Welcome to the 65th
OSU International
Symposium on Molecular Spectroscopy

On behalf of the Executive Committee, Frank DeLucia, Eric Herbst, Anne B. McCoy, and myself, I extend to all our Symposium guests a heartfelt welcome to the 65th Symposium and more broadly to The Ohio State University and Columbus.

The Symposium presents research results in molecular spectroscopy and related fields. The fact that this is the 65th consecutive annual meeting clearly demonstrates the venerableness of the Symposium. The facts that a large number of the talks are given, as usual, by students and that there are more talks in total scheduled at this year’s meeting than ever before demonstrate the Symposium’s continuing vitality. The presentations, which are documented in this Abstract Book, are the heart of the meeting. However information at the Symposium also flows from informal exchanges and discussions. As organizers, we strive to provide an environment that facilitates both kinds of interactions.

The value of the meeting lies in the scientific discussions and your personal experiences this week, whether you are attending for the first time or the fifty-something time. It is our sincere hope that you will find this meeting informative and enjoyable both scientifically and personally. If we can help to enhance your experience, please do not hesitate to ask the Symposium staff or the Executive Committee.

Terry A. Miller
Symposium Chair

Contents

<table>
<thead>
<tr>
<th>SCHEDULE OF TALKS</th>
<th>ABSTRACTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monday (M)...........</td>
<td>Monday (M)...........</td>
</tr>
<tr>
<td>Tuesday (T)..........</td>
<td>Tuesday (T).........</td>
</tr>
<tr>
<td>Wednesday (W).......</td>
<td>Wednesday (W)......</td>
</tr>
<tr>
<td>Thursday (R)........</td>
<td>Thursday (R).......</td>
</tr>
<tr>
<td>Friday (F)..........</td>
<td>Friday (F).........</td>
</tr>
</tbody>
</table>

AUTHOR INDEX........310
ACKNOWLEDGMENTS.....319
65th OSU INTERNATIONAL SYMPOSIUM ON MOLECULAR SPECTROSCOPY
JUNE 21-25, 2010

International Advisory Committee
Jose Alonso, U. Valladolid
David Anderson, U. Wyoming
Vincent Boudon, CNRS-U. Bourgogne
Walther Caminati, U. Bologna
Yasuki Endo, U. Tokyo
Scott Kable, U. Sydney
Zbigniew Kisiel, PAN (Poland)
Yuan-Pern Lee, National Chiao Tung U.
*steering committee member
e-mail: mss@molspect.chemistry.ohio-state.edu

Executive Committee
Terry A. Miller, Chair
Frank C. DeLucia, Eric Herbst
Anne B. McCoy

Please send correspondence to:
Terry A. Miller
International Symposium on Molecular Spectroscopy
Department of Chemistry
100 West 18th Avenue
Columbus, Ohio 43210 USA
http://molspect.chemistry.ohio-state.edu/symposium/

International Advisory Committee
Carl Lineberger, JILA-U. Colorado
Mark Marshall, Amherst College*
Ben McCall, U. IL at Urbana-Champaign*
Scott Reid, Marquette U.*
Hanna Reisler, U. Southern California
David Dale Skatrud, ARO
Li-Hong Xu, U. New Brunswick*
Lucy Ziurys, U. Arizona*, Chair
*steering committee member
614-292-2569 (phone),-1948 (FAX)

Commemorative Session for the 65th Meeting

The Commemorative Session will be in the Auditorium of the Fawcett Center, 5:00pm, Wednesday, June 23, 2010 and will have talks featuring the history and related aspects of the Symposium and its influence on the development of the science over its lifetime. Invited speakers are: Robert Curl, Rice University; Jon Hougen, NIST; David Skatrud, Army Research Office; and Brenda Winnewisser, The Ohio State University.

Special Sessions

For the 65th Symposium, Michael Duncan, University of Georgia, is organizing a mini-symposium entitled, "Metal Containing Molecules". Metal-containing molecules probe the fundamentals of metal bonding, metal-adsorbate interactions, metal-ligand bonding and metal ion solvation. The spectroscopy of these systems is therefore relevant for many areas of chemistry, biochemistry, catalysis, materials and astrophysics. This symposium brings together spectroscopy of all types that focus on metal- and metal-ion-containing molecules, metal atom clusters, and metal-molecular clusters. Invited speakers will include Michael Heaven, Emory University; Lucy Ziurys, University of Arizona; Andre Fielicke, Fritz Haber Institute, Berlin; and Michael Duncan, University of Georgia. A second mini-symposium is being organized by Ben McCall, University of Illinois, Urbana and Jun Ye, JILA/University of Colorado on the subject of "High Precision Spectroscopy and Frequency Combs." This mini-symposium will cover new approaches to molecular spectroscopy enabled by frequency combs. Invited talks for this mini-symposium will be given by Ronald Holzwarth, MPI-Garching; and Ronald Walsworth, Harvard-Smithsonian Center for Astrophysics. A third mini-symposium is being organized by Fleming Crim, University of Wisconsin and Thomas Rizzo, EPFL, entitled "Spectroscopy and Dynamics of Bio-molecules and Ions." This mini-symposium will explore recent progress in obtaining and interpreting highly-resolved vibrational spectra of biomolecules and cluster ions. Invited speakers include Mark Johnson, Yale University; Tom Rizzo, EPFL; and Tim Zwier, Purdue University. A session on theory is being organized by Anne McCoy, John Herbert, and Russell Pitzer, Ohio State University, featuring an invited talk by Tucker Carrington, Queens University.

Picnic

The Symposium picnic will be held on Wednesday evening, June 23, at the Fawcett Center. The cost of the picnic is included in your registration (at below cost to students), so that all may attend the event. The Coblentz Society is the host for refreshments at 7:00pm before the picnic which is scheduled to commence at 7:30pm at the Fawcett Center.
**Sponsorship**

We are pleased to announce our anticipated sponsorship for the 65th Symposium. We anticipate that principal funding will come from the Army Office of Research (ARO). We are most grateful to ARO for their support. We are also receiving support from The Ohio State University. Our Corporate sponsors are Elsevier, BW Tek, Coherent, Journal of Physical Chemistry A and Quantel and ads for each appear at the end of this book. We are pleased to acknowledge Bristol Instruments, Bruker Optics, CVI Melles Griot, Daylight Solutions, Lockheed Martin/Aculight, Newport/Spectra-Physics, Princeton Instruments, Qioptiq/LINOS Photonics, and Scientific Connections as Contributing sponsors. Our sponsors will have exhibits at the Symposium and we encourage you to visit their displays.

**Rao Prize**

The three Rao Prizes for the most outstanding student talks at the 2009 meeting will be presented. The winners are Amanda Case, University of Wisconsin; Andreas Hauser, Graz University of Technology; and George Barratt Park, MIT. The Rao Prize was created by a group of spectroscopists who, as graduate students, benefited from the emphasis on graduate student participation, which has been a unique characteristic of the Symposium. This year three more Rao Prizes will be awarded. The award will be administered by a Prize Committee chaired by Yunjie Xu, University of Alberta and comprised of Kevin Lehmann, Princeton University; John Muenter, University of Rochester; Brooks Pate, University of Virginia; Douglas Petkie, Wright State University, Rebecca Peebles, Eastern Illinois University; and Tim Zwier, Purdue University. Any questions or suggestions about the Prize should be addressed to the Committee. Anyone (especially post-docs) willing to serve on a panel of judges should contact Yunjie Xu (yunjie.xu@ualberta.ca). The Symposium wishes to express its sincere thanks to the long-serving, retiring Committee Chair, Brenda Winnewisser, for her dedicated service.

**Information**

**ACCOMMODATIONS:** The check-in for dormitory accommodations is located in the Lane Avenue Residence Hall (LARH), 328 W. Lane Avenue, will open at 10:00a.m. Sunday, June 20, and remain open 24 hours a day through the Symposium. Meal plans may be purchased upon registration. Inquire upon check-in.

Other hotels close to campus include: The Blackwell, corner of Tuttle Park Place and Woodruff Avenue, 866-247-4003; Red Roof Inn, State Route 315 & Ackerman Rd., 267-9941; University Plaza Hotel, 3110 Olentangy River Rd., 267-7461. **NOTE:** When making reservations with the Blackwell or University Plaza Hotel mention that you are with the Molecular Spectroscopy Symposium and you will be given the OSU discount, if available.

**MAIL:** As in recent years, computer facilities for email will be available. Address your regular mail and packages for delivery during the Symposium to: c/o MOLECULAR SPECTROSCOPY SYMPOSIUM, Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio, 43210, U.S.A. FAX number - (614) 292-1948, Telephone number - (614) 292-2569.

**PARKING:** Parking permits, for the week, are available only from the check-in desk at Lane Avenue Residence Hall. These permits allow you to park in any “C” parking space on campus. The permit must be displayed on the front windshield of your car. Please follow all traffic rules to avoid the issuance of tickets. **NOTE:** The Symposium takes place during the first week of Summer Quarter so parking on campus can be problematic.

**REGISTRATION:** The Registration Desk will be located in Room 2017 McPherson Lab. It will be kept open between 4:00-6:00 p.m. Sunday, and 8:15a.m. - 4:30p.m., Monday through Friday. Those who have prepaid their registration and who are staying in the dorms will receive their registration packet at dormitory check-in. If you have prepaid your registration but are not staying at the dorms, pick up your packet at the Registration Desk. **NOTE:** If the dates of your stay change after Friday, June 11, please settle your dorm account with Lane Avenue Residence Hall directly.

**LIABILITY:** The Symposium fees DO NOT include provisions for the insurance of participants against personal injuries, sickness, theft or property damage. Participants and companions are advised to take whatever insurance they consider necessary. Neither the Symposium organizing committee, its sponsors, nor individual committee members assume any responsibility for loss, injury, sickness, or damages to persons or belongings, however caused. The statements and opinions stated during oral presentations or in written abstracts are solely the author’s responsibilities and do not necessarily reflect the opinions of the organizers.
AUDIO/VIDEO INFORMATION: Computers with your PowerPoint presentations will be available for each session. You must go to the Digital Presentation link on our website and follow the instructions to upload your PowerPoint file and all supporting documents. These files must be submitted to the Symposium by midnight the day BEFORE your presentation session. All submitted files will be loaded on the presentation computer one half-hour prior to the beginning of the session.

Please make careful note of the username (p#) and password provided in the email confirming receipt of your abstract - this username/password combination will be required when you submit your digital presentation. If you are submitting multiple presentations you will need to log on separately with the appropriate username and password for each presentation.

ACKNOWLEDGEMENTS: The Symposium Chair wishes to acknowledge the hard work of numerous people who make this meeting possible. Key among these people are Becky Gregory, who solves everyone’s problems and keeps the meeting running smoothly; and my student assistants, Terrance Codd and Adrian Lange who ensure the sessions go well. We wish to acknowledge the hospitality of the Chemistry Department in tolerating our invasion this year. Sergey Panov originally wrote the script for the electronic aspects of the Symposium; Computer Support in Chemistry, particularly Mike Reed, and Physics helps us modernize it as well as keep it and other aspects of our services operational. Finally, all the students in my group play vital roles in helping make sure nothing falls through the cracks.
Welcome
Carolyn C. Whitacre, Vice President for Research
The Ohio State University

MA01 40 min 9:00
TOWARDS AN IMPROVED MEASUREMENT OF THE ELECTRON’S ELECTRIC DIPOLE MOMENT IN A TRAPPED MOLECULAR ION


MA02 40 min 9:45
MOLECULAR IONS IN THE LABORATORY AND IN SPACE

M. C. MCCARTHY, Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138, and School of Engineering & Applied Sciences, Harvard University, 29 Oxford St., Cambridge, MA 02138.

Intermission

RAO AWARDS 10:50
Presentation of Awards by Brenda Winnewisser, The Ohio State University

2009 Rao Award Winners
Amanda Case, University of Wisconsin-Madison
Andreas Hauser, Graz University of Technology
George Barratt Park, MIT

MA03 40 min 11:05
VIBRATIONAL SPECTROSCOPY OF PHOTOREACTIVE MOLECULES IN ATMOSPHERIC CHEMISTRY

VERONICA VAIDA, Department of chemistry and Biochemistry, University of Colorado, Boulder, CO 80309.
MF. INFRARED/RAMAN (VIBRATIONAL)
MONDAY, JUNE 21, 2010 – 1:30 pm
Room: 160 MATH ANNEX

Chair: GEOFFREY DUXBURY, University of Strathclyde, Glasgow, United Kingdom

MF01 15 min 1:30
SUPERFLUID EFFECTS IN PARA-H₂ CLUSTERS PROBED BY CO₂ ROTATION-VIBRATION TRANSITIONS

HUI LI, ROBERT J. LE ROY, PIERRE-NICHOLAS ROY, Department of Chemistry, University of Waterloo, Waterloo, ON N2L 3G1, Canada; A.R.W. MCKELLAR, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, ON K1A 0R6, Canada.

MF02 15 min 1:47
THEORETICAL AND EXPERIMENTAL STUDY OF THE INFRARED SPECTRA OF CO₂-(para-H₂)₂ TRIMERS

HUI LI, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada; A.R.W. MCKELLAR, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada; ROBERT J. LE ROY, and PIERRE-NICHOLAS ROY, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

MF03 15 min 2:04
QUANTUM MONTE CARLO PREDICTION OF VIBRATIONAL FREQUENCY SHIFTS FOR CO–(p-H₂)ₙ CLUSTERS

HUI LI, ROBERT J. LE ROY and PIERRE-NICHOLAS ROY, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

MF04 15 min 2:21
UNDERSTANDING INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION BY THE ROVIBRATIONAL ANALYSIS OF HIGH RESOLUTION INFRARED SPECTRA: THE CASE OF CHD₂I

CARINE MANCA TANNER, SIEGHARD ALBERT, and MARTIN QUACK, Physical Chemistry, ETH Zurich, Switzerland.

MF05 10 min 2:38
OZONE: FIRST OBSERVATION OF THE 2ν₁+3ν₂+ν₃ BAND

A. BARBE, Groupe de Spectrométrie Moléculaire et Atmosphérique, U.M.R. CNRS 6089, Université de REIMS, Moulin de la Housse, B.P. 1039, 51687 REIMS cedex 2, FRANCE; M.-R. DE BACKER-BARILLY, X. THOMAS, P. VON DER HEYDEN, V.L.G. TUYTEREV, Groupe de Spectrométrie Moléculaire et Atmosphérique, U.M.R. CNRS 6089, Université de REIMS, Moulin de la Housse, B.P. 1039, 51687 REIMS cedex 2, FRANCE.

MF06 10 min 2:50
OZONE: THE KNOWLEDGE OF THE (204) VIBRATIONAL STATE THROUGH THE OBSERVATION OF THE 2ν₁+4ν₃ AND 2ν₁+4ν₃-ν₃ BANDS

GLOBAL MODELING OF HIGH RESOLUTION IR SPECTRA OF $^{12}C_2H_2$

B. AMYAY, M. HERMAN, Service de Chimie quantique et Photophysique CP160/09, Faculté des Sciences, Université Libre de Bruxelles (U.L.B.), Av. Roosevelt, 50, B-1050, Bruxelles, Belgium; A. FAYT, Laboratoire de Spectroscopie Moléculaire, Université Catholique de Louvain, Chemin du Cyclotron, 2, B-1348 Louvain-La-Neuve, Belgium.

ROCK AND ROLL IN HE NANODROPLETS: AGGREGATION AT ULTRACOLD CONDITIONS.

G. W. SCHWAAB, M. HAVENITH, Physical Chemistry II, Ruhr-University Bochum, D-44780 Bochum, Germany; E. SANCHEZ-GARCIA, MPI für Kohlenforschung, Mülheim a.d. Ruhr, Germany; A. METZELTHIN, DPG Bad Honnef; and W. SANDER, Organic Chemistry II, Ruhr-University Bochum.

VAPOR PHASE INFRARED SPECTROSCOPY AND ANHARMONIC AB INITIO FUNDAMENTAL FREQUENCIES OF AMMONIA BORANE

ROBERT L. SAMS, SOTIRIS S. XANTHEAS, and THOMAS A. BLAKE, Pacific Northwest National Laboratory, P.O. Box 999, Mail Stop K8-88, Richland, WA 99352 (PNNL is operated for the US Department of Energy by the Battelle Memorial Institute under contract DE-AC05-76RL01830).

Intermission

STARK SPECTRUM SIMULATION OF $X_2Y_4$ ASYMMETRIC MOLECULES: APPLICATION TO ETHYLENE IN A MFI-TYPE HOST ZEOLITE

M. SANZCHAROV, V. BOUDON, M. LOÈTE, N. ZVEREVA-LOÈTE, A. BALLANDRAS, G. WEBER, Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 5209 CNRS-Université de Bourgogne, 9 avenue Alain Savary, B.P. 47870, F-21078 Dijon Cedex, France; M. ROTGER, Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA), CNRS UMR 6089, Moulin de la Housse, BP 1039, Cases 16-17, F-51687 Reims Cedex 2, France.

HIGH RESOLUTION SPECTROSCOPY OF THE CARBON CAGE ADAMANTANE $C_{10}H_{16}$

V. BOUDON, Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 5209 CNRS-Université de Bourgogne, 9, Av. A. Savary, BP 47870, F-21078 Dijon Cedex, France; O. PIRALI, D. BALCON, M. VERVLOET, Ligne AILES – Synchrotron SOLEIL, L’Orme des Merisiers, F-91192 Gif-sur-Yvette, France; J. OOMENS, Inst. Plasma Phys. Rijnhuizen, FOM, NL-3439 MN Nieuwegein, Netherlands.
MF12 15 min 4:44
IN PURSUIT OF THE FAR-INFRARED SPECTRUM OF CYANOGEN ISO-THIOCYANATE, NCNCS, UNDER THE INFLUENCE OF THE ENERGY LEVEL DISLOCATION DUE TO QUANTUM MONODROMY

MANFRED WINNEWISSER, BRENTA P. WINNEWISSER, IVAN R. MEDVEDEV, FRANK C. DELUCIA, Department of Physics, The Ohio State University, Columbus Ohio, 43210-1106, USA; STEPHEN C. ROSS, Department of Physics and Centre for Laser, Atomic, and Molecular Sciences, University of New Brunswick, P.O. Box 4400, Fredericton NB E3B 5A3, Canada; and JACEK KOPUT, Department of Chemistry, Adam Mickiewicz University, 60-780 Poznan, Poland.

MF13 15 min 5:01
THE TWO MISSING CONFORMERS OF GAS-PHASE ALANINE: A JET-COOLED RAMAN SPECTROSCOPY STUDY

ROMAN M. BALABIN, Department of Chemistry and Applied Biosciences, ETH Zurich, 8093 Zurich, Switzerland.

MF14 15 min 5:18
CONFORMATIONAL EQUILIBRIUM IN GLYCINE: EXPERIMENTAL JET-COOLED RAMAN SPECTRUM

ROMAN M. BALABIN, Department of Chemistry and Applied Biosciences, ETH Zurich, 8093 Zurich, Switzerland.

MF15 15 min 5:35
TIME-RESOLVED ROTATIONAL ENERGY TRANSFER AND SPECTRAL LINE BROADENING IN ACETYLENE. A HIGH RESOLUTION RAMAN STUDY.

J. L DOMENECH, R. Z. MARTINEZ, D. BERMEJO, Instituto de Estructura de la Materia (CSIC), Dept. of Molecular Physics, Serrano 123, E-28006 Madrid, Spain.

MF16 15 min 5:52
HIGH-RESOLUTION INFRARED SPECTRA OF BICYCLO[1.1.1]PENTANE: ANALYSES OF THE $\nu_{14}(e')$ AND $\nu_{18}(a_2^+)$ BANDS

M. A. MARTIN and A. PERRY, Department of Chemistry, Oregon State University, Corvallis, OR, 97332-4003, USA; T. MASIELLO, Department of Chemistry and Biochemistry, California State University, East Bay, Hayward, CA, 94542, USA; K. SCHWARTZ, Department of Chemistry, Oregon State University, Corvallis, OR, 97332-4003, USA; J.W. NIBLER, Department of Chemistry, Oregon State University, Corvallis, OR, 97332-4003, USA; A. WEBER, Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD, 20899-8441, USA; A. MAKI, 15012 24th Ave., S.E., Mill Creek, WA, 98012, USA; T.A. BLAKE, Pacific Northwest National Laboratory, P.O. BOX 999, Mail Stop K8-88, Richland, WA, USA.
MG ELECTRONIC (UV/VIS/NIR)
MONDAY, JUNE 21, 2010 – 1:30 pm
Room: 170 MATH ANNEX

Chair: TIMOTHY SCHMIDT, University of Sydney, Sydney, Australia

MG01 15 min 1:30
SPECTRAL DISSIMILARITIES BETWEEN AZULENE(C_{10}H_{8}) AND NAPHTHALENE(C_{10}H_{8})

MASAAKI BABA, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan.

MG02 15 min 1:47
ROTATIONALLY RESOLVED ELECTRONIC SPECTRA OF 2,6-DIAMINOPYRIDINE: A FOUR-FOLD BARRIER PROBLEM

CASEY L. CLEMENTS, JUSTIN W. YOUNG, and DAVID W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

*Work supported by NSF (CHE-0911117).

MG03 15 min 2:04
ROTATIONALLY RESOLVED STUDIES OF PARA-AMINOPHENOL AND ITS COMPLEXES.

JUSTIN W. YOUNG, PATRICK S. WALSH, ADAM J. FLEISHER and DAVID W. PRATT, Department of Chemistry, University of Pittsburgh, Pa 15260.

*Work supported by NSF (CHE-0911117)

MG04 15 min 2:21
CHARGE REDISTRIBUTION IN THE \( \beta \)-NAPHTHOL-WATER COMPLEX AS MEASURED BY HIGH RESOLUTION STARK SPECTROSCOPY IN THE GAS PHASE.

ADAM J. FLEISHER, DAVID W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260; ALESSANDRO CEMBRAN and JIALI GAO, Department of Chemistry, University of Minnesota, Minneapolis, MN 55455.

*Work supported by NSF (CHE-0911117).

MG05 15 min 2:38
VIBRATIONAL AND ROTATIONAL STRUCTURE AND EXCITED-STATE DYNAMICS OF PYRENE

YASUYUKI KOWAKA, NOLITAKA ASHIZAWA, MASAAKI BABA, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan.

MG06 15 min 2:55
STRUCTURE AND EXCITED-STATE DYNAMICS OF PERYLENE: ULTRAHIGH-RESOLUTION SPECTROSCOPY AND AB INITIO CALCULATION

NOLITAKA ASHIZAWA, YOSHITAKE SUGANUMA, YASUYUKI KOWAKA, MASAAKI BABA, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan.
MERGING OF THE SPLINE-POINTWISE AND MORSE/LONG-RANGE POTENTIAL FUNCTION FORMS FOR DIRECT-POTENTIAL-FIT DATA ANALYSES

JASON TAO, ROBERT J. LE ROY, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada; ASEN PASHOV, Department of Physics, Sofia University, 5 James Bourcheier Blvd, 1164 Sofia, Bulgaria.

Intermission

STARK EFFECT STUDIES OF THE ELECTRONIC SPECTRUM OF 1-PHENYL PYRROLE AT HIGH RESOLUTION. CHARGE TRANSFER STATES\(^a\)

JESSICA A. THOMAS, JUSTIN W. YOUNG, ADAM J. FLEISHER, and DAVID W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

\(^a\)Work supported by NSF CHE-0911117.

ELECTRONIC SPECTRA OF THE JET-COOLED ACETAMINOPHEN

SEUNG JUN LEE, AHREUM MIN, YUSIC KIM and MYONG YONG CHOI, Department of Chemistry (BK21) and Research Institute of Natural Science, Gyeongsang National University, Jinju 660-701, Korea; JINYOUNG CHANG, SANG HAK LEE, Department of Chemistry, Seoul National University, Seoul 151-747, Korea; and SEONG KEUN KIM, Department of Chemistry and Department of Biophysics and Chemical Biology, Seoul National University, Seoul 151-747, Korea.

PHOTOELECTRON SPECTROSCOPY OF DOPED HELIUM NANODROPLETS

EVGENY LOGINOV and MARCEL DRABBELS, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.

CORE LEVEL SPECTROSCOPY AND TAUTOMERISM OF KEY BIOMOLECULES IN THE GAS PHASE

V. FEYER, O. PLEKAN, R. RICHTER, K. C. PRINCE, Sincrotrone Trieste, Basovizza (Trieste), Italy; M. CORENO, CNR-IMIP, Montelibretti (Rome), Italy; B. M. GIULIANO, L. EVANGELISTI, S. ME-LANDRI, W. CAMINATI, Dipartimento di Chimica "G. Ciamici" dell’Università, Bologna, Italy; A. B. TROFIMOV, I. L. ZAYTSEVA, T. E. MOSKOVSKAYA, Irkutsk State University, Irkutsk, Russian Federation; E. V. GROMOV, J. SCHIRMER, Physikalisch-Chemisches Institut, Universität Heidelberg, Heidelberg, Germany.

THE DARK SINGLET STATE AS DOORWAY STATE OF INTERSYSTEM CROSSING IN DNA MONOMERS.

CHRISTIAN REICHARDT, CARLOS E. CRESPO-HERNÁNDEZ, Case Western Reserve University, Department of Chemistry Center for Chemical Dynamics, 2080 Adelbert Road, Cleveland, Ohio 44106.
PHOTODISSOCIATION SPECTRA OF CYCLIC AND NON-CYCLIC NUCLEOTIDES

SYDNEY H. KAUFMAN, JESSE C. MARCUM, and J. MATHIAS WEBER, JILA, NIST, and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309.

ULTRAFAST SINGLET-TRIPLET POPULATION DYNAMICS IN NITRO-AROMATIC COMPOUNDS

R. AARON VOGT, CHRISTIAN REICHARDT, CARLOS E. CRESPO-HERNÁNDEZ, Case Western Reserve University, Department of Chemistry Center for Chemical Dynamics, Cleveland, Ohio 44106, USA.

SPECTROSCOPIC AND THEORETICAL DETERMINATION OF ACCURATE CH/π INTERACTION ENERGIES IN BENZENE-HYDROCARBON CLUSTERS.

A. FUJII, H. HAYASHI, J.W. PARK, T. KAZAMA, Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan; and S. TSUZUKI, National Institute of Advanced Industrial Science and Technology, Tsukuba, 305-8568, Japan.

PUMP-PROBE DELAYED IONIZATION STUDY OF PHENYLACETYLENE

GARY V. LOPEZ, PHILIP M. JOHNSON AND TREVOR J. SEARS, Department of Chemistry, Stony Brook University, Stony Brook, New York 11794; CHIH-HSUAN CHANG, Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973.

UV PHOTODISSOCIATION OF CYCLIC KETONES IN THE GAS-PHASE AND COLD INERT GAS MATRIXES

ANAMIKA MUKHOPADHYAY, Department of Physical Chemistry, Indian Association for the Cultiva- tion of Science, Jadavpur, Kolkata 700032, India; MOITRAYEE MUKHERJEE, ; AMIT K. SAMANTA, ; and TAPAS CHAKRABORTY.
MH. MINI-SYMPOSIUM: METAL CONTAINING MOLECULES

MONDAY, JUNE 21, 2010 – 1:30 pm
Room: 1000 McPHERSON LAB

Chair: MICHAEL DUNCAN, University of Georgia, Athens, Georgia

MH01 30 min 1:30
METAL-CONTAINING MOLECULES BEYOND THE SOLAR SYSTEM: A LABORATORY AND RADIO ASTRO-NOMICAL PERSPECTIVE

L. M. ZIURYS, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.

MH02 15 min 2:05
THE PURE ROTATIONAL SPECTRUM OF ZnOD AND THE STRUCTURE OF ZnOH (X^2A’):

L.N.ZACK, B.J.HARRIS, M.P.BUCCHINO and L. M. ZIURYS, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ, 85721.

MH03 15 min 2:22
MICROWAVE SPECTRA AND STRUCTURES OF H_2S-CuCl AND H_2O-CuCl.

N. R. WALKER, D. E. WHEATLEY, S. L. STEPHENS, F. J. ROBERTS, V. A. MIKHAILOV AND A. C. LEGON, School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K.

MH04 15 min 2:39
MICROWAVE SPECTRA AND STRUCTURES OF H_2O-AgCl AND H_3N-AgCl.

N. R. WALKER, V. A. MIKHAILOV, S. J. HARRIS, F. J. ROBERTS AND A. C. LEGON, School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K.

MH05 15 min 2:56
QUADRUPOLE COUPLING IN AlOH, AlCH_3, CuCN, CuOH, AND CuSH DETERMINED BY FOURIER TRANSFORM MICROWAVE TECHNIQUES

M. SUN, D. T. HALPEN, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721; D. J. CLOUTHIER, Department of Chemistry, University of Kentucky, Lexington, KY 40506; and L. M. ZIURYS, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.

MH06 15 min 3:13
FOURIER TRANSFORM MICROWAVE SPECTRUM OF AlCCH (X^1Σ^+) AND ITS ^13C/D ISOTOPOLOGUES

M. SUN, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721; D. J. CLOUTHIER, Department of Chemistry, University of Kentucky, Lexington, KY 40506; and L. M. ZIURYS, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.
MICROWAVE MEASUREMENTS OF STRUCTURE CHANGES FOR LIGAND MOLECULES BOUND TO TRANSITION METALS

STEPHEN G. KUKOLICH, Department of Chemistry and Biochemistry, The University of Arizona, Tucson, Arizona 85721.

*Supported by THE NATIONAL SCIENCE FOUNDATION

Intermission

HIGH RESOLUTION LASER SPECTROSCOPY OF Mg\textsubscript{12}C\textsubscript{12}CD, Mg\textsubscript{13}C\textsubscript{13}CH AND Mg\textsubscript{12}C\textsubscript{4}H

D. FORTHOMME, C. LINTON, D. W. TOKARYK, Centre for Laser, Atomic, and Molecular Sciences and Physics Department, 8 Bailey Dr., University of New Brunswick, P.O. Box 4400, Fredericton, NB, Canada E3B 5A3; A. G. ADAM, A. D. GRANGER, Centre for Laser, Atomic, and Molecular Sciences and Chemistry Department, 30 Dineen Dr., University of New Brunswick, P.O. Box 4400, Fredericton, NB, Canada E3B 5A3.

EXPLORING THE PHOTOREDUCTION OF Au(III) COMPLEXES IN THE GAS-PHASE

JESSE C. MARCUM, SYDNEY H. KAUFMAN, J. MATHIAS WEBER, JILA, NIST, Department of Chemistry and Biochemistry, The University of Colorado, Boulder, CO.

PULSED-FIELD IONOIZATION ELECTRON SPECTROSCOPY OF LANTHANIDE (Lu, Gd) BENZENE COMPLEXES

MOURAD ROUDJANE, SUDESH KUMARI, and DONG-SHENG YANG, Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.

ROTATIONAL CONFORMERS OF GROUP VI METAL (Cr, Mo, and W) BIS(MESITYLENE) SANDWICH COMPLEXES

SUDESH KUMARI and DONG-SHENG YANG, Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.

ELECTRONIC AND SPECTROSCOPIC PROPERTIES OF A REDOX ACTIVE ANALOG OF 4,4’-BIPYRIDINE INCORPORATING A METAL-METAL QUADRUPLE BOND

PHIL C. BUNTING, BENJAMIN J. LEAR, and MALCOLM H. CHISHOLM, The Ohio State University, Columbus, OH 43210.

EXCITED STATE PROPERTIES OF PADDLEWHEEL COMPLEXES INVOLVING METAL-METAL (M = MO, W) QUADRUPLE BONDS SUPPORTED BY AMIDINATE AND CARBOXYLATE LIGANDS

BRIAN G. ALBERDING, MALCOLM H. CHISHOLM, and TERRY L. GUSTAFSON, The Ohio State University, Department of Chemistry, Columbus, Ohio, 43210.
WATER REACTIVITY WITH TUNGSTEN OXIDES: FORMATION OF H₂ FROM W₂O₇⁻ + H₂O REACTIONS

NICHOLAS J. MAYHALL, DAVID W. ROTHGEB, EKRAM HOSSAIN, CAROLINE CHICK JARROLD, AND KRISHNAN RAGHAVACHARI, Department of Chemistry, Indiana University, 800 E. Kirkwood Avenue, Bloomington, Indiana 47405, USA.

DYNAMICS OF METAL CYANIDES

DANIEL WEIDINGER, Code 6111, Naval Research Laboratory, 4555 Overlook Ave SW Washington, D.C. 20375; DOUGLAS J. BROWN, Chemistry Department, United States Naval Academy, Annapolis, MD 21402; CASSIDY HOUCHINS, Code 6111, Naval Research Laboratory, 4555 Overlook Ave SW Washington, D.C. 20375; and JEFFREY C. OWRUTSKY, Code 6111, Naval Research Laboratory, 4555 Overlook Ave SW Washington, D.C. 20375.
MI. RADICALS AND IONS
MONDAY, JUNE 21, 2010 – 1:30 pm
Room: 1015 McPHERSON LAB

Chair: JU XIN, Bloomsburg University, Bloomsburg, Pennsylvania

MI01 15 min 1:30
MICROWAVE SPECTROSCOPY AND POTENTIAL ENERGY SURFACES OF Ne-OH and Kr-OH

YOSHIHIRO SUMIYOSHI, IPPEI FUNAHARA, KAZUYA SATO, YASUHIRO OHSHIMA, and YASUKI ENDO, Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153-8902, Japan.

*Present address: Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

MI02 15 min 1:47
OBSERVATION OF PURE ROTATIONAL SPECTRA OF trans- and cis-HOCO/DOCO

TAKAHIRO OYAMA, WATARU FUNATO, YOSHIHIRO SUMIYOSHI and YASUKI ENDO, Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo, 153-8902, Japan.

MI03 15 min 2:04
ORTHO-PARA MIXING INTERACTION IN THE VINYL RADICAL DETECTED BY MILLIMETER-WAVE SPECTROSCOPY AND PREDICTION OF FAST ORTHO-PARA CONVERSION RATE

KEIICHI TANAKA, MASATO HAYASHI, MITSUHIKO OHTSUKI, KENSUKE HARADA, and TAKEHIKO TANAKA, Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi, Fukuoka 812-8581, Japan.

MI04 15 min 2:21
OBSERVATION OF THE $\tilde{A} - \tilde{X}$ TRANSITION OF ALLYL PEROXY RADICAL VIA CAVITY RINGDOWN SPECTROSCOPY

PHILLIP S. THOMAS and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus OH 43210.

MI05 15 min 2:38
SPECTROSCOPY AND DISSOCIATION DYNAMICS OF THE 1-METHYLALLYL RADICAL

M. GASSER, J. A. FREY, J. M. HOSTETTLER and A. BACH, Laboratorium für Organische Chemie, ETH Zürich, CH-8093, Switzerland.

MI06 15 min 2:55
HYDROCARBON RADICALS ISOLATED IN HELIUM NANODROPLETS

ALEXANDER M. MORRISON, STEVEN D. FLYNN, TAO LIANG and GARY E. DOUBERLY, Department of Chemistry, University of Georgia, Athens, Georgia 30602.
OBSERVATION OF THE $\tilde{A} - \tilde{X}$ ELECTRONIC TRANSITION OF $\beta$-HYDROXYETHYL PEROXY VIA CAVITY RING DOWN SPECTROSCOPY

RABI CHHANTYAL-PUN, NEAL D. KLINE, PHILLIP S. THOMAS and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus OH 43210.

JET-COOLED $\tilde{A}-\tilde{X}$ SPECTRA OF THE $\beta$-HYDROXYETHYLPEROXY and $\beta$-HYDROXYETHYLPEROXY-OD RADICALS

MING-WEI CHEN, GABRIEL M. P. JUST*, TERRANCE CODD, and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210.

*present address: Lawrence Berkeley National Laboratory, Lawrence Berkeley National Laboratory

Intermission

HIGHER VIBRATIONAL LEVELS OF THE $\tilde{A}^1\Pi_u$ STATE OF C$_3$ OBSERVED BY LASER-INDUCED FLUORESCENCE

CHIAO-WEI CHEN, ANTHONY J. MERER, JUN-MEI CHAO, AND YEN-CHU HSU, Institute of Atomic and Molecular Sciences, Academia Sinica, Box 23-166, Taipei, Taiwan 10617.

EMISSION SPECTROSCOPY FOLLOWING THE MULTIPHOTON PHOTOLYSIS OF HALOMETHANES AT NEAR-ULTRAVIOLET WAVELENGTHS

CHEN-NAN LIU, HSIAANG-FU LIAO, GUANG-YI HOU, SHI-XING YANG, and BOR-CHEN CHANG, Department of Chemistry, National Central University, Jhongli 32001, Taiwan.

SUB-DOPPLER SPECTROSCOPY OF MIXED STATE LEVELS IN CH$_2$

CHIH-HSUAN CHANG, GREGORY E. HALL AND TREVOR J. SEARS, Chemistry Department, Brookhaven National Laboratory, Upton, New York, 11973.

THE ORIGIN BAND OF THE $\tilde{b} - \tilde{a}$ SYSTEM OF CH$_2$

GREGORY E. HALL, AND TREVOR J. SEARS, Department of Chemistry, Brookhaven National Laboratory, Upton, NY, 11973; BOR-CHEN CHANG, Department of Chemistry, National Central University, Jhongli 32001, Taiwan, R.O.C; ZHONG WANG, Shinnecock Building, SUNY Suffolk Eastern Campus, Riverhead NY 11901; JU XIN, ERIC OTRUBA AND TYLER LATSHA, Department of Physics and Engineering Technology, Bloomsburg University, Bloomsburg, PA, 17815.
MI13 15 min 5:08
PRECISE MEASUREMENTS OF ABSORPTION CROSS-SECTIONS OF PEROXY RADICALS BY DUAL WAVELENGTH CAVITY RING-DOWN SPECTROSCOPY

DMITRY G. MELNIK, and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210.

MI14 15 min 5:25
SPECTROSCOPIC IDENTIFICATION OF NEW BENZYL-TYPE RADICALS IN CORONA EXCITATION: CHLORO-α-METHYLBENZYL RADICALS

YOUNG WOOK YOON, SEUNG WOON LEE, SANG KUK LEE, Department of Chemistry, Pusan National University, Pusan 609-735, South Korea; and GI WOO LEE, Korea Basic Science Institute, Pusan 609-735, Korea.

MI15 15 min 5:42
CORRELATED AB INITIO STUDY OF THE GROUND ELECTRONIC STATE OF THE O2-HCN COMPLEX

WAFAA M. FAWZY, Department of Chemistry, Murray State University, Murray, KY 42071.
MJ01  15 min  1:30
CLOSED-CYCLE HE-COOLED ABSORPTION CELLS DESIGNED FOR A BRUKER IFS-125HR: FIRST RESULTS BETWEEN 79 K AND 297 K


MJ02  15 min  1:47
INFRARED SPECTRA OF N₂-BROADENED ¹³CH₄ AT TITAN ATMOSPHERIC TEMPERATURES


MJ03  15 min  2:04
HIGH RESOLUTION INVESTIGATION OF THE ETHANE SPECTRUM AT 7 MICRON (1430 CM⁻¹)

C. DI LAURO, F. LATTANZI, Dipartimento di Chimica Farmaceutica e Tossicologia, Università di Napoli Federico II, I-80131 Naples, Italy; K. SUNG, L. R. BROWN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA; J. VANDER AUWERA, Service de Chimie Quantique et Photophysique, Université Libre de Bruxelles, CP 160/09, 50 avenue F.D. Roosevelt, B-1050 Brussels, Belgium; A.W. MANTZ, Dept. of Physics, Astronomy and Geophysics, Connecticut College, New London, CT 06320, USA; M. A. H. SMITH, Science Directorate, NASA Langley Research Center, Hampton, VA 23681, USA.

MJ04  15 min  2:21
LINE PARAMETERS OF ETHANE (¹²C₂H₆) AT 12 µm WITH CONSTRAINED MULTISPECTRUM FITTING

HIGH RESOLUTION INFRARED SPECTRUM OF ETHYLENE ($^{12}$C$_2$H$_4$) IN THE SPECTRAL REGION 1820 TO 2300 CM$^{-1}$

JEAN-MARIE FLAUD AND F. KWABIA TCHANA, Laboratoire Interuniversitaire des Systèmes Atmosphériques, C.N.R.S., UMR 7583, Universités Paris Est et 7, 61 Avenue du Général de Gaulle, 94010 Créteil Cedex France; WALTER J. LAPPERTY, Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441, USA.

DIRECT DETECTION OF C$_2$H$_2$ IN AIR AND HUMAN BREATH BY CW-CRDS

FLORIAN M. SCHMIDT, OLAVI VAITTINEN, MARKUS METSÄLÄ, and LAURI HALONEN, Laboratory of Physical Chemistry, Department of Chemistry, P.O. Box 55 (A.I. Virtasen aukio 1), FIN-00014 University of Helsinki, Finland.

THE 4$\nu_3$ SPECTRAL REGION OF METHANE

D. CHRIS BENNER, V. MALATHY DEVI, Department of Physics, College of William and Mary, Williamsburg, VA 23187-8795; J. J. O’BRIEN, S. SHAJI, Department of Chemistry and Biochemistry, University of Missouri - St. Louis, St. Louis, MO 63121-4400; P. T. SPIELKER, C. P. HOUCK, J. A. COAKLEY, Department of Physics, Bridgewater College, Bridgewater, VA 22812.

FORMALDEHYDE: THE 5.7µm AND 3.6µm BANDS

D. JACQUEMART, N. LACOME, Université Pierre et Marie Curie-Paris 6; CNRS; Laboratoire de Dynamique, Interactions et Réactivité (LADIR), UMR 7075, Case Courrier 49, 4 Place Jussieu, 75252 Paris Cedex 05, France; A. PERRIN, F. KWABIA TCHANA, Université Paris 12; CNRS; Laboratoire Inter Universitaire des Systèmes Atmosphériques (LISA), UMR 7583, 61 Av du General de Gaulle, 94010 Créteil Cedex France; A. LARAIA, and R.R. GAMACHE, University of Mass Lowell, Department of Environmental, Earth and Atmospheric Sciences, Lowell, MA 01854, USA.

TRACE ATMOSPHERIC DETECTION OF HCHO VIA FIBER LASER-INDUCED FLUORESCENCE DURING BEARPEX 2009

J. DIGANGI, S. HENRY, A. KAMMRATH, E. BOYLE, and F. KEUTSCH, Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706.; J. PAUL, NovaWave Technologies, Redwood City, CA 94065.

LONG-TERM TREND OF CARBON TETRACHLORIDE (CCl$_4$) FROM GROUND-BASED HIGH RESOLUTION INFRARED SOLAR SPECTRA RECODED AT THE JUNGFRAUJOCH

THE REGION OF 3\(\mu\)m FOR THE MOLECULE \(\text{CH}_3\text{Cl}\)

**C. BRAY, N. LACOME, D. JACQUEMART**, Université Pierre et Marie Curie-Paris 6; CNRS; Laboratoire de Dynamique, Interactions et Réactivité (LADIR), UMR 7075, Case Courrier 49, 4 Place Jussieu, 75252 Paris Cedex 05, France; **A. PERRIN**, Université Paris 12; CNRS; Laboratoire Inter Universitaire des Systèmes Atmosphériques (LISA), UMR 7583, 61 Av du General de Gaulle, 94010 Créteil Cedex France.

NEW HIGH RESOLUTION SPECTROSCOPY STUDIES OF METHYL NITRITE \(\text{CH}_3\text{ONO}\)


IR/THZ DOUBLE RESONANCE SIGNATURES AT ATMOSPHERIC PRESSURE

**Dane J. Phillips, Elizabeth A. Tanner**, Kratos Defense and Security Solutions - Digital Fusion Solutions Advanced Technologies Division, 5030 Bradford Dr. Building 1, Suite 210, Huntsville, AL 35805; **Henry O. Everitt**, Army Aviation and Missile RD&E Center, Weapons Sciences Directorate, Redstone Arsenal, AL 35898; **Ivan R. Medvedev**, Department of Physics, 191 W. Woodruff Ave., Ohio State University, Columbus, OH 43210 USA; **Jennifer Holt**, and **Frank C. De Lucia**, Department of Physics, 191 W. Woodruff Ave., Ohio State University, Columbus, OH 43210 USA.

INFRARED/SUBMICROSECOND DOUBLE RESONANCE AS AN APPROACH TO ATMOSPHERIC REMOTE SENSING: MEASUREMENTS AND ENERGY TRANSFER MODELING

**Jennifer Holt**, **Ivan R. Medvedev**, **Christopher F. Neese**, and **Frank C. De Lucia**, Department of Physics, 191 W. Woodruff Ave., Ohio State University, Columbus, OH 43210 USA; **Dane J. Phillips**, Elizabeth A. Tanner, Kratos Defense and Security Solutions - Digital Fusion Solutions Advanced Technologies Division, 5030 Bradford Dr. Building 1, Suite 210, Huntsville, AL 35805; **Henry O. Everitt**, Army Aviation and Missile RD&E Center, Weapons Sciences Directorate, Redstone Arsenal, AL 35898.

ABSOLUTE LINE INTENSITIES OF HONO AND DONO IN THE FAR INFRARED AND REDETERMINATION OF THE ENERGY DIFFERENCE BETWEEN THE TRANS AND CIS SPECIES OF NITROUS ACID

TA01  15 min  8:30
TIME DEPENDENT MEASUREMENTS OF NITROUS OXIDE - FOREIGN GAS COLLISIONAL RELAXATION PROCESSES USING A FREQUENCY DOWN-CHIRPED 7.84 MICRONS QUANTUM CASCADE LASER

K. G. HAY, G. DUXBURY and N. LANGFORD, Department of Physics, SUPA, John Anderson Building, University of Strathclyde, 107 Rottenrow, Glasgow G4 0NG, Scotland, UK; N. TASINATO, Dipartimento di Chimica Fisica, Universita Ca Foscari di Venezia, 30123 Venezia, Italy.

TA02  15 min  8:47
VIBRATIONAL DEPENDENCE OF_excited state intramolecular proton transfer in 2-(2′-PYRIDYL)PYRROLE IN THE GAS PHASE VIA HIGH RESOLUTION ELECTRONIC SPECTROSCOPY. 

PHILIP J. MORGAN, ADAM J. FLEISHER and DAVID W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260; MICHAL KIJAJK and JACEK WALUK, Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland.

aWork supported by NSF (CHE-0911117)
bSynthesis by Randolph P. Thummel, University of Houston, Houston, Texas 77204-5003

TA03  15 min  9:04
INTERNAL DYNAMICS OF WATER ATTACHED TO A PHOTOCYDIC SUBSTRATE: HIGH RESOLUTION ELECTRONIC SPECTROSCOPY OF β-NAPHTHOL-WATER IN THE GAS PHASE.

ADAM J. FLEISHER, JUSTIN W. YOUNG and DAVID W. PRATT, Department of Chemistry, University of Pittsburgh, 15260.

aWork supported by NSF (CHE-0911117).

TA04  15 min  9:21
VIBRATIONAL RELAXATION AND CONTROL IN THE CYCLOHEXADIENE REACTIVE SYSTEM

ADAM D. DUNKELBERGER, RYAN D. KIEDA, F. FLEMING CRIM, Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706.

TA05  15 min  9:38
PHOTOISOMERIZATION DYNAMICS OF STILBENE AND AZOBENZENE DERIVATIVE OBSERVED BY FEMTOSECOND TRANSIENT ABSORPTION SPECTROSCOPY

LESLIE HERMAN, KRISTIN A. BRINEY and F. FLEMING CRIM, The University of Wisconsin-Madison, Department of Chemistry, 1101 University Avenue, Madison, WI 53706.
THE EFFECT OF VIBRATIONAL ENERGY ON THE ISOMERIZATION REACTION OF TRANS-STILBENE IN THE CONDENSED PHASE

KRISTIN A. BRINEY, LESLIE V. HERMAN, DAVE S. BOUCHER and F. FLEMING CRIM, The University of Wisconsin-Madison, Department of Chemistry, 1101 University Avenue, Madison, WI 53706.

Intermission

ELECTRONIC STRUCTURE CALCULATIONS OF INTER-RING TORSIONAL POTENTIALS OF REGIOREGULAR POLY (3-METHYL THIOPHENE) OLIGOMERS

RAMS BHATTA, DAVID S PERRY, Department of Chemistry, The University of Akron, OH 44325-3601.

STUDIES OF TRANSIENT NEUTRAL MOLECULES BY DISSOCIATIVE PHOTODETACHMENT OF COOLED MOLECULAR ANIONS

CHRISTOPHER J. JOHNSON and ROBERT E. CONTINETTI, Department of Physics, Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, CA 92093.

This work supported by the United States Department of Energy

COHERENT EXCITATION PHENOMENA IN TIME-RESOLVED EXPERIMENTS

A. PERALTA CONDE, R. MONTERO, F. CASTANO, AND A. LONGARTE, Departamento de Química-Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apartado 644, ES-48080 Bilbao, Spain.

COHERENT EFFECTS INVOLVING THE EXCITATION AND RELAXATION OF THE COUPLED Lα/Lβ ELECTRONIC EXCITED STATES OF NAPHTHALENE: A TIME DEPENDENT EXPERIMENTAL STUDY

R. MONTERO, A. PERALTA CONDE, F. CASTANO, AND A. LONGARTE, Departamento de Química-Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apartado 644, ES-48080 Bilbao, Spain.

INFLUENCE OF SOLVATION ON 1-AMINONAPHTHALENE PHOTOPHYSICS: ULTRAFAST RELAXATION IN THE ISOLATED MOLECULE, MOLECULAR CLUSTER AND SOLUTION

R. MONTERO, A. PERALTA CONDE, F. CASTANO, AND A. LONGARTE, Departamento de Química-Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apartado 644, ES-48080 Bilbao, Spain.

INTRAMOLECULAR CHARGE TRANSFER DYNAMICS OF 4-(DIMETHYLAMINO)BENZONITRILE: ULTRAFAST BRANCHING FOLLOWED BY A TWO-FOLD DECAY MECHANISM

PEDRO B. COTO, LUIS SERRANO-ANDRÉS, Instituto de Ciencia Molecular (ICMOL), Universitat de València, P.O. Box 22085, ES-46071, Valencia, Spain; THOMAS GUSTAVSSON, Laboratoire Francis Perrin, CEA/DSM/DECAM/SPAM-CNRS URA 2453 CEA/Saclay, 91 191 Gif-sur-Yvette, France; TAKASHIGE FUJIWARA, and EDWARD C. LIM, Department of Chemistry and The Center for Laser and Optical Spectroscopy, The University of Akron, Akron OH 44325-3601.
TB. MINI-SYMPHOSIUM: BIOMOLECULES AND CLUSTER IONS
TUESDAY, JUNE 22, 2010 – 8:30 am
Room: 170 MATH ANNEX

Chair: FLEMING CRIM, University of Wisconsin, Madison, Wisconsin

TB01  INVITED TALK - Abstract Rescheduled at Authors’ Request  30 min  8:30
EXPLORING SOLVENT SHAPE AND FUNCTION USING MASS- AND ISOMER-SELECTIVE VIBRATIONAL SPECTROSCOPY

MARK JOHNSON, Yale University, Department of Chemistry, New Haven, CT.

TB02  15 min  9:05
INFRARED SPECTROSCOPY OF WATER CLUSTER RADICAL CATIONS (H$_2$O)$_n^+$ ($n = 3$ to 11)

KENTA MIZUSE and ASUKA FUJII, Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan.

TB03  15 min  9:22
INFRARED SPECTROSCOPY OF 7-AZAINDOLE TAUTOMERIC DIMER: OBSERVATION OF THE ND STRETCH

HARUKI ISHIKAWA, TAKUMI NAKANO, HIROKI YABUGUCHI, AKIMASA FUJIHARA, KIYOKAZU FUKE, Department of Chemistry, Graduate School of Science, Kobe University, Nada-ku, Kobe 657-8501, Japan.

TB04  15 min  9:39
PROTON BETWEEN BENZENE AND WATER: INFRARED SPECTROSCOPY TO MODEL INTERACTIONS AT THE OIL-WATER INTERFACE

B. BANDYOPADHYAY, T. C. CHENG, and M. A. DUNCAN, Department of Chemistry, University of Georgia, Athens, GA 30602-2556.

TB05  15 min  9:56
INFRARED SPECTRA OF HYDRATED CLUSTERS OF GUANINE NUCLEOSIDES OBSERVED BY IR-UV DOUBLE RESONANCE SPECTROSCOPY

SHU-HEI URASHIMA, HIROYA ASAMI, and HIROYUKI SAIGUSA, Graduate School of Arts and Sciences, Yokohama City University, Yokohama 236-0027, Japan.

Intermission

TB06  15 min  10:30
EFFECTS OF MICROSOLVATION ON A MODEL PEPTIDE CHAIN INVESTIGATED BY IR/UV DOUBLE RESONANCE SPECTROSCOPY

CONFORMATION-SPECIFIC INFRARED SPECTROSCOPY OF $\gamma^2$-PEPTIDE FOLDAMERS: Ac-$\gamma^2$-hPhe-$\gamma^2$-hAla-NHMe AND Ac-$\gamma^2$-hAla-$\gamma^2$-hPhe-NHMe

WILLIAM H. JAMES III, EVAN G. BUCHANAN, CHRISTIAN W. MÜLLER, and TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN 47907; LI GUO, and SAMUEL H. GELL-MAN, Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706.

SINGLE-CONFORMATION SPECTROSCOPIC INVESTIGATION OF PEPTIDE BUILDING BLOCKS IN THE AMIDE I SPECTRAL REGION: COMPARISON OF EXPERIMENT TO DENSITY FUNCTIONAL THEORY AND THE TRANSITION DIPOLE COUPLING MODEL

WILLIAM H. JAMES III, EVAN G. BUCHANAN, CHRISTIAN W. MÜLLER, ESTEBAN E. BAQUERO, JACOB C. DEAN, and TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN 47907; MICHAEL G. D. NIX, School of Chemistry, University of Bristol, Bristol BS8 1TS, UK; SOO HYUK CHOI, LI GUO, and SAMUEL H. GELLMAN, Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706.

VIBRATIONAL ENERGY RELAXATION OF BENZENE DIMER STUDIED BY PICOSECOND TIME-RESOLVED INFRARED-ULTRAVIOLET PUMP-PROBE SPECTROSCOPY

R. KUSAKA and T. EBATA, Department of Chemistry, Graduate School of Science, Hiroshima University, Higashi-Hiroshima, 739-8526, Japan.

APPLICATION OF INFRARED MULTIPHOTON DISSOCIATION SPECTROSCOPY FOR THE STUDY OF CHIRAL RECOGNITION IN PROTONATED SERINE CLUSTERS

FUMIE X. SUNAHORI, GUOCHUN YANG, ELENA N. KITOVA, JOHN S. KLASSEN, AND YUNJIE XU, Department of Chemistry, University of Alberta, Edmonton, Canada T6G 2G2.

USING DIFFERENTIAL ION MOBILITY AS A CONFORMATIONAL FILTER TO SIMPLIFY SPECTRA OF BIOMOLECULAR IONS

THOMAS R. RIZZO, OLEG V. BOYARKIN, CAROLINE SEAIBY and GEORGIOS PAPADOPOULOS, Laboratoire de chimie physique moléculaire (LCPM), École polytechnique fédérale de Lausanne, CH-1015 Lausanne, Switzerland.
TC. MICROWAVE (ROTATIONAL)
TUESDAY, JUNE 22, 2010 – 8:30 am
Room: 1000 McPHERSON LAB

Chair: REBECCA PEEBLES, Eastern Illinois University, Charleston, Illinois

TC01 15 min 8:30
EXTENDED TOWNES-DAILEY ANALYSIS II

STEWARD E. NOVICK, Department of Chemistry, Wesleyan University, Middletown, CT 06459.

TC02 15 min 8:47
RECENT CHANGES IN PGOPHER: A GENERAL PURPOSE PROGRAM FOR SIMULATING ROTATIONAL STRUCTURE

COLIN WESTERN, School of Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS, UK.

TC03 15 min 9:04
REVISITING THE AMMONIA HYPERFINE STRUCTURE WITH SPFIT

BRIAN J. DROUIN, SHANSHAN YU, JOHN C. PEARSON, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099.

TC04 15 min 9:21
ATTEMPTS AT USING IAMCALC TO ANALYZE LOW FREQUENCY ROTATIONAL SPECTRA OF MOLECULES WITH INTERNAL ROTATION AND NUCLEAR SPINS

CHRISTOPHER T. DEWBERRY AND STEPHEN A. COOKE, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH TEXAS, 1155 UNION CIRCLE #305070, DENTON, TX 76203-5017, U.S.A.

TC05 15 min 9:38
A PROPOSAL FOR A GENERAL METHOD FOR DETERMINING SEMI-EXPERIMENTAL EQUILIBRIUM STRUCTURES OF CARBON ATOM BACKBONES

NORMAN C. CRAIG, Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH 44074.

TC06 15 min 9:55
CONSTRUCTION AND DEVELOPMENT OF A NEW LOW-FREQUENCY FOURIER TRANSFORM SPECTROMETER FOR OPERATION IN THE 1-6 GHZ RANGE\(^a\)

LASZLO SARKOZY, STEPHEN G. KUKOLICH, Department of Chemistry and Biochemistry, The University of Arizona, Tucson, AZ 85721.

\(^a\)Supported by THE NATIONAL SCIENCE FOUNDATION

TC07 15 min 10:12
DESIGN AND INITIAL OPTIMISATION OF A BROADBAND (6.5-18 GHz) CHIRPED-PULSE, FOURIER TRANSFORM MICROWAVE SPECTROMETER

N. R. WALKER AND S. L. STEPHENS, School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K.
Intermission

TC08  15 min  10:45
TWO-DIMENSIONAL CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTROSCOPY: INTRODUCTION TO TWO-DIMENSIONAL BROADBAND TECHNIQUES

AMANDA J. SHIRAR, KELLY M. HOTOPP, DAVID S. WILCOX, BRIAN C. DIAN, Department of Chemistry, Purdue University, West Lafayette, IN, 47907.

TC09  15 min  11:02
TWO-DIMENSIONAL CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTROSCOPY: MODELING COHERENCE TRANSFER

DAVID S. WILCOX, KELLY M. HOTOPP, AMANDA J. SHIRAR, BRIAN C. DIAN, Department of Chemistry, Purdue University, West Lafayette, IN, 47907.

TC10  15 min  11:19
STRATEGIES FOR COMPLEX MIXTURE ANALYSIS IN BROADBAND MICROWAVE SPECTROSCOPY.

AMANDA L. STEBER, JUSTIN L. NEILL, MATTHEW T. MUCKLE, AND BROOKS H. PATE, Department of Chemistry, University of Virginia, McCormick Rd., P.O. Box 400319, Charlottesville, VA 22904; D.F. PLUSQUELLIC, Optical Technology Division, NIST, Gaithersburg, MD 20899-8441; V. LATTANZI, S. SPEZZANO, AND M.C. MCCARTHY, Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138, and School of Engineering & Applied Sciences, Harvard University, 29 Oxford St., Cambridge MA 02138.

TC11  15 min  11:36
A K_A-BAND CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTROMETER.

DANIEL P. ZALESKI, JUSTIN L. NEILL, MATTHEW T. MUCKLE, AND BROOKS H. PATE, Department of Chemistry, University of Virginia, McCormick Rd., P.O. Box 400319, Charlottesville, VA 22904; P. BRANDON CARROLL AND SUSANNA L. WIDICUS WEAVER, Department of Chemistry, Emory University, 1515 Dickey Drive, Atlanta, GA 30322.

TC12  15 min  11:53
TWO-DIMENSIONAL CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTROSCOPY: APPLICATIONS TO MULTI-LEVEL SYSTEMS

KELLY M. HOTOPP, DAVID S. WILCOX, AMANDA J. SHIRAR, BRIAN C. DIAN, Department of Chemistry, Purdue University, West Lafayette, IN, 47907.
TD01 15 min  8:30
PULSED JET DISCHARGE MATRIX ISOLATION STUDIES OF RADICALS, IONS, AND WEAKLY BOUND RADICAL-MOLECULE COMPLEXES
AIMABLE KALUME, LISA GEORGE AND SCOTT A. REID, Department of Chemistry, Marquette University, Milwaukee, WI 53233.

TD02 15 min  8:47
MATRIX ISOLATION AND COMPUTATIONAL STUDIES OF THE PHOTOLYSIS OF DIHALOETHANES: PROBING THE PATHWAYS LEADING TO RADICAL AND MOLECULAR PRODUCTS
AIMABLE KALUME, LISA GEORGE AND SCOTT A. REID, Department of Chemistry, Marquette University, Milwaukee, WI 53233; PATRICK Z. EL-KHOURY AND ALEXANDER TARNOVSKY, Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, OH 43403.

TD03 15 min  9:04
MATRIX ISOLATION AND COMPUTATIONAL STUDY OF iso-CF₂Br₂: A ROUTE TO MOLECULAR PRODUCTS IN CF₂Br₂ PHOTOLYSIS
LISA GEORGE, AIMABLE KALUME AND SCOTT A. REID, Department of Chemistry, Marquette University, Milwaukee, WI 53233; PATRICK Z. EL-KHOURY AND ALEXANDER TARNOVSKY, Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, OH 43403.

TD04 15 min  9:21
THE VIBRATIONAL STRUCTURE OF OH RADICAL AND OH-H₂O COMPLEX: A MATRIX ISOLATION STUDY
PRASAD R. JOSHI, LAHOUARI KRIM, Université Pierre et Marie Curie-Paris 6; CNRS; Laboratoire de Dynamique, Interactions et Réactivité (LADIR), UMR 7075, Case Courrier 49, 4 Place Jussieu, 75252 Paris Cedex 05, France.

TD05 15 min  9:38
AN FTIR STUDY OF THE INFLUENCE OF ENVIRONMENT CONDITIONS ON THE SUCCESSIVE HYDROGENATIONS OF CO
C. PIRIM, L. KRIM, UPMC Univ Paris 06, UMR 7075, Laboratoire de Dynamique, Interactions et Réactivité (LADIR), F-75005, Paris, France.

TD06 10 min  9:55
Original Abstract Withdrawn - Post-deadline Abstract
NEAR-IR BAND STRENGTHS OF MOLECULES DILUTED IN N₂ AND H₂O ICES
Intermission

TD07 15 min 10:20
MATRIX ISOLATION FTIR SPECTROSCOPIC AND DFT STUDIES OF MnC₃

M. BEJJANI, C. M. L. RITTBY and W. R. M. GRAHAM, Department of Physics and Astronomy, Texas Christian University, Fort Worth, TX 76129.

TD08 15 min 10:37
THERMAL DECOMPOSITION OF ACETALDEHYDE STUDIED BY MATRIX IR AND PIMS SPECTROSCOPY

ANGAYLE VASILIOU, KRZYSZTOF PIECH, G. BARNEY ELLISON, University of Colorado, Boulder, CO 80309-0215; MARK R. NIMLOS, Center for Renewable Chemical, Technologies & Materials, NREL, 1617 Cole Blvd., Golden, CO 80401; JOHN W. DAILY, Department of Mechanical Engineering, University of Colorado, Boulder, CO 80309-0427; JOHN F. STANTON, Institute for Theoretical Chemistry, Department of Chemistry, University of Texas, Austin, TX 78712-0165.

TD09 15 min 10:54
ORIGINAL ABSTRACT WITHDRAWN - ABSTRACT RESCHEDULED AT AUTHOR’S REQUEST

DIMINISHED CAGE EFFECT IN p-H₂: INFRARED SPECTRA OF CH₃S OBSERVED FROM PHOTOLYSIS OF CH₃SH, CH₃SCH₃, AND CH₃SSCH₃ ISOLATED IN p-H₂

YUAN-PERN LEE, Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan and Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan; MOHAMED BAHOU, Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan.

TD10 15 min 11:11
LONG-WAVELENGTH PHOTOCHEMISTRY OF MATRIX-ISOLATED BIACTETYL

NATHAN G. KUCHMAS and C. A. BAUMANN, Department of Chemistry, The University of Scranton, Scranton, PA 18510-4626.

TD11 15 min 11:28
SOFT X-RAY SPECTROSCOPY OF GLYCYL-GLYCINE ADSORBED ON Cu(110) SURFACE

V. FEYER, O. PLEKAN, V. LYAMAYEV, T. SKALA, K. C. PRINCE, Sincrotrone Trieste, Basovizza (Trieste), Italy; V. CHAB, Institute of Physics, Prague, Czech Republic; N. TSUD, V. MATOLIN, Charles University, Prague, Czech Republic; V. CARRAVETTA, CNR-Institute of Chemical Physical Processes, Pisa, Italy.

TD12 15 min 11:45
IONS AS PROBES OF SUB-PS WATER NETWORK DYNAMICS.

G. W. SCHWAAB, D. A. SCHMIDT, S. FUNKNER, B. BORN, M. HAVENITH a, Department of Physical Chemistry II, Ruhr-University Bochum, D-44780 Bochum, Germany; O. BIRER, Department of Chemistry, Koc University, 34450 Istanbul, Turkey; R. GNANASEKARAN, and D. M. LEITNER, Department of Chemistry, University of Nevada, 89557 Reno, Nevada, USA.

aThe authors acknowledge financial support by the VW Stiftung Az I/84 302, the BMBF (grant 05 KS7PC2), FOR 618 and NSF (grant CHE-0910669).
TE. ATMOSPHERIC SPECIES
TUESDAY, JUNE 22, 2010 – 8:30 am
Room: 2015 McPHERSON LAB

Chair: CURTIS RINSLAND, NASA Langley Research Center, Hampton, Virginia

TE01  15 min  8:30
HIGH SENSITIVITY CRDS OF THE $\alpha^1\Delta_g \rightarrow X^3\Sigma_g^-$ BAND OF OXYGEN NEAR 1.27 $\mu$m: MAGNETIC DIPOLE AND ELECTRIC QUADRUPOLE TRANSITIONS IN SPECTRA OF FIVE ISOTOPOLOGUES

O. M. LESHCISHINA, S. KASSI, L. WANG, Université Joseph Fourier/CNRS, Laboratoire de Spectrométrie Physique, 38402 Saint Martin d’Hères, FRANCE; I. E. GORDON, L. S. ROTHMAN, Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge MA 02138-1516, USA; A. CAMPARGUE, Université Joseph Fourier/CNRS, Laboratoire de Spectrométrie Physique, 38402 Saint Martin d’Hères, FRANCE.

TE02  15 min  8:47
PRESSURE BROADENING AND SPECTRAL OVERLAP IN THE MILLIMETER WAVE SPECTRUM OF OZONE

COREY CASTO AND FRANK C. DE LUCIA, Department of Physics, The Ohio State University, Columbus, OH 43210-1106.

TE03  15 min  9:04
TEMPERATURE DEPENDENT OZONE ABSORPTION CROSS SECTIONS FOR SATELLITE SPECTROMETERS: NEW LABORATORY MEASUREMENTS

ANNA SERDYUCHENKO, VICTOR GORSHELEV, MARK WEBER, JOHN P. BURROWS, INSTITUTE FOR ENVIRONMENTAL PHYSICS, UNIVERSITY OF BREMEN, OTTO-HAHN ALLEE 1, D-28359 BREMEN, GERMANY.

TE04  15 min  9:21
FAR-INFRARED EMISSION SPECTROSCOPY OF ROVIBRATIONALY EXCITED WATER VAPOR


TE05  15 min  9:38
THEORETICAL CALCULATION OF THE N$_2$ BROADENED HALF-WIDTHS OF H$_2$O

R. H. TIPPING, Department of Physics and Astronomy, University of Alabama, Tuscaloosa, AL 35487; Q. MA, NASA/Goddard Institute for Space Studies and Department of Applied Physics and Applied Mathematics, Columbia University, 2880 Broadway, New York, NY 10025.

TE06  15 min  9:55
NEW MEASUREMENTS OF H$_2$ $^{16}$O LINE INTENSITIES AROUND 8800 CM$^{-1}$ AND 1300 CM$^{-1}$

C. OUDOT, L. REGALIA, LE WANG, L. DAUMONT , X. THOMAS, P. VON DER HEYDEN, D. DECA-TOIRE, Groupe de Spectromètrie Moléculaire et Atmosphérique, UMR 6089, Faculté des sciences, BP 1039, 51687 REIMS CEDEX2 - FRANCE.
Intermission

TE07 15 min 10:30
EMPIRICAL LOWER STATE ENERGIES OF $^{13}$CH$_4$ AT 1.66 $\mu$m USING 296 K AND 81 K SPECTRA

O. M. LYULIN, Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, 1, Akademicheskii av., 634055 Tomsk; S. KASSI, A. CAMPARGUE, Laboratoire de Spectrométrie Physique (associated with CNRS, UMR 5588), Université Joseph Fourier de Grenoble, B.P. 87, 38402 Saint-Martin-d’Hères Cedex, France; K. SUNG, L. R. BROWN, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109, U.S.A..

TE08 15 min 10:47
REAL TIME DIAGNOSTICS OF JET ENGINE EXHAUST PLUMES USING A CHIRPED QC LASER SPECTROMETER

K. G. HAY, G. DUXBURY and N. LANGFORD, Department of Physics, SUPA, John Anderson Building, University of Strathclyde, 107 Rottenrow, Glasgow G4 0NG, Scotland, UK.

TE09 15 min 11:04
MULTI-WAVELENGTH MEASUREMENT OF BUS EXHAUSTS USING A FOUR QC LASER SPECTROMETER

K. G. HAY, D. WILSON, G. DUXBURY and N. LANGFORD, Department of Physics, SUPA, John Anderson Building, University of Strathclyde, 107 Rottenrow, Glasgow G4 0NG, Scotland, UK.

TE10 15 min 11:21
THE COF$_2$ ROTATIONAL SPECTRUM NEAR 1 THz; IMPROVED MOLECULAR CONSTANTS FOR THE GROUND AND FIRST EXCITED STATES OF $\nu_2$, $\nu_3$, $\nu_5$, and $\nu_6$

E. A. COHEN, and B. J. DROUIN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099.

TE11 15 min 11:38
A SUBMILLIMETER CHEMICAL SENSOR

CHRISTOPHER F. NEESE, IVAN R. MEDVEDEV, FRANK C. DE LUCIA, Department of Physics, 191 W. Woorduff Ave., Ohio State University, Columbus, OH 43210 USA; GRANT M. PLUMMER, Enthalpy Analytical, Inc., 2202 Ellis Rd., Durham, NC 27703 USA; CHRISTOPHER D. BALL, AARON J. FRANK, Battelle Memorial Institute, 505 King Ave., Columbus, OH 43201 USA.
## TF. MINI-SYMPOSIUM: METAL CONTAINING MOLECULES

**TUESDAY, JUNE 22, 2010 – 1:30 pm**  
**Room: 160 MATH ANNEX**

**Chair: NICHOLAS WALKER, University of Bristol, Bristol, United Kingdom**

<table>
<thead>
<tr>
<th>Session</th>
<th>Title</th>
<th>Duration</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>TF01</td>
<td>INVITED TALK</td>
<td>30 min</td>
<td>1:30</td>
</tr>
<tr>
<td></td>
<td>SIZE SELECTIVE FAR-INFRARED SPECTROSCOPY OF TRANSITION METAL CLUSTERS IN A MOLECULAR BEAM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ANDRÉ FIELICKE, Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin, Germany.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TF02</td>
<td>15 min</td>
<td>2:05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>INFRARED SPECTROSCOPY OF METAL LIGAND AND METAL OXIDE LIGAND COMPLEXES</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ALLEN M. RICKS and MICHAEL A. DUNCAN, Department of Chemistry, University of Georgia, Athens, Ga.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TF03</td>
<td>15 min</td>
<td>2:22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>INFRARED SPECTROSCOPY OF DOUBLY-CHARGED METAL-WATER COMPLEXES</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B. BANDYOPADHYAY and M. A. DUNCAN, Department of Chemistry, University of Georgia, Athens, GA 30602-2556.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TF04</td>
<td>15 min</td>
<td>2:39</td>
<td></td>
</tr>
<tr>
<td></td>
<td>THE OPTICAL STARK SPECTRUM OF THE $A^3\Phi_4 - X^3\Phi_4$ BAND SYSTEM OF IRIDIUM MONOFLUORIDE, IrF</td>
<td></td>
<td></td>
</tr>
<tr>
<td>XIUJJUAN ZHUANG AND TIMOTHY C. STEIMLE, Department of Chemistry and Biochemistry, Arizona State University, Tempe,AZ 85287; COLAN LINTON, Center for Lasers, Atomic and Molecular Sciences and Physics Department, University of New Brunswick, Fredericton, NB Canada E3B 5A3.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TF05</td>
<td>15 min</td>
<td>2:56</td>
<td></td>
</tr>
<tr>
<td></td>
<td>THE VISIBLE SPECTRUM OF TITANIUM DIOXIDE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>XIUJJUAN ZHUANG AND TIMOTHY C. STEIMLE, Department of Chemistry and Biochemistry, Arizona State University, Tempe,AZ 85287; RAMYA NAGARAJIANN AND JOHN P. MAIER, Department of Chemistry, University of Basel, Basel Switzerland.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TF06</td>
<td>15 min</td>
<td>3:13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SEARCH FOR THE LOW-LYING ELECTRONICALLY EXCITED STATES OF UO$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I. O. ANTONOV, M. C. HEAVEN, Department of Chemistry, Emory University, Atlanta, GA 30322.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Intermission**
TF07  15 min  3:45
STUDY OF THE ZEEMAN EFFECT IN THE [17.6]7.5 X18.5 TRANSITION IN HOLMIUM MONOXIDE (HoO)

COLAN LINTON, Center for Lasers, Atomic and Molecular Sciences and Physics Department, University of New Brunswick, Fredericton, NB Canada E3B 5A3; HAILING WANG AND TIMOTHY C. STEIMLE, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287.

TF08  10 min  4:02
INTRACAVITY LASER ABSORPTION SPECTROSCOPY OF PLATINUM FLUORIDE IN THE NEAR INFRARED

LEAH C. O'BRIEN, KIMBERLY HANDLER, RACHEL A. HARRIS, Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026-1652; JAMES J. O'BRIEN, MEREDITH REDICK, BECCA STEINBERG, Department of Chemistry and Biochemistry and Center for Nanoscience, University of Missouri, St Louis, MO 63121-4499.

TF09  10 min  4:14
INTRACAVITY LASER ABSORPTION SPECTROSCOPY OF PLATINUM SULFIDE IN THE NEAR INFRARED

JAMES J. O'BRIEN, Department of Chemistry and Biochemistry and Center for Nanoscience, University of Missouri, St Louis, MO 63121-4499; LEAH C. O'BRIEN, KIMBERLY HANDLER, Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026-1652.

TF10  15 min  4:26
HOW CATION-PI INTERACTIONS ENHANCE AND STRUCTURE THE BINDING OF METAL IONS TO AMINO ACIDS AND PEPTIDES. DIALANINE PROBED BY IRMPD SPECTROSCOPY AS A PRIME EXAMPLE

ROBERT C. DUNBAR, Chemistry Department, Case Western Reserve Univ., Cleveland, OH 44106; JEFFREY STEILL, FOM Institute for Plasma Physics, Nieuwegein, Netherlands; JOS OOMENS, FOM Institute for Plasma Physics, Nieuwegein, and University of Amsterdam, Netherlands.

TF11  15 min  4:43
ANION PHOTOELECTRON SPECTROSCOPY OF Mo-V BINARY TRANSITION METAL SUBOXIDE CLUSTERS

CAROLINE CHICK JARROLD, JENNIFER E. MANN, SARAH E. WALLER, and DAVID W. ROTHGEB, Department of Chemistry, Indiana University, 800 E. Kirkwood Avenue, Bloomington, IN 47405.

TF12  15 min  5:00
MICROSOLVATION OF Ni^{2+} AND Co^{2+} BY ACETONITRILE AND WATER: PHOTODISSOCIATION DYNAMICS OF M^{2+}(CH_3CN)_n(H_2O)_m

MANORI PERERA, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801; RICARDO B. METZ, Department of Chemistry, University of Massachusetts, Amherst, MA 01002.

TF13  15 min  5:17
ELECTRONIC SPECTROSCOPY AND VIBRATIONALLY MEDIATED PHOTODISSOCIATION OF Co^{2+}(H_2O), Co^{2+}(D_2O) and Co^{2+}(HOD)

ABDULKADIR KOCAK, G. AUSTEIN-MILLER and R. B. METZ, Department of Chemistry, University of Massachusetts, Amherst, MA 01003.
TF14 15 min 5:34
QUADRUPLY BONDED M$_2$ COMPLEXES INCORPORATING THIENYLETHYNYL AND THIENYLVINYL CARBOXYLATES

CARLY R. REED, MALCOLM H. CHISHOLM, and CLAUDIA TURRO, Ohio State University, Department of Chemistry, Columbus, Ohio 43210.

TF15 15 min 5:51
USING ELECTROABSORPTION SPECTROSCOPY TO GAIN INSIGHT INTO THE GROUND- AND EXCITED-STATE MIXED VALENCE PROPERTIES OF A SERIES OF DIMERS FORMED FROM METAL-METAL QUADRUPLY BONDED UNITS

BENJAMIN J. LEAR, PHIL. C. BUNTING, and MALCOLM H. CHISHOLM, The Ohio State University, Columbus, OH 43210.
TG. ELECTRONIC (UV/VIS/NIR)
TUESDAY, JUNE 22, 2010 – 1:30 pm
Room: 170 MATH ANNEX

Chair: GABRIEL JUST, Lawrence Berkeley National Laboratory, Berkeley, California

<table>
<thead>
<tr>
<th>TG01</th>
<th>DIRECT OBSERVATION OF RYDBERG–RYDBERG TRANSITIONS IN CALCINIUM ATOMS</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>TG02</th>
<th>RYDBERG STATES OF XENON COLLISION DIMERS IN THE VUV ENERGY REGION</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WAN-CHUN PAN, I-CHIA CHEN, Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan; TZU-PING HUANG, and YIN-YU LEE, National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TG03</th>
<th>TWO-STEP EXCITATION OF Rb AND Cs ATOMS ON He NANODROPLETS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MORITZ THEISEN, FLORIAN LACKNER, and WOLFGANG E. ERNST, Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, 8010 Graz, Austria; FRANCESCO ANCILOTTO, Dipartimento di Fisica ‘G. Galilei’, Università di Padova, via Marzolo 8, 35131 Padova, Italy; CARLO CAL-LEGARI, Sincrotrone Trieste, Strada Statale 14 - km 163.5, 34149 Basovizza, Trieste, Italy.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TG04</th>
<th>LASER-INDUCED FLUORESCENCE OF RUBIDIUM DIMER: OBSERVATION OF TWO NEW VIBRONIC BAND SYSTEMS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>JIANDE HAN and MICHAEL C. HEAVEN, Department of Chemistry, Emory University, Atlanta, GA 30322.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TG05</th>
<th>COUPLED-CHANNEL ANALYSIS OF THE $^3\Pi – d^3\Pi$ COMPLEX IN NaK; POTENTIAL ENERGY CURVES AND SPIN-ORBIT FUNCTIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ANASTASIA DROZDOVA and AMANDA J. ROSS, LASIM, Université Lyon 1 &amp; CNRS, 43 Bd du 11 novembre 1918, F-69622 Villeurbanne, France; ANDREY V. STOLYAROV, Department of Chemistry, Moscow State University, 119992 Moscow, Russia; WLODZIMIERZ JASTRZĘBSKI, Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland; and PAWEŁ KOWALCZYK, Institute of Experimental Physics, Warsaw University, ul. Hoża 69, 00-681 Warsaw, Poland.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TG06</th>
<th>CaF: ALL SPECTRA AND ALL DYNAMICS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R. W. FIELD, J. J. KAY, S. L. COY, V. S. PETROVIĆ, S. N. ALTUNATA, and B. M. WONG, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139; Ch. JUNGEN, Laboratoire Aim Cotton du CNRS, Université de Paris Sud, F-91405 Orsay, France.</td>
</tr>
</tbody>
</table>
Intermission

TG07 15 min 3:20
LASER-INDUCED FLUORESCENCE STUDIES OF THE JET-COOLED CARBON DIOXIDE AND NITROUS OXIDE CATIONS

MOHAMMED A. GHARAIBEH and DENNIS J. CLOUTHIER, Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.

TG08 15 min 3:37
ELECTRONIC SPECTRA OF LiNH$_3$ AND YbNH$_3$

N. BHALLA, L. VARRIALE, N. M. TONGE AND A. M. ELLIS, Department of Chemistry, University of Leicester, Leicester, LE1 7RH, United Kingdom.

TG09 15 min 3:54
THE OPTICAL SPECTRUM OF ATOMIC CLUSTERS Si$_3$ and S$_3$

DAMIAN L. KOKKIN, NEIL J. REILLY, MICHAEL C. McCARTHY, and PATRICK THADDEUS, Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138, and School of Engineering & Applied Sciences, Harvard University, 29 Oxford St., Cambridge, MA 02138; JOHN F. STANTON, Department of Chemistry & Biochemistry, The University of Texas at Austin, 1 University Station A5300 Austin, TX 78712.

TG10 15 min 4:11
OPTICAL SPECTROSCOPY OF SILICON-CARBON CLUSTERS: Si$_2$C and Si$_3$C

NEIL J. REILLY, DAMIAN L. KOKKIN, MICHAEL C. McCARTHY, and PATRICK THADDEUS, Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138, and School of Engineering & Applied Sciences, Harvard University, 29 Oxford St., Cambridge, MA 02138.

TG11 15 min 4:28
LASER INDUCED FLUORESCENCE SPECTROSCOPY OF THE SiNSi RADICAL I: THE $^3 \Delta_u - ^2 \Pi_g$ TRANSITION

MASARU FUKUSHIMA, TAKASHI ISHIWATA, Faculty of Information Sciences, Hiroshima City University, Hiroshima 731-3194, Japan; CHIHAYA MOTOYOSHI, YOSHIHIRO SUMIYOSHI, and YASUKI ENDO, Department of Basic Science, The University of Tokyo, Meguro 153-8902, Japan.

TG12 15 min 4:45
LASER INDUCED FLUORESCENCE SPECTROSCOPY OF THE SiNSi RADICAL II: IDENTIFICATIONS OF THE $^3 \Sigma^+$ STATES

CHIHAYA MOTOYOSHI, YOSHIHIRO SUMIYOSHI, YASUKI ENDO, Department of Basic Science, The University of Tokyo, Tokyo 153-8902, Japan; MASARU FUKUSHIMA and TAKASHI ISHIWATA, Faculty of Information Sciences, Hiroshima City University, Hiroshima 731-3194, Japan.

TG13 15 min 5:02
SUB-DOPPLER SPECTROSCOPY OF THE $^1 \Sigma^+$ - $^1 \Pi$ ELECTRONIC TRANSITION OF CBr$_2$

EYAD H AL-SAMRA and COLIN WESTERN, School of Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS, UK.
ROTATIONALLY RESOLVED $\tilde{B} \leftarrow \tilde{X}$ ELECTRONIC SPECTRA OF THE ISO-PROPOXY RADICAL AND OTHER SECONDARY ALKOXY RADICALS

J. LIU and T. A. MILLER, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, OH 43210, USA.

LASER INDUCED FLUORESCENCE SPECTROSCOPY OF THE JET-COOLED TRANSIENT SPECIES AsD$_2$ AND AsHD

ROBERT A. GRIMMINGER and DENNIS J. CLOUTHIER, Department of Chemistry, University of Kentucky, Lexington, KY, 40506-0055.

OH LASER-INDUCED FLUORESCENCE MEASUREMENTS in NANOSECOND PULSE DISCHARGE PLASMAS

INCHUL CHOI, IGOR V. ADAMOVICH and WALTER R. LEMPert, Michael A. Chaszeyka Nonequilibrium Thermodynamics Laboratory, Department of Mechanical Engineering, The Ohio State University, Columbus, OH 43210.
TH. MICROWAVE (ROTATIONAL)
TUESDAY, JUNE 22, 2010 – 1:30 pm
Room: 1000 McPherson Lab

Chair: JENNIFER VAN WIJNGAARDEN, University of Manitoba, Winnipeg, Canada

TH01 15 min 1:30
MICROWAVE SPECTRA AND STRUCTURE OF N₂ CO₂

DANIEL J. FROHMAN, EDWIN S. CONTRERAS, ROSS S. FIRESTONE, STEWART E. NOVICK, Department of Chemistry, Wesleyan University, Middletown, CT 06459; WILLIAM KLEMPERER, Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138.

TH02 15 min 1:47
MILLIMETER-WAVE SPECTROSCOPY OF THE vdW BANDS OF He-HCN NEAR THE DISSOCIATION LIMIT.

KENSUKE HARADA and KEIICHI TANAKA, Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashiku, Fukuoka, 812-8581 Japan.

TH03 15 min 2:04
OBSERVATION OF THE WEAKLY BOUND (HCl)₂H₂O CLUSTER BY CHIRPED-PULSE FTMW SPECTROSCOPY

ZBIGNIEW KISIEL, Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland; ALBERTO LESARRI, Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47011 Valladolid, Spain; JUSTIN NEILL, MATT MUCKLE, BROOKS PATE, Department of Chemistry, University of Virginia, McCormick Rd., Charlottesville, VA 22904-4319.

TH04 15 min 2:21
THE HCCIF₂–HCCH COMPLEX: MICROWAVE SPECTRUM, STRUCTURE AND C–H···π INTERACTIONS

REBECCA A. PEEBLES, JOHN M. Sexton, ASHLEY A. ELLIOTT, AMANDA L. STEBER and SEAN A. PEEBLES, Department of Chemistry, Eastern Illinois University, 600 Lincoln Ave., Charleston, IL 61920; JUSTIN L. NEILL, MATT T. MUCKLE and BROOKS H. PATE, Department of Chemistry, University of Virginia, McCormick Rd., PO Box 400319, Charlottesville, VA 22904.

TH05 15 min 2:38
THE FT MICROWAVE SPECTRA AND STRUCTURE OF THE ARGON AND NEON VAN DER WAALS COMPLEXES OF CYANOCYCLOBUTANE

WALLACE C. PRINGLE, DANIEL J. FROHMAN, WILLIAM NDUGIRE, STEWART E. NOVICK, Department of Chemistry, Wesleyan University, Middletown, CT 06459.

TH06 15 min 2:55
FOURIER TRANSFORM MICROWAVE SPECTRA OF CO₂-ETHYLENE SULFIDE,CO₂-ETHYLENE OXIDE AND CO₂-PROPYLENE OXIDE COMPLEXES

YUKARI ORITA, YOSHIYUKI KAWASHIMA, Department of Applied Chemistry, Faculty of Engineering, Kanagawa Institute of Technology, Atsugi, Kanagawa 243-0292, JAPAN; and EIZI HIROT A, The Graduate University for Advanced Studies, Hayama, Kanagawa 240-0193, JAPAN.
TH07 10 min 3:12

ROTATIONAL SPECTROSCOPIC INVESTIGATIONS OF $CH_4$ - $H_2S$ COMPLEX

AISWARYA LAKSHMI P. and E. ARUNAN, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India.

Intermission

TH08 15 min 3:40

MICROWAVE SPECTRUM AND PARTIAL GAS PHASE STRUCTURE OF A FORMIC ACID-FORMAMIDE COMPLEX

ADAM M. DALY, STEPHEN G. KUKOLICH, Department of Chemistry and Biochemistry, 1306 E. University, Tucson, Arizona 85721; BRYAN SARGUS, Catalina Foothills High School Teacher, Tucson, Arizona 85718.

Supported by THE NATIONAL SCIENCE FOUNDATION

TH09 15 min 3:57

MICROWAVE SPECTRUM OF THE HYDROGEN BONDED COMPLEX BETWEEN PROPIOLIC AND FORMIC ACID

ADAM M. DALY, STEPHEN G. KUKOLICH, Department of Chemistry and Biochemistry, 1306 E. University, Tucson, Arizona 85721.

Supported by THE NATIONAL SCIENCE FOUNDATION

TH10 15 min 4:14

MICROSOLVATION OF $\beta$-PROPIOLACTONE AS REVEALED BY CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTROSCOPY.

JUSTIN L. NEILL, MATT T. MUCKLE, AND BROOKS H. PATE, Department of Chemistry, University of Virginia, McCormick Rd., P.O. Box 400319, Charlottesville, VA 22904; I. PENA, C. PEREZ, AND J.L. ALONSO, Grupo de Espectroscopía Molecular (GEM), Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47005 Valladolid, Spain.

TH11 15 min 4:31

THE EFFECT OF VICINAL VERSUS GEMINAL SUBSTITUTION OF HYDROGEN BY CHLORINE: MICROWAVE SPECTRA AND MOLECULAR STRUCTURES OF THE COMPLEXES OF 1-CHLORO-1-FLUOROETHYLENE AND (E)-1-CHLORO-2-FLUOROETHYLENE WITH HYDROGEN FLUORIDE

HELEN O. LEUNG, MARK D. MARSHALL, ALEX J. LEE, AARON T. BOZZI, PAUL M. COHEN, and MABLE LAM, Department of Chemistry, Amherst College, P.O. Box 5000, Amherst, MA 01002-5000.

TH12 15 min 4:48

THE STRUCTURE OF THE 1-CHLORO-1-FLUOROETHYLENE–ACETYLENE COMPLEX

HELEN O. LEUNG, MARK D. MARSHALL, AND DAVID D. GRIMES, Department of Chemistry, Amherst College, P.O. Box 5000, Amherst, MA 01002-5000.
TH13 15 min 5:05
DETERMINING THE GROUND STATE GEOMETRY OF THE (E)-1-CHLORO-1,2-DIFLUOROETHYLENE–HYDROGEN FLUORIDE COMPLEX USING MICROWAVE SPECTROSCOPY

Aaron T. Bozzi, Helen O. Leung and Mark D. Marshall, Department of Chemistry, Amherst College, P.O. Box 5000, Amherst, MA 01002-5000.

TH14 15 min 5:22
FTMW STUDY OF THE CHIRALITY RECOGNITION BETWEEN TWO DIFFERENT CHIRAL MOLECULES: THE GLYCIDOL-PROPYLENE OXIDE COMPLEX

Javix Thomas, Fumie X. Sunahori, Nicole Borho, and Yunjie Xu, Department of Chemistry, University of Alberta, Edmonton, AB, T6G 2G2, Canada.

TH15 15 min 5:39
MICROWAVE SPECTROSCOPY OF TRANS-ETHYL METHYL ETHER IN THE TORSIONALLY EXCITED STATE 3

Kaori Kobayashi, Keigo Murata, Shozo Tsunekawa, Department of Physics, University of Toyama, 3190 Gofuku, Toyama, 930-8555 Japan; and Nobukimi Ohashi, Kanazawa University, Japan.
TI. THEORY
TUESDAY, JUNE 22, 2010 – 1:30 pm
Room: 1015 McPHERSON LAB

Chair: RUSSELL PITZER, The Ohio State University, Columbus, Ohio

TI01 15 min 1:30
MODELING SIMULTANEOUS STARK AND ZEEMAN EFFECTS

WILTON L. VIRGO, KATHY J. CHEN and SARAH A. HYDE, Department of Chemistry, Wellesley College, Wellesley, MA 02481.

TI02 15 min 1:47
CHARACTERIZATION AND FORMATION PROCESSES OF $C_3^{-}$, $C_4H$ and $C_4H^-$

M.L. SENENT, Departamento de Astrofísica Molecular e Infrarroja, Instituto de Estructura de la Materia, C.S.I.C., Serrano 121, Madrid 28006, SPAIN; V. BRITES, M. HOCHLAF, Université Paris-Est, Laboratoire de Modélisation et Simulation Multi Echelle, MSME FRE 3160 CNRS, 5 boulevard Descartes, 77454 Marne-la-Vallée, FRANCE.

TI03 15 min 2:04
CHARACTERIZATION OF $C_3HSi^-$

N. INOSTROZA, Departamento de Astrofísica Molecular e Infrarroja, Instituto de Estructura de la Materia, C.S.I.C., Serrano 121, Madrid 28006, SPAIN; M.L. SENENT, Departamento de Astrofísica Molecular e Infrarroja, Instituto de Estructura de la Materia, C.S.I.C., Serrano 121, Madrid 28006, SPAIN.

TI04 10 min 2:21
AB INITIO INVESTIGATION OF NH$_3$-O$_2$ EXCIPLEX

L. M. HAUPERT, G. SIMPSON, AND L. V. SLIPCHENKO, Department of Chemistry, Purdue University, West Lafayette, IN 47907.

TI05 15 min 2:33
EQUILIBRIUM STRUCTURES OF MOLECULES FEATURING BONDS BETWEEN SECOND-ROW ELEMENTS

SVEN THORWIRTH, I. Physikalisches Institut, Universität zu Köln, Germany and Max-Planck-Institut für Radioastronomie, Bonn, Germany; MICHAEL E. HARDING, Institute for Theoretical Chemistry, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712, USA.

TI06 15 min 2:50
CALCULATION OF VIBRATIONAL ENERGY LEVELS: VPT2 VS. A VARIATIONAL APPROACH

M. E. HARDING, J. VÁZQUEZ, J. F. STANTON, Institute for Theoretical Chemistry, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712, USA.
TIO7 15 min 3:07
BOND-STRETCH ISOMERISM IN SFCI AND OTHER SULFUR HALIDES

JEFF LEIDING, DAVID E. WOON and THOM H. DUNNING, JR., Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana IL, 61801.

Intermission

TIO8 15 min 3:40
NEW METHODS FOR EXPLORING QM:MM POTENTIAL ENERGY LANDSCAPES

HRANT P. HRAITCHIAN, Gaussian, Inc., Wallingford, CT 06492, USA.

TIO9 15 min 3:57
DESCRIBING THE HYDRATED ELECTRON WITH A POLARIZABLE ELECTRON-WATER PSEUDOPOTENTIAL

LEIF D. JACOBSON, JOHN M. HERBERT, Department of Chemistry, The Ohio State University, Columbus, OH 43210.

TIO10 15 min 4:14
INSIGHTS INTO THE PA NEUTRAL ATOM: FROM AN EVALUATION OF PA^{2+} OUTER-CORE CORRELATION ENERGY CALCULATIONS

MICHAEL K. MROZIK, RUSSELL M. Pitzer, DEPT. OF CHEMISTRY, THE OHIO STATE UNIVERSITY; BRUCE E. BURSTEN, UNIVERSITY OF TENNESSEE-KNOXVILLE.

TIO11 15 min 4:31
CONNECTIONS BETWEEN THE RAYLEIGH-SCHRÖDINGER AND VAN VLECK PERTURBATION THEORIES AND THEIR APPLICATION TO RESONANCES IN MOLECULAR VIBRATIONS

D. A. MATTHEWS, J. VÁZQUEZ, AND J. F. STANTON, Institute for Theoretical Chemistry, The University of Texas at Austin, Austin, Texas 78712.

TIO12 15 min 4:48
NEW PERSPECTIVE ON PF_{n} (n=1–5) FROM THE RECOUPLED PAIR BONDING MODEL: A QUANTUM CHEMICAL STUDY

D. E. WOON and T. H. DUNNING, JR., Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

TIO13 15 min 5:05
A QUANTUM CHEMICAL STUDY OF FAMILIAR AND EXOTIC LOW-LYING SINGLET AND TRIPLET STATES OF CH_{2}, CF_{2}, AND CHF

LU XU, D. E. WOON, and T. H. DUNNING, JR., Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801.
APPLICATION OF THE RECOUPLED PAIR BONDING MODEL TO BOUND DOUBLET AND QUARTET STATES OF HSO, SOH, OSF AND SOF

TYLER Y. TAKESHITA, D. E. WOON, and T. H. DUNNING, JR., Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

THE SWITCHING/GAUSSIAN METHOD FOR POLARIZABLE CONTINUUM MODELS WITH APPLICATIONS TO AQUEOUS MOLECULAR DYNAMICS AND VIBRATIONAL SPECTRA

ADRIAN W. G. LANGE, JOHN M. HERBERT, 100 W. 18th Ave, Columbus, OH 43210.

DETERMINATION OF EXCITON LENGTH IN AQUEOUS B-DNA USING LONG-RANGE-CORRECTED TIME-DEPENDENT DENSITY FUNCTIONAL THEORY (LRC-TDDFT)

RYAN M. RICHARD, JOHN M. HERBERT, Department of Chemistry, The Ohio State University, Columbus, OH 43210.
NEW MICROWAVE SPECTRUM AND GLOBAL FIT OF METHYL ACETATE GROUND STATE

J. KLEINER, M. TUDORIE, Laboratoire Interuniversitaire des Systèmes Atmosphériques, CNRS et Universités Paris 7 et Paris 12, 61 av. Général de Gaulle, 94010, Créteil, France; J. T. HOUGEN, Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441, USA; S. MELANDRI, Dipartimento di Chimica "G. Ciamiciani", via Selmi 2, 40126 Bologna, Italy; W. STAHL, L. SUTIKDJIA, Institut für Physikalische Chemie, Raum 234, RWTH Aachen, Landoltweg 2 52062 Aachen.

3-D SUBMILLIMETER SPECTROSCOPY OF ASTRONOMICAL ‘WEEDS’ — EXPERIMENTAL AND THEORETICAL ASPECTS OF DATA PROCESSING AND CATALOGING

IVAN R. MEDVEDEV, SARAH M. FORTMAN, CHRISTOPHER F. NEESE, and FRANK C. DE LUCIA, Department of Physics, 191 W. Woodruff Ave., Ohio State University, Columbus, OH 43210 USA.

3-D SUBMILLIMETER SPECTROSCOPY OF ASTRONOMICAL ‘WEEDS’ – LATEST RESULTS

SARAH M. FORTMAN, IVAN R. MEDVEDEV, CHRISTOPHER F. NEESE, and FRANK C. DE LUCIA, Department of Physics, 191 W. Woodruff Ave., Ohio State University, Columbus, OH 43210 USA.

THE MICROWAVE SPECTRUM OF THE HCOOCD₂H SPECIES OF METHYL FORMATE

L. H. COUDERT, LISA, CNRS/Universités Paris Est et Paris Diderot, 61 Avenue du Général de Gaulle, 94010 Créteil, France; T. R. HUET, L. MARGULÉS, R. MOTIYENKO, Laboratoire PhLAM, UMR 8523 CNRS, Bât. P5, Université des Sciences et Technologies de Lille 1, 59655 Villeneuve d’Ascq Cedex, France; and H. MOLLENDAL, Centre for Theoretical and Computational Chemistry (CTCC), University of Oslo, P. O. Box 1033, Blindern, 0315 Oslo, Norway.

This work is supported by the ANR-08-BLAN-0054 and ANR-08-BLAN-0225 contracts.

THE ROTATION-TORSION SPECTRUM OF CH₂DOH

A. EL HILALI, L. H. COUDERT, LISA, CNRS/Universités Paris Est et Paris Diderot, 61 Avenue du Général de Gaulle, 94010 Créteil, France; L. MARGULÉS, R. MOTIYENKO, Laboratoire PhLAM, UMR 8523 CNRS, Bât. P5, Université des Sciences et Technologies de Lille 1, 59655 Villeneuve d’Ascq Cedex, France; and S. KLEE, Physikalisch-Chemisches Institut, Justus-Liebig-Universität Gießen, 35392 Gießen, Germany.

This work is supported by the ANR-08-BLAN-0225 contract.
THE TORSIONAL SPECTRUM OF MONO-DEUTERATED METHANOL CH$_2$DOH

A. EL HILALI, L. H. COUDERT, LISA, CNRS/Universités Paris Est et Paris Diderot, 61 Avenue du Général de Gaulle, 94010 Créteil, France; and S. KLEE, Physikalisch-Chemisches Institut, Justus-Liebig-Universität Gießen, 35392 Gießen, Germany.

Intermission

SUBMILLIMETER-WAVE SPECTRUM OF CH$_2$D$^+$

T. AMANO, Department of Chemistry and Department of Physics and Astronomy, University of Waterloo, Waterloo, ON, Canada N2L 3G1.

THE $J = 1 \leftarrow 0$ ROTATIONAL TRANSITIONS OF $^{12}$CH$^+$, $^{13}$CH$^+$ and $^{12}$CD$^+$

T. AMANO, Department of Chemistry and Department of Physics and Astronomy, University of Waterloo, Waterloo, ON, Canada N2L 3G1.

QUANTUM CHEMICAL PREDICTIONS OF THE DIPOLE MOMENTS AND DIPOLE POLARIZABILITIES FOR 200+ KNOWN AND POSTULATED NEUTRAL ASTROMOLECULES

D. E. WOON, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801; E. HERBST, Departments of Physics, Chemistry, and Astronomy, The Ohio State University, Columbus, OH 43210.

TERAHERTZ SPECTROSCOPY OF EXCITED WATER

SHANSHAN YU, JOHN C. PEARSON AND BRIAN J. DROUIN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109; ADAM WALTERS, Centre d’Etude Spatiale des Rayonnements, Université de Toulouse [UPS], CNRS [UMR 5187], 9 avenue du Colonel Roche, BP 44346, F-31028 Toulouse Cedex 4, France; HOLGER S.P. MÜLLER AND SANDRA BRÜNKEN, I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany.

COMPREHENSIVE SUBMILLIMETER WAVE STUDIES OF THE ISOTOPIC SPECIES OF A MAJOR WEED: METHYL FORMATE

L. MARGULÈS, R. MOTIYENKO, T. R. HUET, Laboratoire PhLAM, CNRS UMR 8523, Université de Lille 1, 59655 Villeneuve d’Ascq Cedex, France; L. H. COUDERT, I. KLEINER, LISA, CNRS UMR 7583, Université Paris 7 and Paris 12, 94010 Créteil Cedex France; M. CARVAJAL, Departamento de Fisica Aplicada, Universidad de Huelva, Spain; H. MOLLENDAL, Centre for Theoretical and Computational Chemistry (CTCC), University of Oslo, P. O. Box 1033, Blindern, NO-0315 Oslo, Norway; and J.-C. GUILLEMIN, Sciences Chimiques de Rennes-Ecole Nationale Supérieure de Chimie de Rennes-CNRS, 35700 Rennes, France.
SUBMILLIMETER WAVE SPECTROSCOPY AND ISM SEARCH FOR A CHIRAL MOLECULE: 2-AMINOPROPANENITRILE

L. MARGULÈS, R. MOTIYENKO, Laboratoire PhLAM, CNRS UMR 8523, Université de Lille 1, 59655 Villeneuve d’Ascq Cedex, France.; H. MOLLENDAL, Centre for Theoretical and Computational Chemistry (CTCC), University of Oslo, P. O. Box 1033, Blindern, NO-0315 Oslo, Norway; J.-C. GUILLEMIN, Sciences Chimiques de Rennes-Ecole Nationale Supérieure de Chimie de Rennes-CNRS, 35700 Rennes, France; and A. BELLOCHE, Max-Planck-Institut für Radioastronomie, Auf dem Hügel 69, D-53121 Bonn, Germany.

TERAHERTZ AND FIR SYNCROTRON SPECTRA OF METHYL MercAPTAN, CH₃SH

LI-HONG XU, R. M. LEES, Centre for Laser, Atomic and Molecular Sciences (CLAMS), Department of Physics, University of New Brunswick, Saint John, N.B., Canada E2L 4L5; H. S. P. MÜLLER, C. P. EN-DRES, O. BAUM, F. LEWEN, S. SCHLEMMER, I. Physikalisches Institut, Universität zu Köln, 50937 Köln; K. M. MENTEN, MPIfR, 53121 Bonn, Germany.

THE SUBMILLIMETER SPECTRUM OF GLYCOLALDEHYDE FROM 500 GHz TO 1.2 THz

P. BRANDON CARROLL, Department of Chemistry, Emory University, Atlanta, GA 30322; BRIAN J. DROUIN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, 91109; and SUSANNA L. WIDICUS WEAVER, Department of Chemistry, Emory University, Atlanta, GA 30322.

LABORATORY DETECTION OF THE TRANS-GAUCHE CONFORMER OF ETHYL FORMATE.

JUSTIN L. NEILL, MATT T. MUCKLE, DANIEL P. ZALESKI, AND BROOKS H. PATE, Department of Chemistry, University of Virginia, McCormick Rd., P.O. Box 400319, Charlottesville, VA 22904; V. LAT-TANZI, S. SPEZZANO, AND M.C. MCCARTHY, Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138, and School of Engineering & Applied Sciences, Harvard University, 29 Oxford St., Cambridge MA 02138.
WA. PLENARY

WEDNESDAY, JUNE 23, 2010 – 8:30 am

Room: AUDITORIUM, INDEPENDENCE HALL

Chair: MALCOLM CHISHOLM, The Ohio State University, Columbus, Ohio

<table>
<thead>
<tr>
<th>Session</th>
<th>Time</th>
<th>Title</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>WA01</td>
<td>40 min</td>
<td>HIGH RESOLUTION SPECTROSCOPY AND DYNAMICS: FROM JET COOLED RADICALS TO GAS-LIQUID INTERFACES</td>
<td>E. SHARP-WILLIAMS, M. A. ROBERTS, J. R. ROSCIOLI, A. W. GISLER, M. ZIEMKIEWICZ, D. J. NESBITT. JILA, University of Colorado and National Institute of Standards and Technology, Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0440; F. DONG, Los Gatos Research, 67 E. Evelyn Ave. Suite 3, Mountain View, CA 94041; B. G. PERKINS, JR., Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Ave Building 6-026, Cambridge, MA 02139.</td>
</tr>
<tr>
<td>WA02</td>
<td>40 min</td>
<td>GLOBAL CALCULATIONS USING POTENTIAL FUNCTIONS AND EFFECTIVE HAMILTONIAN MODELS FOR VIBRATION-ROTATION SPECTROSCOPY AND DYNAMICS OF SMALL POLYATOMIC MOLECULES</td>
<td>VLADIMIR TUYTEREV. Groupe de Spectrométrie Moléculaire et Atmosphérique, U.M.R. CNRS 6089, Université de REIMS, Moulin de la Housse, B.P. 1039, 51687 REIMS cedex 2, FRANCE.</td>
</tr>
<tr>
<td>WA03</td>
<td>40 min</td>
<td>PROBING FUNDAMENTAL PHYSICS WITH COLD AND ULTRACOLD MOLECULES</td>
<td>E.A. HINDS, B.E. SAUER, J.J. HUDSON, M.R. TARBU TT, D.M. KARA. Centre for Cold Matter, Imperial College London, SW7 2AZ.</td>
</tr>
</tbody>
</table>

Intermission

COBLENTZ AWARD

Presentation of Award by Ian Lewis, Kaiser Optical Systems

WA04  Coblentz Society Award Lecture

INTERROGATING HYDROCARBON RADICALS

TIMOTHY W. SCHMIDT. School of Chemistry, The University of Sydney, NSW 2006, Australia.
WF01 15 min 1:30
INCORPORATING DAMPING FUNCTIONS INTO THE MORSE/LONG-RANGE POTENTIAL FUNCTION FORM IMPROVES BOTH LONG-RANGE AND VERY SHORT-RANGE BEHAVIOUR

ROBERT J. LE ROY, CARL HAUGEN and JASON TAO, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

WF02 15 min 1:47
ELECTRONIC TRANSITIONS OF IRIDIUM MONOBORIDE

A. S-C. CHEUNG, H.F. PANG, Y.W. NG, AND G. CHEN, Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong.

WF03 15 min 2:04
ELECTRIC QUADRUPOLE TRANSITIONS IN THE $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ BAND OF OXYGEN: A CASE STUDY

J. E. GORDON, Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge MA 02138-1516, USA; S. KASSI, A. CAMPARGUE, Université Joseph Fourier/CNRS, Laboratoire de Spectrométrie Physique, 38402 Saint Martin d’Hères, FRANCE; G. C. TOON, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA.

WF04 15 min 2:21
OSCILLATOR STRENGTHS IN THE VISIBLE ABSORPTION SPECTRUM OF I$_2$

J. TELLINGHUISEN, Department of Chemistry, Vanderbilt University, Nashville, TN 37235.

WF05 15 min 2:38
ULTRAFAST PHOTOCHEMISTRY OF BROMOFORM IN SOLUTION PROBED IN THE DEEP-UV- TO NEAR-IR SPECTRAL RANGE

SUMAN KALYAN PAL, PATRICK EL-KHOURY, ANDREY SERGEEVICH MERESHCHENKO, AND ALEXANDER N. TARNOVSKY, Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio, USA.

WF06 15 min 2:55
X-RAY SPECTROSCOPY OF BROMINE COMPOUNDS AND BIOMEDICAL APPLICATIONS

SULTANA N. NAHAR, Dept of Astronomy, Ohio State University; YI LUO, LINH LE, Biophysics Program, Ohio State University; A.K. PRADHAN, Dept of Astronomy, Ohio State University; E. CHOWDHURY, Physics Dept, Ohio State University; R. PITZER, Dept of Chemistry,Ohio State University, Columbus, OH 43210; M. MONTENEGRO, Catholic University of Chile.
**WF07**

15 min 3:12

DUBLY HYDROGEN BONDED BIS-(4-HYDROXYPHENYL)METHANE DIMERS.

**CHIRANTHA P. RODRIGO, WILLIAM H. JAMES III, TIMOTHY S. ZWIER**, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-2084.*

**WF08**

15 min 3:29

NON-SYMMETRIC PUSH-PULL MOLECULES IN THE GAS PHASE: HIGH RESOLUTION STARK SPECTROSCOPY OF M-AMINOBENZOIC ACID.\(^a\)

**ADAM J. FLEISHER, PHILIP J. MORGAN and DAVID W. PRATT**, *Department of Chemistry, University of Pittsburgh, 15260.*

\(^a\)Work supported by NSF (CHE-0911117).

**WF09**

15 min 3:46

GAS PHASE ELECTRONIC SPECTROSCOPY OF 5-FLUOROSALICYLIC ACID.\(^a\)

**JUSTIN W. YOUNG, ADAM J. FLEISHER and DAVID W. PRATT**, *Department of Chemistry, University of Pittsburgh, Pa 15260.*

\(^a\)Work supported by NSF(CHE-0911117)

**WF10**

10 min 4:03

LASER INDUCED CHLOROPHYLL FLUORESCENCE SPECTRA OF CAJANUS CAJAN L PLANT GROWING UNDER CADMIUM STRESS

**RAM GOPAL**, *Laser Spectroscopy and Nanomaterial Lab, Department of Physics (UGC-CAS) University of Allahabad, Allahabad-211002, INDIA.; and J. K. PANDEY, M.N.Saha Center of Space Studies, IIDS, Nehru Science Center, University of Allahabad, Allahabad-211002, INDIA.*
### WG01 15 min 1:30

**Oscillator Strengths and Predissociation Rates for Rydberg Transitions in CO between 930 and 935 Å**

S. R. Federman, Y. Sheffer, Department of Physics and Astronomy, University of Toledo, Toledo, OH 43606; M. Eidelsberg, J. Lemaire, F. Rostas, Observatoire de Paris Meudon and Université de Cergy-Pontoise; J. H. Fillion, Université UMPC, Paris VI.

*The authors acknowledge the support of the SOLEIL synchrotron facility through time allocation and the DESIRS beam-line team. This work was funded in part by NASA and the CNRS-PCMI program.*

### WG02 15 min 1:47

**Exotic Metal Molecules in Oxygen-Rich Envelopes: Detection of AlOH (X^1Σ^+) in VY Canis Majoris**

E. D. Tenenbaum and L. M. Ziurys, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.

### WG03 15 min 2:04

**Confirmation of KCN in the Circumstellar Envelope of IRC+10216**

R. L. Pulliam, L. M. Ziurys, Department of Chemistry and Biochemistry, Department of Astronomy, Steward Observatory, University of Arizona, Tucson, AZ 85721; C. Savage, Applied Electromagnetics (IAT-2), Los Alamos National Laboratory, Los Alamos, NM 87545.

### WG04 10 min 2:21

**CS and HCO⁺ in Planetary Nebulæ**


### WG05 15 min 2:33

**Comparing the Ortho-to-Para Ratios of H₂ and H₃⁺ in Diffuse Interstellar Clouds**

Nick Indriolo, Department of Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801; Takeshi Oka, Department of Astronomy & Astrophysics and Department of Chemistry, University of Chicago, Chicago, IL 60637; Thomas R. Geballe, Gemini Observatory, Hilo, HI 96720; Kenneth H. Hinkle, National Optical Astronomy Observatories, Tucson, AZ 85726; Geoffrey A. Blake, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125; Benjamin J. McCall, Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801.
THE NEARLY PERFECT CORRELATION BETWEEN THE DIFFUSE INTERSTELLAR BANDS \( \lambda\lambda 6196.0 \) AND \( 6613.6 \)

BENJAMIN J. McCall, University of Illinois at Urbana-Champaign, Urbana, IL 61801; MEREDITH M. DROSBACK, University of Virginia, Charlottesville, VA 22904; JULIE A. THORBURN, Carthage College, Kenosha, WI 53140; DONALD G. YORK, University of Chicago, Chicago, IL 60637; SCOTT D. FRIEDMAN, Space Telescope Science Institute, Baltimore, MD 21218; LEWIS M. HOBBS, University of Chicago, Yerkes Observatory, Williams Bay, WI 53191; BRIAN L. RACHFORD, Embry-Riddle Aeronautical University, Prescott, AZ 86301; THEODORE P. SNOW, University of Colorado, Boulder, CO 80309; PAULE SONNENTRUCKER, Johns Hopkins University, Baltimore, MD 21218; DANIEL E. WELTY, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

A NEW ATLAS OF THE DIFFUSE INTERSTELLAR BANDS: HD 183143

LEWIS M. HOBBS, University of Chicago, Yerkes Observatory, Williams Bay, WI 53191; DONALD G. YORK, University of Chicago, Chicago, IL 60637; JULIE A. THORBURN, Carthage College, Kenosha, WI 53140; THEODORE P. SNOW, University of Colorado, Boulder, CO 80309; MICHAEL BISHOF, University of Chicago, Chicago, IL 60637; SCOTT D. FRIEDMAN, Space Telescope Science Institute, Baltimore, MD 21218; BENJAMIN J. McCall, University of Illinois at Urbana-Champaign, Urbana, IL 61801; TAKESHI OKA, University of Chicago, Chicago, IL 60637; BRIAN L. RACHFORD, Embry-Riddle Aeronautical University, Prescott, AZ 86301; PAULE SONNENTRUCKER, Johns Hopkins University, Baltimore, MD 21218; DANIEL E. WELTY, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

NH AND CH IN THE ACE SATELLITE SOLAR SPECTRUM

P. F. BERNATH, Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK; R. S. RAM, Department of Chemistry, University of Arizona, Tucson, AZ 85721, USA; R. COLIN, Service de Chimie Quantique et Photophysique, Université Libre de Bruxelles (ULB), 50, av. F.D. Roosevelt, 1050 Brussels, Belgium.

THE GAS-PHASE SPECTRA OF RESONANCE-STABILIZED RADICALS AND THE RED RECTANGLE EMISSION

NAHID CHALYAVI, TYLER P. TROY, MASAKAZU NAKAJIMA, KLAAS NAUTA, SCOTT H. KABLE, and TIMOTHY W. SCHMIDT, School of Chemistry, The University of Sydney, NSW 2006, Australia.

MOLECULAR HYDROGEN FORMATION IN THE EARLY UNIVERSE: NEW IMPLICATIONS FROM LABORATORY MEASUREMENTS

HOLGER KRECKEL\(^a\), HJALMAR BRUHNS, KENNETH A. MILLER, DANIEL W. SAVIN, Columbia Astrophysics Laboratory, Columbia University, New York, NY 10027, USA; MARTIN CIZEK, Charles University Prague, Faculty of Mathematics and Physics, Institute of Theoretical Physics, 180 00 Praha 8, Czech Republic; SIMON C.O. GLOVER, Zentrum für Astronomie der Universität Heidelberg, Institut für Theoretische Astrophysik, 69120 Heidelberg, Germany; XAVIER URBAIN, Department of Physics/PAMO, Université Catholique de Louvain, Louvain-la-Neuve B-1348, Belgium.

\(^a\)Present address: Department of Chemistry, University of Illinois, Urbana, IL 61801, USA, Email: hkreckel@illinois.edu
WH. MICROWAVE (ROTATIONAL)
WEDNESDAY, JUNE 23, 2010 – 1:30 pm
Room: 1000 McPHERSON LAB

Chair: STEPHEN COOKE, University of North Texas, Denton, Texas

WH01 15 min 1:30
MICROWAVE STUDY OF A HYDROGEN-TRANSFER-TRIGGERED METHYL-GROUP INTERNAL ROTATION IN 5-METHYLTROPOLONE

VADIM V. ILYUSHIN, INSTITUTE OF RADIO ASTRONOMY OF NASU, CHERVONOPRAPORNA 4, 61002 KHARKOV, UKRAINE; EMILY A. CLOESSNER, DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY, COLLEGE OF CHARLESTON, CHARLESTON, SC 29424, USA; YUNG-CHING CHOU, DEPARTMENT OF NATURAL SCIENCE, TAIPEI MUNICIPAL UNIVERSITY OF EDUCATION, TAIPEI 10048, TAIWAN; LAURA B. PICRAUX, SUN CHEMICAL, CINCINNATI, OH 45232, USA; JON T. HOUGEN, OPTICAL TECHNOLOGY DIVISION, NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY, GAITHERSBURG, MD 20899-8441, USA; RICHARD LAVRICH, DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY, COLLEGE OF CHARLESTON, CHARLESTON, SC 29424, USA.

WH02 10 min 1:47
ROTATIONAL SPECTRA AND MOLECULAR CONFORMATION OF TWO CONFORMERS OF LEUCINAMIDE

ANDREW R. CONRAD and MICHAEL J. TUBERGEN, Department of Chemistry, Kent State University, Kent, Ohio 44242; RICHARD J. LAVRICH, Department of Chemistry and Biochemistry, College of Charleston, 66 George Street, Charleston, South Carolina 29424.

WH03 15 min 1:59
MICROWAVE SPECTRUM, STRUCTURAL PARAMETERS AND QUADRUPOLE COUPLING FOR AZABORINE AND 1-ETHYL-AZABORINE

ADAM DALY, STEPHEN G. KUKOLICH, Department of Chemistry and Biochemistry, The University of Arizona, Tucson, Arizona 85721; CHAKREE TANJAROON, Department of Chemistry and Physics, Arkansas State University, Jonesboro, AR 72467; ADAM J. V. MARWITZ and SHIH-YUAN LIU, Department of Chemistry, University of Oregon, Eugene, OR 97403.

*Supported by THE NATIONAL SCIENCE FOUNDATION

WH04 15 min 2:16
ROTATIONAL INVESTIGATION OF TROPANE ALKALOIDS

EMILIO J. COCINERO, Departamento de Química Física, Universidad del País Vasco, 48080 Bilbao, Spain; ALBERTO LESARRI, Departamento de Química Física y Química Inorgánica, Universidad de Valladolid, 47011 Valladolid, Spain; PATRICIA ECJIA, Departamento de Química Física, Universidad del País Vasco, 48080 Bilbao, Spain; JENS-UWE GRABOW, Institut für Physikalische Chemie und Elektrochemie, Gottfried-Wilhelm-Leibniz-Universität Hannover, Callinstrasse 3A, 30167 Hannover, Germany; JOSE A. FERNÁNDEZ, FERNANDO CASTANO, Departamento de Química Física, Universidad del País Vasco, 48080 Bilbao, Spain.
WH05 10 min 2:33
CONFORMATIONAL LANDSCAPE OF NICOTINOIDS: SOLVING THE "CONFORMATIONAL DISPARITY" OF ANABASINE

ALBERTO LESARRI, Departamento de Química Física y Química Inorgánica, Universidad de Valladolid, 47011 Valladolid, Spain; EMILIO J. COCINERO, Departamento de Química Física, Universidad del País Vasco, 48080 Bilbao, Spain; LUCA EVANGELISTI, Dipartimento di Chimica "G. Ciamiciam", Università di Bologna, 40126 Bologna, Italy; RICHARD D. SUENRAM, Department of Chemistry, University of Virginia, Charlottesville, VA 22904, USA; WALther CAMINAtI, Dipartimento di Chimica "G. Ciamiciam", Università di Bologna, 40126 Bologna, Italy; JENs-UWE GRABOW, Institut für Physikalische Chemie und Elektrochemie, Gottfried-Wilhelm-Leibniz-Universität Hannover, Callinstraße 3A, 30167 Hannover, Germany.

WH06 15 min 2:45
MICROWAVE SPECTROSCOPY OF ALKALOIDS: THE CONFORMATIONAL SHAPES OF NICOTINE


WH07 15 min 3:02
LARGE AMPLITUDE MOTIONS AND INFORMATION TRANSFER ALONG CONJUGATED BONDS: THE CASE OF PARATOLUALDEHYDE

HILKKA SAAL, JENS-UWE GRABOW, Gottfried-Wilhelm-Leibniz-Universität, Institut für Physikalische Chemie und Elektrochemie, Lehrgebiet A, Callinstraße 3A, D-30167 Hannover, Germany; ANGELA R. HIGHT-WALKER, JON T. HOUGEN, Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441, USA; WALther CAMINAtI, Universita di Bologna, Dipartimento di Chimica G. Ciamiciam, via F. Selmi 2, 40126 Bologna, Italy; ISABELLE KLEINER, Laboratoire Interuniversitaire des Systèmes Atmosphériques, CNRS et Universités Paris 7 et Paris 12, 61 av. Général de Gaulle, 94010, Créteil, France.

WH08 15 min 3:19
DDS-BASED FAST SCAN SPECTROMETER

E. A. ALEKSEEV, Institute of Radio Astronomy of NASU, Chervonopraporna 4, 61002 Kharkov, Ukraine; R. A. MOTIYENKO, L. MARGULÈS, Laboratoire PhLAM, CNRS UMR 8523, Université de Lille 1, 59655 Villeneuve d’Ascq Cedex, France.

WH09 15 min 3:36
PROGRESS TOWARDS CHIRPED-PULSE FOURIER TRANSFORM THZ SPECTROSCOPY

KEVIN O. DOUGLASS, DAVID F. PLUSQUELLIC, NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY, OPTICAL TECHNOLOGY DIVISION, GAITHERSBURG, MD 20899; EYAL GERECHT, NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY, ELECTROMAGNETICS DIVISION, BOULDER, CO 80305.
EXPERIMENTAL DETERMINATION OF THE ROTATIONAL PARTITION FUNCTION BY A PASSIVE SPECTROMETER

HIROYUKI OZEKI, H. ISHIWATA, Department of Environmental Science, Toho University, Funabashi 274-8510, Japan; KAORI KOBAYASHI, Department of Physics, University of Toyama, 3190 Gofuku, Toyama, 930-8555 Japan; K. KIKUCHI, T. YAMADA, M. MAEZAWA, and S. KOHJIRO, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8568, Japan.
WI. MINI-SYMPOSIUM: METAL CONTAINING MOLECULES

WEDNESDAY, JUNE 23, 2010 – 1:30 pm

Room: 1015 McPHERSON LAB

Chair: J. MATHIAS WEBER, JILA, University of Colorado, Boulder, Colorado

WI01 INVITED TALK

UNUSUAL BONDING MECHANISMS IN BERYLLIUM COMPOUNDS

IVAN O. ANTONOV, BEAU J. BARKER, VLADIMIR E. BONDBEY, JEREMY M. MERRITT and MICHAEL C. HEAVEN, Department of Chemistry, Emory University, Atlanta, GA 30322.

WI02

PFI-ZEKE SPECTROSCOPY OF Be₂O

I. O. ANTONOV, M. C. HEAVEN, Department of Chemistry, Emory University, Atlanta, GA 30322.

WI03

VIBRATIONAL SPECTROSCOPY OF BINARY METAL OXIDE CLUSTERS

L. JIANG, T. WENDE, G. MEIJER, K. R. ASMIS, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany; P. CLAES, S. BHATTACHARYA, P. LIEVENS, Laboratorium voor Vaste-Stoffysica en Magnetisme, Katholieke Universiteit Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium.

WI04

ELECTRONIC SPECTROSCOPY OF Li(NH₃)₄

N. BHALLA, L. VARRIALE, N. M. TONGE, A. M. ELLIS, Department of Chemistry, University of Leicester, Leicester, LE1 7RH, United Kingdom.

WI05

ACCIDENTAL CONICAL INTERSECTIONS IN MIXED TRIMERS OF POTASSIUM AND RUBIDIUM: A VIBRONIC ANALYSIS OF THE 4⁴B₂ AND 3⁴A₁ STATES

A. W. HAUSER, G. AUBÖCK, C. CALLEGARI and W. E. ERNST, Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria.

*present address: Sincrotrone Trieste, Strada Statale 14 - km 163.5, 34149 Basovizza, Trieste, Italy

WI06

FEMTOSECOND SPECTROSCOPY OF ALKALI TRIMERS ON HELIUM NANODROPLETS

C. GIESE, B. GRÜNER, L. FECHNER, M. MUDRICH, F. STIENKEMEIHER, Physikalisches Institut, Universitat Freiburg, Hermann-Herder-Strasse 3, 79104 Freiburg, Germany; A. W. HAUSER and W. E. ERNST, Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria.
W107
GROWING OF METAL-MOLECULE CLUSTERS IN HELIUM DROPLETS

EVGENY LOGINOV, LUIS GOMEZ and ANDREY VILESOV, Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482.

W108
IR SPECTRA OF LARGE TAILOR-MADE Ag-MOLECULE (METHANE, ETHANE, ETHYLENE, ACETYLENE) CLUSTERS PRODUCED IN HELIUM NANODROPLETS

EVGENY LOGINOV, LUIS GOMEZ and ANDREY VILESOV, Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482.
WJ01 15 min 1:30
ROVIBRONIC INTERACTIONS IN NO₃: HISTORICAL OVERVIEW, PRESENT STATUS AND FUTURE PROSPECT OF HIGH-RESOLUTION SPECTROSCOPIC STUDIES

EIZI HIROTA, The Graduate University of Advanced Studies, Hayama, Kanagawa 240-0293, Japan; KENTAROU KAWAGUCHI, Department of Chemistry, Faculty of Science, Okayama University, 3-1-1, Tsushima-Naka, Okayama 700-8530, Japan; TAKASHI ISHIWATA, Graduate School of Information Sciences, Hiroshima City University, 3-4-1 Otsuka-Higashi, Hiroshima 731-3194, Japan.

WJ02 15 min 1:47
HIGH-ACCURACY DIABATIC TREATMENT OF NO₃ ENERGY LEVELS

JOHN F. STANTON, Department of Chemistry & Biochemistry, The University of Texas at Austin, 1 University Station A5300 Austin, TX 78712.

WJ03 15 min 2:04
SOLVING THE PUZZLE OF TETRATICOM, 23-VALENCE-ELECTRON MOLECULES

MARILYN E. JACOX, Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441.

WJ04 15 min 2:21
JET-COOLED CAVITY RING-DOWN SPECTROSCOPY OF THE $\tilde{A}^2E'' \rightarrow \tilde{X}^2A'_2$ VIBRONIC TRANSITION OF NO₃

MING-WEI CHEN, GABRIEL M. P. JUSTa, TERRANCE CODD, and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210.

a presents address: Lawrence Berkeley National Laboratory, Lawrence Berkeley National Laboratory

WJ05 15 min 2:38
ULTRAHIGH-RESOLUTION SPECTROSCOPY AND THE ZEEMAN EFFECT OF THE $B^2E' \leftarrow X^2A'_2$ TRANSITION OF NITRATE RADICAL NO₃

SHUNJI KASAHARA, KOHEI TADA, Molecular Photoscience Research Center, Kobe University, Kobe 657-8501, Japan; MASAAKI BABA, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan; TAKASHI ISHIWATA, Faculty of Information Sciences, Hiroshima City University, Hiroshima 731-3194, Japan; EIZI HIROTA, The Graduate University for Advanced Studies, Kanagawa 240-0193, Japan.

WJ06 15 min 2:55
INSIGHT INTO THE JAHN-TELLER EFFECT IN THE NITRATE RADICAL VIA THE A-X HOT BANDS

KANA TAKEMATSU, NATHAN EDDINGSAAS, and MITCHIO OKUMURA, Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125; JOHN STANTON, Department of Chemistry, University of Texas at Austin, Austin, TX 78712.
FTIR SPECTROSCOPY OF NO$_3$: OBSERVATION AND ANALYSIS OF THE 1127 cm$^{-1}$ BAND.

K. KAWAGUCHI, N. SHIMIZU, R. FUJIMORI, Department of Chemistry, Faculty of Science, Okayama University, 3-1-1, Tsushima-Naka, Okayama 700-8530, JAPAN; T. ISHIWATA, Graduate School of Information Sciences, Hiroshima City University, 3-4-1 Otuka-Higashi, Hiroshima 731-3194, JAPAN; I. TANAKA, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro, Tokyo 152-8550, Japan; and E. HIROTA, The Graduate University for Advanced Studies, Hayama, Kanagawa 240-0193, JAPAN.

NUCLEAR SPIN DEPENDENCE OF THE REACTION OF H$_3^+$ WITH H$_2$

KYLE N. CRABTREE, BRIAN A. TOM, CARRIE A. KAUFFMAN, BENJAMIN J. McCALL, Department of Chemistry, University of Illinois, Urbana, IL 61801.  

*Current Address: Department of Chemistry, United States Air Force Academy, CO 80840

FOURIER TRANSFORM INFRARED EMISSION SPECTROSCOPY AND AB INITIO STUDY OF HBO AND BO

G. LI, R. J. HARGREAVES, and P. F. BERNATH, Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK.

INFRARED PHOTODISSOCIATION SPECTROSCOPY OF HYDROGEN CLUSTERS

T. C. CHENG, B. BANDYOPADHYAY, M.A. DUNCAN, Department of Chemistry, University of Georgia, Athens, GA 30602-2556; Y. WANG, S. CARTER, B.J. BASTIAAN J.M. BOWMAN, Department of Chemistry, Emory University, Atlanta, GA 30322.
WK. COMMEMORATIVE SESSION
JUNE 23, 2010 – 5:00 pm
Room: FAWCETT CENTER AUDITORIUM

Chair: FRANK DE LUCIA, The Ohio State University, Columbus, Ohio

Greeting
Gordon Gee, President
The Ohio State University

WK01 20 min 5:05
65 SCARLET AND GRAY BOOKLETS

BRENDA P. WINNEWISER, Department of Physics, The Ohio State University, Columbus, Ohio 43210.

WK02 20 min 5:30
THE SYMPOSIUM: A PERSONAL PERSPECTIVE

ROBERT CURL, Department of Chemistry and Rice Quantum Institute, Rice University, Houston, TX 77005, USA.

WK03 20 min 5:55
HIGH PRECISION IN AN IMPRECISE WORLD: THE IMPORTANCE OF THE MOLECULAR SPECTROSCOPY SYMPOSIUM TO THE ARMY

DAVID SKATRUD, Army Research Office, Research Triangle Park, NC, 27709-2211.

WK04 20 min 6:20
POTENTIAL REWARDS FROM THE BEGINNING TO THE END OF A SPECTROSCOPIC CAREER DERIVED FROM ATTENDANCE AT A GRADUATE-STUDENT AND POSTDOCTORAL-FELLOW ORIENTED SYMPOSIUM

JON T. HOUGEN, OPTICAL TECHNOLOGY DIVISION, NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY, GAITHERSBURG, MD 20899-8441, USA.
RA01  15 min  8:30
INTERSYSTEM CROSSING: A STEP BEYOND STATISTICS


RA02  15 min  8:47
COLLISIONAL X- AND A-STATE KINETICS OF CN USING TRANSIENT SUB-DOPPLER HOLE BURNING

MICHAEL L. HAUSE, TREvor J. SEARS, and GREGORY E. HALL, Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973-5000.

RA03  15 min  9:04
AMMONIA CLUSTER DISSOCIATION VIA NH STRETCH EXCITATION

AMANDA S. CASE, CORNELIA G. HEID and F. FLEMING CRIM, The University of Wisconsin-Madison, Department of Chemistry, 1101 University Avenue, Madison, WI 53706.

RA04  15 min  9:21
PHOTODISSOCIATION DYNAMICS OF THE S\(_1\) AND S\(_2\) STATES OF CH\(_3\)ONO: ENERGY DISTRIBUTION IN THE CH\(_3\)O PHOTOFRAGMENT

CHRISTOPHER J. ANNESLEY, ANDREW E. BERKE, F. FLEMING CRIM, Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706.

RA05  15 min  9:38
DIFFUSION MONTE CARLO CALCULATIONS OF MINIMUM ENERGY PATHS FOR THE ISOTOPIC VARIANTS OF THE CH\(_3\) + H\(_2\) ↔ CH\(_3\)H ↔ CH\(_3\)H + H\(_2\) REACTION

CHARLOTTE E. HINKLE, ANNE B. McCoy, Department of Chemistry, The Ohio State University, Columbus, OH 43210.

RA06  15 min  9:55
TIME-RESOLVED PHOTOELECTRON STUDIES OF IBr\(^-\): A CLASSICAL AND QUANTUM TUG-OF-WAR

SAMANTHA HORVATH and ANNE B. McCoy, Department of Chemistry, The Ohio State University, Columbus, OH 43210.

RA07  15 min  10:12
HYDROGEN EXCHANGE BEFORE DISSOCIATION IN THE PHOTOLYSIS OF ACETALDEHYDE: A NON-TRANSITION STATE MECHANISM.

Intermission

RA08  10 min  10:45

VELOCITY-MAPPED ION IMAGING OF METHYL NITRITE PHOTODISSOCIATION

NICLAS A. WEST, AIDAN J. KLOBUCHAR, JEFFREY A. BARTZ, Department of Chemistry, Kalamazoo College, 1200 Academy Street, Kalamazoo, MI 49006.

RA09  10 min  10:57

PHOTODISSOCIATION OF METHYL NITRITE FROM THE S2 STATE – ION IMAGES AND VECTOR CORRELATIONS

AIDAN J. KLOBUCHAR and JEFFREY A. BARTZ, Department of Chemistry, Kalamazoo College, 1200 Academy Street, Kalamazoo, MI 49006.

RA10  15 min  11:09

ROTATIONAL DEPENDENCE OF INTRAMOLECULAR DYNAMICS IN ACETYLENE AT LOW VIBRATIONAL EXCITATION AS DEDUCED FROM HIGH RESOLUTION SPECTROSCOPY

DAVID S. PERRY, ANTHONY MILLER, Department of Chemistry, The University of Akron, Akron OH 44325-3601; B. AMYAY, A. FAYT, and M. HERMAN, Laboratoire de Chimie Quantique et Photophysique, Université libre de Bruxelles, B-1050 Brussels, Belgium.

RA11  15 min  11:26

ROTATIONAL AND VIBRATIONAL ENERGY TRANSFER FROM THE FIRST OVERTONE STRECH OF ACETYLENE

M. C. HEAVEN, JIANDE HAN, and KEITH FREEL, Department of Chemistry, Emory University, Atlanta, GA 30322.

RA12  15 min  11:43

PHOTODISSOCIATION DYNAMICS OF THE PHENYL RADICAL VIA PHOTOFRAGMENT TRANSLATIONAL SPECTROSCOPY

BOGDAN NEGRU, SCOTT J. GONCHER, AMY L. BRUNSVOLD, DANIEL M. NEUMARK, College of Chemistry, University of California, Berkeley, California 94720, and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA.
RB. MINI-SYMPOSIUM: BIOMOLECULES AND CLUSTER IONS  
THURSDAY, JUNE 24, 2010 – 8:30 am  
Room: 170 MATH ANNEX  
Chair: THOMAS RIZZO, Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland

RB01  INVITED TALK - Abstract Rescheduled at Authors’ Request  30 min  8:30
COMBINING LASER SPECTROSCOPY AND MASS SPECTROMETRY FOR CONFORMATION-SPECIFIC STUDIES OF GAS-PHASE BIOMOLECULES

THOMAS R. RIZZO, OLEG V. BOYARKIN, JAIME A. STEARNS, MONIA GUIDI, CAROLINE SEAIBY, NATALIA NAGORNova and ANNETTE SVENDSEN, Laboratoire de chimie physique moléculaire (LCPM), École polytechnique fédérale de Lausanne, CH-1015 Lausanne, Switzerland.

RB02  15 min  9:05
EXAMINATION OF H₂CO–X⁺ AND NH₂CH₂COOH–X⁺ COMPLEXES [X⁺ = Li⁺, Na⁺, K⁺] USING ELECTRONIC STRUCTURE THEORY

ANNIE L. LESIAK, SAMANTHA HORVATH, and ANNE B. McCOY, Department of Chemistry, The Ohio State University, Columbus, OH 43210.

RB03  15 min  9:22
ORIGINS OF IR INTENSITY IN OVERTONES AND COMBINATION BANDS IN HYDROGEN BONDED SYSTEMS

SAMANTHA HORVATH and ANNE B. McCOY, Department of Chemistry, The Ohio State University, Columbus, OH 43210.

RB04  15 min  9:39
VIBRATIONAL PREDISSOCIATION SPECTRA IN THE SHARED PROTON REGION OF PROTONATED FORMIC ACID WIRES

HELEN GERARDI, CHRIS LEAVITT, and MARK JOHNSON, Yale University, Department of Chemistry, New Haven, CT.

RB05  15 min  9:56
TRIGGERING INTRA-CLUSTER ELECTRON CAPTURE WITH VIBRATIONAL EXCITATION: AN IR STUDY OF THE CH₃NO₂(H₂O)₆ ANION

KRISTIN J. BREEN, TIMOTHY L. GUASCO and MARK A. JOHNSON, Sterling Chemistry Laboratory, Yale University, PO Box 208107, New Haven, CT 06520.

Intermission

RB06  INVITED TALK  30 min  10:30
FOLDAMERS, CROWNS, AND WATER: CONNECTIONS BETWEEN ISOLATED MOLECULES AND SOLUTION-PHASE BEHAVIOR

WILLIAM H. JAMES III, EVAN G. BUCHANAN, CHRISTIAN W. MÜLLER , and TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN 47907; LI GUO, and SAMUEL H. GELL-MAN, Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706.
RB07 15 min 11:05
HYDRATION OF A LARGE ANIONIC CHARGE DISTRIBUTION - NAPHTHALENE-WATER CLUSTER ANIONS

J. MATHIAS WEBER, CHRISTOPHER L. ADAMS, JILA, NIST, and Department of Chemistry and Bio-
chemistry, University of Colorado at Boulder, 440 UCB, Boulder, CO 80309-0440, USA.

RB08 15 min 11:22
LASER SPECTROSCOPIC STUDY ON ENCAPSULATION STRUCTURE OF FUNCTIONAL MOLECULES IN SU-
PERSONIC JETS

T. EBATA, Department of Chemistry, Graduate School of Science, Hiroshima University, Higashi-Hiroshima,
739-8526, Japan.

RB09 15 min 11:39
CONFORMATION-SPECIFIC INFRARED AND ULTRAVIOLET SPECTROSCOPY OF DIBENZO-15-CROWN-5-
(H₂O)₁-CLUSTER: RESHAPING A BINDING POCKET

EVAN G. BUCHANAN, CHIRANTHA P. RODRIGO, ANNA K. GUTBERLET and TIMOTHY S. ZWIER,
Department of Chemistry, Purdue University, West Lafayette, IN 47907.

RB10 15 min 11:56
CONFORMATION-SPECIFIC SPECTROSCOPY OF A PROTOTYPICAL γ-PEPTIDE-WATER COMPLEX: Ac-γ²-
hPhe-NHMe-(H₂O)₁

EVAN G. BUCHANAN, WILLIAM H. JAMES III, and TIMOTHY S. ZWIER, Department of Chemistry,
Purdue University, West Lafayette, IN 47907; LI GUO, and SAMUEL H. GELLMAN, Department of Chem-
istry, University of Wisconsin-Madison, Madison, WI 53706.
RC01 10 min 8:30
MICROWAVE SPECTRUM OF $^{12}\text{C}^{16}\text{O}$

S.A. TASHKUN, S.N. MIKHAILENKO, Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, 634055, Tomsk, RUSSIA.

RC02 15 min 8:42
CAN THE INVERSION-VIBRATION-ROTATION PROBLEM IN THE $\nu_1$ AND $2\nu_2$ STATES OF NH$_3$ BE SOLVED TO EXPERIMENTAL ACCURACY?

J.C. PEARSON, S. YU and B.J. DROUIN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109, USA; O. PIRALI, M.-A. MARTIN, M. VERVLOET and D. BALCON, Ligne AILES–Synchrotron SOLEIL, L’Orme des Merisiers Saint-Aubin, 91192 Gif-sur-Yvette, France; C. P. EN-DRES, I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany.

RC03 15 min 8:59
THz SPECTROSCOPY OF THE $a^1\Delta_g$ STATE OF O$^{18}$O and $^{18}$O$_2$.

HARSHAL GUPTA, SHANSHAN YU, BRIAN J. DROUIN, AND CHARLES E. MILLER, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109; HOLGER S. P. MÜLLER, I. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, Köln, Germany.

RC04 10 min 9:16
FOURIER TRANSFORM MICROWAVE LABORATORY DETECTION OF HSiNH$_2$

VALERIO LATTANZI, M.C. McCARTHY, P. THADDEUS, Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, and School of Engineering and Applied Science, Harvard University, Cambridge, MA 02138; and SVEN THORWIRTH, Max-Planck-Institut für Radioastronomie, Bonn, Germany, and I. Physikalisches Institut, Universität zu Köln, Germany.

RC05 10 min 9:28
SILICON-PHOSPHORUS BONDING: LABORATORY DETECTION OF HPSiH$_2$ EMPLOYING HIGH RESOLUTION MICROWAVE SPECTROSCOPY

VALERIO LATTANZI, M.C. McCARTHY, P. THADDEUS, Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, and School of Engineering and Applied Science, Harvard University, Cambridge, MA 02138; and SVEN THORWIRTH, Max-Planck-Institut für Radioastronomie, Bonn, Germany, and I. Physikalisches Institut, Universität zu Köln, Germany.

RC06 15 min 9:40
CHIRPED PULSE FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF SnCl

GARRY S. GRUBBS II AND STEPHEN A. COOKE, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH TEXAS, 1155 UNION CIRCLE #305070, DENTON, TX 76203-5017, U.S.A.
HYPERFINE STRUCTURE IN THE PURE ROTATIONAL SPECTRUM OF $^{208}\text{Pb}^{35}\text{Cl}$

CHRISTOPHER T. DEWBERRY, GARRY S. GRUBBS II, KERRY C. ETCHISON AND STEPHEN A. COOKE, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH TEXAS, 1155 UNION CIRCLE #305070, DENTON, TX 76203-5017, U.S.A.

THE MILLIMETER/SUBMILLIMETER SPECTRUM OF CYANOPHOSPHINE, $\text{PH}_2\text{CN}$ ($\tilde{X}^1\text{A}^\prime$)

D. T. HALFEN, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721; D. J. CLOUTHIER, Department of Chemistry, University of Kentucky, Lexington, KY 40506; and L. M. ZIURYS, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.

HIGH-RESOLUTION MICROWAVE SPECTROSCOPY OF IMINOSILICON, HNSI

M. C. MCCARTHY, P. THADDEUS, Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, U.S.A. and School of Engineering and Applied Sciences, Harvard University, 29 Oxford Street, Cambridge, MA 02138, U.S.A.; FILIPPO TAMASSIA, Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna, Vle Risorgimento 4, I-40136 Bologna, Italy; S. THORWIRTH, Max-Planck-Institut für Radioastronomie, 53121 Bonn, Germany, and I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany.

MICROWAVE SPECTRUM AND AB INITIO CALCULATIONS FOR DIFLUOROSILYL ISOCYANATE, HF$_2$SiNCO

SEAN A. PEEBLES, DANIEL A. OBENCHAIN and REBECCA A. PEEBLES, Department of Chemistry, Eastern Illinois University, 600 Lincoln Avenue, Charleston, IL 61920; MICHAEL H. PALMER, School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK; GAMIL A. GUIRGIS, ZICHAO WANG and JONEL LIRJONI, Department of Chemistry and Biochemistry, College of Charleston, Charleston, SC 29424.

ANOMALOUS HYPERFINE STRUCTURE OF NSF$_3$ IN THE DEGENERATE VIBRATIONAL STATE $v_5=1$: LIFTING OF THE PARITY DEGENERACY BY THE FLUORINE SPIN-ROTATION INTERACTION

H. HARDER, S. MACHOLL, H. MAEDER, Institut für Physikalische Chemie, Universität Kiel, 24098 Kiel, Germany; L. FUSINA, Dipartimento di Chimica Fisica e Inorganica, Università di Bologna, 40136 Bologna, Italy; I. OZIER, Department of Physics and Astronomy, University of British Columbia, BC V6T 1Z1, Canada.

TOWARD A GLOBAL MODEL OF LOW-LYING VIBRATIONAL STATES OF CH$_3$CN: THE $v_4 = 1$ STATE AT 920 cm$^{-1}$ AND ITS INTERACTIONS WITH NEARBY STATES

HOLGER S. P. MÜLLER, I. Physikalisches Institut, Universität zu Köln, 50937 Köln; B. J. DROUIN, J. C. PEARSON, L. R. BROWN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA; I. KLEINER, LISA, Université Paris 12 & Paris 7 & CNRS, 94010 Créteil, France; R. L. SAMS, PNNL, Richland, WA 99352, USA.
TOWARDS UNDERSTANDING QUANTUM MONODROMY IN QUASI-SYMMETRIC MOLECULES: FASSST ROTATIONAL SPECTRA OF CH$_3$NCO AND CH$_3$NCS

ZBIGNIEW KISIEL, Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland; SARAH FORTMAN, IVAN R. MEDVEDEV, MANFRED WINNEWISER, FRANK C. DE LUCIA, Department of Physics, The Ohio State University, Columbus, OH 43210; JACEK KOPUT, Department of Chemistry, Adam Mickiewicz University, 60-780 Poznań, Poland.
RD. MINI-SYMPOSIUM: PRECISION/FREQUENCY COMBS
THURSDAY, JUNE 24, 2010 – 8:30 am
Room: 1015 McPherson Lab

Chair: BEN McCALL, University of Illinois, Urbana, Illinois

RD01 30 min 8:30
BROADBAND SPECTROSCOPY WITH DUAL COMBS AND CAVITY ENHANCEMENT

RONALD HOLZWARTH, Max-Planck-Institute for Quantum Optics, 81748 Garching, Germany and Menlo Systems GmbH, 82152 Martinsried, Germany; BIRGITTA BERNHARDT, AKIRA OZAWA, THOMAS UDEM, THEODOR W. HÄNSCH, Max-Planck-Institute for Quantum Optics, 81748 Garching, Germany; PATRICK JACQUET, MARION JACQUEY, GUY GUELACHVILI, Laboratoire de Photophysique Moleculaire, CNRS, Bâtiment 350, Université Paris-Sud, 91405 Orsay, France; YOHEI KOBAYASHI, Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan; NATHALIE PICQUE, Max-Planck-Institute for Quantum Optics, 81748 Garching, Germany and Laboratoire de Photophysique Moleculaire, CNRS, Bâtiment 350, Université Paris-Sud, 91405 Orsay, France.

RD02 15 min 9:05
TUNABLE LASER SPECTROSCOPY REFERENCED WITH DUAL FREQUENCY COMBS


RD03 15 min 9:22
TUNABLE MID-IR FREQUENCY COMB FOR MOLECULAR SPECTROSCOPY

TODD A. JOHNSON and SCOTT A. DIDDAMS, National Institute of Standards and Technology, Boulder, Colorado 80305.

RD04 15 min 9:39
SENSITIVE AND INSTANTANEOUS MOLECULAR DETECTION FROM BROADBAND CAVITY-ENHANCED DUAL COMB SPECTROSCOPY

B. BERNHARDT1, M. JACQUEY2, A. OZAWA1, P. JACQUET2, Y. KOBAYASHI1, T. UDEM1, R. HOLZWARTH1, G. GUELACHVILI2, T. W. HÄNSCH1,4, N. PICQUÉ5,2,4, 1Max Planck Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany; 2Institut des Sciences Moléculaires d’Orsay, CNRS, Université Paris Sud, Bât 350, 91405 Orsay, France; 3The Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581 Japan; 4Ludwig Maximilians-Universität München, Fakultät für Physik, Schellingstrasse 4/III, 80799 München, Germany.

RD05 15 min 9:56
VERSATILE AND SENSITIVE DUAL COMB FOURIER TRANSFORM SPECTROSCOPY

M. JACQUEY, P. JACQUET, J. MANDON, R. THON, G. GUELACHVILI, Institut des Sciences Moléculaires d’Orsay, CNRS, Université Paris-Sud, Bâtiment 350, 91405 Orsay Cedex, France; T. W. HÄNSCH, Max Planck Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany; Ludwig Maximilians-Universität München, Fakultät für Physik, Schellingstrasse 4/III, 80799 München, Germany; N. PICQUÉ, Institut des Sciences Moléculaires d’Orsay, CNRS, Université Paris-Sud, Bâtiment 350, 91405 Orsay Cedex, France; Max Planck Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany; Ludwig Maximilians-Universität München, Fakultät für Physik, Schellingstrasse 4/III, 80799 München, Germany.
Intermission

RD06 15 min 10:30
THEORY FOR DIRECT FREQUENCY COMB SPECTROSCOPY

DANIEL FELINTO, CARLOS E. E. LÓPEZ, Departamento de Física, Universidade Federal de Pernambuco, 50670-901 Recife, PE - Brazil.

RD07 15 min 10:47
POWER SCALING OF VUV AND XUV FREQUENCY COMBS

DYLAN YOST, ARMAN CINGOZ, JUN YE, JILA, National Institute of Standards and Technology and University of Colorado, Department of Physics, University of Colorado, Boulder, CO 80309-0440; AXEL RUEHL, MARTIN E. FERMANN, INGMAR HARTL, IMRA America, Inc., 1044 Woodridge Ave., Ann Arbor, MI 48105, USA.

RD08 15 min 11:04
PRECISION MEASUREMENT OF THE IONIZATION AND DISSOCIATION ENERGIES OF H₂, HD AND D₂

DANIEL SPRECHER, JINJUN LIU, and FRÉDÉRIC MERKT, ETH Zürich, Laboratorium für Physikalische Chemie, Wolfgang-Pauli-Strasse 10, 8093 Zürich, Switzerland; CHRISTIAN JUNGEN, Laboratoire Aimé Cotton, CNRS II, Bâtiment 505, Campus d’Orsay, 91405 Orsay Cedex, France; WIM UBACHS, Laser Centre, Department of Physics and Astronomy, Vrije Universiteit, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands.

RD09 15 min 11:21
DUAL COMB FOURIER TRANSFORM SPECTROSCOPY

T.W. HÄNSCH¹,², N. PICQUÉ¹,²,³, ¹ Max Planck Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany; ²Ludwig Maximilians-Universität München, Fakultät für Physik, Schellingstrasse 4/III, 80799 München, Germany; ³Institut des Sciences Moléculaires d’Orsay, CNRS, Université Paris-Sud, Bâtiment 350, 91405 Orsay, France. Email: nathalie.picque@mpg.de.

RD10 15 min 11:38
DUAL COMB FOURIER TRANSFORM SPECTROSCOPY IN THE GREEN REGION

R.J. KNIZE¹,², B. BERNHARDT², N. PICQUÉ²,³,⁴, T.W. HÄNSCH²,³,⁴, ¹ Laser and Optics Research Center, U.S. Air Force Academy, Suite 2A31, 2354 Fairchild Drive, Colorado Springs, Colorado 80840, U.S.A; ² Max Planck Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany; ³ Institut des Sciences Moléculaires d’Orsay, CNRS, Université Paris-Sud, Bâtiment 350, 91405 Orsay Cedex, France; ⁴Ludwig Maximilians-Universität München, Fakultät für Physik, Schellingstrasse 4/III, 80799 München, Germany.

RD11 15 min 11:55
SCALING OF YB-FIBER FREQUENCY COMBS

AXEL RUEHL, ANDRIUS MARCINKEVIČIUS, MARTIN E. FERMANN and INGMAR HARTL, IMRA America Inc., 1044 Woodridge Avenue, Ann Arbor, Mi 48105-9774, USA.
RE01 15 min 8:30
THE PERFORMANCE OF A CONTINUOUS SUPERSONIC EXPANSION DISCHARGE SOURCE

CARRIE A. KAUFFMAN, KYLE N. CRABTREE, Department of Chemistry, University of Illinois, Urbana, IL 61801; BENJAMIN J. MCCALL, Departments of Chemistry and Astronomy, University of Illinois, Urbana, IL 61801.

RE02 15 min 8:47
FOURIER TRANSFORM INFRARED SPECTROSCOPY OF THE H$_2$F$^+$ $\nu_1$, $\nu_3$ AND $\nu_2$ BANDS

R. FUJIMORI, Y. HIRATA, K. KAWAGUCHI, Department of Chemistry, Faculty of Science, Okayama University, 3-1-1, Tsushima-Naka, Okayama 700-8530, JAPAN; I. MORINO, Satellite Remote Sensing Research Section, Center for Global Environmental Research, National Institute for Environmental Studies Onogawa 16-2, Tsukuba, Ibaraki 305-8506, JAPAN.

RE03 15 min 9:04
MEASUREMENT OF ROTATIONAL LEVELS OF THE HOMONUCLEAR HELIUM DIMER CATION BY EXTRAPOLATION OF RYDBERG SERIES

DANIEL SPRECHER, JINJUN LIU, TOBIAS KRÄHENMANN, MARTIN SCHAFFER, and FRÉDÉRIC MERKT, ETH Zürich, Laboratorium für Physikalische Chemie, Wolfgang-Pauli-Strasse 10, 8093 Zürich, Switzerland.

RE04 15 min 9:21
THE INFRARED SPECTRA OF BF$_3$ CATION AND BF$_2$OH CATION TRAPPED IN SOLID NEON

MARILYN E. JACOX and WARREN E. THOMPSON, Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441.

RE05 15 min 9:38
CAVITY ENHANCED VELOCITY MODULATION SPECTROSCOPY

BRIAN SILLER, ANDREW MILLS, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801; BENJAMIN J. McCALL, Departments of Chemistry and Astronomy, University of Illinois and Urbana-Champaign, Urbana, IL 61801.

RE06 15 min 9:55
TOWARDS HIGH RESOLUTION CAVITY ENHANCED SPECTROSCOPY WITH FAST ION BEAMS

ANDREW MILLS, BRIAN SILLER, MANORI PERERA, HOLGER KRECKEL, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801; BENJAMIN J. McCALL, Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801.
RE07 15 min 10:12
CATION SPECTROSCOPY OF 3,4-DIFLUOROANILINE

WEN BIH TZENG, Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, 1 Section 4, Roosevelt Road, Taipei 10617, Taiwan.

Intermission

RE08 15 min 10:45
PHOTODISSOCIATION OF ACETALDEHYDE AND THE PHOTOIONIZATION CROSS SECTION OF HCO

V. ALVIN SHUBERT and STEPHEN T. PRATT, Argonne National Laboratory, Chemical Sciences and Engineering Division, Argonne, IL 60439.

RE09 15 min 11:02
THEORETICAL PREDICTIONS OF THE STRUCTURES AND ENERGETICS OF ClF$_n^+/-$ ($n$=1−5) IONS: EXTENDED STUDIES OF HYPERVALENT SPECIES USING THE RECOUPLED PAIR BONDING MODEL

L. CHEN, D. E. WOON, and T. H. DUNNING, JR., Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

RE10 15 min 11:19
SUPEROXIDE PHOTOELECTRON ANGULAR DISTRIBUTIONS: VIBRATIONAL DEPENDENCE AS A CONSEQUENCE OF BORN-OPPENHEIMER BEHAVIOR

RICHARD MABBS, MATTHEW VAN DUZOR, FOSTER MBAIWA and JIE WIE, Department of Chemistry, Washington University, One Brookings Dr., Campus Box 1134 Saint Louis, Missouri 63130, USA; STEPHEN GIBSON, STEVEN CAVANAGH and B. R. LEWIS, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, Australian Capital Territory 0200, Australia.

RE11 15 min 11:36
THE PHOTOELECTRON ANGULAR DISTRIBUTION AS A PROBE OF ENERGETICALLY INDISTINGUISABLE CHANNELS IN PHOTODETACHMENT

MATTHEW VAN DUZOR, FOSTER MBAIWA, JIE WIE and RICHARD MABBS, Department of Chemistry, Washington University, One Brookings Dr., Campus Box 1134 Saint Louis, Missouri 63130, USA.

RE12 15 min 11:53
VIBRATIONAL AUTODETACHMENT IN NITROALKANE ANIONS

CHRISTOPHER L. ADAMS, J. MATHIAS WEBER, JILA, NIST, and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309, USA.
RF01 15 min 1:30
THE INTERSTELLAR DETECTION OF HSCN IN Sgr B2(N)

D. T. HALFEN, L. M. ZIURYS, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721; M. C. MCCARTHY, C. GOTTLEIB, and P. THADDEUS, Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138, and School of Engineering & Applied Sciences, Harvard University, 29 Oxford St., Cambridge, MA 02138.

RF02 15 min 1:47
THE [HNCS]/[HSCN] RATIO IN SGRB2 AND TMC-1

G. ADANDE, D.T. HALFEN, L.M. ZIURYS, Department of Chemistry, Steward Observatory, University of Arizona, Tucson.

RF03 15 min 2:04
DETECTION OF INTERSTELLAR UREA WITH CARMA

H.-L. KUO, L. E. SNYDER, D. N. FRIEDEL, L. W. LOONEY, Department of Astronomy, University of Illinois at Urbana-Champaign; B. J. McCALL, Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana IL 61801; A. J. REMIJAN, NRAO, Charlottesville VA 22903; F.J. LOVAS, Optical Technology Division, NIST, Gaithersburg MD 20899-8441; J. M. HOLLIS, NASA/GSFC, Code 606, Greenbelt MD 20771.

RF04 15 min 2:21
METHANOL PHOTODISSOCIATION BRANCHING RATIOS AND THEIR INFLUENCE ON INTERSTELLAR ORGANIC CHEMISTRY

JACOB C. LAAS and SUSANNA L. WIDICUS WEAVER, Department of Chemistry, Emory University, Atlanta, GA 30322; ROBIN T. GARROD, Department of Astronomy, Cornell University, Ithaca, NY 14853.

RF05 15 min 2:38
CHEMISTRY IN THE MOLECULAR DISKS OF ACTIVE GALACTIC NUCLEI

NANASE HARADA, Department of Physics, The Ohio State University, Columbus OH 43210; ERIC HERBST, Departments of Physics, Astronomy, and Chemistry, The Ohio State University, Columbus, OH 43210.

RF06 15 min 2:55
TWO SIGHTLINES TOWARD THE GALACTIC CENTER WITH REMARKABLE H$_3^+$ and CO SPECTRA

TAKESHI OKA, Department of Astronomy and Astrophysics, and Department of Chemistry, the University of Chicago, IL 60637; T. R. GEBALLE, Gemini Observatory, Hilo, HI 96720.
Intermission

RF07 15 min 3:30
LINEAR ANALYSIS OF INFRARED CO SPECTRA

TAKESHI OKA, Department of Astronomy and Astrophysics, and Department of Chemistry, The Enrico Fermi Institute, the University of Chicago, IL 60637; Han Xiao, Department of Statistics, the University of Chicago, Chicago, IL 60637; T. R. GEBALLE, Gemini Observatory, Hilo, HI 96720.

RF08 10 min 3:47
INCLUSION OF REACTIONS WITH BARRIERS IN HOT CORE MODELS

GEORGE E. HASSEL, Department of Physics, The Ohio State University, Columbus, OH 43210; ERIC HERBST, Departments of Physics, Astronomy and Chemistry, The Ohio State University, Columbus, OH 43210; NANASE HARADA, Department of Physics, The Ohio State University, Columbus, OH 43210.

RF09 15 min 3:59
THE STRATOSPHERIC OBSERVATORY FOR INFRARED ASTRONOMY (SOFIA)

R. D. GEHRZ, Department of Astronomy, University of Minnesota, 116 Church Street, S. E., Minneapolis, MN 55455; E. E. BECKLIN, Universities Space Research Association, NASA Ames Research Center, MS 211-3, Moffett Field, CA 94035.

RF10 15 min 4:16
INFRARED SPECTROSCOPIC STUDIES OF THE PHYSICS AND CHEMISTRY OF STELLAR EVOLUTION WITH THE STRATOSPHERIC OBSERVATORY FOR INFRARED ASTRONOMY (SOFIA)

R. D. GEHRZ, Department of Astronomy, University of Minnesota, 116 Church Street, S. E., Minneapolis, MN 55455; E. E. BECKLIN, Universities Space Research Association, NASA Ames Research Center, MS 211-3, Moffett Field, CA 94035.

RF11 15 min 4:33
THE JPL MILLIMETER AND SUBMILLIMETER SPECTRAL LINE CATALOG

BRIAN J. DROUIN, SHANSHAN YU, JOHN C. PEARSON, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099.

RF12 15 min 4:50
ANALYSIS OF THE $\lambda = 1.3 \text{ mm}$ SPECTRUM OF ORION-KL

MARY L. RADHUBER, JAY A. KROLL, and SUSANNA L. WIDICUS WEAVER, Department of Chemistry, Emory University, Atlanta, GA 30322.

RF13 15 min 5:07
BROADBAND, HIGH RESOLUTION SPECTROSCOPY WITH NRAO FACILITIES

ANTHONY J. REMIJAN, NRAO, 520 Edgemont Road, Charlottesville, VA 22903.
RF14 10 min 5:24
ASTROCHEMISTRY WITH THE UPGRADED COMBINED ARRAY FOR RESEARCH IN MILLIMETER-WAVE ASTRONOMY

D. N. FRIEDEL, Department of Astronomy, University of Illinois, Urbana, IL 61801.

RF15 15 min 5:36
THE $^{14}$N/$^{15}$N ISOTOPE RATIO IN DENSE MOLECULAR CLOUDS

G. ADANDE, L. M. ZIURYS, Department of Chemistry, Steward Observatory, University of Arizona, Tucson.

RF16 15 min 5:53
QUANTUM CHEMICAL STUDIES OF LOW-ENERGY PATHWAYS TO ORGANIC SPECIES ON INTERSTELLAR ICY GRAIN MANTLES

D. E. WOON and L. CHEN, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801.
RG. MINI-SYMPOSIUM: METAL CONTAINING MOLECULES
THURSDAY, JUNE 24, 2010 – 1:30 pm
Room: 170 MATH ANNEX

Chair: CAROLINE JARROLD, Indiana University, Bloomington, Indiana

RG01 30 min 1:30
Journal of Molecular Spectroscopy Review Lecture
INFRARED PHOTODISSOCIATION SPECTROSCOPY OF CATION-MOLECULAR COMPLEXES

MICHAEL A. DUNCAN, Department of Chemistry, University of Georgia, Athens, GA 30602.

RG02 15 min 2:05
INFRARED SPECTROSCOPY OF $\text{M}^+\text{(CH}_4\text{)}_n\text{(H}_2\text{O)}_{3-4} \text{ CLUSTERS (M=Li, Na): INDUCING H}_2\text{O} \cdot \cdot \cdot \text{H}_2\text{O AND H}_2\text{O} \cdot \cdot \cdot \text{CH}_4 \text{ HYDROGEN BONDS IN METHANATED CLUSTERS}$

OSCAR RODRIGUEZ JR. and JAMES M. LISY, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

RG03 10 min 2:22
GROUND AND EXCITED STATES OF PLATINUM DIMER: TIME-DEPENDENT RELATIVISTIC DENSITY FUNCTIONAL THEORY STUDY

HOSSEIN Z. JOOYA AND LEAH C. O’BRIEN, Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026-1652.

RG04 10 min 2:34
INTRACAVITY LASER ABSORPTION SPECTROSCOPY OF PLATINUM DIMER IN THE NEAR INFRARED

LEAH C. O’BRIEN, Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026-1652;
JAMES J. O’BRIEN, Department of Chemistry and Biochemistry and Center for Nanoscience, University of Missouri, St Louis, MO 63121-4499.

RG05 15 min 2:46
PHOTOELECTRON AND PHOTOION SPECTROSCOPY OF SCANDIUM-METHYLBENZENE COMPLEXES

JUNG SUP LEE, YUXIU LEI, SUDESH KUMARI, and DONG-SHENG YANG, Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.

RG06 15 min 3:03
MASS-ANALYZED THRESHOLD IONIZATION OF LaO$_2$

LU WU, CHANGHUA ZHANG, SERGIY KRASNOKUTSKI, and DONG-SHENG YANG, Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.

RG07 15 min 3:20
ELECTRONIC SPECTROSCOPY OF COBALT-NEON

T. C. CHENG, S. HASBROUCK, M.A. DUNCAN, Department of Chemistry, University of Georgia, Athens, GA 30602-2556.
VECTO R CORRELATION IN THE PHOTODISSOCIATION OF METAL NITROS YLS

J EFFREY A. B A RTZ, AMBER L. P EDEN, and R YAN D. K IEDA, Department of Chemistry, Kalamazoo College, 1200 Academy Street, Kalamazoo, MI 49006.

In termission

LASER EXCITATION SPECTROSCOPY OF $^{58}$NiH IN A MAGNETIC FIELD

C YRIL RICHARD, HEATHER HARKER, PATRICK CROZET and AMANDA J. ROSS, LASIM, Université Lyon I & CNRS, 43 Bd du 11 novembre 1918, F-69622 Villeurbanne, France; DENNIS TOKARYK, Department of Physics and Center for Laser, Atomic, and Molecular Sciences, University of New Brunswick, Fredericton, Canada E3B 5A3.

ZEEMAN PAT TE RNS IN FOURIER TRANSFORM RESOLVED FLUORESCENCE SPECTRA OF NiH

A MANDA J. ROSS, PATRICK CROZET, HEATHER HARKER and CYRIL RICHARD, LASIM, Université Lyon I & CNRS, 43 Bd du 11 novembre 1918, F-69622 Villeurbanne, France; and STEPHEN H. ASHWORTH, School of Chemistry, University of East Anglia, Norwich NR4 7TJ, UK.

HIGH RESOLUTION LASER EXCITATION SPECTROSCOPY OF BARIUM MONOSULFIDE

G. L I, J.-G. W ANG, and P. F. B E RNATH, Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK.

INVESTIGATING THE EXCITED ELECTRONIC STATES OF BaOH VIA LASER SPECTROSCOPY AND AB INITIO CALCULATION: FURTHER EVIDENCE OF PERTURBATION FROM THE $A'^2\Delta$ STATE

J. D. T ANDY, J.-G. W ANG, P. F. B E RNATH, Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK; J. LIÉVIN, Service de Chimie Quantique et Photophysique, Université Libre de Bruxelles, CPI 160/09, 50 av F.D. Roosevelt, B-1050 Bruxelles, Belgium.

SPECTROSCOPY IN SUPPORT OF PARITY NONCONSERVATION MEASUREMENTS: THE $A^2\Pi - X^2\Sigma^+$ (0,0) BAND OF BARIUM MONOF LUORIDE

A NH LE, SARAH FREY AND TIMOTHY C. STEIMLE, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287.

OPTICAL STARK SPECTROSCOPY OF THE $B^1A'' - X^1\Lambda'$ of CuOH

F ANG W ANG AND TIMOTHY C. STEIMLE, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287.
FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF CuCCH ($X^1\Sigma^+$)

M. SUN, D. T. HALFEN, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721; D. J. CLOUTHIER, Department of Chemistry, University of Kentucky, Lexington, KY 40506; and L. M. ZIURYS, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.
RH. MICROWAVE (ROTATIONAL)
THURSDAY, JUNE 24, 2010 – 1:30 pm
Room: 1000 McPHERSON LAB

Chair: THERESA HUET, University of Lille I, Villeneuve, France

RH01 10 min 1:30
TRANSIENT/PERMANENT CHIRALITY: ROTATIONAL SPECTRA OF THE DIMERS OF ISOPROPA NOL

LUCA EVANGELISTI, FEDERICO PESCI and WALThER CAMINATI, Dipartimento di Chimica "G. Ciamicon" dell’Università, Via Selmi 2, 1-40126 Bologna, Italy.

RH02 15 min 1:42
TRIPLE RESONANCE FOR A THREE-LEVEL SYSTEM OF A CHIRAL MOLECULE


RH03 15 min 1:59
CHIRALITY OF AND GEAR MOTION IN ISOPROPYL METHYL SULFILE: A FOURIER TRANSFORM MICROWAVE STUDY

YOSHIYUKI KAWASHIMA, KEISUKE SAKIEDA, Department of Applied Chemistry, Faculty of Engineering, Kanagawa Institute of Technology, Atsugi, Kanagawa 243-0292, JAPAN; and EIZI HIROT A, The Graduate University for Advanced Studies, Hayama, Kanagawa 240-0193, JAPAN.

RH04 15 min 2:16
CHIRPED-PULSED FTMW SPECTRUM OF 4-FLUOROBENZYL ALCOHOL. STRUCTURE AND TORSIONAL MOTIONS IN THE GROUND ELECTRONIC STATE PHASE

RYAN G. BIRD and DAVID W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pa 15213; JUSTIN L. NEILL and BROOKS H. PATE, Department of Chemistry, University of Virginia, Charlottesvi lle, Va 22904.

*a Work supported by NSF (CHE-0618740 and -0911117).

RH05 15 min 2:33
A STUDY OF 4,4-DIMETHYLAMINOBEZONITRILE BY CHIRPED-PULSED FOURIER TRANSFORM MICROWAVE SPECTROSCOPY

RYAN G. BIRD, VALERIE J. ALSTADT, and DAVID W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pa 15213; JUSTIN L. NEILL and BROOKS H. PATE, Department of Chemistry, University of Virginia, Charlottesville, Va 22904.

*a Work supported by NSF (CHE-0618740 and -0911117).

RH06 15 min 2:50
CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTRUM OF THE LOW GLOBAL WARMING POTENTIAL REFRIGERANT ALTERNATIVE, 2,3,3,3-TETRAFLUOROPROPENE

MARK D. MARSHALL, HELEN O. LEUNG, Department of Chemistry, Amherst College, P.O. Box 5000, Amherst, MA 01002-5000; JOHN S. MUENTER, Department of Chemistry, University of Rochester, Rochester, NY 14627.
A 480 MHz CHIRPED-PULSE FOURIER-TRANSFORM MICROWAVE SPECTROMETER: CONSTRUCTION AND MEASUREMENT OF THE ROTATIONAL SPECTRA OF DIVINYL SILANE AND 3,3-DIFLUOROPENTANE

DANIEL A. OBENCHAIN, AMANDA L. STEBER, ASHLEY A. ELLIOTT, REBECCA A. PEEBLES and SEAN A. PEEBLES, Department of Chemistry, Eastern Illinois University, 600 Lincoln Avenue, Charleston, IL 61920; CHARLES J. WURREY, Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110; GAMIL A. GUIRGIS, Department of Chemistry and Biochemistry, College of Charleston, Charleston, SC 29424.

CHIRPED-PULSE FTMW SPECTRA OF FLUORINATED MOLECULES: 1,1,1-TRIFLUORO-2-BUTANONE AND 3,3,3-TRIFLUOROPROPIONIC ACID

L. EVANGELISTI, Dipartimento di Chimica “G. Ciamici” dell’Università, Via Selmi 2, I-40126 Bologna, Italy; J. VAN WUNGAARDEN, Department of Chemistry, University of Manitoba, Winnipeg, MB, Canada R3T 2N2.

MICROWAVE SPECTROSCOPY OF BIS-(TRIFLUOROMETHYL) PEROXIDE, CF$_3$OOCF$_3$

LU KANG, Department of Biology, Chemistry, and Physics, Southern Polytechnic State University, Marietta, GA 30060; STEWART E. NOVICK, Department of Chemistry, Wesleyan University, Middletown, CT 06457.

MICROWAVE SPECTROSCOPY AND STRUCTURES OF PERFLUOROHEXANE AND 1H-HEPTAFLUOROPROPAINE

JOSEPH A. FOURNIER, ROBERT K. BOHN, Dept. of Chemistry, Univ. of Connecticut, Storrs, CT 06269-3060; JOHN A. MONTGOMERY, JR., Dept. of Physics, Univ. of Connecticut, Storrs, CT 06269-3046.

THE SHAPES OF CHLOROPENTAFLUOROACETONE AND 1,3-DICHLOROTETRAFLUOROACETONE IN THE GAS PHASE

GAUTAM KADIWAR, CHRISTOPHER T. DEWBERRY, GARRY S. GRUBBS II AND STEPHEN A. COOKE, Department of Chemistry, University of North Texas, 1155 Union Circle #305070, Denton, TX 76203-5017, U.S.A.

ROTATIONAL ANALYSIS OF BANDS IN THE HIGH-RESOLUTION INFRARED SPECTRA OF trans, trans- AND cis, cis-1,4-DIFLUOROBUTADIENE-2-d$_1$

NORMAN C. CRAIG, DEACON J. NEMCHICK, CLAY C. EASTERDAY, ETHAN C. GLOR, and DREW F. K. WILLIAMSON, Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH 44074; THOMAS A. BLAKE and ROBERT L. SAMS, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352.
FIRST MICROWAVE TRANSITIONS IN THE ROTATIONAL SPECTRUM OF $\nu_{17}$ OF ACETONE ASSIGNED BY MW-MW DOUBLE RESONANCE

P. GRONER, Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110-2499; M. UNRATH, D. CHRISTEN, Institute of Physical and Theoretical Chemistry, University of Tübingen, D-72076 Tübingen, Germany.

THE MILLIMETER-WAVE ROTATIONAL SPECTRUM OF PHENYLACETYLENE

ZBIGNIEW KISIEL, ADAM KRAŚNICKI, Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland.

ROTATIONAL CONSTANTS FOR M-METHYLBENZALDEHYDE: A STUDY IN LOW BARRIER TORSIONAL SPLITTING

AMANDA J. SHIRAR, KELLY M. HOTOPP, DAVID S. WILCOX, BRIAN C. DIAN, Department of Chemistry, Purdue University, West Lafayette, IN, 47907.
RI. INFRARED/RAMAN (VIBRATIONAL)
THURSDAY, JUNE 24, 2010 – 1:30 pm
Room: 1015 McPHERSON LAB

Chair: OLIVIER PIRALI, Laboratoire de Photophysique Moleculaire, CNRS, Orsay, France

RI01 15 min 1:30
FEMTO-FANTASIO: A VERSATILE EXPERIMENTAL SET-UP TO INVESTIGATE MOLECULAR COMPLEXES


RI02 10 min 1:47
INVESTIGATION OF VAN DER WAALS COMPLEXES IN A FREE EXPANSION OF $C_2H_2/X$ (X=NOBLE GAS) USING CW CAVITY RING-DOWN SPECTROSCOPY IN THE OVERTONE RANGE


RI03 10 min 1:59
AB INITIO INVESTIGATION OF $C_2H_2/X$ VAN DER WAALS COMPLEXES (X=NOBLE GAS, CO$_2$, N$_2$O).


RI04 15 min 2:11
INFRARED SPECTROSCOPY OF Li(METHYLAMINE)$_n$(NH$_3$)$_m$ CLUSTERS

N. BHALLA, L. VARRIALE, N. M. TONGE AND A. M. ELLIS, Department of Chemistry, University of Leicester; Leicester, LE1 7RH, United Kingdom.

RI05 15 min 2:28
HIGH RESOLUTION SPECTRA OF CARBON DIOXIDE CLUSTERS IN THE $\nu_3$ BAND REGION

A.R.W. MCKELLAR, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, ON K1A 0R6, Canada; MAHIN AFSHARI, M. DEHGHANY, and N. MOAZZEN-AHMADI, Department of Physics and Astronomy, University of Calgary, 2500 University Dr., N.W., Calgary, AB T2N 1N4, Canada.

RI06 15 min 2:45
INFRARED SPECTRA OF ACETYLENE-D$_2$ CLUSTERS

F. MIVEHVAR, J. NOROOZ OLIAEE, M. DEHGHANY, N. MOAZZEN-AHMADI, Department of Physics and Astronomy, University of Calgary, Calgary, AB T2N 1N4, Canada; A.R.W. MCKELLAR, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, ON K1A 0R6, Canada.
RI07 15 min 3:02

A NEW POTENTIAL ENERGY SURFACE FOR N₂O–He, AND PIMC SIMULATIONS PROBING INFRARED SPECTRA AND SUPERFLUIDITY

LECHENG WANG, DAIQIAN XIE, School of Chemistry and Chemical Engineering, Nanjing University, No.22 Hankou Road, Nanjing, Jiangsu, China, 210093; HUI LI, ROBERT J. LE ROY, and PIERRE-NICHOLAS ROY, Guelph-Waterloo Centre for Graduate Work in Chemistry and Biochemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

Intermission

RI08 15 min 3:40

INFRARED SPECTRA OF (CO₂)₂-OCS COMPLEX: INFRARED OBSERVATION OF TWO DISTINCT BARREL-SHAPED ISOMERS

J. NOROOZ OLIAEE, M. DEHGHANY, F. MIVEHVAR, N. MOAZZEN-AHMADI, Department of Physics and Astronomy, University of Calgary, Calgary, AB T2N 1N4, Canada; A.R.W. MCKELLAR, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, ON K1A 0R6, Canada.

RI09 15 min 3:57

FUNDAMENTALS AND TORSIONAL COMBINATION BANDS OF TWO ISOMERS OF THE OCS-CO₂ COMPLEX

J. NOROOZ OLIAEE, M. DEHGHANY, F. MIVEHVAR, MAHIN AFSHARI, N. MOAZZEN-AHMADI, Department of Physics and Astronomy, University of Calgary, 2500 University Dr., N.W., Calgary, Alberta T2N 1N4, Canada; A.R.W. McKELLAR, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, K1A 0R6, Canada.

RI10 10 min 4:14

INFRARED SPECTROSCOPY OF LARGE-SIZED PHENOL-WATER CLUSTERS PhOH-(H₂O)ₙ (10 ≤ n ≤ 50)

TORU HAMASHIMA, KENTA MIZUSE and ASUKA FUJII, Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan.

RI11 15 min 4:26

INFRARED SPECTRA OF OCS-C₆H₆, OCS-C₆H₆-He AND OCS-C₆H₆-Ne VAN DER WAALS COMPLEXES

M. DEHGHANY, J. NOROOZ OLIAEE, MAHIN AFSHARI, N. MOAZZEN-AHMADI, Department of Physics and Astronomy, University of Calgary, 2500 University Dr., N.W., Calgary, Alberta T2N 1N4, Canada; A.R.W. McKELLAR, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, K1A 0R6, Canada.

RI12 15 min 4:43

INFRARED SPECTRA OF SIZE-SELECTED METHANOL CLUSTERS USING IR-VUV PHOTORIZATION

HUI-LING HAN, Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan; YUAN-PERN LEE, Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan and Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan.
RI13 15 min 5:00
INFRARED PREDISSOCIATION SPECTRA OF Cl⁻(CH₃OH)ₙAr CLUSTER IONS, n=1-3

JORDAN P. BECK, JAMES M. LISY, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

RI14 10 min 5:17
LONG RANGE PROTON-MIGRATION IN VUV PHOTOIONIZATION OF ACETONE CLUSTERS

KEN-ICHI HANAUE, YOSHIYUKI MATSUDA, KEISUKE OHTA, NAOHIKO MIKAMI and ASUKA FU-JII, Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan.

RI15 15 min 5:29
OVERTONE SPECTROSCOPY OF PEROXYACETIC ACID AND PEROXYFORMIC ACID : INFLUENCE OF INTRAMOLECULAR HYDROGEN BONDING

MONTU K. HAZRA, MICHELLE KUANG, and AMITABHA SINHA, Department of Chemistry and Biochemistry, University of California-San Diego 9500 Gilman Drive, La Jolla, California 93093-0314.

RI16 10 min 5:46
STUDY OF SURFACE ENHANCED RAMAN SCATTERING OF ALIZARIN AND CRYSTAL VIOLET DYES

RAM GOPAL and RAJ KUMAR SWARNKAR, Laser Spectroscopy and Nanomaterials Lab, Department of Physics (UGC-CAS), University of Allahabad, Allahabad-211002, India.

RI17 15 min 5:58
INFRARED SPECTROSCOPY PROBING OF BLUE-SHIFTING CHO HYDROGEN-BONDED COMPLEXES BETWEEN CYCLIC KETONES AND HALOFORMS

ANAMIKA MUKHOPADHYAY, Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India; AMIT K. SAMANTA; BIMAN BANDYOPADHYAY; PRASENJIT PANDEY; and TAPAS CHAKRABORTY.
RJ01  
**INVITED TALK**  30 min  1:30
CALCULATING RO-VIBRATIONAL SPECTRA OF VAN DER WAALS MOLECULES

XIAOGANG WANG and TUCKER CARRINGTON, Jr., Chemistry Department, Queen’s University, Kingston, Canada.

RJ02  15 min  2:05
PREDICTION OF VIBRATIONAL ENERGY LEVELS USING A MIXED APPROACH OF NUMERICAL AND ANALYTICAL INTEGRATION

J. VÁZQUEZ, M. E. HARDING, J. F. STANTON, Institute for Theoretical Chemistry, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712; J. GAUSS, Institut für Physikalische, Universität Mainz, Jakob Welder Weg 11, D-55128 Mainz, Germany.

RJ03  15 min  2:22
COMPUTATION OF INFRARED SPECTROSCOPIC FEATURES USING SYMMETRY

J. VÁZQUEZ, J. F. STANTON, Institute for Theoretical Chemistry, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712.

RJ04  15 min  2:39
NINE DIMENSIONAL THEORETICAL STUDIES ON METHOXY FREE RADICAL

JAYASHREE NAGESH and E. L. SIBERT III, Department of Chemistry and Theoretical Chemistry Institute, University of Wisconsin-Madison, WI 53706.

RJ05  15 min  2:56
VIBRATIONAL DYNAMICS AROUND THE CONICAL INTERSECTION OF METHOXY

J. NAGESH and E. L. SIBERT III, Department of Chemistry and Theoretical Chemistry Institute, University of Wisconsin-Madison, WI 53706.

RJ06  15 min  3:13
CALCULATING ANHARMONIC VIBRATIONAL STATES WITHOUT A PRE-EXISTING POTENTIAL ENERGY SURFACE

ANDREW S. PETIT and ANNE B. McCOY, Department of Chemistry, The Ohio State University, Columbus, OH 43210.
DIMETHYL ETHER THREE DIMENSIONAL SPECTRA

M. Villa, Departamento de Química, Universidad Autónoma Metropolitana, Av. San Rafael Atlixco 186, Col Vicentina, Iztapalapa, Mexico D.F. 09340, MEXICO; MA. L. Senent, Departamento de Astrofísica Molecular e Infrarroja, Instituto de Estructura de la Materia, C.S.I.C., Serrano 113B, Madrid 28006, SPAIN.

THEORETICAL STUDIES ON THE ELECTRONIC SPECTRA OF AlCl

Sunil K. Mishra, Sushil Srivastav and Vipin B. Singh, Department of Physics, Udaipur Pratap Autonomous College, Varanasi-221002, India.

aPresent address: Department of Physics, Agrasen Kannaya PG College, Varanasi

Intermission

REACTION PATH HAMILTONIAN CALCULATION OF TUNNELING SPLITTING IN PROTONATED METHANOL AND METHYLMETHANE.

A. R. Sharma, J. M. Bowman, Cherry L. Emerson Center for Scientific Computation, Department of Chemistry, Emory University, Atlanta GA 30322, USA; S. C. Carter, Department of Chemistry, University of Reading, RG6 2AD, England.

ELECTRONIC STRUCTURE AND SINGLE-TRIPLET ENERGY SPLITTINGS IN ETHYNYL CYCLOBUTADIENES

Stephanie J. Thompson, Frank Lee Emmert III, and Lyudmila V. Slipchenko, Department of Chemistry, Purdue University, West Lafayette, IN 47907.

ELECTRONIC STRUCTURE OF THE FLEXIBLE BICHROMOPHORE DIPHENYL METHANE

Frank Lee Emmert III, and Lyudmila V. Slipchenko, Department of Chemistry, Purdue University, West Lafayette, IN 47907.

VIBRATION-ROTATION-TUNNELING STATES OF THE BENZENE DIMER: AN AB INITIO STUDY

Ad van der Avoird, P.R. Bunker, Melanie Schnell, Gert von Helden, and Gerhard Meijer, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany; Rafal Podszwa and Krzysztof Zalewicz, Department of Physics and Astronomy, University of Delaware, Newark, DE 19716; Claude LeForestier, Institut Charles Gerhardt Montpellier, Université Montpellier 2, 34095 Montpellier, Cedex 05, France; and Rob van Harrevelt, Theoretical Chemistry, Institute for Molecules and Materials, Radboud University Nijmegen, 6525 AJ Nijmegen, The Netherlands.
TENSORIAL FORMALISM FOR ROVIBRONIC SPECTROSCOPY OF $C_{3v}$ MOLECULES SPECTROSCOPY OF $XY_3Z$ ($C_{3v}$) MOLECULES WITH AN EVEN OR ODD NUMBER OF ELECTRONS: A TENSORIAL FORMALISM ADAPTED TO THE $SU(2) \otimes C_1 \supset C_{\infty v}^{S} \supset C_{3v}^{S}$ GROUP CHAIN

A. EL HILALI, LISA, CNRS/Universités Paris Est et Paris Diderot, 61 Avenue du Général de Gaulle, 94010 Créteil, France; V. BOUDON, Laboratoire interdisciplinaire Carnot de Bourgogne, UMR 5209 CNRS–Université de Bourgogne, 9, Avenue Alain Savary, BP 47870, F-21078 Dijon Cedex, France.

GROUP PARAMETRIZED TUNNELING AND LOCAL SYMMETRY CONDITIONS

WILLIAM HARTER, JUSTIN MITCHELL, Department of Physics, University of Arkansas, Fayetteville, AR 72701.

SYMMETRY-BASED TUNNELINGS IN HIGH-RESOLUTION ROVIBRATIONAL SPECTRA OF OCTAHEDRAL MOLECULES

JUSTIN MITCHELL, WILLIAM HARTER, Department of Physics, University of Arkansas, Fayetteville, AR 72701.
FA. INFRARED/RAMAN (VIBRATIONAL)
FRIDAY, JUNE 25, 2010 – 8:30 am
Room: 160 MATH ANNEX
Chair: JOSEPH R. ROSCIO, University of Colorado, Boulder, Colorado

FA01 15 min 8:30
HIGHEST RESOLUTION FOURIER TRANSFORM INFRARED SPECTROSCOPY WITH AN ELEVEN CHAMBER BRUKER INTERFEROMETER AT THE SWISS SYNCHROTRON

S. ALBERT, K.K. ALBERT, M. QUACK, PHYSICAL CHEMISTRY, ETH ZÜRICH, CH-8093 ZÜRICH, SWITZERLAND; PH. LERCH, L. QUARONI, SWISS LIGHT SOURCE, PAUL-SCHERRER-INSTITUTE, CH-5232 VILLIGEN, SWITZERLAND; A. KEENS, BRUKER OPTICS, D-76275 ETTLINGEN, GERMANY.

FA02 15 min 8:47
HIGH-RESOLUTION SPECTROSCOPY OF THE ν8 BAND OF METHYLENE BROMIDE USING A QUANTUM CAScade LASER-BASED CAVITY RINGDOWN SPECTROMETER

JACOB T. STEWART, BRIAN E. BRUMFIELD, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801; MATTHEW D. ESCARRA, CLAIRE F. GMACHL, Department of Electrical Engineering, Princeton University, Princeton Institute for the Science and Technology of Materials, Princeton, NJ 08544; BENJAMIN J. McCALL, Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

FA03 10 min 9:04
FTIR SPECTROMETERS UTILIZING MID-INFRARED QUANTUM CASCADE LASERS.

CHRISTIAN PFLUGL, LORAN DIEHL, FEDERICO CAPASSO, School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, 02138; MARK F. WITINSKI, Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts, 02138; SERGEY SHILOV, PANG WANG, THOMAS TAGE, Bruker Optics, 19 Fortune Drive, Billerica, Massachusetts, 01821.

FA04 15 min 9:16
MID- AND LONGWAVE INFRARED TOTAL AND DIFFUSE REFLECTANCE MEASUREMENTS USING AN INTEGRATING SPHERE WITH A TWO-SAMPLE-PORT DESIGN

THOMAS A. BLAKE and TIMOTHY J. JOHNSON, Pacific Northwest National Laboratory, P.O. Box 999, Mail Stop K8-88, Richland, WA 99352 (PNNL is operated for the US Department of Energy by the Battelle Memorial Institute under contract DE-AC05-76RL0 1830); MICHAEL JUETTE and ARNO SIMON, Bruker Optik GmbH Rudolf-Plank-Straße 27, D-76275 Ettingen Germany.

FA05 15 min 9:33
VIBRATIONAL SPECTRA OF CHLOROFORM, FREON-11 AND SELECTED ISOTOPOMERS IN THE TERAHERTZ REGION

CHRISTA HAASE, JINJUN LIU and FRÉDÉRIC MERKT, Laboratorium für Physikalische Chemie, ETH-Zürich, 8093 Zürich, Switzerland.

aCurrent address: Department of Chemistry, Laser Spectroscopy Facility, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210, USA.
FA06 15 min 9:50

EXPERIMENTAL ENERGY LEVELS OF HD\textsuperscript{18}O AND D\textsubscript{2}\textsuperscript{18}O

S.N. MIKHAILENKO, O.V. NAUMENKO, S.A. TASHKUN, Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, 634055, Tomsk, RUSSIA; A.-W. LIU, S.-M. HU, Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, CHINA.

FA07 15 min 10:07

SPECTRA OF ETHANE IN He DROPLETS IN THE 3 \(\mu\)m RANGE

LUIS GOMEZ, EVGENIY LOGINOV, DMITRY SKVORTSOV, HIROMICHI HOSHINA, and ANDREY F. VILESOV, Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482.

Intermission

FA08 15 min 10:40

PURE ROTATIONAL CARS THERMOMETRY IN NANOSECOND PULSE BURST AIR AND HYDROGEN-AIR PLASMAS

YVETTE ZUZEK, INCHUL CHOI, SHERRIE BOWMAN, IGOR V. ADAMOVICH AND WALTER R. LEMPERT, Department of Mechanical Engineering, The Ohio State University, 201 W. 19th Ave., Columbus OH, 43210.

FA09 10 min 10:57

INVESTIGATION OF A SPARK IGNITION INTERNAL COMBUSTION ENGINE VIA IR SPECTROSCOPY

STEPHENA. SAKAI, ALLEN R. WHITE, Department of Mechanical Engineering, Rose-Hulman Institute of Technology, Terre Haute, IN; KEVIN GROSS, Department of Engineering Physics, Air Force Institute of Technology, Dayton, OH; REBECCA B. DEVASHER, Department of Chemistry, Rose-Hulman Institute of Technology, Terre Haute, IN.

FA10 10 min 11:09

DIRECT AND COLLISIONAL EXCITATION OF AUTOMOTOVE FUEL COMPONENTS)

ALLEN R. WHITE, KYLE WILSON, STEPHENA. SAKAI, Department of Mechanical Engineering, Rose-Hulman Institute of Technology, 5500 Wabash Ave., Terre Haute, IN 47803; REBECCA B. DEVASHER, Department of Chemistry, Rose-Hulman Institute of Technology, 5500 Wabash Ave., Terre Haute, IN 47803.

FA11 15 min 11:21

STRUCTURES OF TWO ISOMERS OF NITROUS OXIDE TETRAMER FROM THEIR INFRARED SPECTRA

J. NOROOZO.LIAEE, F. MIVEHVAR, M. DEHGANY, MOAZZEN-AHMADI, Department of Physics and Astronomy, University of Calgary, Calgary, AB T2N 1N4, Canada; A.R.W. MCKELLAR, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, ON K1A 0R6, Canada.

FA12 15 min 11:38

VIBRATIONAL PREDISSOCIATION SPECTRA OF THE Ar-T AGGED [CH\textsubscript{4} - H\textsubscript{3}O\textsuperscript{+}] BINARY COMPLEX: SPECTROSCOPIC SIGNATURE OF HYDROGEN BONDING TO AN ALKANE

SOLVEIG GAARN OLESEN, STEEN HAMMERUM, Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen , Denmark; TIMOTHY LAURENCE GAUSCO, GARY HOWARD WEDDLE, MARK ALBERT JOHNSON, Sterling Chemistry Laboratory, Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520.
FA13  
15 min 11:55

COHERENCE-CONVERTED POPULATION TRANSFER FTMW-IR DOUBLE RESONANCE SPECTROSCOPIC OF CH3OD IN THE C-H STRETCH REGION

SYLVESTRE TWAGIRAYEZU, DAVID S. PERRY, Department of Chemistry, The University of Akron, Akron OH 44325; JUSTIN L. NEILL, MATT T. MUCKLE, BROOKS H. PATE, Department of Chemistry, University of Virginia, McCormick Rd., Charlottesville, VA 22904.

FA14  
Post-deadline Abstract  
15 min 12:12

PULSE BURST LASER SYSTEM FOR HIGH SPEED LASER AND COMBUSTION MEASUREMENTS

NAIBO JIANG, MATT WEBSTER, KATHRYN GABET, RANDY PATTON, JEFFEREY SUTTON AND WALTER LEMPERT, Department of Mechanical Engineering, The Ohio State University, Columbus, OH 43210; JOSEPH MILLER AND TERRENCE MEYER, Department of Mechanical Engineering, Iowa State University, Ames, IA 50011; JENIFER INMAN, BRETT BATHEL, STEVE JONES AND PAUL DANEHY, NASA Langley Research Center, Hampton VA, 23681.

FA15  
Post-deadline Abstract  
15 min 12:29

FAR INFRARED HIGH RESOLUTION SYNCHROTRON FTIR SPECTROSCOPIC OF THE LOW FREQUENCY BENDING MODES OF DMSO

ARNAUD CUISSET, IRINA SMIRNOVA, ROBIN BOCQUET, FRANCIS HINDLE, GAEL MOURET, DMITRII A. SADOVSKII, Laboratoire de Physico-Chimie de l’Atmosphère, CNRS UMR-8101, Université du Littoral Côte d’Opale, 189A Ave. Maurice Schumann, 59140 Dunkerque, France; OLIVIER PIRALI, PASCALE ROY, Ligne AILES (Advance InfraRed Line Exploited for Spectroscopy), synchrotron SOLEIL, L’Orme des Merisiers, Saint Aubin, BP 48, 91192 Gif-sur-Yvette, France..

FA16  
Post-deadline Abstract  
10 min 12:46

ANHARMONIC RESONANCES AMONG LOW-LYING VIBRATIONAL LEVELS OF METHYL ISO-CYANIDE (H3CNC)

P. PRACNA, J. URBAN, J. Heyrovský Institute of Physical Chemistry, v.v.i., Academy of Sciences of the Czech Republic, 18223 Prague 8, Czech Republic; Š. URBAN, J. VARGA, Department of Analytical Chemistry, Institute of Chemical Technology, 16628 Prague 6, Czech Republic; V.-M. HORNEMAN, Department of Physical Sciences, University of Oulu, Linnanmaa, FIN-90570 Oulu, Finland.
FB. MATRIX/CONDENSED PHASE
FRIDAY, JUNE 25, 2010 – 8:30 am
Room: 170 MATH ANNEX

Chair: MARILYN JACOX, NIST, Gaithersburg, Maryland

FB01  15 min  8:30
MOLECULAR HYDROGEN ADSORPTION IN METAL-ORGANIC FRAMEWORKS

S. FITZGERALD, M. FRIEDMAN, J. GOTDANK, B. THOMPSON, Department of Physics and Astronomy, Oberlin College, Oberlin, OH 44074; J. ROWSELL, Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH 44074.

FB02  15 min  8:47
STRUCTURE OF COLD, MIXED PARAHYDROGEN-DEUTERIUM CLUSTERS

RUSSELL SLITER and ANDREY F. VILESOV, Department of Chemistry, University of Southern California, Los Angeles, CA 90089.

FB03  15 min  9:04
PHOTODISSOCIATION OF NO ISOLATED IN SOLID PARAHYDROGEN

DAVID T. ANDERSON, LEIF O. PAULSON and SHARON C. KETTWICH, Department of Chemistry, University of Wyoming, Laramie, WY 82071-3838.

FB04  15 min  9:21
HYPERFINE MATRIX SHIFT AND EPR-LINESHAPE ANISOTROPY OF METHYL RADICALS IN SOLID NE, AR, KR AND P-H\textsubscript{2} MATRICES

YURIJ A. DMITRIEV\textsuperscript{a}, Ioffe Physical-Technical Institute, 26 Politekhnicheskaya str., 194021 St. Petersburg, Russia; and NIKOLAS-PLOUTARCH BENETIS, Department of Pollution Control, Technological Educational Institution, TEI, West Macedonia, Kozani 501 00, Greece.

\textsuperscript{a}Support by Russian Foundation for Basic Research under grant 08-02-90409-Ukr\_a is gratefully acknowledged

FB05  15 min  9:38
HIGH RESOLUTION STUDIES OF THE \nu\textsubscript{3} BAND OF METHYL FLUORIDE IN SOLID PARAHYDROGEN USING A QUANTUM CASCADE LASER

A.R.W. MCKELLAR, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, ON K1A 0R6, Canada; ASAO MIZOGUCHI and HIDETO KANAMORI, Department of Physics, Tokyo Institute of Technology, Ohokayama 2-12-1, Meguro-ku, Tokyo, 152-8551 Japan.

FB06  15 min  9:55
ALKALI-METAL ATOMS AS SPIN LABELS ON HELIUM NANODROPLETS

MARKUS KOCH, MARTIN RATSCHEK, CARLO CALLEGARI\textsuperscript{a}, and WOLFGANG E. ERNST, Institute of Experimental Physics, TU Graz, Petersgasse 16, 8010 Graz, Austria.

\textsuperscript{a}Present address: Sincrotrone Trieste, Strada Statale 14 - km 163.5, 34149 Basovizza, Trieste, Italy
Intermission

FB07 15 min 10:30
STARK SPECTROSCOPY OF CH$_3$F SOLVATED IN HELIUM NANODROPLETS

ALEXANDER M. MORRISON, STEVEN D. FLYNN, TAO LIANG and GARY E. DOUBERLY, Department of Chemistry, University of Georgia, Athens, Georgia 30602.

FB08 15 min 10:47
INFRARED LASER SPECTROSCOPY OF (HCl)$_m$(H$_2$O)$_n$ CLUSTERS IN HELIUM NANODROPLETS

S. D. FLYNN, A. M. MORRISON, T. LIANG, G. E. DOUBERLY, Department of Chemistry, University of Georgia, Athens, GA 30602.

FB09 15 min 11:04
HYDRATED HCl COMPLEXES, (HCl)$_m$(H$_2$O)$_n$, IN HELIUM NANODROPLETS: OH STRETCHING MODES

SEUNG JUN LEE and MYONG YONG CHOI, Department of Chemistry (BK21) and Research Institute of Natural Science, Gyeongsang National University, Jinju, 660-701, Korea; DIMITRY SKVORTSOV and ANDREY F. VILESOV, Department of Chemistry, University of Southern California, Los Angeles, CA 90089, USA.

FB10 15 min 11:21
HYDRATED HCl COMPLEXES, (HCl)$_m$(H$_2$O)$_n$, IN HELIUM NANODROPLETS: HCl STRETCHING MODES

MYONG YONG CHOI and SEUNG JUN LEE, Department of Chemistry (BK21) and Research Institute of Natural Science, Gyeongsang National University, Jinju, 660-701, Korea; DIMITRY SKVORTSOV and ANDREY F. VILESOV, Department of Chemistry, University of Southern California, Los Angeles, CA 90089, USA.

FB11 10 min 11:38
Post-deadline Abstract
FOURIER TRANSFORM INFRARED SPECTRAL INVESTIGATION OF THE $\nu_6$ BAND OF CYCLIC-C$_3$H$_2$

PRADEEP RISIKRISHNA VARADWAI, RYUJI FUJIMORI, KENTAROU KAWAGUCHI, Department of Chemistry, Faculty of Science, Okayama University, 3-1-1, Tsushima-Naka, Okayama 700-8530, JAPAN.

FB12 10 min 11:50
Post-deadline Abstract
MICROWAVE SPECTRA OF FLUOROFORMYOXYL AND FLUOROSULFATE RADICALS

Š. URBAN, J. VARGA, L. KOLESNIKOVÁ, Z. MELTZEROVÁ, T. UHLÍKOVÁ, J. KOUCKÝ, P. KANIA, Department of Analytical Chemistry, Institute of Chemical Technology, 16628 Prague 6, Czech Republic; H. BECKERS, H. WILLNER, Bergische Universität Wuppertal, FB 9, Anorganische Chemie, Gaußstr. 20, 42097 Wuppertal, Germany.
FC01 15 min 8:30
TORSIONALLY EXCITED DIMETHYL ETHER IN THE LABORATORY AND IN SPACE

C. P. ENDRES, H. S. P. MÜLLER, F. LEWEN, T. F. GIESEN, S. SCHLEMMER, I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany; B. J. DROUIN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099, USA; S. BISSCHOP, Center for Star and Planet Formation, University of Copenhagen, DK-1350, Copenhagen, Denmark; P. GRONER, Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110, USA.

FC02 15 min 8:47
THE ROTATIONAL SPECTRUM OF SINGLY AND DOUBLY 13C-SUBSTITUTED DIMETHYLETHER

MONIKA KOERBER, CHRISTIAN P. ENDRES, FRANK LEWEN, THOMAS F. GIESEN, STEPHAN SCHLEMMER, I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany; ROLAND POHL, AXEL KLEIN, Institut für Anorganische Chemie, Universität zu Köln, 50939 Köln, Germany.

FC03 10 min 9:04
ACETYLENE 12C2H2 LABORATORY MEASUREMENTS FOR ASTROPHYSICAL APPLICATIONS

D. JACQUEMART, L. GOMEZ, N. LACOME, Université Pierre et Marie Curie-Paris 6; CNRS: Laboratoire de Dynamique, Interactions et Réactivité (LADIR), UMR 7075, Case Courrier 49, 4 Place Jussieu, 75252 Paris Cedex 05, France; J.-Y. MANDIN, Université Pierre et Marie Curie-Paris 6; CNRS: Laboratoire de Physique Moléculaire pour l’atmosphère et l’astrophysique (LPMAA), UMR 7092, Case courrier 76, 75252 Paris Cedex 05, France; O. PIRALI, and P. ROY, Synchrotron SOLEIL, L’Orme des Merisiers Saint-Aubin, 91192 Gif-sur-Yvette cedex, France.

FC04 15 min 9:16
TERAHERTZ AND FAR-INFRARED SPECTROSCOPY OF HIGH-J TRANSITIONS OF THE GROUND AND v2 = 1 STATES OF NH3

O. PIRALI, M.-A. MARTIN, M. VERVLOET and D. BALCON, Ligne AILES–Synchrotron SOLEIL, L’Orme des Merisiers Saint-Aubin, 91192 Gif-sur-Yvette, France; S. YU, J. PEARSON and B. DROUIN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109, USA; C. P. ENDRES, I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany; T. SHIRAISHI, K. KOBAYASHI, and F. MATSUSHIMA, Department of Physics, University of Toyama, Gofuku, Toyama 930-8555, Japan.

FC05 15 min 9:33
ISOMER-SPECIFIC SPECTROSCOPY OF GAS-PHASE α-HYDRONAPHTHYL, β-HYDRONAPHTHYL, AND 1,2,3-TRIHYDRONAPHTHYL RADICALS

JOSHUA A. SEBREE, TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN 47907; VADIM V. KISLOV, ALEXANDER M. MEBEL, Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199.
SYNCHROTRON-BASED HIGHEST RESOLUTION FOURIER TRANSFORM INFRARED SPECTROSCOPY OF NAPHTHALENE (C_{10}H_{8}): ROVIBRATIONAL ANALYSIS OF THE $\nu_{46}$ BAND

S. ALBERT, K.K. ALBERT, M. QUACK, PHYSICAL CHEMISTRY, ETH ZÜRICH, CH-8093 ZÜRICH, SWITZERLAND; PH. LERCH, SWISS LIGHT SOURCE, PAUL-SCHERRER-INSTITUTE, CH-5232 VILLI-GEN, SWITZERLAND.

N$_2$ COLLISIONAL BROADENING OF METHANE IN THE THZ REGION MEASURED AT THE SOLEIL SYNCHROTRON

V. BOUDON, T. GABARD, Institut Carnot de Bourgogne, UMR 5209 CNRS-Université de Bourgogne, 9. Av. A. Savary, BP 47870, F-21078 Dijon Cedex, France; O. PIRALI, P. ROY, J.-B. BRUBACH, Ligne AILES – Synchrotron SOLEIL, L’Orme des Merisiers, F-91192 Gif-sur-Yvette, France; L. MANCERON, Laboratoire de Dynamique, Interactions et Réactivité, UMR 7075 – Université Pierre et Marie Curie – CNRS, Case 49, 4 Place Jussieu, F-75252, Paris Cedex, France; J. VANDER AUWERA, Service de Chimie Quantique et Photophysique, Université Libre de Bruxelles, CP 160/09, 50 avenue F.D. Roosevelt, B-1050 Brussels, Belgium.

ANALYSIS OF HIGH RESOLUTION LABORATORY PROPANE SPECTRA ($\nu_{21}$, 922 cm$^{-1}$) AND THE INTERPRETATION OF TITAN’S INFRARED SPECTRA$^a$.

V. KLA VANS, Department of Astronomy, University of Maryland, College Park, MD 20742; C. NIXON, T. HEWAGAMA, Department of Astronomy, University of Maryland, College Park, MD 20742 at NASA Goddard Space Flight Center, Greenbelt, MD 20771; and D. E. JENNINGS, NASA Goddard Space Flight Center, Greenbelt, MD 20771.

$^a$This work was supported by the NASA Cassini Data Analysis Program, grant number NNX09AK55G.

OBSERVING A COLUMN-DEPENDENT $\zeta$ IN THE HORSEHEAD PDR

P.B. RIMMER, Department of Physics, Ohio State University, Columbus, OH 43210; O. MORATA, Institute of Astronomy and Astrophysics, Academia Sinica, Taipei 11677, Taiwan; E. ROUEFF, Observatoire de Paris, LUTH and Université Denis Diderot, Place J. Janssen 92190 Meudon, France; E. HERBST, Departments of Astronomy, Physics, and Chemistry, Ohio State University, Columbus, OH 43210.

CONSTRAINING THE FLUX OF LOW-ENERGY COSMIC RAYS ACCELERATED BY THE SUPERNova REMNANT IC 443

NICK INDRIOLO, Department of Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801; GEOFFREY A. BLAKE, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125; MIWA GOTO, Max Planck Institute for Astronomy, Königstuhl 17, Heidelberg D-69117, Germany; TOMONORI USUDA, Subaru Telescope, Hilo, HI 96720; THOMAS R. GEBALLE, Gemini Observatory, Hilo, HI 96720; TAKESHI OKA, Department of Astronomy & Astrophysics and Department of Chemistry, University of Chicago, Chicago, IL 60637; BENJAMIN J. MCCALL, Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801.
FC11 15 min 11:34
DARK WATER - IMPLICATIONS OF RECENT COLLISIONAL COOLING MEASUREMENTS

BRIAN J. DROUIN, MICHAEL J. DICK, JOHN C. PEARSON, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099; EDWIN BERGIN, Department of Astronomy, University of Michigan, Ann Arbor, MI 48109-1090.

FC12 10 min 11:51
PROGRESS IN COMPUTING ACCURATE INFRARED LINELISTS FOR CO$_2$

XINCHUAN HUANG, SETI Institute, 515 N. Whisman Road, Mountain View, CA, 94043; DAVID W. SCHWENKE, MS T27B-1, NASA Ames Research Center, Moffett Field, CA, 94035; and TIMOTHY J. LEE, MS 245-1, NASA Ames Research Center, Moffett Field, CA, 94035.

FC13 10 min 12:03
A GAS GRAIN MODEL OF INTERSTELLAR CLOUD CORES WITH MOMENT EQUATIONS TO TREAT SURFACE CHEMISTRY

YEZHE PEI, Department of Physics, The Ohio State University, Columbus, OH 43210; ERIC HERBST, Department of Physics, Astronomy and Chemistry, The Ohio State University, Columbus, OH 43210.

FC14 Post-deadline Abstract 15 min 12:15
STRUCTURE OF THE LARGE MOLECULE DISTRIBUTION IN THE TAURUS MOLECULAR CLOUD

GLEN I. LANGSTON and KYLE WOOLARD, National Radio Astronomy Observatory, Green Bank, WV 24915.

FC15 Post-deadline Abstract 15 min 12:32
ROTATIONAL SPECTRA OF THE MOLECULAR IONS H$_2$NCO$^+$ AND NCO$^-$

VALERIO LATTANZI, CARL A. GOTTLIEB, PATRICK THADDEUS, and MICHAEL C. McCARTHY, Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, and School of Engineering and Applied Science, Harvard University, Cambridge, MA 02138; and SVEN THORWIRTH, Max-Planck-Institut für Radioastronomie, Bonn, Germany, and I. Physikalisches Institut, Universität zu Köln, Germany.

FC16 Post-deadline Abstract 15 min 12:49
CHEMICAL CHARACTERIZATION OF THE FIRST STAGES OF PROTOPLANETARY DISK FORMATION

U. HINCELIN, V. WAKELAM, S. GUILLOTÉAU and F. HERSANT, Université de Bordeaux, Observatoire Aquitain des Sciences de l'Univers, 2 rue de l’Observatoire, BP 89, F-33271 Floirac Cedex, France, and, CNRS, UMR 5804, Laboratoire d’Astrophysique de Bordeaux, 2 rue de l’Observatoire, BP 89, F-33271 Floirac Cedex, France.
FD. MINI-SYMPOSIUM: PRECISION/FREQUENCY COMBS
FRIDAY, JUNE 25, 2010 – 8:30 am
Room: 1015 McPHERSON LAB

Chair: SCOTT DIDDAMS, NIST, Boulder, Colorado

FD01
INVITED TALK
30 min 8:30
LASER FREQUENCY COMBS FOR PRECISION RADIAL VELOCITY MEASUREMENTS IN ASTROPHYSICS

RONALD WALSWORTH, Harvard-Smithsonian, Cambridge, MA.

FD02
15 min 9:05
PRECISION CAVITY ENHANCED VELOCITY MODULATION SPECTROSCOPY

ANDREW MILLS, BRIAN SILLER, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801; BENJAMIN J. McCALL, Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

FD03
15 min 9:22
CAVITY-ENHANCED DIRECT FREQUENCY COMB VELOCITY MODULATION SPECTROSCOPY

LAURA SINCLAIR, KEVIN COSSEL, WILLIAM AMES, JUN YE AND ERIC CORNELL, JILA, University of Colorado Boulder and the National Institute for Standards and Technology, Boulder, Colorado 80309.

FD04
15 min 9:39
APPLICATIONS OF CAVITY-ENHANCED DIRECT FREQUENCY COMB SPECTROSCOPY

KEVIN C. COSSEL, FLORIAN ADLER, JILA, National Institute of Standards and Technology and University of Colorado Department of Physics, University of Colorado, Boulder, Colorado 80309-0440, USA; PIOTR MASŁOWSKI, JILA, National Institute of Standards and Technology and University of Colorado Department of Physics, University of Colorado, Boulder, Colorado 80309-0440, USA and Instytut Fizyki, Uniwersytet Mikolaja Kopernika, ul. Grudziadzka 5/7, 87-100 Torun, Poland; and JUN YE, JILA, National Institute of Standards and Technology and University of Colorado Department of Physics, University of Colorado, Boulder, Colorado 80309-0440, USA.

FD05
15 min 9:56
FREQUENCY STABILIZATION OF HIGH-POWER 3.3 µm CW LASER WITH A FREQUENCY COMB SYSTEM

SUSUMU KUMA and TAKAMASA MOMOSE, Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, British Columbia V6T1Z1, Canada.

Intermission

FD06
15 min 10:30
TWO-PHOTON TRANSITIONS VIA OPTICAL FREQUENCY COMB TO FORM ULTRACOLD MOLECULES

SVETLANA MALINOVS'KAYA, WUFU SHI, Department of Physics and Engineering Physics, Stevens Institute of Technology, Hoboken, NJ 07030.
PROGRESS REPORT ON A PORTABLE Ti:SAPPHIRE COMB LASER WITH FREQUENCIES REFERRING TO CESIUM ATOM TWO-PHOTON TRANSITIONS

WANG-YAU CHENG, CHIEN-MING WU, TZ-WEI LIU, YO-HUAN CHEN, IAMS, Academia Sinica, No. 1, Roosevelt Rd., Sec. 4, Taipei, Taiwan.

MID-INFRARED FREQUENCY COMB SPECTROSCOPY WITH TWO Cr^{2+}:ZnSe FEMTOSECOND OSCILLATORS

P. JACQUET¹, B. BERNHARDT², E. SOROKIN³, R. THON¹, T. BECKER², I.T. SOROKINA⁴, N. PICQUE¹,²,³, T. W. HÄNSCH²,³ ¹ Institut des Sciences Moléculaires d’Orsay, C.N.R.S., Université Paris-Sud, Bât 350, 91405 Orsay Cedex, France; ² Max Planck Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany; ³ Institut für Photonik, TU Wien, Gusshausstrasse 27/387, A-1040 Vienna, Austria; ⁴ Norwegian University of Science and Technology, Department of Physics, N-7491 Trondheim, Norway; ⁵ Ludwig Maximilians-Universität München, Fakultät für Physik, Schellingstrasse 4/III, 80799 München, Germany.

SENSITIVITY SCALING OF DUAL FREQUENCY COMB SPECTROSCOPY


HIGH PRECISION MID-IR SPECTROSCOPY OF $^{12}$C$^{16}$O$_2$ NEAR 2.7 $\mu$m

WEI-JO TING, JOW-TSONG SHY, Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 30013, R.O.C.

SPECTROSCOPY WITH COMB-REFERENCED DIODE LASERS

MATTHEW CICH, GARY V. LOPEZ, PHILIP M. JOHNSON AND TREVOR J. SEARS, Department of Chemistry, Stony Brook University, Stony Brook, New York 11794; CHRISTOPHER P. MCRAVEN, Homer L. Dodge Department of Physics and Astronomy, The University of Oklahoma, Norman, OK 72019-2061.

A THz PHOTOMIXING SYNTHESIZER BASED ON A FIBER FREQUENCY COMB FOR HIGH RESOLUTION ROTATIONAL SPECTROSCOPY

FRANCIS HINDLE, GAEL MOURET, ARNAUD CUISSET, CHUN YANG, SOPHIE ELIET, ROBIN BOCQUET, Laboratoire de Physico-Chimie de l’Atmosphère, Université du Littoral Côte d’Opale, 189A Ave. Maurice Schumann, 59140 Dunkerque, France.
FE. DYNAMICS
FRIDAY, JUNE 25, 2010 – 8:30 am
Room: 2015 McPHERSON LAB

Chair: PHILLIP THOMAS, The Ohio State University, Columbus, Ohio

FE01 15 min 8:30
PHOTOCHEMISTRY OF MONOCHLORO COMPLEX OF COPPER (II) IN SOLUTION BY MEANS OF TRANSIENT ABSORPTION TIME-RESOLVED ULTRAFAST SPECTROSCOPY

A. S. MERESHCHENKO, P. EL-KHOURY, S. PAL, A. N. TARNOVSKY, Bowling Green University, Department of Chemistry and Center for Photochemical Sciences, Bowling Green, Ohio 43403.

FE02 10 min 8:47
ULTRAFAST EXCITED-STATE DYNAMICS IN MODEL HEXABROMOPLATINATE (IV) AND HEXABROMOOSMIATE (IV) DIANIONS IN THE CONDENSED PHASE

I. L. ZHELDAKOV, A. S. MERESHCHENKO, A. N. TARNOVSKY, Bowling Green University, Department of Chemistry and Center for Photochemical Sciences, Bowling Green, Ohio 43403.

FE03 15 min 8:59
DYNAMICS AND MECHANISM OF (6-4) PHOTOPRODUCT REPAIR IN DAMAGED DNA BY PHOTOLYASE

J. LI, Z. LIU, C. TAN, X. GUO, L. WANG and D. ZHONG, Departments of Physics, Chemistry, and Biochemistry, Programs of Biophysics, Chemical Physics, and Biochemistry, 191 West Woodruff Avenue, The Ohio State University, Columbus, Ohio 43210; A. SANCAR, Department of Biochemistry and Biophysics, University of North Carolina School of Medicine, Chapel Hill, North Carolina 27599.

FE04 15 min 9:16
MAPPING THYMINE DIMER SPLITTING IN DAMAGED DNA BY PHOTOLYASE

ZHEYUN LIU, CHUANG TAN, JIANG LI, XUNMIN GUO, LIJUAN WANG, and DONGPING ZHONG, Department of Physics, Chemistry, and Biochemistry, The Ohio State University, Columbus, OH 43210.

FE05 15 min 9:33
2D IR LINE SHAPES FOR DETERMINING THE STRUCTURE OF A PEPTIDE IN A BILAYER

ANN MARIE WOYS, Y. S. LIN, J. S. SKINNER, M. T. ZANNI, Department of Chemistry, University of Wisconsin, Madison, WI 53706; A. S. REDDY, J. J. DE PABLO, Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706.

Intermission

FE06 15 min 10:10
CHEMICAL DYNAMICS IN ENERGETIC MATERIALS INCORPORATING ALUMINUM NANOPARTICLES

WILLIAM K. LEWIS, BARBARA A. HARRUFF, K. A. SHIRAL FERNANDO, MARCUS J. SMITH, ELENA A. GULIANTS, Nanochemistry and Nanoengineering Group, University of Dayton Research Institute, Dayton, OH 45469; CHRISTOPHER E. BUNKER, Propulsion Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH 45433.
SOLVENT-MEDIATED ELECTRON LEAPFROGGING: CHARGE TRANSFER IN IBr\(^-\)(CO\(_2\)) PHOTODISSOCIATION

SAMANTHA HORVATH and ANNE B. McCOY, Department of Chemistry, The Ohio State University, Columbus, OH 43210; LEONID SHEPS, ELISA M. MILLER, MATTHEW A. THOMPSON, ROBERT PARSON, and W. CARL. LINEBERGER, JILA, Department of Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, CO 80309.

THE ROLE OF VIBRATIONAL EXCITATION ON THE DYNAMICS OF THE F(2P) + HCl → FH + Cl(2P) HYDROGEN-TRANSFER REACTION

SARA E. RAY, GÉ W. M. VISSERS and ANNE B. McCOY, Department of Chemistry, The Ohio State University, Columbus, OH 43210.

ULTRAFAST SOLVATION DYNAMICS OF FLAVODOXIN IN THREE OXIDATION STATES

TING-FANG HE, CHIH-WEI CHANG, and DONGPING ZHONG, Programs of Ohio State Biochemistry, Biophysics, and Chemical Physics, and Departments of Physics, Chemistry, and Biochemistry, The Ohio State University, Columbus, OH 43210.

DYNAMICS AND MECHANISM OF EFFICIENT DNA REPAIR REVIEWED BY ACTIVE-SITE MUTANTS

CHUANG TAN, ZHEYUN LIU, JIANG LI, XUNMIN GUO, LIJUAN WANG and DONGPING ZHONG, Departments of Physics, Chemistry, and Biochemistry, Programs of Biophysics, Chemical Physics, and Biochemistry, The Ohio State University, Columbus, Ohio, 43210.

REACTION DYNAMICS OF THE BROMINE-BROMOFORM COMPLEX IN SOLUTION

THOMAS J. PRESTON, MAITREYA DUTTA and F. FLEMING CRIM, The University of Wisconsin-Madison, Department of Chemistry, 1101 University Avenue, Madison, WI 53706.

VIBRATIONAL SPECTROSCOPY AND DYNAMICS OF THE HYDRAZOIC AND ISOTHIOCYANIC ACIDS IN PROTIC AND APROTIC SOLVENTS


\(^{a}\)CH and DW acknowledge the Naval Research Laboratory - National Research Council Research Associateship.
Welcome

Carolyn C. Whitacre, Vice President for Research
The Ohio State University

MA01 40 min 9:00
TOWARDS AN IMPROVED MEASUREMENT OF THE ELECTRON’S ELECTRIC DIPOLE MOMENT IN A TRAPPED MOLECULAR ION


Many proposed extensions to the standard model of particle physics predict that the electrons electric dipole moment (eEDM) should be nonzero, yet all measurements to date are consistent with zero. We are attempting to improve the current limit a factor of one hundred, by taking advantage of the very large internal electric field in a polar molecule, and the very long coherence times possible with trapped ions. Our favorite candidates are $\text{HfF}^+$ and $\text{ThF}^+$. I’ll discuss the difficulties of doing an experiment that requires the application of a uniform electric bias field to an ion, and touch on the techniques we’ve developed for doing massively parallel survey spectroscopy on ionic species.

Intermission
VIBRATIONAL SPECTROSCOPY OF PHOTOREACTIVE MOLECULES IN ATMOSPHERIC CHEMISTRY

VERONICA VAIDA, Department of chemistry and Biochemistry, University of Colorado, Boulder, CO 80309.

Vibrational overtone spectra of oxidized atmospheric chromophores are presented and analyzed to energies where chemistry through vibrational overtone pumping is possible. Experimental near infrared and visible spectra complemented by dynamical theory are presented to elucidate the light initiated reaction dynamics of pyruvic and of glyoxilic acid photo-decarboxylation. The role of water is investigated by making use of vibrational spectra of hydrates of the title compounds. Consequences of water and sunlight mediated chemistry to formation of secondary organic aerosol in the atmosphere will be discussed.

SUPERFLUID EFFECTS IN PARA-H₂ CLUSTERS PROBED BY CO₂ ROTATION-VIBRATION TRANSITIONS

HUI LI, ROBERT J. LE ROY, PIERRE-NICHOLAS ROY, Department of Chemistry, University of Waterloo, Waterloo, ON N2L 3G1, Canada; A.R.W. MCKELLAR, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, ON K1A 0R6, Canada.

The prospect of directly observing superfluidity in para-H₂ is a tantalizing but elusive goal. Like ⁴He, para-H₂ is a light zero-spin boson. However, H₂–H₂ intermolecular interactions, though weak, are stronger than He–He interactions, and hydrogen is a solid below about 14 K. This makes detection of superfluidity in bulk hydrogen problematical, to say the least. But there are still possibilities for para-H₂ in the form of clusters or in nano-confined environments, and superfluid transition temperatures as high as \(\sim 6\) K have been predicted.¹

Spectroscopic observations of (para-H₂)_N–CO₂ clusters² were at first very difficult to interpret for \(N > 5\). However, with the help of path integral Monte Carlo simulations and an accurate new H₂–CO₂ intermolecular potential surface³ which explicitly incorporates dependence on the CO₂ \(\nu_3\) asymmetric stretch, it is now possible to achieve a remarkably consistent picture of (para-H₂)_N–CO₂ clusters in the size range \(N = 1 \sim 20\). By combining the experimental spectroscopic measurements and theoretical simulations, we determine the size evolution of the superfluid response of the CO₂-doped para-H₂ clusters, which peaks for the “magic” number \(N = 12\).

¹V.L. Ginzburg and A.A. Sobyanin, JETP Lett. 15, 343 (1972).

THEORETICAL AND EXPERIMENTAL STUDY OF THE INFRARED SPECTRA OF CO₂-(para-H₂)₂ TRIMERS

HUI LI, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada; A. R. W. MCKELLAR, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A OR6, Canada; ROBERT J. LE ROY, and PIERRE-NICHOLAS ROY, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

The infrared spectra of several isotopologues of the CO₂-(para-H₂)₂ trimer have been predicted by applying exact basis-set calculations to a global potential energy surface which is defined as a sum of the accurately known two-body para-H₂–CO₂ and para-H₂–para-H₂ potentials.⁴ These results are compared with new spectroscopic measurements, for which sixteen transitions have been assigned. A reduced-dimension treatment of the para-H₂ rotation has been employed by performing an exact hindered-rotor average.⁵ Three-body effects and the quality of the potential are discussed. We present a new technique for representing the three-dimensional para-H₂ density in the body-fixed frame. It shown the two para-H₂ molecules are localized much more closely together than is the case for the two He atoms in the analogous CO₂–(He)₂ system.

QUANTUM MONTE CARLO PREDICTION OF VIBRATIONAL FREQUENCY SHIFTS FOR CO-(p-H₂)ᵓ CLUSTERS

HUI LI, ROBERT J. LE ROY and PIERRE-NICHOLAS ROY, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

Since para-H₂ molecules are spin zero bosons (like ⁴He atoms) they might also show superfluid behavior at low temperatures. Results of recent spectroscopic studies of molecules embedded in helium droplets suggests that a new route for investigating superfluidity of para-hydrogen (p-H₂) would be to consider p-H₂ clusters doped with a single chromophore molecule (such as CO, CO₂, N₂O, or OCS). High resolution infrared spectra of CO in (H₂)ᵓ cluster have been studied by the McKellar and coworkers, who observed R(0) transitions which have been assigned for n up to 9 for b-type transitions and to n = 14 for a-type series, with the help of reptation Monte Carlo simulations. Recently, Raston and coworkers indirectly determined band origin shifts for C-O stretching in small clusters with n up 7. Such studies stimulated our efforts to predict vibrational frequency shifts for larger clusters, and to perform critical comparisons between experimental and theoretical shifts in smaller clusters.

Predicting vibrational band origins shifts requires a potential energy surface which depends on the monomer vibrational coordinate(s). We recently determined a five-dimensional ‘Morse/Long-Range’ potential energy surface for CO-H₂ which explicitly depends on the C-O vibrational coordinate, and also incorporates the correct angle-dependent inverse-power long-range behaviour. We have now used this new potential in quantum Monte Carlo simulations to predict both the rotational dynamics and the shift of the C-O band origin for CO doped in p-H₂ clusters, in order to provide definitive theoretical evidence regarding whether superfluidity occurs for p-H₂ cluster doped with CO, and if so, at what cluster size it begins.

UNDERSTANDING INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION BY THE ROVIBRATIONAL ANALYSIS OF HIGH RESOLUTION INFRARED SPECTRA: THE CASE OF CHD₃I

CARINE MANCA TANNER, SIEGHERD ALBERT, and MARTIN QUACK, Physical Chemistry, ETH Zurich, Switzerland.

In our group we pursue two experimental approaches to investigate Intramolecular Vibrational Redistribution (IVR): this process can be studied by time-resolved femtosecond pump-probe experiments, or the corresponding time-dependent quantum dynamics can be obtained from stationary spectra in the IR at high frequency resolution by a time-dependent analysis using the underlying Hamiltonian and time evolution operator. Recent work in our group has shown that CH₃I and its deuterated isotopomers have different IVR-times, revealing different intramolecular coupling schemes for the initially excited vibrational levels. The present work is part of a larger effort to understand IVR in these molecules on the basis of high resolution spectra in the 500-12000 cm⁻¹ region. In previous work we have analyzed the strong Fermi-resonance coupling between the CH-stretching and bending modes in CHD₃I at modest resolution, demonstrating very fast redistribution times on the order of 100 fs. We refer to this recent paper for the past literature on the topic. Here we present detailed rovibrational analysis of ν₁ and several other fundamentals of CHD₃I recorded with our high resolution FTIR spectrometer Bruker ZP2001 with resolutions up to 0.0008 cm⁻¹. We discuss our new results in relation to our recent work on the overtone spectra and dynamics and to the femtosecond pump-probe results.
This work continues the systematic study of ozone in the infrared. Thanks to available predictions of band centres and rotational constants and the improvement of signal/noise ratios of observed spectra, we are able to observe weaker and weaker bands. It is the case of the $2\nu_1+3\nu_2+\nu_3$ band, which lies in the 5160 cm$^{-1}$ spectral range. The spectrum has been recorded with the FTS of GSMA, with a path length of 36 metres and a pressure of 41.0 Torr. The transitions are derived with a precision better than $1 \times 10^{-3}$ cm$^{-1}$ for wavenumbers and 10% for the intensities.

The analysis has been performed using effective Hamiltonian, and transition moment operators. 430 transitions have been assigned, with $J = 34$, $K_a = 11$. They are reproduced with an rms $= 2 \times 10^{-3}$ cm$^{-1}$, close to the experimental accuracy. Only one level (243) has found to be slightly perturbed (Obs-Calc=-0.011 cm$^{-1}$). The perturber has easily been identified, as the $242$ level of the (302) state. It is particularly interesting that this level was known, derived from our analysis of the (302)-(001) band with a shift (Obs-Calc=+0.011 cm$^{-1}$), confirming the validity of both analyses. We present here the results, with spectroscopic parameters (including the resonance with the (302) state, effective transition moment operators, integrated band intensities, portion of created linelists available for databanks and examples of agreements between observed and calculated spectra.

---


The (204) vibrational state of ozone, early labelled (006), was considered as dark in a previous analyse of the \( \nu_1 + 4\nu_3 \) band. Since that time, the improvement of signal/noise ratios reaching 5000 in the 5000 cm\(^{-1}\) spectral range allows now to observe very weak features which may be tentively assigned. A first spectrum has been recorded, in the 4700 cm\(^{-1}\) spectral range with the FTS of GSMA, with a path length of 36 metres and a pressure of 41.0 Torr. The transitions are derived with a precision better than \( 1 \times 10^{-3} \) cm\(^{-1}\) for wavenumbers and 10% for the intensities. A typical A-type band shape has been assigned to the \( 2\nu_1 + 4\nu_3 - \nu_3 \) band. The ASSIGN code has allowed assigning lines up to \( J = 20 \) and \( K_a = 4 \), leading to available rotational constants for the (204) state. With these ones, we have searched for the cold \( 2\nu_1 + 4\nu_3 \) band in other spectra in the 5760 cm\(^{-1}\) spectral range. Despite many difficulties, we finally succeed to assign lines corresponding to \( K_a = 0 \) and 1, and relatively large values of \( J \). Using suitable Hamiltonian model taking account of resonances with the (105) and (312) vibrational states, we finally assign 18 lines up to \( J_{\text{max}} = 26 \), \( K_a = 0, 1 \) for the cold band and 125 transitions, with \( J_{\text{max}} = 25 \), \( K_{\text{max}} = 8 \) for the hot band. Concerning the intensities, accounting of the weakness of the transitions, only a rough estimation of \( \mu'_Z = 0.8 \times 10^{-4} \) \( \phi_X \) (Debye) is given for the cold band. For the hot band, a fit on 72 transitions has been performed, leading to the value of \( \mu'_Z = 0.1166 \times 10^{-2} \) \( \phi_X \) (Debye). We present here all the results for the spectroscopic parameters, effective transition moment operators, integrated band intensities, portion of created line lists available for databanks and examples of agreements between observed and calculated spectra.

---

**GLOBAL MODELING OF HIGH RESOLUTION IR SPECTRA OF \(^{12}\)C\(_2\)H\(_2\)**

**B. AMYAY, M. HERMAN, Service de Chimie quantique et Photophysique CP160/09, Faculté des Sciences, Université Libre de Bruxelles (U.L.B.), Av. Roosevelt, 50, B-1050, Bruxelles, Belgium; A. FAYT, Laboratoire de Spectroscopie Moléculaire, Université Catholique de Louvain, Chemin du Cyclotron, 2, B-1348 Louvain-La-Neuve, Belgium.**

A global approach has been developed to calculate vibration-rotation spectra of acetylene in its ground electronic state, now including Coriolis interaction. The acetylene spectroscopic data base has been recently extended and the most recent set of effective Hamiltonian parameters resulting from the fit of experimental line positions gathered from literature up to 9000 cm\(^{-1}\) will be presented. This global model is essential to perform assignments and intensity simulations of high resolution spectra of acetylene, of astrophysical interest. Recent results will be highlighted concerning the FIR, MIR and NIR ranges.

---


ROCK AND ROLL IN HE NANODROPLETS: AGGREGATION AT ULTRACOLD CONDITIONS.

G. W. SCHWAAB, M. HAVENITH, Physical Chemistry II, Ruhr-University Bochum, D-44780 Bochum, Germany; E. SANCHEZ-GARCIA, MPI für Kohlenforschung, Mülheim a.d. Ruhr, Germany; A. METZELTHIN, DPG Bad Honnef; and W. SANDER, Organic Chemistry II, Ruhr-University Bochum.

Helium nanodroplets provide a unique environment to study intermolecular interactions. Their large pickup cross section allows the embedding of low vapor pressure compounds in the $10^{-7}$ to $10^{-4}$ mbar range. Evaporation of He atoms cools droplet and dopant molecules to 0.37 K typically within 1 ns. The superfluid He acts as soft matrix that shifts energy levels only slightly compared to gas phase values. Aggregation of molecules with large dipole moments in a typical droplet with radius of 5 nm is dominated by long range electrostatic interactions, e.g. dipole-dipole interactions. Famous examples are HCN aggregates with up to 12 monomers or formic acid dimer where the formation of a polar acyclic structure was observed.

In contrast, the interaction energy governing the step by step aggregation of molecules with small or even vanishing dipole moment in helium nanodroplets is small compared to the thermal energy at 0.37 K. In these cases short range interactions and even rotation will stabilize certain conformers while at the same time preventing the formation of others. Examples for both aggregation processes obtained from high resolution infrared spectroscopy in combination with extensive calculations on different levels of theory will be presented.

Support by the DFG Forschergruppe 618 is gratefully acknowledged

VAPOR PHASE INFRARED SPECTROSCOPY AND ANHARMONIC AB INITIO FUNDAMENTAL FREQUENCIES OF AMMONIA BORANE

ROBERT L. SAMS, SOTIRIS S. XANTHEAS, and THOMAS A. BLAKE, Pacific Northwest National Laboratory, P.O. Box 999, Mail Stop K8-88, Richland, WA 99352 (PNNL is operated for the US Department of Energy by the Battelle Memorial Institute under contract DE-AC05-76RL01830).

Ammonia borane (NH$_3$BH$_3$) has garnered considerable interest in recent years as a solid state hydrogen storage material for fuel cells. While many papers have been published on its physical and chemical properties, its vapor phase infrared spectrum has not yet been reported. A 1973 paper by Smith, Seshardi, and White$^a$ reported the matrix isolation spectrum of ammonia borane and this has been used as the infrared spectrum of the isolated molecule since.

Using a White cell with an optical path set to 68 meters and a room temperature sample, an adequate pressure-pathlength burden was achieved that allowed the moderate resolution spectrum of ammonia borane to be recorded using a Bruker IFS 120HR Fourier transform spectrometer. Additionally, first principles CCSD(T) and MP2 electronic structure calculations of the fundamental mode frequencies were performed. The harmonic frequencies were computed at the CCSD(T) level whereas anharmonic corrections were estimated at the MP2 levels of theory. The molecule has an ethane-like structure (eclipsed conformation) of C$_{3v}$ symmetry with five A$_1$ symmetry vibrational modes, an inactive A$_2$ torsional mode and six degenerate E symmetry modes. Of the five A$_1$ modes, four were observed: sym. B$-$H stretch at 2298.6 cm$^{-1}$ (2444 cm$^{-1}$ calculated); sym. NH$_3$ deformation 1281.8 (1271); sym. BH$_3$ deformation 1176.5 (1182); B$-$N stretch 610 (593). The B$-$N stretch mode is very weak. Of the six E symmetry modes, four were observed: asym. N$-$H stretch 3419.2 (3376); asym. B$-$H stretch 2407.9 (2369); asym. NH$_3$ deformation 1613.8 (1531); and the asym. BH$_3$ deformation 1042.2 (1127).


Intermission
We present the $D_{2h}TDS−ST$ ($D_{2h}−STARK$ Top Data System) program suite developed to simulate Stark spectra of any IR active rovibrational polyad of $X_2Y_4$ ($D_{2h}$) asymmetric-top molecules. It is based on the $D_{2h}TDS$ package, released for studying any rovibrational band or polyad in the absence of an electric field$^a,b$. The $D_{2h}TDS−ST$ suite consists in a series of FORTRAN programs called by a script. For calculation of Stark spectra we obtained the expressions of the dipole moment and polarizability operators of $X_2Y_4$ molecules, using a tensorial formalism$^c$ analogous to the one developed for tetrahedral and octahedral molecules$^d$. The developed program suite was used to estimate an effective average field in a cavity of a MFI-type host zeolite by comparison, with vibrational absorption spectra of ethylene in MFI-zeolite that have been recorded.


Adamantane $C_{10}H_{16}$ is the smallest member of the diamondoid family which consist of diamond-like carbon cages where all carbon atoms are $sp^3$ hybridised and terminated with hydrogen atoms. The unambiguous presence of presolar diamond nanocrystals in meteorites led several astrophysical groups to look for the signature of this family of molecules in the interstellar medium; mostly comparing IR observations with low resolution laboratory results$^a,b$. Using the Bruker IFS 125 coupled to a multipass cell (absorption path length of 150 m) of the AILES beamline at SOLEIL, we recorded the IR spectrum of gas phase adamantane in the 300–3000 cm$^{-1}$ spectral region with an unapodized resolution of about 0.001 cm$^{-1}$. While the most intense 3 μm bands appear as unresolved broad features, seven fundamental bands show rotationally resolved structures typical of $T_d$ spherical tops. The analysis of all the resolved bands has been performed thanks to the XTDS and SPVIEW softwares developed in Dijon for such molecules$^c$. Each band can be considered as isolated and we get very good fits of line positions, with a root mean square deviation better than $5 \times 10^{-4}$ cm$^{-1}$ for $J$ values up to 100 or more in each case. The resulting synthetic spectra will permit an active search of this very stable species in different sources of the interstellar medium.

IN PURSUIT OF THE FAR-INFRARED SPECTRUM OF CYANOGEN ISO-THIOCYANATE, NCNCS, UNDER THE INFLUENCE OF THE ENERGY LEVEL DISLOCATION DUE TO QUANTUM MONODROMY

MANFRED WINNEWISSER, BRENDA P. WINNEWISSER, IVAN R. MEDVEDEV, FRANK C. DELUCIA, Department of Physics, The Ohio State University, Columbus Ohio, 43210-1106, USA; STEPHEN C. ROSS, Department of Physics and Centre for Laser, Atomic, and Molecular Sciences, University of New Brunswick, P.O. Box 4400, Fredericton NB E3B 5A3, Canada; and JACEK KOPUT, Department of Chemistry, Adam Mickiewicz University, 60-780 Poznan, Poland.

Quantum Monodromy has a strong impact on the ro-vibrational energy levels of chain molecules whose bending potential energy function has the form of the bottom of a champagne bottle (i.e. with a hump or punt) around the linear configuration. NCNCS is a particularly good example of such a molecule and clearly exhibits a distinctive monodromy-induced dislocation of the energy level pattern at the top of the potential energy hump. The generalized semi-rigid bender (GSRB) wave functions are used to show that the expectation values of any physical quantity which varies with the large amplitude bending coordinate will also have monodromy-induced dislocations. This includes the electric dipole moment components. High level ab initio calculations not only provided the molecular equilibrium structure of NCNCS, but also the electric dipole moment components \( \mu_a \) and \( \mu_b \) as functions of the large-amplitude bending coordinate. The calculated expectation values of these quantities indicate large ro-vibrational transition moments that will be discussed in pursuit of possible far-infrared bands. To our knowledge there is no NCNCS infrared spectrum reported in the literature.

---

THE TWO MISSING CONFORMERS OF GAS-PHASE ALANINE: A JET-COOLED RAMAN SPECTROSCOPY STUDY

ROMAN M. BALABIN, Department of Chemistry and Applied Biosciences, ETH Zurich, 8093 Zurich, Switzerland.

The jet-cooled spontaneous Raman spectrum of an amino acid – alanine (Ala, 2-aminopropanoic acid; \( \text{H}_2\text{NCH(CH}_3\text{)}\text{COOH} \)) – is reported. The low-frequency vibrational spectrum (below 500 cm\(^{-1}\)) was recorded and assigned using quantum chemical data: \textit{ab initio} (MP2) and density functional theory (DFT; BLYP, B3LYP, and PBE0/PBE1PBE). Band polarization measurements were used to confirm the vibrational assignments. The acquired medium resolution spectra (HWHM of approximately 4 cm\(^{-1}\)) allow the different alanine conformations to be distinguished. Four alanine conformers were observed and identified: two previously reported by microwave (MW) spectroscopy studies and two that were previously unreported. A set of reasons for why these conformers eluded previous studies are discussed. Selective collisional relaxation processes in the jet (associated with low interconversion barriers between different alanine conformations) that depopulate the high-energy conformers were experimentally demonstrated. Conclusions about conformational equilibrium in peptide/protein building block are made.
CONFORMATIONAL EQUILIBRIUM IN GLYCINE: EXPERIMENTAL JET-COOLED RAMAN SPECTRUM

ROMAN M. BALABIN, Department of Chemistry and Applied Biosciences, ETH Zurich, 8093 Zurich, Switzerland.

The first observation of a gas-phase spontaneous Raman spectrum of an amino acid – glycine (Gly, H₂NCH₂COOH) – is reported. A molecular beam source was combined with a high sensitivity Raman setup to record a low-frequency (below 500 cm⁻¹) vibrational spectrum. Ab initio (first principles; MP2) and density functional theory (DFT; BLYP, B3LYP, and PBE0/PBE1PBE) calculations with the aug-cc-pVTZ Dunning-type basis set were used to support vibrational assignments. Jet-cooling of glycine molecules was observed by varying the laser-nozzle distance. The acquired medium resolution spectra (4 cm⁻¹) allow the different glycine conformations to be distinguished. The structures of the two most stable glycine conformers, previously observed by electron diffraction and microwave spectroscopy, have been confirmed. Evidence is reported for a third conformation (gauche-trans-trans), which has not been previously experimentally reported. Band polarization measurements were used to confirm the vibrational assignments.

TIME-RESOLVED ROTATIONAL ENERGY TRANSFER AND SPECTRAL LINE BROADENING IN ACETYLENE. A HIGH RESOLUTION RAMAN STUDY.

J. L. DOMENECH, R. Z. MARTINEZ, D. BERMEJO, Instituto de Estructura de la Materia (CSIC), Dept. of Molecular Pysics, Serrano 123, E-28006 Madrid, Spain.

The quasi-cw stimulated Raman technique is a powerful tool for the determination of collisional broadening and line-mixing parameters, which bear a very direct relationship with the rotational energy transfer rate constants matrix at the state-to-state level. Indeed, the broadening coefficients and the analysis of line-mixing profiles, frequently combined with a rate-law analysis, have provided a wealth of information on collision physics for many gas systems throughout the years. We report on new high resolution measurements of the broadening coefficients on the Q-branch of the ν₂ band of acetylene.

Furthermore, last year at this meeting, we reported on a new technique for the determination of state-to-state rotational energy transfer rate constants, based on a time-resolved double-resonance Raman-Raman scheme. It uses the quasi-continuous stimulated Raman-loss technique for the probe stage. Through a systematic recording of the time evolution of rotational populations from a single initially populated J level, it allows the direct determination of most elements of the rate-constant matrix without resorting to fitting or scaling laws.

The comparison of the results obtained from the high resolution spectroscopic approach with those from the time-resolved dynamics experiment provides insight into the collision mechanisms and some of the assumptions or simplifications usually made in rate-law analysis.
HIGH-RESOLUTION INFRARED SPECTRA OF BICYCLO[1.1.1]PENTANE: ANALYSES OF THE $\nu_{14}(e')$ AND $\nu_{18}(a_2^{2''})$ BANDS

M. A. MARTIN and A. PERRY, Department of Chemistry, Oregon State University, Corvallis, OR, 97332-4003, USA; T. MASIELLO, Department of Chemistry and Biochemistry, California State University, East Bay, Hayward, CA, 94542, USA; K. SCHWARTZ, Department of Chemistry, Oregon State University, Corvallis, OR, 97332-4003, USA; J.W. NIBLER, Department of Chemistry, Oregon State University, Corvallis, OR, 97332-4003, USA; A. WEBER, Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD, 20899-8441, USA; A. MAKI, 15012 24th Ave., S.E., Mill Creek, WA, 98012, USA; T.A. BLAKE, Pacific Northwest National Laboratory, P.O. BOX 999, Mail Stop K8-88, Richland, WA, USA.

Infrared spectra of the $\nu_{14}(e')$ 540 cm$^{-1}$ and $\nu_{18}(a_2^{2''})$ 835 cm$^{-1}$ bands of bicyclo[1.1.1]pentane have been recorded at a resolution sufficient (0.0015 cm$^{-1}$) to resolve for the first time individual rovibrational lines. This report presents the ground state constants for this molecule determined from two of the ten infrared-active fundamental bands. The fitted transitions were judged to be free of perturbations of their upper state levels. A combined total of more than 6000 lines with $J$ and $K$ quantum numbers of the two bands ranging up to about 60 were fit with an obs-calc RMS deviation of 0.00021 cm$^{-1}$. The following principal constants (in units of cm$^{-1}$) of the rovibrational ground state were obtained: $B_0 = 0.23994136(30)$, $D_{J} = 5.9959(96) \times 10^{-8}$, and $D_{JK} = -1.5052(98) \times 10^{-8}$. The band centers were found to be $\nu_{14} = 540.326397(19)$ cm$^{-1}$ and $\nu_{18} = 832.92902(3)$ cm$^{-1}$. The values in parentheses represent the uncertainties (2 standard deviations) in the last digits of the value of the constants. The results are compared with those obtained for [1.1.1]propellane and with those computed at the ab initio anharmonic level using the B3LYP density functional method with a cc-pVTZ basis set.
MG. ELECTRONIC (UV/VIS/NIR)
MONDAY, JUNE 21, 2010 – 1:30 pm
Room: 170 MATH ANNEX
Chair: TIMOTHY SCHMIDT, University of Sydney, Sydney, Australia

MG01 15 min 1:30
SPECTRAL DISSIMILARITIES BETWEEN AZULENE(C_{10}H_{8}) AND NAPHTHALENE(C_{10}H_{8})

MASAAKI BABA, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan.

Polycyclic aromatic hydrocarbons (PAHs) are of great interest in the molecular structure and excited-state dynamics, and there have been extensive spectroscopic and theoretical studies. Azulene and naphthalene are bicyclic aromatic hydrocarbons composed of odd- and even-membered rings, respectively. First, they were discriminated by a theory of mutual polarizability.  

a Naphthalene is an alternant hydrocarbon, but azulene is not. In contrast, spectral resemblances were found by John Platt et al.,  
b and were explained by their simple model of molecular orbital. However, the absorption and emission feature of the S_1 and S_2 states is completely different each other. We have investigated each rotational and vibrational structures, and radiative and nonradiative processes by means of high-resolution spectroscopy  
c d and ab initio calculation. The equilibrium structures in the S_0, S_1, and S_2 states are similar. This small structural change upon electronic excitation is common to PAH molecules composed of six-membered rings. The fluorescence quantum yield is high because radiationless transitions such as intersystem crossing (ISC) to the triplet state and internal conversion (IC) to the S_0 state are very slow in the S_1 state. In contrast, the S_1 state of azulene is nonfluorescent and the S_1 ← S_0 excitation energy is abnormally small. We consider that the potential energy curve of a b_2 vibration is shallower in the S_1 state, and therefore the vibronic coupling with the S_0 state is strong to enhance the IC process remarkably. This situation is, of course, due to its peculiar characteristics of odd-membered rings and molecular symmetry, which are completely different from the naphthalene molecule.

---


MG02 15 min 1:47
ROTATIONALLY RESOLVED ELECTRONIC SPECTRA OF 2,6-DIAMINOPYRIDINE: A FOUR-FOLD BARRIER PROBLEM

CASEY L. CLEMENTS, JUSTIN W. YOUNG, and DAVID W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

High resolution, rotationally resolved electronic spectra of four bands of 2,6-diaminopyridine were obtained. They were found to have zigzagging inertial defects that point to a double minimum excited state potential energy surface along the amino group inversion coordinate. The possibility of two isomers, differing in the position of the amino group hydrogens above or below the plane of the ring, leads to a four-fold barrier problem. The observed spectra, in combination with high level ab initio calculations, make it possible to distinguish which of the species is the more stable form, and provide information about the barrier heights that govern their interconversion.

---

Work supported by NSF (CHE-0911117).
ROTATIONALLY RESOLVED STUDIES OF \textit{PARA}-AMINOPHENOL AND ITS COMPLEXES.\textsuperscript{a}

JUSTIN W. YOUNG, PATRICK S. WALSH, ADAM J. FLEISHER and DAVID W. PRATT, \textit{Department of Chemistry, University of Pittsburgh, Pa 15260.}

In biological systems, solvent molecules play a significant role through non-covalent interactions. From this, the desire to understand the properties of solvent molecules bound to different functional groups of a bio-molecule follows. The goal of this study is to use rotationally resolved electronic spectroscopy to determine the position of attachment and intermolecular motions of a single solvent molecule linked to three possible receptor sites in \textit{para}-aminophenol; the hydroxyl group, the amino group, and the aromatic ring.

\textsuperscript{a}Work supported by NSF(CHE-0911117)

---

CHARGE REDISTRIBUTION IN THE $\beta$-NAPHTHOL-WATER COMPLEX AS MEASURED BY HIGH RESOLUTION STARK SPECTROSCOPY IN THE GAS PHASE.\textsuperscript{a}

ADAM J. FLEISHER, DAVID W. PRATT, \textit{Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260}; ALESSANDRO CEMBRAN and JIALI GAO, \textit{Department of Chemistry, University of Minnesota, Minneapolis, MN 55455.}

The extensively studied photoacid $\beta$-naphthol exhibits a large decrease in $pK_a$ upon irradiation with ultraviolet light, in the condensed phase.\textsuperscript{b} $\beta$-naphthol is almost 10 million times more acidic in the excited electronic state, compared to the ground state. Motivated by this fact, we report here the measurement of the electronic dipole moments of the $\beta$-naphthol-water complex in both electronic states, from which estimates of the charge transfer from solute to solvent in both states will be made. Comparisons to \textit{ab initio} and density functional theory calculations will also be reported.\textsuperscript{c}

\textsuperscript{a}Work supported by NSF (CHE-0911117).
\textsuperscript{b}N. Mataga and T. Kubota, \textit{Molecular Interactions and Electronic Spectra} (Marcel Dekker, New York, 1970).

---

VIBRATIONAL AND ROTATIONAL STRUCTURE AND EXCITED-STATE DYNAMICS OF PYRENE

YASUYUKI KOWAKA, NOLITAKA ASHIZAWA, MASAAKI BABA, \textit{Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan.}

Pyrene is one of the prototypical compact polycyclic aromatic hydrocarbons (PAHs), and it is important to investigate its molecular structure precisely, because it does not conform to Hückel’s $4n + 2$ rule. We analyzed high-resolution and ultrahigh-resolution spectra of jet-cooled pyrene and elucidated the vibrational and rotational structures in the $S_0$ $^1A_g$ and $S_1$ $^1B_{3u}$ states.\textsuperscript{a} We conclude that the molecule is planar with $D_{2h}$ symmetry. The rotational constants and vibrational normal energies are very similar for the $S_0$ and $S_1$ states, indicating that its geometrical structure and potential energy curves are not changed much upon electronic excitation. This small change is common to large PAH molecules because the changes of bond orders by one electron excitation is diluted with a large number of $\pi$ electrons. The rates of Radiationless transitions in the $S_1$ state are closely related with the molecular structure and the potential energy curves. Intersystem crossing (ISC) to the triplet state is expected to be very slow in planar PAHs. Internal conversion (IC) to the $S_0$ state does not occur, if the molecular structure and potential energy curves are identical for the $S_0$ and $S_1$ states. In perylene, the fluorescence lifetime is 1400 ns, and the fluorescence quantum yield is considerably high. These properties are attributed to its small changes in molecular structure and potential energy curves upon $S_1 \leftrightarrow S_0$ excitation.

\textsuperscript{a}M. Baba, Y. Kowaka \textit{et al.}, \textit{J. Chem. Phys.}, \textbf{131}, 224318 (2009)
Perylene is one of the prototypical compact polycyclic aromatic hydrocarbons (PAHs). The fluorescence quantum yield in the $S_1$ state is considerably high. It is strange because radiationless transitions such as intersystem crossing (ISC) to the triplet state and internal conversion (IC) to the $S_0$ state are expected to be fast due to high density of coupling levels. We observed the ultrahigh-resolution spectrum of the $S_1 \rightarrow S_0$ transition of jet-cooled perylene, and determined the rotational constants in these two states. The inertial defect is positive and small, so that the molecule is considered to be planar with $D_{2h}$ symmetry. The obtained rotational constants of the $S_1$ state is very similar to those of the $S_0$ state. It indicates that the structural change upon electronic transition is very small. We performed ab initio calculation, and the calculated geometrical molecular structure and vibrational energies were in good coincidence with the experimental results. The observed high fluorescence quantum yield shows that radiationless transitions are all slow in the $S_1$ state of perylene. The slow IC can be attributed to the small scale of its structural change. We also observed the ultrahigh-resolution spectrum in the magnetic field of 0.5 Tesla. Zeeman broadening was very small, indicating that the singlet-triplet interaction is very weak, and that ISC is minor in the $S_1$ state. In specific vibronic levels, the fluorescence lifetimes are remarkably short. We conclude that the main process is IC, and the accepting mode is in-plane ($\alpha_g$) deformation vibration in the $S_1$ state.


In recent years it has become increasingly common to analyze diatomic molecule spectroscopic data by using fully quantum mechanical direct potential fits (DPFs) to determine the potential energy function(s) of the state(s) in question. However, the efficacy of this approach is strongly dependent on the quality of the analytic model used for the potential function. The two best models introduced to date are the ‘Morse/Long-Range’ (MLR) function$^a$ which provides particularly compact, accurate and flexible functions which explicitly incorporate correct long-range and sensible short-range behaviour, and the ‘Spline Point-wise Potential’ (SPP) form which is particularly successful for treating states with irregularly shaped potentials with a double-minimum or a ‘shelf’.$^b$ The present work shows that a merging of these two forms effected by representing the exponent coefficient function of the MLR model by a spline passing through a compact mesh of values yields most of the advantages of both approaches. Preliminary illustrative applications to the ground states of Ca$_2$ and NaRb will be presented.


STARK EFFECT STUDIES OF THE ELECTRONIC SPECTRUM OF 1-PHENYLPYRROLE AT HIGH RESOLUTION. CHARGE TRANSFER STATES?\textsuperscript{a}

JESSICA A. THOMAS, JUSTIN W. YOUNG, ADAM J. FLEISHER, and DAVID W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

We report Stark effect studies of the $S_1 - S_0$ electronic spectrum of 1-phenylpyrrole (1PP) at high resolution. Analyses of these data yield values of the magnitudes and orientations of the permanent electric dipole moments of both electronic states. When combined with an earlier analysis of the vibrationally resolved spectrum,\textsuperscript{b} the results provide new insights into the extent to which the $S_1$ state of 1PP is a charge transfer state.

\textsuperscript{a}Work supported by NSF CHE-0911117.  
\textsuperscript{b}J.A. Thomas, \textit{et al.}, \textit{64}th International Symposium on Molecular Spectroscopy, TB06, 2009.

ELECTRONIC SPECTRA OF THE JET-COOLED ACETAMINOPHEN

SEUNG JUN LEE, AHREUM MIN, YUSIC KIM and MYONG YONG CHOI, Department of Chemistry (BK21) and Research Institute of Natural Science, Gyeongsang National University, Jinju 660-701, Korea; JINYOUNG CHANG, SANG HAK LEE, Department of Chemistry, Seoul National University, Seoul 151-747, Korea; and SEONG KEUN KIM, Department of Chemistry, and Department of Biophysics and Chemical Biology, Seoul National University, Seoul 151-747, Korea.

Resonant two-photon ionization (R2PI), laser induced fluorescence (LIF) and UV-UV double resonance spectra of the jet-cooled acetaminophen, widely used as a pain reliever and fever reducer, were obtained in the gas phase. Conformational characterizations for acetaminophen will be presented with an aid of spectroscopic techniques and DFT B3LYP calculations.

PHOTOELECTRON SPECTROSCOPY OF DOPED HELIUM NANODROPLETS

EVGENY LOGINOV and MARCEL DRABBELS, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.

The photoionization of aromatic molecules (aniline, phenol, and toluene) in helium droplets was studied with photoelectron spectroscopy. The photoelectron spectra resemble closely those of gas phase molecules except for the droplet size dependent shift. This shift is caused by the lowering of the ionization threshold upon solvation and can be readily estimated. The individual peaks in photoelectron spectra are broadened, which is thought to partially reflect the rearrangement of helium upon ion solvation. The droplet size and kinetic energy dependences of the peak broadening towards lower energy may be attributed to the relaxation of the photoelectrons as they pass through a helium droplet. ZEKE spectroscopy of surface-doped helium droplets will be discussed.
The nucleobases cytosine, thymine and uracil are pyrimidine derivatives. They pair with their complementary purines, guanine and adenine, through hydrogen bonding to form DNA and RNA chains. The tautomeric forms of DNA bases are capable of unusual base pairing like thymine-guanine and cytosine-adenine and create mutations, which are the precursors of some molecular-based diseases. Low energy spectroscopies such as microwave, laser and infrared techniques are commonly used as methods to investigate the conformational and tautomeric equilibria of biomolecules, while the high energy technique of x-ray photoemission spectroscopy (XPS) has yielded a smaller amount of significant structural information about biomolecules in the gas phase. In the present studies we successfully apply XPS to the study of five nucleic acid base tautomers, as well as the prototypical system 2-hydroxypyridimine and the related molecules S-methyl-2-thiouracil and 2-thiouracil in the vapor phase. XPS is a quantitative technique, allowing the experimental determination of the populations of keto and enol tautomers at known equilibrium temperatures: it is difficult to obtain this information otherwise. The effect of different substituents on stability of tautomers has been revealed. Quantum chemistry calculations have been carried out in order to obtain information about the structure, relative stability and difference in populations of the tautomers and conformers under study.

The excited state dynamics of 9-methylpurine (9MP) were studied with broadband transient absorption spectroscopy in the time regime from femtoseconds to 3 nanoseconds. Excitation of 9MP in aqueous solutions at 266 nm results in ultrafast internal conversion from the initially excited $S_2(\pi\pi^*)$ state to the $S_1$ state. Quantum chemical calculations that include bulk and explicit solvent interactions show that the $S_1$ state has significant $n\pi^*$ character. Population of the $S_1$ state is followed by intersystem crossing (ISC) to the $T_1(\pi\pi^*)$ state on a time scale of hundreds of picoseconds. Vanishingly small fluorescence yields were measured, supporting the dark character of the $S_1$ state as well as the high triplet yield in 9MP. Analogous experiments in acetonitrile show a decrease in the ISC lifetime by almost 50% but an equally high triplet yield. The results presented in this work demonstrate the important role that the dark singlet state has in modulating the excited-state dynamics of DNA monomers in solution.

We have studied the UV photodepletion and photofragment action spectra of deprotonated adenosine monophosphate and guanosine monophosphate as well as their cyclic analogs. We observe the same anionic fragments as in earlier experiments on collision-induced dissociation of deoxyribonucleotides, although their relative intensities are quite different, especially with respect to the abundance of the deprotonated base anions. The suppression and amplification of spectral features provides information about the threshold energies for the active fragment channels.
The electronic energy relaxation of 2-nitronaphthalene (2NN), 1-nitronaphthalene (1NN) and 2-methyl-1-nitronaphthalene (2M1NN) were studied in various solvents using broadband transient absorption spectroscopy with femtosecond time resolution. As was previously shown for 1NN\(^a\), excitation of the nitronaphthalene compounds at 340 nm populates the S\(_1\)(\(\pi\pi^*\)) state, which is proposed to bifurcate into two almost barrierless nonradiative decay channels. The first channel connects the S\(_1\) state with a receiver T\(_n\) state that has strong n\(\pi^*\) character. Intersystem crossing is followed by internal conversion to the lowest triplet state, which is populated with excess vibrational energy. The ensuing vibrational cooling dynamics in the triplet manifold depends on both the solvent and the nitronaphthalene compound studied. The second minor channel involves conformational relaxation of the S\(_1\) state to populate a dissociative singlet state that has significant charge-transfer character and negligible oscillator strength. It is proposed that the relative yield of the two initial nonradiative decay channels depends on the nitronaphthalene compound studied and correlates with their steady-state photochemistry. Quantum chemical calculations including solvent effects substantiate the assignment of the experimental observations.


Accurate interaction energies in benzene-X clusters (X=ethane, propane, n-butane, and cyclohexane) were determined by two-color two-photon ionization spectroscopy. The experimental interaction energies agree well with those evaluated by high precision ab initio calculations at the CCSD(T)(basis set limit) level. The magnitude of the interaction energy is proportional to the averaged polarizability of the hydrocarbon moiety, indicating that the CH/\(\pi\) interaction is dominated by the dispersion force.
PUMP-PROBE DELAYED IONIZATION STUDY OF PHENYLACETYLENE

GARY V. LOPEZ, PHILIP M. JOHNSON AND TREVOR J. SEARS, Department of Chemistry, Stony Brook University, Stony Brook, New York 11794; CHIH-HSUAN CHANG, Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973.

Pump-probe photoionization experiments on the origin of the $S_1 \leftarrow S_0$ transition of phenylacetylene (PA) have revealed the production of long lived ($\gg 100 \mu\text{sec}$ lifetime) species with low ionization potential where short lifetimes ($\text{nsec}$ lifetime) are expected if simple intersystem crossing takes place. The pump-probe delay photoionization decay curve for the band origin, previously presented by Hofstein et al., and four other assigned strong bands in the $S_1 \leftarrow S_0$ transition of PA have been obtained in recent experiments. Following $S_1 \leftarrow S_0$ excitation, the decay consists of a prompt short-lived component matching the measured singlet fluorescence lifetime and a second, very long-lived, component. The ratios between the singlet channel signal to that of the long-lived species for these bands are not the same: 3.03±0.38, 1.48±0.33, 1.75±0.19, 3.11±0.36 and 2.77±0.35 for the origin, $\nu_{15}$, $\nu_{6a}$, $\beta_{cc}$ and $\nu_1$, respectively. The fact that the $\nu_{15}$ and $\nu_{6a}$ modes have low ratios suggests that the normal coordinates of these modes could lie near the reaction path for the formation of the long lived species. Thus, these results combined with theoretical calculations may potentially give an indication of the identity of the long-lived species.

Acknowledgments: Work at Brookhaven National Laboratory was carried out under Contract No. DE-AC02-98CH10886 with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences.

UV PHOTODISSOCIATION OF CYCLIC KETONES IN THE GAS-PHASE AND COLD INERT GAS MATRIXES

ANAMIKA MUKHOPADHYAY, Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India; MOITRAYEE MUKHERJEE, AMIT K. SAMANTA, and TAPAS CHAKRABORTY.

Photodissociation (PD) is a natural means for removal of volatile organic materials from atmosphere. We have studied UV-PD reactions (excitation wavelengths = 254 and 266 nm) of various cyclic and acyclic ketones in the gas phase, and studied also how the reaction channels are altered when the molecules are embedded in cold inert gas matrixes. The gas-phase PD products are characterized by quadrupole mass spectrometry followed by low-energy electron-impact ionization and also by gas-phase FTIR spectroscopy of irradiated gases. PD yields are estimated by measuring the depletion of parent molecular ion signal following introduction of UV laser pulses into molecular beam before ionization and comparing the results with respect to a standard. The mechanisms of PD reactions are suggested by identifying the transient intermediates by mass spectrometry, and energy partitioning among the PD products are estimated by analyzing the shapes of the time-of-flight signals.
MH01 30 min 1:30
METAL-CONTAINING MOLECULES BEYOND THE SOLAR SYSTEM: A LABORATORY AND RADIO ASTRO-NOMICAL PERSPECTIVE

L. M. ZIURYS, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.

Although the history of interstellar molecules began around 1970, with the millimeter-wave detection of CO in the Orion Nebula, metal-containing species have been somewhat elusive for astronomical searches. Only in the past two decades have metal-bearing molecules been identified in space, starting with metal halides (NaCl, KCl, AlCl, and AlF), and then metal cyanide and isocyanide species (MgNC, MgCN, NaCN, and AlNC). Moreover, the metal-containing molecules seemed to be present in a single astronomical object: the envelope of a dying, carbon-rich star, IRC+10216. However, with improvements both in laboratory spectroscopy and telescope sensitivity, it is becoming clear that the relevance of metal-containing species in astrophysics is increasing. Metal oxide and hydroxide species, such as AlO and AlOH, have recently been identified in interstellar space. Metal-containing molecules are now being found in other astronomical sources, such as the oxygen-rich shell surrounding VY Canis Majoris, a supergiant star. These new astronomical discoveries will be presented, as well as the laboratory measurements that made them possible. New directions in rotational spectroscopy of metal-bearing molecules will also be discussed.

MH02 15 min 2:05
THE PURE ROTATIONAL SPECTRUM OF ZnOD AND THE STRUCTURE OF ZnOH (X^2A'):

L.N.ZACK, B.J.HARRIS, M.P.BUCCHINO and L. M. ZIURYS, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ, 85721.

The pure rotational spectrum of ZnOD in its (X^2A') state has been measured using millimeter/submillimeter direct absorption spectroscopy. The molecule was synthesized by reacting zinc vapor with D_2O under DC discharge conditions. The K-ladder structure characteristic of asymmetric tops has been clearly observed in the zinc isotopologues ^64ZnOD, ^66ZnOD, and ^68ZnOD, just as in the ZnOH species. A spin-rotation splitting of ~170-180 MHz for ZnOD is observed for each K component. Constants were obtained by fitting the data to a Watson s-reduced Hamiltonian. Measurement of the ZnOD spectrum, has allowed for a complete r_0 and r_m(1) structure determination for ZnOH. The r_m(1) bond length for Zn-O is 1.7945 Å and 0.9669 Å for O-H, respectively. The Zn-O-H bond angle is 114.2 degrees. We are initiating a study using Fourier transform microwave spectroscopy in order to measure the hyperfine structure due to the hydrogen. The spectral analysis of ZnOD will be presented, as well as conclusions about the structure of ZnOH.
MICROWAVE SPECTRA AND STRUCTURES OF H₂S-CuCl AND H₂O-CuCl.

N. R. WALKER, D. E. WHEATLEY, S. L. STEPHENS, F. J. ROBERTS, V. A. MIKHAILOV AND A. C. LEGON, School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K.

A Balle-Flygare FT-MW spectrometer coupled to a laser ablation source has been used to measure the pure rotational spectra of H₂S-CuCl and H₂O-CuCl. Both molecules are generated via laser ablation (532 nm) of a metal rod in the presence of CCl₄, argon, a low partial pressure of H₂S or H₂O and are stabilized by supersonic expansion. Rotational constants and centrifugal distortion constants have been measured for eight isotopologues of H₂S-CuCl with substitutions available at the copper, chlorine and hydrogen atoms. Transitions in the spectra of nine isotopologues of H₂O-CuCl have been measured with isotopic substitutions achieved for every atom. The spectra of both H₂S-CuCl and H₂O-CuCl are consistent with a linear arrangement of sulphur or oxygen, metal and chlorine atoms. The structure of H₂S-CuCl is pyramidal with Cₛ symmetry. The structure of H₂O-CuCl is either C₂ᵥ planar at equilibrium or Cₛ pyramidal but with a low potential-energy barrier to planarity such that the v=0 and 1 states associated with the motion that inverts the configuration at the O atom are well separated. Nuclear quadrupole coupling constants have been measured for the chlorine and copper atoms in each molecule. Nuclear spin-rotation constants have been determined for the copper atom.

MICROWAVE SPECTRA AND STRUCTURES OF H₂O-AgCl AND H₃N-AgCl.

N. R. WALKER, V. A. MIKHAILOV, S. J. HARRIS, F. J. ROBERTS AND A. C. LEGON, School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K.

A Balle-Flygare FT-MW spectrometer coupled to a laser ablation source has been used to measure the pure rotational spectra of H₂O-AgCl and H₃N-AgCl. Both molecules are generated via laser ablation (532 nm) of a metal rod in the presence of CCl₄, argon, a low partial pressure of H₂O or NH₃ and are stabilized by supersonic expansion. Rotational constants and centrifugal distortion constants have been measured for eight isotopologues of H₂O-AgCl with substitutions at the silver, chlorine, oxygen and hydrogen atoms. B₀ and C₀ have been independently determined for six isotopologues and the spectra are consistent with a linear arrangement of oxygen, silver and chlorine atoms. The structure is either C₂ᵥ planar at equilibrium or Cₛ pyramidal but with a low potential-energy barrier to planarity such that the v=0 and 1 states associated with the motion that inverts the configuration at the O atom are well separated. Preliminary data from a study of H₃N-AgCl will also be presented. Several transitions have been observed and tentatively assigned to hyperfine components of the 2_{02}-1_{01}, 3_{03}-2_{02} and 4_{04}-3_{03} transitions of H₃N-¹⁰⁷Ag³⁵Cl and H₃N-¹⁰⁹Ag³⁵Cl. These data are consistent with a C₃ᵥ structure.

QUADRUPOLE COUPLING IN AlOH, AlCH₃, CuCN, CuOH, AND CuSH DETERMINED BY FOURIER TRANSFORM MICROWAVE TECHNIQUES

M. SUN, D. T. HALFEN, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721; D. J. CLOUTHIER, Department of Chemistry, University of Kentucky, Lexington, KY 40506; and L. M. ZIURYS, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.

The microwave spectra of AlOH (X¹Σ⁺), AlCH₃ (X¹Σ⁺), CuCN (X¹Σ⁺), CuOH (X¹A′), and CuSH (X¹A′) have been measured using Fourier transform techniques. Both aluminum species were created in a dc discharge by the reaction of a mixture of Al(CH₃)₃ in argon carrier gas. The copper species were created in a pulsed dc discharge using copper pin electrodes and a gas mixture with cyanogen (CuCN), methanol (CuOH) or H₂S (CuSH). Four rotational transitions for both ⁶³CuCN and ⁶⁵CuCN were measured in the frequency range of 8 to 34 GHz, while the J = 1 → 0 rotational transitions were measured for the other species. From these data, aluminum and copper quadrupole coupling constants were determined for these species. The results will be discussed with the implications for bonding in these molecules.
FOURIER TRANSFORM MICROWAVE SPECTRUM OF AlCCH (X^1Σ^+) AND ITS ^13C/D ISOTOPOLOGUES

M. SUN, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721; D. J. CLOUTHIER, Department of Chemistry, University of Kentucky, Lexington, KY 40506; and L. M. ZIURYS, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.

The microwave spectrum of AlCCH (X^1Σ^+) has been measured using Fourier transform microwave (FTMW) techniques in the frequency range of 9-40 GHz. This molecule was created in a supersonic expansion by the reaction of trimethyl aluminum, Al(CH₃)₃, and acetylene, C₂H₂, or methane, CH₄, diluted in argon carrier gas, using a pulsed nozzle coupled with a dc discharge. Spectra of Al^{12}C^{13}CH, Al^{13}C^{12}CH, Al^{13}C^{13}CH, Al^{12}C^{12}CD have also been recorded. From these data, rotational constants and Al and D hyperfine parameters have been determined, as well as the r_m(1) structure. AlCCH is a model system for heteroatom dicarbide species.

MICROWAVE MEASUREMENTS OF STRUCTURE CHANGES FOR LIGAND MOLECULES BOUND TO TRANSITION METALS

STEPHEN G. KUKOLICH, Department of Chemistry and Biochemistry, The University of Arizona, Tucson, Arizona 85721.

Precise values for structural parameters for transition metal complexes have been obtained from high-resolution PBFT microwave measurements. The changes in structural parameters for the small organic molecule ligands are relatively large and well-determined. Results for C₆H₆-Os-(CO)₄, C₂H₄-Fe-(CO)₄, C₂H₂-Re-(O)₂CH₃, C₆H₆-Cr-(CO)₃ and C₄H₆-Fe-(CO)₃ will be discussed and compared. For the Ethylene Osmium Tetracarbonyl complex, the experimental ethylene C-C bond length is 1.432 Å, which falls between the free ethylene value of 1.339 Å and the ethane value of 1.534 Å. The angle between the plane of the CH₂ group and the extended ethylene C-C bond (out-of-plane angle) is 26°. Ethylene structural changes are larger for the Os complex than for the similar Fe complex. For Acetylene Methyl dioxoRhenium, the C-C bond length is increased by 0.08 Å to 1.29 Å. The H-C-C interbond angles are reduced from 180° to 146°, and 147°. The planar, D_{6h} structure of free benzene is changed to a C₃v structure with alternating C-C bond lengths due to interaction with Cr-(CO)₃ in the complex. The structural changes are small but significant, since the benzene reactivity is changed. For Butadiene Iron Tricarbonyl, the terminal CH₂ groups are rotated by 28° out of the butadiene plane and the CH₂ plane is folded away from the butadiene C1-C2 axis by 27° in a direction away from the iron atom. Free butadiene has a trans planar conformation, much different from the distorted cis conformation in the complex. These structural changes are usually accompanied by significant changes in reactivity, which has proved useful for transition metal catalysts and metal containing enzymes.

Intermission
Carbon and magnesium are abundant elements in the interstellar medium, so it is possible that carbon chain molecules containing a magnesium atom may exist in this environment. With this in mind, radical molecules of the form MgC\textsubscript{2}\textsubscript{n}H (n = 1,2,3) have been frequent subjects of both experimental and theoretical studies. In this presentation we will discuss our high-resolution experiments of the \textbf{A}^2Π \rightarrow \textbf{X}^2Σ^+ transitions in the isotopologues Mg\textsubscript{12}C\textsubscript{12}CD and Mg\textsubscript{13}C\textsubscript{13}CH, which complement our earlier investigation of this spectrum in Mg\textsubscript{12}C\textsubscript{12}CH. The data permit us to determine the lengths of individual bonds to high precision. In addition, we have expanded on previous studies of the \textbf{A}^2Π \rightarrow \textbf{X}^2Σ^+ transition of Mg\textsubscript{12}C\textsubscript{4}H, conducted at medium resolution. The parameters obtained from our high-resolution spectra are compared with those obtained from theoretical structure calculations.


---

EXPLORING THE PHOTOREDUCTION OF Au(III) COMPLEXES IN THE GAS-PHASE

JESSE C. MARCUM, SYDNEY H. KAUFMAN, J. MATHIAS WEBER, JILA, NIST, Department of Chemistry and Biochemistry, The University of Colorado, Boulder, CO.

We have used photodissociation spectroscopy to probe the electronic structure and photoreduction of Au(III) in gas-phase complexes containing Cl\textsuperscript{−} and OH\textsuperscript{−}. The gas-phase electronic spectrum of [AuCl\textsubscript{4}]\textsuperscript{−} closely resembles the aqueous solution spectrum, showing a lack of strong solvatochromic shifts. Substitution of Cl\textsuperscript{−} ligands with OH\textsuperscript{−} results in a strong blue shift, in agreement with ligand-field theory. Upon excitation, [AuCl\textsubscript{4}]\textsuperscript{−} can dissociate by loss of either one or two neutral Cl atoms, resulting in the reduction of gold from Au(III) to Au(II) and Au(I) respectively. The hydroxide substituted complex, [AuCl\textsubscript{2}(OH)\textsubscript{2}]\textsuperscript{−}, demonstrates similar behavior but the only observable fragment channel is the loss of two neutral OH ligands, leading only to Au(I).

PULSED-FIELD IOIONIZATION ELECTRON SPECTROSCOPY OF LANTHANIDE (Lu, Gd) BENZENE COMPLEXES

MOURAD ROUDJANE, SUDESH KUMARI, and DONG-SHENG YANG, Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.

Over the last 25 years, organometallic chemistry of f elements has attracted considerable attentions of both experimentalists and theoreticians. We have recently succeeded in producing Ln-benzene (Ln = Lu, Gd) complexes in laser-vaporization supersonic molecular beams and in measuring their vibronic spectra using single-photon pulsed field ionization-zero electron kinetic energy (PFI-ZEKE) spectroscopy. We obtained for the first time the adiabatic ionization energy (AIE) and metal-benzene vibrational frequencies. The AIE of the Lu-benzene complex is 44461 (5) cm\textsuperscript{−1}, and the Lu-benzene stretching frequencies are 204 and 270 cm\textsuperscript{−1} in the neutral and ion, respectively. For the Gd-benzene complex, its AIE is 40830 (5) cm\textsuperscript{−1}, and the metal-ligand stretching frequencies of the neutral and ionic species are 256 and 298 cm\textsuperscript{−1}. We will discuss the electronic transitions involved in the PFI-ZEKE spectra of the two complexes by combining the experimental measurements with quantum chemical calculations and spectral simulations.
ROTATIONAL CONFORMERS OF GROUP VI METAL (Cr, Mo, and W) BIS(MESITYLENE) SANDWICH COMPLEXES

SUDESH KUMARI, and DONG-SHENG YANG, *Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.*

Group VI metal bis(mesitylene) sandwich complexes were produced by interactions between laser-vaporized metal atoms and mesitylene vapor in pulsed molecular beams, identified by photoionization time-of-flight mass spectrometry, and studied by pulsed-field-ionization zero-electron-kinetic-energy spectroscopy and density functional theory calculations. Although transition metal bis(arene) sandwiches may adopt eclipsed and staggered conformations, the group VI metal bis(mesitylene) complexes were determined to be in the eclipsed form. In this configuration, two rotational conformers, with methyl group dihedral angles of 0° and 60°, were identified for each complex. The adiabatic ionization energies of the 0° and 60° rotamers were measured to be 40557/40359, 42138/41697, and 41452/41000 cm⁻¹ for the Cr, Mo, and W complexes, with the uncertainty of ∼5 cm⁻¹. The ground electronic states of the 0°(D₃h)/60°(D₃d) rotamers are ¹A'₁/¹A₁g in the neutral form and ²A'₁/²A₁g in the ionized form.

ELECTRONIC AND SPECTROSCOPIC PROPERTIES OF A REDOX ACTIVE ANALOG OF 4,4’-BIPYRIDINE INCORPORATING A METAL-METAL QUADRUPLE BOND

PHIL C. BUNTING, BENJAMIN J. LEAR, and MALCOLM H. CHISHOLM, *The Ohio State University, Columbus, OH 43210.*

The synthesis of the metal-metal quadruple bond containing complex, (MM)(TiPB)₂(nic)₂, where M= Mo or W, TiPB= Triisopropylbenzoate, and nic= isonicotinate, is reported. This is envisioned as an inorganic analog of 4,4’-bipyridine, which is used to bridge two tris(pentafluorophenyl)borane units. The electronic and spectroscopic properties of both the parent compounds and the borane adducts are discussed. For both the molybdenum and tungsten complexes, addition of the borane significantly stabilizes the HOMO and, to a larger extent, the LUMO of the complexes. This results in a redshift in the metal to ligand charge transfer band for the neutral complexes and stabilizes the -1, mixed valence, state of the complexes.

EXCITED STATE PROPERTIES OF PADDLEWHEEL COMPLEXES INVOLVING METAL-METAL (M = MO, W) QUADRUPLE BONDS SUPPORTED BY AMIDINATE AND CARBOXYLATE LIGANDS

BRIAN G. ALBERDING, MALCOLM H. CHISHOLM, and TERRY L. GUSTAFSON, *The Ohio State University, Department of Chemistry, Columbus, Ohio, 43210.*

Spectroscopic studies of the trans-substituted compounds M₂(O₂CCCH₃)₂[(N’Pr)₂CCCR]₂ (where M = Mo or W and R = aromatic hydrocarbon) have been carried out. These complexes have been shown to possess optically active excited states in both the singlet and triplet manifolds that can be classified as either charge transfer or metal centered in character. The nature of the excited states has been assigned based on steady state absorbance and emission studies and supported by electronic structure calculations. Furthermore, excited state dynamics have been determined from both ns- and fs-transient absorption spectroscopies. Comparisons will be made between molybdenum and tungsten.
WATER REACTIVITY WITH TUNGSTEN OXIDES: FORMATION OF H₂ FROM W₂Oₙ⁻ + H₂O REACTIONS

NICHOLAS J. MAYHALL, DAVID W. ROTHGEB, EKRAM HOSSAIN, CAROLINE CHICK JARROLD, AND KRISHNAN RAGHAVACHARI, Department of Chemistry, Indiana University, 800 E. Kirkwood Avenue, Bloomington, Indiana 47405, USA.

In a recent mass spectrometry/photoelectron spectroscopy study on the reactions between W₂Oₙ⁻ (ₙ = 2–6) and water, Jarrold and coworkers (J. Chem. Phys., 130, 124312 2009) observed interesting differences in the reactivity of the different cluster ions. Particularly noteworthy is the observation that the only product with the incorporation of hydrogens is a single peak corresponding to W₂O₆H²⁻. As reactions between metal oxide clusters and small molecules such as water have high potential for catalytic applications, we aim to obtain a mechanistic understanding of this observed reactivity. Using electronic structure calculations, we have identified and characterized multiple modes of reactivity between unsaturated tungsten oxide clusters (W₂O₄⁻ (ₙ = 4–6)) and water. By calculating the free energy corrected reaction profiles, our results provide an explanation for the formation of W₂O₆H²⁻. We propose a mechanism in which water reacts with a metal oxide cluster and eliminates H₂. The results from our calculations show that this is nearly a barrierless process for all sub-oxide clusters with the exception of W₂O₅⁻.

DYNAMICS OF METAL CYANIDES

DANIEL WEIDINGER, Code 6111, Naval Research Laboratory, 4555 Overlook Ave SW Washington, D.C. 20375; DOUGLAS J. BROWN, Chemistry Department, United States Naval Academy, Annapolis, MD 21402; CASSIDY HOUCHINS, Code 6111, Naval Research Laboratory, 4555 Overlook Ave SW Washington, D.C. 20375; and JEFFREY C. OWRUTSKY, Code 6111, Naval Research Laboratory, 4555 Overlook Ave SW Washington, D.C. 20375.

Time resolved IR spectroscopy was used to characterize the vibrational energy relaxation (VER) dynamics of the CN stretching bands of aqueous molecular metal cyanides and networked metal cyanides, such as Prussain Blue, in reverse micelles. The vibrational and rotational relaxation dynamics of the CN stretching bands near 2000 cm⁻¹ for aqueous molecular cyanides Au(CN)₂⁻, Ni(CN)₄⁻², Pt(CN)₄²⁻, Co(CN)₆⁻³, Mn(CN)₄²⁻, and Ru(CN)₆⁻¹ have been investigated using ultrafast pump-probe spectroscopy. While the spectra and dynamics of Ru(CN)₆⁻¹ are similar to those previously reported for ferrocyanide, VER times are significantly longer (>30 ps) in the other molecules. Mn(CN)₆⁻³ represents an intermediate case with a relaxation time of about 15 ps in water. The VER dynamics extend and reinforce the established trends of metal cyanide CN band frequencies and intensities. Prussian Blue and its ruthenium analog were also studied using visible pump-IR probe and IR pump-IR probe spectroscopy. The VER dynamics are similar to the monometal cyanides and there is evidence for CN band excitation following back electron transfer based on the comparison of visible and infrared pump results.
MI. RADICALS AND IONS
MONDAY, JUNE 21, 2010 – 1:30 pm
Room: 1015 McPHERSON LAB

Chair: JU XIN, Bloomsburg University, Bloomsburg, Pennsylvania

MI01 15 min 1:30
MICROWAVE SPECTROSCOPY AND POTENTIAL ENERGY SURFACES OF Ne-OH and Kr-OH

YOSHIHIRO SUMIYOSHI, IPPEI FUNAHARA, KAZUYA SATO, YASUHIRO OHSHIMA, and YASUKI ENDO, Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153-8902, Japan.

Three-dimensional potential energy surfaces for Ne-OH/OD and Kr-OH/OD have been determined from the data by Fourier-transform microwave spectroscopy with fine and hyperfine structures. For Ne-OH, data of rovibrational transitions between the levels with $P = 0.5$ and $1.5$ have been utilized as well as those of the pure rotational transitions. Simultaneous least-squares analyses utilizing the data of the two isotopologues were performed, where all the freedom of motions for an atom-diatom system in the Jacobi coordinate, $R$, $\theta$, and $r$, were considered. The initial values for the least-squares analyses were obtained by high-level ab initio calculations at the UCCSD(T)-F12 theory with the basis set of aug-cc-pV5Z for Ne-OH and aug-cc-pVQZ for Kr-OH. Dependences of the intermolecular interaction energy on the bond length of the OH monomer of the two complexes are compared with that of Ar-OH, where the interaction potential of Ar-OH has been redetermined using the new initial potential parameters by UCCSD(T)-F12/aug-cc-pV5Z.

$^a$Present address: Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

MI02 15 min 1:47
OBSERVATION OF PURE ROTATIONAL SPECTRA OF trans-, and cis-HOCO/DOCO

TAKAHIRO OYAMA, WATARU FUNATO, YOSHIHIRO SUMIYOSHI and YASUKI ENDO, Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo, 153-8902, Japan.

Rotational spectra of trans-, cis-HOCO and DOCO have been observed using an Fourier transform microwave(FTMW) spectrometer and the FTMW-mmw-DR technique. The cis-conformer was observed for the first time in the gas phase. The HOCO radical was produced in a supersonic jet by discharging a gas mixture of CO and H$_2$O diluted in Ar. The molecular constants including the hyperfine coupling constants have been precisely determined. The determined $r_0$ structure of the two conformers are consistent with those of ab initio calculations. The fermi constants of the two conformers indicate that the spin densities on the hydrogen nuclei are different between the two conformers.
ORTHODO-PARA MIXING INTERACTION IN THE VINYL RADICAL DETECTED BY MILLIMETER-WAVE SPECTROSCOPY AND PREDICTION OF FAST ORTHO-PARA CONVERSION RATE

KEIICHI TANAKA, MASATO HAYASHI, MITSUHIKO OHTSUKI, KENSUKE HARADA, and TAKEHIKO TANAKA, Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashiku, Fukuoka 812-8581, Japan.

Ortho-para mixing interaction due to the coupling of nuclear and electron spins was detected for the first time by millimeter-wave spectroscopy of deuterated vinyl radicals, H$_2$CCD and D$_2$CCD, of which the ground states are split by the tunneling motion of the $\alpha$ deuteron into two components $0^+$ and $0^-$, whose separations have been determined to be $\Delta E_0 = 1186.644(16)$ and $771.978(18)$ MHz, respectively. The observed tunneling-rotation spectra are significantly perturbed by the ortho-para mixing interaction expressed by $\langle 0^\pm | H' | 0^\mp \rangle = (\delta \alpha_e^{(\beta)}/2) S \cdot (I_{\beta 1} - I_{\beta 2})$, where $I_{\beta 1}$ and $I_{\beta 2}$ are spins of the two hydrogen nuclei in the $\beta$ position and $S$ is the electron spin, which connects rotational levels in the $0^+$ and $0^-$ states, one being an ortho level and the other a para level. The $\delta \alpha_e^{(\beta)}$ constants for H$_2$CCD and D$_2$CCD have been determined to be $68.06(53)$ and $10.63(94)$ MHz, respectively, consistent each other within the isotopic mass relation. The ortho and para states are mixed by about 0.097% and 0.0123% due to this interaction. $^a$ The $\delta \alpha_e^{(\beta)}$ constant for H$_2$CCH should be similar to that for H$_2$CCD because of the same probability density of the unpaired electron at the $\beta$ protons, but could not be determined independently in our previous study. It is because the mixing of para- and ortho-levels of about 0.00044% is much smaller than that for H$_2$CCD due to the large tunneling splitting of $\Delta E_0 = 16271.8429(59)$ MHz. $^b$

The rate constant of para to ortho ($I_{\beta} = 0 \rightarrow 1$) conversion is predicted as $1.2 \times 10^5$ s$^{-1}$ torr$^{-1}$ for H$_2$CCD, suggesting extremely rapid mutual conversion between ortho and para nuclear spin isomers of H$_2$CCD, which is more than $10^6$ times faster compared with that in closed shell molecules such as H$_2$CO and H$_2$CCH$_2$.


OBSERVATION OF THE $\tilde{A} - \tilde{X}$ TRANSITION OF ALLYL PEROXY RADICAL VIA CAVITY RINGDOWN SPECTROSCOPY

PHILLIP S. THOMAS and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus OH 43210.

Organic peroxy radicals are important chemical intermediates produced in combustion and by atmospheric oxidation of hydrocarbons. Peroxies containing the allyl functionality are particularly important as these are generated in large quantities by the OH-initiated oxidation of isoprene, the most abundant non-methane biogenic hydrocarbon. A structural diagnostic for the parent compound, the allyl peroxy radical, is therefore of great importance. We have recently measured the room temperature $\tilde{A} - \tilde{X}$ electronic absorption spectrum of allyl peroxy via cavity ringdown spectroscopy. Photolysis of allyl bromide at 193 nm or 248 nm in the presence of O$_2$ results in observation of signals belonging to both allyl peroxy and HO$_2$ radicals, with the longer wavelength conditions being more favorable towards allyl peroxy formation. By comparing the experimental spectra with predictions from ab initio and density functional calculations, we have assigned the band origins and vibrational structure to conformers of allyl peroxy. Three of the five possible conformers (T$_1$G$_2$, G$_1$G$_2$, G$_1'$G$_2$) can be identified in the room temperature spectrum; the apparent absence of the remaining two conformers is rationalized on the basis of low Boltzmann factors and/or oscillator strengths. Computed OICC torsional potentials are presented and their implications on the spectroscopy are discussed. This work represents an extension of recent progress in measuring $\tilde{A} - \tilde{X}$ absorption spectra of alkyl peroxy radicals to unsaturated species.
SPECTROSCOPY AND DISSOCIATION DYNAMICS OF THE 1-METHYLALLYL RADICAL

M. GASSER, J. A. FREY, J. M. HOSTETTLER and A. BACH, Laboratorium für Organische Chemie, ETH Zürich, CH-8093, Switzerland.

The $\tilde{A} \rightarrow \tilde{X}$ band system of jet-cooled 1-methylallyl radical ($\text{C}_4\text{H}_7$) was observed for the first time using resonance-enhanced multiphoton ionization combined with electronic ground state depletion spectroscopy. Analysis of the vibronic structure reveals transitions to the non-planar $\tilde{A}$ valence excited state with an electronic origin for the $Z$-isomer of 1-methylallyl at 23 979 cm$^{-1}$.

Time- and frequency-resolved photoionization of the hydrogen atom product from electronically excited 1-methylallyl radical and its isotopologue $\text{CH}_3\text{C}_3\text{D}_4$ provides information on the dissociation dynamics. The measured dissociation rates and kinetic energy release combined with results from high level $ab\text{ initio}$ calculations suggests unimolecular decomposition to 1,3-butadiene and hydrogen with no evidence for nonstatistical behavior in dissociation.

HYDROCARBON RADICALS ISOLATED IN HELIUM NANODROPLETS

ALEXANDER M. MORRISON, STEVEN D. FLYNN, TAO LIANG and GARY E. DOUBERLY, Department of Chemistry, University of Georgia, Athens, Georgia 30602.

We report high resolution infrared spectra in the C-H stretch region for small hydrocarbon radicals isolated in helium nanodroplets. Stark Spectroscopy of the symmetric CH$_2$ stretch of the ethyl radical provides the first experimentally measured dipole moment for this species.

OBSERVATION OF THE $\tilde{A} - \tilde{X}$ ELECTRONIC TRANSITION OF $\beta$-HYDROXYETHYL PEROXY VIA CAVITY RING DOWN SPECTROSCOPY

RABI CHHANTYAL-PUN, NEAL D. KLINE, PHILLIP S. THOMAS and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus OH 43210.

Peroxy radicals, formed by the addition of oxygen to organic radicals, are key intermediates in combustion and atmospheric chemistry. $\beta$-hydroxyethyl peroxy ($\text{HO}_2\text{CH}_2\text{OO}/\beta$-HEP) in particular is a key intermediate in the OH radical mediated oxidation of ethene in the atmosphere and the combustion of ethanol. Historically, $\tilde{B} - \tilde{X}$ transitions of peroxy radicals have been monitored in kinetic studies. However, this system cannot be used to extract detailed structural information due to predissociation in the $\tilde{B}$ state. Recently, the $\tilde{A} - \tilde{X}$ transitions, which are weak but structured and specific to conformers and isomers, have been studied for a number of aliphatic and aromatic peroxy radicals using the sensitive cavity ring down spectroscopy (CRDS) technique. In this work we present for the first time the observation and analysis of the $\tilde{A} - \tilde{X}$ transition of the $\beta$-HEP using CRDS. Aided by $ab\text{ initio}$ and DFT calculations, we tentatively assign our spectrum to low energy conformers involving different G($\pm 120^\circ$) and T($O^\circ$) orientations of the three dihedral angles between the OOC and OCC, the OCC and CCO, and the CCO and COH planes.
JET-COOLED $\tilde{A}$-$\tilde{X}$ SPECTRA OF THE $\beta$-HYDROXYETHYLPEROXY and $\beta$-HYDROXYETHYLPEROXY-OD RADICALS

MING-WEI CHEN, GABRIEL M. P. JUSTa, TERRANCE CODD, and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210.

The $\beta$-hydroxyethylperoxy (HOCH$_2$CH$_2$OO, $\beta$-HEP) radical in the atmosphere arises from the reaction of ethene (CH$_2$CH$_2$) and hydroxyl radical (OH), followed by the reaction with oxygen (O$_2$). It is also an important intermediate in the oxidation of ethanol, a component of automotive fuel. High-resolution, jet-cooled cavity ring-down spectroscopy (resolution of $\Delta \nu \approx 250$MHz, considering the instrumental linewidth and the residual Doppler broadening) has been applied to observe the $\tilde{A}$-$\tilde{X}$ origin band of the most stable conformer of both $\beta$-HEP and mono-deuterated $\beta$-HEP (DOCH$_2$CH$_2$OO, $\beta$-HEP-OD). Broadened rotational contours are observed for both isotopologues, but more resolved structure is shown in the $\beta$-HEP-OD spectrum. The evolutionary algorithm approach is applied to analyze the spectra, which gives fitted rotational constants and the homogeneous linewidths for both isotopologues using an asymmetric-top model for the rotational Hamiltonian. Evidence corresponding to a narrower homogeneous linewidth in the $\beta$-HEP-OD spectra implies that the broad rotational contour of $\beta$-HEP likely involves the motion of the hydrogen of the OH group.

aPresent address: Lawrence Berkeley National Laboratory, Lawrence Berkeley National Laboratory

INTERMISSION

HIGHER VIBRATIONAL LEVELS OF THE $\tilde{A}^1\Pi_u$ STATE OF C$_3$ OBSERVED BY LASER-INDUCED FLUORESCENCE

CHIAO-WEI CHEN, ANTHONY J. MERER, JUN-MEI CHAO, AND YEN-CHU HSU, Institute of Atomic and Molecular Sciences, Academia Sinica, Box 23-166, Taipei, Taiwan 10617.

The vibrational structure of the $\tilde{A}^1\Pi_u$ electronic state of C$_3$ in the region 26000-31000 cm$^{-1}$ has been re-examined, using laser excitation spectra of jet-cooled molecules. Rotational constants and vibrational energies have been determined for over 60 previously unreported vibronic levels; a number of other levels have been re-assigned. The vibrational structure is complicated by interactions between levels of the upper and lower Born-Oppenheimer components of the $\tilde{A}^1\Pi_u$ state, and by the effects of the double minimum potential in the $Q_3$ coordinate, recognized by Izuha and Yamanouchi. The present work shows that there is also strong anharmonic resonance between the overtones of the $\nu_1$ and $\nu_3$ vibrations. For instance, the $\Sigma^+_u$ vibronic levels 2 $1^+1$ and 0 $1^+3$ are nearly degenerate in zero order, but as a result of the resonance they give rise to two levels 139 cm$^{-1}$ apart, centered about the expected position of the 2 $1^+1$ level. Similarly, the 202 level lies 60 cm$^{-1}$ lower than expected because of interaction with the 400 and 004 levels. With these irregularities recognized, every observed vibrational level up to 29550 cm$^{-1}$ (a vibrational energy of nearly 5000 cm$^{-1}$) can now be assigned.

EMISSION SPECTROSCOPY FOLLOWING THE MULTIPHOTON PHOTOLYSIS OF HALOMETHANES AT NEAR-ULTRAVIOLET WAVELENGTHS

CHEN-NAN LIU, HSIANG-FU LIAO, GUANG-YI HOU, SHI-XING YANG, and BOR-CHEN CHANG,
Department of Chemistry, National Central University, Jhongli 32001, Taiwan.

Emission spectroscopy including nascent emission and laser-induced dispersed fluorescence was adopted to investigate the multiphoton photolysis mechanism of halomethanes at near-ultraviolet wavelengths in a slow flow system. In the 266 nm photolysis of the interested halomethanes (CHBr$_3$, CHBr$_2$Cl, CHBrCl$_2$, CH$_2$Br$_2$, CHI$_3$, CH$_2$I$_2$, and CH$_3$I), several excited species such as CH ($A^2\Delta$, $B^2\Sigma^-$, and $C^2\Sigma^+$), atomic Br or I, and $C_2$ ($d^3\Pi_g$) were observed in the nascent emission spectra. Halomethylene (CHX, X= Br, Cl, I), the reactive intermediates, were not observed in nascent emission spectra, but they can be found using laser-induced dispersed fluorescence spectroscopy following excitation of their $\tilde{A}^1A''(0,v_2,0)$--$\tilde{X}^1A'(0,0,0)$ transitions. Interestingly, CHBr was seen only in the photolysis of CHBr$_3$, whereas CHCl was only discovered when the precursor is CHBr$_2$Cl or CHBrCl$_2$. The photolysis laser power dependence and emission waveform measurements were also conducted. In addition, nascent emission spectra following the photolysis at longer near-ultraviolet wavelengths (280 nm and 355 nm) were acquired. The results show the distinctive differences between the photolysis of bromomethanes (CHBr$_3$, CHBr$_2$Cl, CHBrCl$_2$, and CH$_2$Br$_2$) and that of iodomethanes (CHI$_3$, CH$_2$I$_2$, and CH$_3$I). Our recent progress will be presented.

SUB-DOPPLER SPECTROSCOPY OF MIXED STATE LEVELS IN CH$_2$

CHIH-HSUAN CHANG, GREGORY E. HALL AND TREVOR J. SEARS, Chemistry Department, Brookhaven National Laboratory, Upton, New York, 11973.

Saturation dip spectroscopy has been used to measure rovibronic transitions in the $\tilde{b}^1B_1$ -- $\tilde{a}^1A_1$ band system of CH$_2$ at sub-Doppler resolution. The radical was made by 308 nm excimer laser photolysis of a slowly flowing, low-pressure, sample of ketene (CH$_2$CO), optionally with added inert buffer gas. Typical observed linewidths in the pure precursor are approximately 8 MHz (FWHM), due to a combination of collisional lifetime and pump-probe beam crossing angle. Due to the non-zero $^1\text{H}$ proton nuclear spin, CH$_2$ exists as two distinct variants, ortho-CH$_2$ with $I^\text{H}=1$ and para-CH$_2$ with $I^\text{H}=0$. In ortho-CH$_2$, each rotational level consists of a triplet of hyperfine components corresponding to levels with $F=J,J\pm1$. Most singlet CH$_2$ transitions show unresolved hyperfine structure in our experiment, since the largest splitting is due to $I,J$ coupling, typically of the order of kHz. However, a small number of rotational levels in the $v=0$ level of the lower $\tilde{a}$ state are known to be perturbed by accidentally near degenerate $^5\Sigma^+$-state levels via spin-orbit coupling. Spectra involving such levels in ortho-CH$_2$ exhibit resolvable triplet, $I,S$, hyperfine splittings, with the splittings providing a direct measure of triplet state character of the level. We have measured hyperfine splittings for a number of pairs of perturbed levels confirming and refining previous estimates of the singlet-triplet mixing coefficients. Measurements of the pressure-dependent saturation recovery rates with different collision partners can give new insights into dephasing, velocity-changing and inelastic collisions relevant to pressure broadening and intersystem crossing mechanisms.

Acknowledgments: Work at Brookhaven National Laboratory was carried out under Contract No. DE-AC02-98CH10886 with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences.

THE ORIGIN BAND OF THE $\tilde{b} - \tilde{a}$ SYSTEM OF CH$_2$

GREGORY E. HALL, AND TREVOR J. SEARS, Department of Chemistry, Brookhaven National Laboratory, Upton, NY, 11973; BOR-CHEN CHANG, Department of Chemistry, National Central University, Jhongli 32001, Taiwan, R.O.C.; ZHONG WANG, Shinnecock Building, SUNY Suffolk Eastern Campus, Riverhead NY 11901; JU XIN, ERIC OTRUBA AND TYLER LATSHA, Department of Physics and Engineering Technology, Bloomsburg University, Bloomsburg, PA, 17815.

Optical double resonance measurements of several rovibronic transitions in the $\tilde{b}^1B_1 \leftarrow \tilde{a}^1A_1$ origin band of CH$_2$ were reported at the 2008 Symposium.$^a$ Although these assignments are unambiguous, the data are sparse and the spectral resolution was limited by the pulsed laser used. We have therefore recorded the complete absorption spectrum between approximately 8200 cm$^{-1}$ and 8400 cm$^{-1}$ at Doppler-limited resolution using an extended cavity diode laser source. This region includes the expected positions of both the $K_a = 0 \leftarrow 1$ and $K_a = 1 \leftarrow 0$ subbands. Although the calculated intensities for these transitions are small,$^b$ the observed spectra have good signal-to-noise ratio and many additional transitions are seen. We have assigned all the expected transitions involving $K_a' = 0$, and part of the subband with $K_a' = 1$. However definitive assignment of transitions involving $J' = 4$ and higher in the second subband have so far eluded us, and additional optical double resonance measurements are needed to decide between several possible assignments.

Acknowledgments: Work at Brookhaven National Laboratory was carried out under Contract No. DE-AC02-98CH10886 with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences. Support from the Department of Energy Faculty and Student Teams Program for Bloomsburg University is gratefully acknowledged.

$^a$Z. Wang et al., paper WG03, 63rd OSU International Symposium on Molecular Spectroscopy.

SPECTROSCOPIC IDENTIFICATION OF NEW BENZYL-TYPE RADICALS IN CORONA EXCITATION: CHLORO-\(\alpha\)-METHYLBENZYL RADICALS

YOUNG WOOK YOON, SEUNG WOON LEE, SANG KUK LEE, Department of Chemistry, Pusan National University, Pusan 609-735, South Korea; and GI WOO LEE, Korea Basic Science Institute, Pusan 609-735, Korea.

Using a pinhole-type glass nozzle coupled with corona excited supersonic expansion (CESE), precursors \(\alpha\)- and \(p\)-chloroethylbenzenes seeded in a large amount of inert carrier gas helium were corona discharged to produce jet-cooled benzyl-type radicals. The vibronic emission spectra were recorded with a long path monochromator to observe vibronic bands of benzyl-type radicals in the visible region. The analysis of the spectra shows the evidence of the \(\alpha\)- and \(p\)-chlorobenzyl radicals as typical products in corona excitation as well as the \(\alpha\)- and \(p\)-chloro-\(\alpha\)-methylbenzyl radicals as unexpected species. After subtracting the bands belonging to chlorobenzyl radicals, we could construct the vibronic emission spectra of the \(\alpha\)- and \(p\)-chloro-\(\alpha\)-methylbenzyl radical in the \(D_1 \rightarrow D_0\) electronic transition at the gas phase. By comparing with those of \textit{ab initio} calculation and of the known vibrational mode frequencies with similar structures, we could obtain the electronic transition and assign the vibrational modes to the bands observed.


CORRELATED \textit{AB INITIO} STUDY OF THE GROUND ELECTRONIC STATE OF THE \(O_2\)-HCN COMPLEX

WAFAA M. FAWZY, Department of Chemistry, Murray State University, Murray, KY 42071.

The potential energy surface of the \(O_2(X^3\Sigma_g^-)-HCN\) complex has been investigated using the CCSD(T) level of theory with the aug-cc-pVDZ and aug-cc-pVTZ basis sets. Results of calculations with the aug-cc-pVTZ basis set provided a minimum energy structure of a planar bent geometry with a well depth of about 320 cm\(^{-1}\). In Jacobi coordinates, the angles between the internuclear axes of the \(O_2\) and the HCN monomers with respect to the axis that connects their centers of masses in the complex are 48° and 6°, respectively. The distance between centers of masses of moieties of the complex is 3.9 Å. Currently, calculations with the aug-cc-pVQZ basis set as well as effects of the BSSE corrections are being investigated. Results of the current work will be discussed and compared to results of our previous \textit{ab initio} study of the \(O_2(X^3\Sigma_g^-)-H_2\) and \(O_2(X^3\Sigma_g^-)-HF\) complexes.
Gas absorption cells specifically designed to achieve stable temperatures down to ∼70 K to fit inside the sample compartment of an evacuated Bruker (IFS-125HR) Fourier Transform spectrometer (FTS) have been developed at Connecticut College, and tested at the Jet Propulsion Laboratory (JPL). In operation, the temperature-controlled cooling by a closed-cycle helium refrigerator achieved a temperature stability of ±0.01 K. The unwanted absorption features initially observed from cryo-deposits formed on the outside cell windows were eliminated by adding an internal vacuum shroud box around the coolable cell to isolate it from residual gases in the evacuated FTS chambers. The effects of vibrations arising from the closed-cycle helium refrigerator upon the FTS spectra were characterized. Using this set up, high resolution spectra of several methane isotopologues (such as $^{12}$CH$_4$, $^{13}$CH$_4$ and $^{12}$CH$_3$D) broadened by N$_2$, were recorded in the 1230 to 1850 cm$^{-1}$ spectral region. Such data are needed to characterize the temperature dependence of line shapes at very low temperatures for remote sensing of outer planets and their moons. Results from the initial analysis of the R(2) manifold of the $\nu_4$ fundamental band of $^{13}$CH$_4$ are discussed to examine whether the N$_2$-broadened half width coefficients follow a simple exponential temperature-dependence over the entire 80 - 296 K temperature range. This initial test was very successful, proving that a high precision Fourier transform spectrometer can be easily configured for spectroscopic studies at very low temperatures relevant to planetary atmospheres.$^a$

$^a$Research described in this paper was performed at Connecticut College, the College of William and Mary, NASA Langley Research Center and the Jet Propulsion Laboratory, California Institute of Technology, under contracts and cooperative agreements with the National Aeronautics and Space Administration.
INFRARED SPECTRA OF N$_2$-BROADENED $^{13}$CH$_4$ AT TITAN ATMOSPHERIC TEMPERATURES


High-resolution spectra of the $\nu_4$ fundamental band of $^{13}$CH$_4$ broadened by N$_2$ at temperatures relevant to the atmosphere of Titan (80 K to 296 K) have been recorded using new temperature-controlled absorption cells installed in the sample compartment of a Bruker (IFS-125HR) Fourier Transform spectrometer (FTS) at the Jet Propulsion Laboratory (JPL). Details of the cells and spectrometer performance have been discussed in the previous talk.$^a$ Early analysis of these spectra using multispectrum fitting has determined half widths, pressure-induced shifts, line mixing parameters and their temperature dependences for R-branch transitions from R(0) through R(6). In addition to the initial R(2) study mentioned in the previous talk, the analysis for the other J-manifolds examined in detail whether or not the N$_2$-broadened half width coefficients follow the simple power-law temperature-dependence over the entire temperature range from 80 K to 296 K. The results are compared with other published measurements of N$_2$-broadened methane parameters at low temperatures.$^b$

$^a$A. W. Mantz et al., Closed-cycle He-cooled absorption cells designed for a Bruker IFS-125HR: First results between 79 K and 297 K, this session.

$^b$Research described in this paper was performed at Connecticut College, the College of William and Mary, NASA Langley Research Center and the Jet Propulsion Laboratory, California Institute of Technology, under contracts and cooperative agreements with the National Aeronautics and Space Administration.

HIGH RESOLUTION INVESTIGATION OF THE ETHANE SPECTRUM AT 7 MICRON (1430 CM$^{-1}$)

C. DI LAURO, F. LATTANZI, Dipartimento di Chimica Farmaceutica e Tossicologia, Università di Napoli Federico II, I-80131 Naples, Italy; K. SUNG, L. R. BROWN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA; J. VANDER AUWERA, Service de Chimie Quantique et Physique, Université Libre de Bruxelles, CP 160/09, 50 avenue F.D. Roosevelt, B-1050 Brussels, Belgium; A.W. MANTZ, Dept. of Physics, Astronomy and Geophysics, Connecticut College, New London, CT 06320, USA; M. A. H. SMITH, Science Directorate, NASA Langley Research Center, Hampton, VA 23681, USA.

Building upon our previous contributions,$^a$ we are re-investigating the ethane spectrum between 1330 and 1610 cm$^{-1}$. For this, spectral data were obtained at room and cold (130 K) temperatures with two Bruker Fourier transform spectrometers (at 0.002 cm$^{-1}$ resolution in Brussels and at 0.003 cm$^{-1}$ resolution in Pasadena). Over 3300 lines were assigned to $\nu_6$, $\nu_8$, $\nu_4 + \nu_{12}$ and $2\nu_4 + \nu_9$ cold bands, and one hot band ($\nu_4 + \nu_8 - \nu_4$). Note that $\nu_6$, $\nu_8$, $\nu_9$, and $\nu_{12}$ are near 1379, 1472, 823, and 1195 cm$^{-1}$, respectively, and $\nu_4$ is the torsional mode near 289 cm$^{-1}$. Our new analysis includes an improved implementation of the theoretical Hamiltonian needed to interpret the very complex spectral structures caused by numerous interactions between these 5 vibrational modes. From this, an empirical line list of positions and estimated intensities is being generated for planetary applications.

Part of the research described in this paper was performed at the Jet Propulsion Laboratory, California Institute of Technology, Connecticut College, and NASA Langley under contracts and grants with the National Aeronautics and Space Administration.

LINE PARAMETERS OF ETHANE ($^{12}$C$_2$H$_6$) AT 12 µm WITH CONSTRAINED MULTISPECTRUM FITTING


A multispectrum nonlinear least squares technique was applied to simultaneously fit 43 infrared absorption spectra of C$_2$H$_6$ between 795 and 850 cm$^{-1}$. The high resolution (0.0016-0.005 cm$^{-1}$) spectra were recorded with two different Bruker Fourier transform spectrometers at PNNL and JPL to support Earth and planetary atmosphere studies, e.g. Titan’s cold stratosphere. Accurate line positions and absolute intensities at room temperature were retrieved for over 1750 transitions of ν$_9$. N$_2$- and self-broadened halfwidth coefficients with their temperature dependences were obtained for over 1330 lines using sample temperatures between $\sim$150 and 298 K. Constraints to intensity ratios, torsional splittings, halfwidth coefficients and their temperature dependence exponents were incorporated in the analysis to determine these parameters for both torsional split components. The variations of the observed halfwidth coefficients and their temperature dependences with respect to J, K quanta are discussed. No pressure-induced shifts were measured or even required to fit the spectra to their noise levels. Present results are compared with previously reported measurements and predictions.

**MJ05**

HIGH RESOLUTION INFRARED SPECTRUM OF ETHYLENE ($^{12}$C$_2$H$_4$) IN THE SPECTRAL REGION 1820 TO 2300 CM$^{-1}$

JEAN-MARIE FLAUD AND F. KWABIA TCHANA, Laboratoire Interuniversitaire des Systèmes Atmosphériques, C.N.R.S., UMR 7583, Universités Paris Est et 7, 61 Avenue du Général de Gaulle, 94010 Créteil Cedex France; WALTER J. LAFFERTY, Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441, USA.

While the fundamental bands of ethylene have been studied at high resolution, most of the combination bands have not been recorded. In this study, we have recorded the $^{12}$C$_2$H$_4$ bands in the 1820 to 2300 cm$^{-1}$ region which consists of a myriad of weak combination bands. Over 10,000 lines were measured. The strongest of these bands are the A-type band, ν$_7$+ν$_8$, centered at 1889 cm$^{-1}$, the A-type band, ν$_6$+ν$_{10}$, at 2048 cm$^{-1}$, and the B-type band, ν$_3$+ν$_{10}$, at 2173 cm$^{-1}$. In addition, there are numerous lines from much weaker bands. All the bands observed are perturbed by Coriolis interactions, and, at this point, we are attempting to fit all the lines to within experimental error using an Hamiltonian matrix including eighth vibrational states among which four are dark states. The most striking resonance is that of the ν$_7$+ν$_8$ band whose energy levels are crossed by the very much weaker ν$_4$+ν$_8$ band where the intensities of the K=7 lines are enhanced due to mixing with the stronger band.
DIRECT DETECTION OF C$_2$H$_2$ IN AIR AND HUMAN BREATH BY CW-CRDS

Florian M. Schmidt, Ola Vaittinen, Markus Metsälä, and Laura Halonen, Laboratory of Physical Chemistry, Department of Chemistry, P.O. Box 55 (A.I. Virtasen aukio 1), FIN-00014 University of Helsinki, Finland.

Continuous wave cavity ring-down spectroscopy (cw-CRDS) is an established cavity-enhanced absorption technique that can provide the necessary sensitivity, selectivity and fast acquisition time for many applications involving the detection of trace species. We present a simple but highly sensitive cw-CRDS spectrometer based on an external cavity diode laser operating in the near-infrared region. This instrument allows us to directly detect acetylene (C$_2$H$_2$) mixing ratios in air with a detection limit of 120 parts per trillion by volume (pptv) measuring on a C$_2$H$_2$ absorption line at 6565.620 cm$^{-1}$. Acetylene is a combustion product that is routinely used in environmental monitoring as a marker for anthropogenic emissions. In a recent work, the spectrometer was employed to measure the level of acetylene in indoor and outdoor air in Helsinki.$^a$ Continuous flow measurements with high time resolution (one minute) revealed strong fluctuations in the acetylene mixing ratio in outdoor air during daytime.

Due to its non-invasive nature and fast response time, the analysis of exhaled breath for medical diagnostics is an excellent and straightforward alternative to methods using urine or blood samples. In an ongoing study, the cw-CRDS instrument is used to establish the baseline level of acetylene in the breath of the healthy population. An elevated amount of acetylene in breath could indicate exposure to combustion exhausts or other volatile organic compound (VOC) rich sources. The latest results of this investigation will be presented.


THE 4$\nu_3$ SPECTRAL REGION OF METHANE

D. Chris Benner, V. Malathy Devi, Department of Physics, College of William and Mary, Williamsburg, VA 23187-8795; J. J. O’Brien, S. Shaji, Department of Chemistry and Biochemistry, University of Missouri - St. Louis, St. Louis, MO 63121-4400; P. T. Spicker, C. P. Houck, J. A. Coakley, Department of Physics, Bridgewater College, Bridgewater, VA 22812.

The near infrared bands of methane were the first observed in the outer planets and Titan. In this spectral region very long paths within the atmospheres of these objects make scattering and pressure and temperature inhomogeneities important. The spectrum is complex, and long absorption paths in the laboratory are difficult to cool to outer solar system temperatures. At room temperature many significant spectral lines appear per Doppler width, so the absorption is usually modeled statistically using unrealistic assumptions. These models generally do not provide transmissions that are multiplicative, so scattering and inhomogeneous atmospheres cannot be properly modeled.

The intracavity laser spectrometer at the University of Missouri-St. Louis was used to obtain low temperature (99-161K), low pressure (0.12-7.13 Torr), long path (3.14-5.65 km) and high resolution (0.01 cm$^{-1}$ HWHM) spectra of methane covering the entire 890nm feature (10925-11500 cm$^{-1}$), the deepest band in the CCD spectral region. At these temperatures the spectral lines originating from higher energy levels are not visible, and the Doppler width is substantially smaller than at room temperature. The result is a dense, but manageable spectrum from which line positions, intensities and lower state energies are derived on a line by line basis by the College of William and Mary multispectrum nonlinear least squares fitting program.$^a$ The results allow the simulation of the methane spectrum at infinite resolution at temperatures less than $\sim$160K, even for complex atmospheric paths.$^b$


$^b$Support for the work at William and Mary was provided by NASA through grant NNX08AF06G. Support for the work at UM-St. Louis provided by NASA through grant NAG5-12013, from NSF through grant CHE-0213356 and by the University of Missouri Research Board.

Intermission
FORMALDEHYDE: THE 5.7 µm AND 3.6 µm BANDS

D. JACQUEMART, N. LACOME, Université Pierre et Marie Curie-Paris 6; CNRS; Laboratoire de Dynamique, Interactions et Réactivité (LADIR), UMR 7075, Case Courrier 49, 4 Place Jussieu, 75252 Paris Cedex 05, France; A. PERRIN, F. KWABIA TCHANA, Université Paris 12; CNRS; Laboratoire Inter Universitaire des Systèmes Atmosphériques (LISA), UMR 7583, 61 Av du General de Gaulle, 94010 Créteil Cedex France; A. LARAIA, and R.R. GAMACHE, University of Mass Lowell, Department of Environmental, Earth and Atmospheric Sciences, Lowell, MA 01854, USA.

The goal of this study was to achieve absolute line intensities and reliable line broadening parameters for the strong 5.7 µm and 3.6 µm bands of formaldehyde (H₂CO) and to generate, for both spectral regions, a complete linelist for atmospheric applications.

High-resolution Fourier transform spectra were recorded at LADIR for the whole 1600 - 3200 cm⁻¹ spectral range and for different path-length-pressure products conditions. Using these spectra, a large set of H₂CO individual line intensities and of self- and N₂-broadening linewidths were measured.

The calculated band intensities derived for the 5.7 µm and 3.6 µm bands are in excellent agreement with the values achieved recently by medium resolution band intensity measurements. It has to be mentioned that intensities in the 3.6 µm achieved in this work are, on the average, about 28 % stronger than those quoted in the HITRAN 2004 database. The linelist of positions and intensities based on this work has been included in the HITRAN 2008 database.

Concerning the linewidths, empirical expansions and theoretical calculations (semi-classical Robert-Bonamy formalism) have been performed and compared to the measurements. Rotational dependences have been studied, and the temperature dependence of the N₂-broadening coefficients has been calculated.

---

TRACE ATMOSPHERIC DETECTION OF HCHO VIA FIBER LASER-INDUCE D FLUORESCENCE DURING BEARPEX 2009

J. DIGANGI, S. HENRY, A. KAMMRATH, E. BOYLE, and F. KEUTSCH, Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706.; J. PAUL, NovaWave Technologies, Redwood City, CA 94065.

Formaldehyde (HCHO) plays an important role in atmospheric chemistry as it is an oxidation product of volatile organic compounds (VOCs), a major source for HOₓ radicals. We will present results from field measurements taken during Biosphere Effects on Aerosols and Photochemistry Experiment (BEARPEX) 2009 using Fiber Laser-Induced Fluorescence (FILIF) detection of HCHO. Central to the FILIF technique is the first of a new class of UV fiber lasers from NovaWave Technologies. By using this narrow bandwidth (< 300 MHz) UV laser to excite a rotational feature in the 410 1A1A2 ←X1A1 band at 353 nm, this technique is capable of very high HCHO sensitivity and selectivity. The combination of low power consumption and weight, compact size, and ruggedness, provides an instrument ideally suited to field measurements.
LONG-TERM TREND OF CARBON TETRACHLORIDE (CCl\(_4\)) FROM GROUND-BASED HIGH RESOLUTION INFRARED SOLAR SPECTRA RECORDED AT THE JUNGFRAUJOCH


The long-term trend of carbon tetrachloride (CCl\(_4\)) has been retrieved from infrared high resolution solar absorption spectra encompassing the 1999 to 2010 time period. The measurements were recorded with a Fourier transform spectrometer at the northern mid-latitude, high altitude Jungfraujoch station in Switzerland (46.5°N latitude, 8.0°E longitude, 3580 m altitude). Total columns were derived from the region of the strong CCl\(_4\) \(\nu_3\) band at 794 cm\(^{-1}\) accounting for all interfering molecules (e.g. H\(_2\)O, O\(_3\)) with significant improvement in the residuals obtained by also taking into account the line mixing in a nearby CO\(_2\) Q branch, a procedure not implemented in previous remote sensing CCl\(_4\) retrievals though its importance has been noted in several papers. The time series shows a statistically-significant long-term decrease in the CCl\(_4\) total atmospheric burden of (-1.180.10 %/yr), at the 95% confidence level, using 2005 as reference. Furthermore, fit to the total column data set also reveals a seasonal cycle with a peak-to-peak amplitude of 10.2%, with minimum and maximum values found in mid-February and early August, respectively. This seasonal modulation can however be attributed to tropopause height changes throughout the season. The results quantify the continued impact of the regulations implemented by the Montreal Protocol and its strengthening amendments and adjustments for a molecule with high global warming potential. Although a statistically significant decrease in the total column is inferred, the CCl\(_4\) molecule remains an important contributor to the stratospheric chlorine budget and burden.

THE REGION OF 3\(\mu\)m FOR THE MOLECULE CH\(_3\)Cl

C. BRAY, N. LACOME, D. JACQUEMART, Université Pierre et Marie Curie-Paris 6; CNRS; Laboratoire de Dynamique, Interactions et Réactivité (LADIR), UMR 7075, Case Courrier 49, 4 Place Jussieu, 75252 Paris Cedex 05, France; A. PERRIN, Université Paris 12; CNRS; Laboratoire Inter Universitaire des Systèmes Atmosphériques (LISA), UMR 7583, 61 Av du General de Gaulle, 94010 Créteil Cedex France.

Methyl chloride is of interest for atmospheric applications, since this molecule is directly involved in the catalytic destruction of ozone in the lower stratosphere. At the present time no complete and accurate spectroscopic line list is available in atmospheric databases such as HITRAN or GEISA. High resolution FT spectra (Bruker IFS 120, unapodized FWHM resolution of 0.001 cm\(^{-1}\)) of natural methyl chloride CH\(_3\)Cl have been recorded at the LADIR. The 3-\(\mu\)m spectral region containing the \(\nu_1\), \(3\nu_6\), \(\nu_4\) and \(2\nu_5\) interacting bands as well as several dark states has been studied for both \(^{12}\)CH\(_3\)\(^{35}\)Cl and \(^{12}\)CH\(_3\)\(^{37}\)Cl isotopologues. The goal of this work is to generate a complete and accurate line list for atmospheric applications. The preliminary study will be presented: using the recorded spectra and a theoretical calculation, new assignments have been performed for the whole 3-\(\mu\)m spectral region. Moreover, a multispectrum fitting procedure has been used to retrieve absolute line positions and intensities from 6 experimental spectra recorded at different pressures of CH\(_3\)Cl.
NEW HIGH RESOLUTION SPECTROSCOPY STUDIES OF METHYL NITRITE CH$_3$ONO

V. SIRONNEAU, P. CHELIN, F. KWABIA TCHANA, I. KLEINER, Laboratoire Interuniversitaire des Systèmes Atmosphériques, CNRS et Universités Paris 7 et Paris 12, 61 av. Général de Gaulle, 94010, Créteil, France; J. ORPHAL, Institute for Meteorology and Climate Research, Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany; O. PIRALI, Synchrotron SOLEIL, L’Orme des Merisiers Saint-Aubin, 91192 Gif-sur-Yvette, France; J-C. GUILLEMIN, Sciences Chimiques de Rennes -École Nationale Supérieure de Chimie de Rennes -CNRS -35700 Rennes, France; L. MARGULES, R. MIOTYENKO, Laboratoire de Physique des Lasers, Atomes, et Molécules, UMR CNRS 8523, Université de Lille I, F-59655 Villeneuve d’Ascq Cédex, France; S. COOKE, W. J. YOUNGBLOOD, A. AGNEW, C. T. DEWBERRY, Department of Chemistry, University of North Texas, P.O. Box 305070, Denton, TX, 76203, U.S.A.

Methyl nitrite CH$_3$ONO is an important species in atmospheric chemistry involved in photochemical oxidation of volatile organic compounds. The cis conformer (more stable by about 298 cm$^{-1}$) has a high internal rotation potential barrier for the methyl group (731 cm$^{-1}$) whereas for the trans conformer the barrier to internal rotation is extremely low (10 cm$^{-1}$), leading to large internal rotation splittings. Only one high resolution infrared study was performed prior to this study. For the first time, high-resolution spectrum of CH$_3$ONO was recorded in the far infrared region (30-500 cm$^{-1}$) using the synchrotron SOLEIL far-infrared beamline (AILES) and a Fourier transform (FT) spectrometer. Some 987 lines were assigned for the cis isomer up to J=65 and combined with 66 previously recorded microwave lines. In addition, high-resolution spectrum of the $\nu_9$ band of the cis isomer around 627.9 cm$^{-1}$ was also recorded using the FT spectrometer at LISA. New microwave data is currently recorded to improve the knowledge of both the cis and trans ground state parameters.

---

IR/THz DOUBLE RESONANCE SIGNATURES AT ATMOSPHERIC PRESSURE

DANE J. PHILLIPS, ELIZABETH A. TANNER, Kratos Defense and Security Solutions - Digital Fusion Solutions Advanced Technologies Division, 5030 Bradford Dr. Building I, Suite 210, Huntsville, AL 35805; HENRY O. EVERITT, Army Aviation and Missile RD&E Center, Weapons Sciences Directorate, Redstone Arsenal, AL 35898; IVAN R. MEDVEDEV, CHRISTOPHER F. NEESE, JENNIFER HOLT, and FRANK C. DE LUCIA, Department of Physics, 191 W. Woodruff Ave., Ohio State University, Columbus, OH 43210 USA.

IR/THz double resonance (DR) spectroscopy, historically used to investigate molecular collision dynamics and THz molecular lasers at low pressures (< 1 Torr), shows promise for trace gas remote sensing at atmospheric pressure. Molecular specificity is obtained through the rare coincidence(s) between molecule-specific ro-vibrational energy levels and CO$_2$ laser lines. The resulting molecule-specific, DR-induced, THz spectroscopic signatures strongly depend on the type of ro-vibrational transition involved ($P$, $Q$, or $R$), the type of vibrational level excited (stretching or bending), and the molecular mass. To illustrate these sensitivities, calculated DR spectra of prototypical molecules such as methyl fluoride, methyl chloride, and methyl cyanide will be discussed. Although atmospheric pressure broadening obfuscates pure rotational spectra, we show how it can enhance the DR signature in two ways: by relaxing the pump coincidence requirement and by adding the DR signatures of multiple nearby transitions. We will present estimates of this enhancement, including cases where the coincidences that produce the strongest DR signatures at atmospheric pressure do not exist at low pressures.
INFRARED/SUBMILLIMETER DOUBLE RESONANCE AS AN APPROACH TO ATMOSPHERIC REMOTE SENSING: MEASUREMENTS AND ENERGY TRANSFER MODELING

JENNIFER HOLT, IVAN R. MEDVEDEV, CHRISTOPHER F. NEESE, and FRANK C. DE LUCIA, Department of Physics, 191 W. Woodruff Ave., Ohio State University, Columbus, OH 43210 USA; DANE J. PHILLIPS, ELIZABETH A. TANNER, Kratos Defense and Security Solutions - Digital Fusion Solutions Advanced Technologies Division, 5030 Bradford Dr. Building I, Suite 210, Huntsville, AL 35805; HENRY O. EVERITT, Army Aviation and Missile RD&E Center, Weapons Sciences Directorate, Redstone Arsenal, AL 35898.

While there have been a number of proposals for spectroscopic remote sensing in the millimeter and submillimeter spectral region, pressure broadening at atmospheric pressure has made this difficult. There are two major problems. First the linewidths (5 GHz) are so broad that the number of resolution elements in the atmospheric windows is small enough that specificity is severely compromised. Less obviously, without the narrow Doppler limited lines of laboratory spectroscopy, it is difficult to separate the spectral signatures from other much larger power variations. We will show that IR/SMM double resonance is an interesting alternative. In this approach, short infrared pump pulses modify the submillimeter signature, providing a modulation for detection. Moreover, the combination of pump frequency, probe frequency, and time signature provide a three-dimensional identification matrix for significantly increased specificity. Experimental results from a system based on a CO$_2$ TEA laser and fast submillimeter probe will be presented. These results are analyzed in the context of a collisional energy transfer model, with collisions being dominated by the air which dilutes the spectroscopic sample.

ABSOLUTE LINE INTENSITIES OF HONO AND DONO IN THE FAR INFRARED AND REDETERMINATION OF THE ENERGY DIFFERENCE BETWEEN THE TRANS AND CIS SPECIES OF NITROUS ACID

V. SIRONNEAU, J.-M. FLAUD, I. KLEINER, P. CHELIN, Laboratoire Interuniversitaire des Systèmes Atmosphériques, CNRS et Universités Paris 7 et Paris 12, 61 av. Général de Gaulle, 94010, Créteil, France; J. ORPHAL, Institute for Meteorology and Climate Research, Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany.

Nitrous acid is an important species in the atmosphere of the Earth since it is a significant daytime source of OH radicals, known to play an important role in tropospheric ozone formation. It is also a molecule of interest for molecular dynamics and ab-initio calculations. In this work, relative line intensities of trans- and cis-HONO and DONO have been measured using absorption spectra in the far-infrared previously recorded by high-resolution Fourier-transform spectroscopy. These relative line intensities measurements were fitted in a least-squared procedure leading to the determination of the b-component of the permanent dipole moments for those species and their rotational corrections. Scaling those values to the absolute values derived from Stark effect measurements allowed us to re-determine the energy difference between the two isomers ($\Delta E_{\text{HONO}}$) to be $107\pm26$ cm$^{-1}$. This value is in good agreement with previous experimental studies calculations and with recent high-level ab-initio calculations.

---


TIME DEPENDENT MEASUREMENTS OF NITROUS OXIDE - FOREIGN GAS COLLISIONAL RELAXATION PROCESSES USING A FREQUENCY DOWN-CHIRPED 7.84 MICRONS QUANTUM CASCADE LASER

K. G. HAY, G. DUXBURY and N. LANGFORD, Department of Physics, SUPA, John Anderson Building, University of Strathclyde, 107 Rottenrow, Glasgow G4 0NG, Scotland, UK; N. TASINATO, Dipartimento di Chimica Fisica, Universita Ca Foscari di Venezia, 30123 Venezia, Italy.

Intra-pulse quantum cascade laser (QCL) spectrometers are able to produce both saturation and molecular alignment of the gas sample. This is due to the rapid sweep of the radiation through the absorption features. The intra-pulse time domain spectra closely resemble those recorded in coherent optical nutation experiments. In this presentation the frequency down-chirped technique is employed to investigate nitrous oxide - foreign gas collisions. We have demonstrated that the measurements may be characterised by the induced polarization dominated and collision dominated measurement limits. The first of these is directly related to the time dependence of the long range collision cross sections. Among the collisional partners considered, carbon dioxide shows a very unusual behaviour of rapid polarization damping, resulting in the production of symmetrical line shapes at very low gas buffer pressures. The carbon dioxide absorptions are modelled by solving the coupled Maxwell-Bloch equations and the role played by the low transition dipole moment of the $^{16}$O$^{12}$C$^{18}$O isotopomer is discussed.

VIBRATIONAL DEPENDENCE OF EXCITED STATE INTRAMOLECULAR PROTON TRANSFER IN 2-(2'-PYRIDYL)PYRROLE IN THE GAS PHASE VIA HIGH RESOLUTION ELECTRONIC SPECTROSCOPY. $^{ab}$

PHILIP J. MORGAN, ADAM J. FLEISHER and DAVID W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260; MICHAL KIJK and JACEK WALUK, Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland.

Rotationally resolved fluorescence excitation spectra of the $S_1 \leftarrow S_0$ origin band and +144 cm$^{-1}$ vibrational band transitions of 2-(2'-Pyridyl)pyrrole (2PP) have been recorded in the collision free environment of a molecular beam. Analyses of these data provide new information about the changes in geometry that occur when 2PP absorbs light. Additionally, significant line broadening is observed in both spectra, which we attribute to an excited state intramolecular proton transfer (ESIPT) reaction. The dynamics and vibrational mode dependence of ESIPT in 2PP will be discussed.

$^a$Work supported by NSF (CHE-0911117)

$^b$Synthesis by Randolph P. Thummel, University of Houston, Houston, Texas 77204-5003
TA03

INTERNAL DYNAMICS OF WATER ATTACHED TO A PHOTOACIDIC SUBSTRATE: HIGH RESOLUTION ELECTRONIC SPECTROSCOPY OF $\beta$-NAPHTHOL-WATER IN THE GAS PHASE.\textsuperscript{a}

ADAM J. FLEISHER, JUSTIN W. YOUNG and DAVID W. PRATT, Department of Chemistry, University of Pittsburgh, 15260.

An understanding of the structure and internal dynamics of water attached to the photoacid $\beta$-napthol is attainable through rotationally resolved electronic spectroscopy. Here, we present rotational constants for the 1:1 acid-base cluster in both $S_0$ and $S_1$, which provide the location of water within the cluster, as well as the barrier height to internal rotation of water in each electronic state. The barrier height decreases slightly upon excitation, from 206 cm$^{-1}$ in $S_0$, to 182 cm$^{-1}$ in $S_1$. There is also little evidence of a large change in water location, orientation, or overall hydrogen bond length upon irradiation with UV light. Thus, a single water molecule has relatively little affect on the substrate photo-acidity measured in the liquid phase.

\textsuperscript{a}Work supported by NSF (CHE-0911117).

TA04

VIBRATIONAL RELAXATION AND CONTROL IN THE CYCLOHEXADIENE REACTIVE SYSTEM

ADAM D. DUNKELBERGER, RYAN D. KIEDA, F. FLEMING CRIM, Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706.

We have shown previously that reactions in molecular beams can be effectively controlled through vibrational excitation of reactant species. We have demonstrated that the short timescale for vibrational relaxation makes such vibrational control difficult in the solution phase. In this work, we apply our recently developed vibrational mediation techniques to the cyclohexadiene reactive system. The ring-opening photoreaction of cyclohexadiene is a simple model for more complicated photochromic systems. The electronic excited state of cyclohexadiene decays on a faster timescale than is typical for vibrational relaxation in solution, making it an attractive target for vibrational control. We present preliminary results of experiments probing the timescale of vibrational relaxation in cyclohexadiene, the first step toward attempting vibrational control of the reactive system.

TA05

PHOTOISOMERIZATION DYNAMICS OF STILBENE AND AZOBENZENE DERIVATIVE OBSERVED BY FEMTOSECOND TRANSIENT ABSORPTION SPECTROSCOPY

LESLIE HERMAN, KRISTIN A. BRINEY and F. FLEMING CRIM, The University of Wisconsin-Madison, Department of Chemistry, 1101 University Avenue, Madison, WI 53706.

Ultrafast femtosecond pump and probe transient electronic absorption spectroscopy experiments were performed to gain insights into the photoisomerization dynamics in the condensed phase of two prototypical molecules, stilbene and a derivative of azobenzene. For example, in the stilbene case, a UV pump - continuum probe experiment measures the excited state dynamics, allowing us to compare the isomerization reaction starting from either the cis or the trans isomer. Information on how energy flows in the ground state molecule can also be obtained with an IR pump (either CH stretch overtone or stretch-bend combination) - UV probe setup. These data are critical in order to understand how vibrations could affect the isomerization process, as a vibrational mediation of this phenomena represents the ultimate goal of these experiments.
THE EFFECT OF VIBRATIONAL ENERGY ON THE ISOMERIZATION REACTION OF TRANS-STILBENE IN THE CONDENSED PHASE

KRISTIN A. BRINEY, LESLIE V. HERMAN, DAVE S. BOUCHER and F. FLEMING CRIM, The University of Wisconsin-Madison, Department of Chemistry, 1101 University Avenue, Madison, WI 53706.

We study the effect of vibrational energy on the isomerization reaction of trans-stilbene in deuterated chloroform. We first excite a ground-state C-H stretch overtone or a stretch-bend combination and allow vibrational relaxation to occur within the molecule before photoinitiating the excited-state isomerization with an ultraviolet photon. Once the stilbene molecule is on the excited state, we monitor the isomerization dynamics via broadband transient absorption spectroscopy. We measure an excited-state lifetime of 55 ± 9 ps when exciting through the C-H stretch overtone and a lifetime of 56 ± 7 ps for excitation through the stretch-bend combination. The trans-stilbene excited-state lifetime after single photon vertical excitation is 52 ± 6 ps with the total added energy being the same for all measurements. Unlike in gas phase studies, where vibrational motion can change the outcome of a chemical reaction, there is no observed difference in the reaction dynamics when exciting this condensed phase system with a single photon versus exciting through a ground-state vibrational mode. Interactions with the solvent cause fast vibrational relaxation on the excited state, though the insensitivity of the rate to vibrational energy may also be due to excess vibrational energy not being promptly partitioned into modes along the isomerization coordinate.

Intermission

ELECTRONIC STRUCTURE CALCULATIONS OF INTER-RING TORSIONAL POTENTIALS OF REGIOREGULAR POLY (3-METHYL THIOPHENE) OLIGOMERS

RAM S BHATTA, DAVID S PERRY, Department of Chemistry, The University of Akron, OH 44325-3601.

The inter-ring torsional potentials of poly (3-methyl thiophene) (P3MT) oligomers are investigated by means of electronic structure calculations. Single layer and ONIOM calculations were performed at B3LYP level with 6-31++G(d,p) basis on the partially optimized geometries of dimer, tetramer and hexamer of P3MT oligomers. Potential energy surfaces are computed as a function of the multiple inter-ring torsional angles involved. The following conclusions are reached: (i) A mixture of cis and trans geometries can be expected in a disordered polymer. (ii) The cis-trans barrier is low enough to allow cis-trans conversion at room temperature. (iii) In the dimer, the potential energy minima are about 30° from the cis and trans planar geometries, but planar geometries are stabilized as the chain length increases. (iv) The extended conjugation causes the torsional potential about one inter-ring bond to be coupled to other torsions along the oligomer chain.
STUDIES OF TRANSIENT NEUTRAL MOLECULES BY DISSOCIATIVE PHOTODETACHMENT OF COOLED MOLECULAR ANIONS

CHRISTOPHER J. JOHNSON and ROBERT E. CONTINETTI, Department of Physics, Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, CA 92093.

We have recently integrated and cryogenically cooled a “Zajfman-style” linear electrostatic ion trap with a Photoelectron-Photofragment Coincidence (PPC) spectrometer. We are able to trap precursor anions for several seconds in a cryogenic environment, allowing them to radiatively cool to ground or near-ground states. Our design features a time- and position-sensitive velocity map imaging electron detector intra-cavity to capture electrons photodetached at the center of the trap, and a multiparticle time- and position-sensitive neutral detector downstream to detect resultant neutral fragments. By recording coincidence events as a function of trapping time we remove ambiguities caused by internally excited anions. The experimental apparatus has been verified on the benchmark systems O$_3$ and O$_4$ by dissociative photodetachment of O$_3^-$ and O$_4^-$ respectively. While both systems have been extensively studied previously in our lab, new dynamics have been resolved in each beyond those already reported. We have also extended our previous investigation of the OH+CO $\rightarrow$ H+CO$_2$ radical reaction, which included significant contributions from internally excited anions, to cooled HOCO$^-$ precursor anions. The new study reveals significant changes in our measurements of energetics and dissociation dynamics on the HOCO potential energy surface.

---

This work supported by the United States Department of Energy


---

COHERENT EXCITATION PHENOMENA IN TIME-RESOLVED EXPERIMENTS

A. PERALTA CONDE, R. MONTERO, F. CASTANO, AND A. LONGARTE, Departamento de Química-Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apartado 644, ES-48080 Bilbao, Spain.

The influence of coherent phenomena on femtosecond pump-probe experiments in molecular systems has been investigated. The signature of Coherent Population Return (CPR) has been observed, and satisfactorily described by means of a coherently excited two-state model. This analysis has been extended to a more general situation where N two-level sub-systems interact independently with the radiation. The obtained results permit us to explain why for such complex systems the incoherent treatment provides an accurate description of the population dynamics. Furthermore, the distribution of states inside and outside the excitation laser bandwidth, rather than the state density as it is accepted, is found to be the key parameter for determining the applicability of the incoherent approach.
COHERENT EFFECTS INVOLVING THE EXCITATION AND RELAXATION OF THE COUPLED $L_a/L_b$ ELECTRONIC EXCITED STATES OF NAPHTHALENE: A TIME DEPENDENT EXPERIMENTAL STUDY

R. MONTERO, A. PERALTA CONDE, F. CASTANO, AND A. LONGARTE, Departamento de Química-Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apartado 644, ES-48080 Bilbao, Spain.

The ultrafast dynamics of the non-adiabatic coupling between the $L_a(S_2)/L_b(S_1)$ electronic excited states of naphthalene has been investigated, regarding the coherent aspects of the preparation and subsequent relaxation of the system. This electronic coupling represents a well known case of non-adiabatic behavior that has been used for years as a benchmark to test theoretical models. The jet cooled naphthalene molecule was prepared in the $L_a$ and $L_b$ states by femtosecond pump pulses in the UV region (318-268 nm), while the temporal evolution of the system was tracked by multiphoton ionization of the molecule with probe pulses centered at 800 nm. The time dependent signals collected at excitation wavelengths corresponding to the weak $S_0-L_b$ transition are dominated by the CPR (Coherent Population Transfer) effect induced by the blue-shifted stronger $S_0-L_a$ absorption. The CPR effect results in the transient population of the $L_a$ state during the interaction of the pump pulse with the system, revealing the coherent nature of the excitation process. The transients collected after excitation to the $L_a$ state reveal the ultrafast relaxation to the strongly coupled $L_b$ state. The electronic and/or vibrational nature of the periodic recurrences observed along the relaxation of the electronic population will be discussed.

INFLUENCE OF SOLVATION ON 1-AMINONAPHTHALENE PHOTOPHYSICS: ULTRAFAST RELAXATION IN THE ISOLATED MOLECULE, MOLECULAR CLUSTER AND SOLUTION

R. MONTERO, A. PERALTA CONDE, F. CASTANO, AND A. LONGARTE, Departamento de Química-Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apartado 644, ES-48080 Bilbao, Spain.

The electronic spectroscopy and photophysics of naphthalene (NPH) and its mono-substituted derivatives is highly influenced by the non-adiabatic coupling between its two lowest electronic excited states, $S_1$ ($L_b$) and $S_2$ ($L_a$) and with the ground state. Trying to understand better the nature of these couplings and the influence of solvation on it, the relaxation dynamics of 1-aminonaphthalene (AMN) isolated in a supersonic expansion and forming molecular clusters of the form AMN(H$_2$O)$_n=1-3$, was tracked following excitation to the $S_1$ and $S_2$ excited states in the range (30000-37500 cm$^{-1}$), at the ultrafast time scale. The experiments were carried out in a time of flight mass spectrometer, using a well known pump-probe ionization scheme (1+n) that involves the probe of the molecule by single or multiphoton ionization. While in the case of NPH the $L_a(S_2)$ state relaxes to the lower $L_b(S_1)$ at ultrafast rate ($\tau=30$ fs) through a conical intersection placed nearby the $L_a$ surface minimum, for AMN, no dynamical signature of the surface crossing is found. However, two additional relaxation channels, internal conversion to the ground state and intersystem crossing, have been observed for the $L_a$ state. The solvation by water molecules induces dramatic changes in the relaxation of the AMN molecule. The inclusion of a single water molecule deactivates the IC channel to the ground state, while for the clusters containing two or three water molecules, ultrafast IC between the $L_a$ to $L_b$ and excited states is observable in the transients. The photophysical behavior observed in the molecular clusters, will be also compared with experiments in solution, where the relaxation dynamics is resolved by fluorescence up-conversion. The role of individual solvent-solute interactions will be discussed.
4-(Dimethylamino)benzonitrile (DMABN) is a paradigm molecule system that exhibits dual fluorescence and intramolecular charge transfer (ICT) in polar solvents. Although numbers of different experimental and theoretical methods have been carried out to date for elucidating the basic mechanism of its energy relaxation, there are still some crucial problems that remain unanswered.

The time-resolved transient absorption and time-resolved fluorescence upconversion will be presented, as combined with ab initio CASPT2//CASSCF calculations, which indicate that a more complex mechanism may be suggested in the ICT reaction in a polar environment. A scheme of ultrafast branching relaxation followed by two-fold decay is proposed in which, whereas the fully twisted ICT (TICT) state is responsible for the transient absorption, a distinct partially twisted ICT (pTICT) structure is for the fluorescent ICT state, both displaying clearly different decay rates.
TB. MINI-SYMPOSIUM: BIOMOLECULES AND CLUSTER IONS

TUESDAY, JUNE 22, 2010 – 8:30 am
Room: 170 MATH ANNEX

Chair: FLEMING CRIM, University of Wisconsin, Madison, Wisconsin

TB01  INVITED TALK - Abstract Rescheduled at Authors’ Request  30 min  8:30
EXPLORING SOLVENT SHAPE AND FUNCTION USING MASS- AND ISOMER-SELECTIVE VIBRATIONAL SPECTROSCOPY

MARK JOHNSON, Yale University, Department of Chemistry, New Haven, CT.

We illustrate the new types of information that can be obtained through isomer-selective “hole-burning” spectroscopy carried out in the vibrational manifolds of Ar-tagged cluster ions. Three examples of increasing complexity will be presented where the changes in a solute ion are correlated with different morphologies of a surrounding solvent cage. In the first, we discuss the weak coupling limit where different hydration morphologies lead to small distortions of a covalent ion. We then introduce the more interesting case of the hydrated electron, where different shapes of the water network lead to dramatic changes in the extent of delocalization in the diffuse excess electron cloud. We then turn to the most complex case involving hydration of the nitrosonium ion, where different arrangements of the same number of water molecules span the range in behavior from simple solvation to actively causing a chemical reaction. The latter results are particularly interesting as they provide a microscopic, molecular-level picture of the “solvent coordinate” commonly used to describe solvent mediated processes.

TB02  15 min  9:05
INFRARED SPECTROSCOPY OF WATER CLUSTER RADICAL CATIONS (H₂O)ₙ⁺ (n = 3 to 11)

KENTA MIZUSE and ASUKA FUJII, Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan.

To obtain structural information about radical cationic hydrogen-bonded water networks, we have measured size-selected infrared spectra of the water cluster cations (H₂O)ₙ⁺ (n = 3–11) in the OH stretching region. The spectra of smaller-sized clusters (n ≤ 6) show a free OH band associated with the OH radical. This band indicates that nominal water cluster cations (H₂O)ₙ⁺ form H⁺(H₂O)ₙ−₁OH type structures, and that the OH radical lies in the network terminal. For larger-sized clusters, the analyses of the hydrogen-bonded OH stretching bands aided by quantum chemical calculations evidence the existence of the OH radical in the clusters. Detailed cluster structures will be discussed on the basis of the experimental spectra.
INFRARED SPECTROSCOPY OF 7-AZAINDOLE TAUTOMERIC DIMER: OBSERVATION OF THE ND STRETCH

HARUKI ISHIKAWA, TAKUMI NAKANO, HIROKI YABUGUCHI, AKIMASA FUJIHARA, KIYOKAZU FUKE, Department of Chemistry, Graduate School of Science, Kobe University, Nada-ku, Kobe 657-8501, Japan.

7-azaindole (7-AI) dimer is a very attractive species as a model system of nucleic-acid base pair. The 7-AI dimer is known to exhibit the excited-state double proton transfer (DPT) reaction. The tautomeric dimer produced in the DPT reaction goes back to normal form in the electronic ground state, in solution. In general, the proton-transfer reaction is a fundamental and an important elementary reaction in various chemical and biological systems. However, the ground-state reverse DPT reaction is not thoroughly studied, so far. Thus, we carry out infrared (IR) spectroscopy of the jet-cooled 7-AI tautomeric dimer. In our previous study, we measured IR spectra of the tautomeric dimer and its deuterated species in the NH stretch region and discussed the vibrational dynamic based on the band profiles\textsuperscript{a}. In order to obtain more precise information about the deuteration effect, we have observed the ND stretch bands of the deuterated dimers in the present study.

The deuteration of the NH hydrogen provides three deuterated species, such as the NH-NH, NH-ND, and ND-ND dimers. The NH stretch band of the NH-NH dimer appears at 2680 cm\textsuperscript{-1}. It exhibits a less-structured and broad profile whose width is \(\sim 245\) cm\textsuperscript{-1}. On the contrary, the NH-ND dimer exhibits a narrower NH stretch band width. This difference is attributed to a change in the vibrational energy flow between the two monomer units in the dimer. In the present study, we have succeeded in measuring the ND stretch bands of the NH-ND and the ND-ND dimers. The ND stretch band of the ND-ND dimer appears at 2120 cm\textsuperscript{-1} and its width is found to be \(\sim 90\) cm\textsuperscript{-1}, whereas that of the NH-ND dimer is red-shifted and exhibits rather narrow width. Based on these observations, the single-deuteration effect on the vibrational dynamics and its relation to the DPT reaction is discussed in the paper.


PROTON BETWEEN BENZENE AND WATER: INFRARED SPECTROSCOPY TO MODEL INTERACTIONS AT THE OIL-WATER INTERFACE

B. BANDYOPADHYAY, T. C. CHENG, and M. A. DUNCAN, Department of Chemistry, University of Georgia, Athens, GA 30602-2556.

The proton affinity of benzene is slightly higher (753.6 kJ/mol) than the proton affinity of water (693.8 kJ/mol) in the isolated gas phase. It is then natural to ask about the location of the proton in the protonated benzene -water complex. Another important question is the effect of solvation on proton accommodation on this system. As benzene is non-polar and water is polar, these kinds of complexes are ideal systems to model molecular interaction at the hydrophobic-hydrophilic interface. In our lab, protonated benzene-water complexes are produced via pulsed discharge in a supersonic expansion cluster source. The cold, mass selected ions are investigated via infrared photodissociation spectroscopy in the range of 1000-4000 cm\textsuperscript{-1}. Quantum mechanical calculations were further implemented to obtain the structures and vibrational frequencies. Infrared spectra of the protonated (benzene)\textsubscript{m}-(water)\textsubscript{n} complexes will be discussed, where m=1-2 and n=1-4.
INFRARED SPECTRA OF HYDRATED CLUSTERS OF GUANINE NUCLEOSIDES OBSERVED BY IR-UV DOUBBLE RESONANCE SPECTROSCOPY

SHU-HEI URASHIMA, HIROY ASAMI, and HIROYUKI SAIGUSA, Graduate School of Arts and Sciences, Yokohama City University, Yokohama 226-0027, Japan.

Mono- and dihydrated clusters of guanosine and 2'-deoxyguanosine are produced by laser-desorption supersonic-jet cooling and their structures are identified by IR-UV double resonance spectroscopy combined with theoretical calculation. The results show that specific hydration structures around the sugar group exist in both nucleosides. It is also demonstrated that the dihydrated structures are strongly influenced by the presence or absence of the 2'-hydroxy group on the sugar.

Intermission

EFFECTS OF MICROSOVLATION ON A MODEL PEPTIDE CHAIN INVESTIGATED BY IR/UV DOUBLE RESONANCE SPECTROSCOPY


IR/UV double resonance spectroscopy of gas phase 1:1 complexes of the capped phenylalanine amino acid with water or methanol has been carried out. The IR spectra in the amide NH and water OH stretches spectral region of UV-selected conformations have resolved absorption bands which have been assigned by comparison with scaled harmonic frequency calculations of the most stable conformations optimized at the B97-D/TZVPP level. The effects of solvation on the structural properties have been investigated by comparison with the conformations observed on the isolated capped phenylalanine. The solvation by one molecule turns out to strongly impact the energy landscape by favoring specific folded structures.

CONFORMATION-SPECIFIC INFRARED SPECTROSCOPY OF γ2-PEPTIDE FOLDAMERS: Ac-γ2-hPhe-γ2-hAla-NHMe AND Ac-γ2-hAla-γ2-hPhe-NHMe

WILLIAM H. JAMES III, EVAN G. BUCHANAN, CHRISTIAN W. MÜLLER, and TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN 47907; LI GUO, and SAMUEL H. GELL-MAN, Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706.

IR/UV double-resonance spectroscopy has been used to study the intrinsic conformational preferences of naturally occurring and synthetic peptides. These studies demonstrated the power of double-resonance methods and highlighted the ability of even short peptide mimics to form a variety of intramolecular hydrogen bonded architectures. Currently, we are extending these studies to a series of model γ2-peptides, which differ from α-peptides by virtue of having two additional, substitutable methylene units separating amide groups in the peptide backbone. Initial studies centered on the conformation-specific infrared spectra of Ac-γ2-hPhe-NHMe, where three unique conformational isomers (two hydrogen-bonded and one intramolecular amide stacked) were observed under the isolated-molecule conditions of a jet-cooled environment. This talk will focus on two larger γ2-peptides, Ac-γ2-hPhe-γ2-hAla-NHMe and Ac-γ2-hAla-γ2-hPhe-NHMe. Utilizing resonant ion-dip infrared spectroscopy, the single-conformation infrared spectra of eight resolved conformers of the two molecules were recorded in the amide NH stretch region. The resulting infrared spectra of the tri-amides contain evidence for structures comprised of one, two, and three intramolecular amide-amide hydrogen bonds, the last of which is unprecedented for a tri-amide. In an effort to make firm conformational assignments, the spectroscopic data will be compared to the results of harmonic vibrational frequency calculations using traditional DFT and dispersion-corrected DFT methods, the results of which will be discussed.
SINGLE-CONFORMATION SPECTROSCOPIC INVESTIGATION OF PEPTIDE BUILDING BLOCKS IN THE AMIDE I SPECTRAL REGION: COMPARISON OF EXPERIMENT TO DENSITY FUNCTIONAL THEORY AND THE TRANSITION DIPOLE COUPLING MODEL

WILLIAM H. JAMES III, EVAN G. BUCHANAN, CHRISTIAN W. MÜLLER, ESTEBAN E. BAQUERO, JACOB C. DEAN, and TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN 47907; MICHAEL G. D. NIX, School of Chemistry, University of Bristol, Bristol BS8 1TS, UK; SOO HYUK CHOI, LI GUO, and SAMUEL H. GELLMAN, Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706.

IR/UV double-resonance spectroscopy has been utilized to elucidate the intrinsic conformational preferences of naturally occurring α-peptides and synthetic β-, α/β-, and γ-peptides. These studies used as the primary spectral probe the amide NH stretch region, demonstrating the power of double-resonance methods and highlighting the ability of even short peptide mimics to form a variety of intramolecular hydrogen bonded architectures. In this talk, we extend our studies of the full complement of some 30 conformations of these molecules into the mid-infrared, where the Amide I region (1600-1800 cm\(^{-1}\)) can provide complementary insight to the nature of the hydrogen bonding involved. Our goal is to provide a unique data set on which to test current theories of Amide I coupling used in the analysis of multi-dimensional infrared spectra of peptides in solution. The spectroscopic data will be compared with density functional theory (DFT) calculations and the transition dipole coupling (TDC) model. The results present the dependence of the C=O stretch vibrations on hydrogen bonding, inter-amide distance, and through-bond and through-space coupling.

VIBRATIONAL ENERGY RELAXATION OF BENZENE DIMER STUDIED BY PICOSECOND TIME-RESOLVED INFRARED-ULTRAVIOLET PUMP-PROBE SPECTROSCOPY

R. KUSAKA and T. EBATA, Department of Chemistry, Graduate School of Science, Hiroshima University, Higashi-Hiroshima, 739-8526, Japan.

The benzene dimer is excited to the CH stretching vibrational levels by a picosecond IR pulse, and the time evolution of the population of the pumped and redistributed levels are probed by (1+1)REMPI with a picosecond UV pulse. In order to accomplish IR excitation localized in the site of the T-shaped dimer, two dimer isotopomers [(1) Top=C\(_6\)H\(_6\), Stem=C\(_6\)D\(_6\), (2) Top=C\(_6\)D\(_6\), Stem=C\(_6\)H\(_6\)] are used. From the time profiles of the pumped and the relaxed levels, the rate constants of intracluster vibrational redistribution (ICVR) at each site and subsequent vibrational predissociation (VP) are discussed.

APPLICATION OF INFRARED MULTIPHOTON DISSOCIATION SPECTROSCOPY FOR THE STUDY OF CHIRAL RECOGNITION IN PROTONATED SERINE CLUSTERS

FUMIE X. SUNAHORI, GUOCHUN YANG, ELENA N. KITOVA, JOHN S. KLASSEN, AND YUNJIE XU, Department of Chemistry, University of Alberta, Edmonton, Canada T6G 2G2.

Serine is an amino acid which has long been known to form magic-number ionic clusters, serine octamer [Ser\(_8^+\) + H\(^+\)]. It has been shown\(^a\) that serine octamers exhibit strong preference for homochirality, but its structure is still unclear. We have used infrared multiphoton dissociation (IRMPD) spectroscopic technique coupled with a Fourier transform ion cyclotron (FRICR) mass spectrometer to investigate the structures of protonated serin octamer and dimer as well as the chiral recognition in these clusters. With the use of ICR cell, the ions can be stored for a sufficient time so that measurements of IRMPD spectra become possible with a CW OPO laser in the 3000-4000 cm\(^{-1}\) region. As an aid to interpret the observed spectra, molecular structures and vibrational frequencies of the octamer and dimer have been predicted by using the B3LYP/6-311++G** calculations. Differences in chiral selectivity between the serine octamer and dimer will be discussed.

As one pushes spectroscopic studies to biological molecules of increasing size, the presence of multiple stable conformers with slightly different spectra can become a major source of spectral congestion. In such cases, the use of non-spectroscopic methods to separate different conformers could greatly simplify the electronic and vibrational spectra of large, flexible species.

This talk will give an update on our work using Field Asymmetric Ion Mobility Spectrometry (FAIMS) as a conformational filter for biomolecular ions produced in the gas phase by electrospray. After conformational preselection by FAIMS, the ions are injected into a cold, 22-pole ion trap where their electronic spectrum reveals the remaining degree of conformational heterogeneity. We will present our most recent results using the nonapeptide bradykinin.
TC. MICROWAVE (ROTATIONAL)

TUESDAY, JUNE 22, 2010 – 8:30 am

Room: 1000 McPHERSON LAB

Chair: REBECCA PEEBLES, Eastern Illinois University, Charleston, Illinois

TC01  15 min  8:30
EXTENDED TOWNES-DAILEY ANALYSIS II

STEWART E. NOVICK, Department of Chemistry, Wesleyan University, Middletown, CT 06459.

Last year at this conference, I presented the Extended (to three dimensions) Townes-Dailey analysis for calculating p-orbital populations from measured nuclear quadrupole coupling tensors. That analysis was limited to molecules containing atoms from the third row and higher. That is, the analysis was limited to unhybridized p-orbitals. Here I will generalize the method to include hybridized orbitals.

*S. E. Novick, OSU International Symposium on Molecular Spectroscopy, RH04 (2009)

TC02  15 min  8:47
RECENT CHANGES IN PGOPHER: A GENERAL PURPOSE PROGRAM FOR SIMULATING ROTATIONAL STRUCTURE

COLIN WESTERN, School of Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS, UK.

Key features of the PGOPHER program include the simulation and fitting of the rotational structure of linear molecules and symmetric and asymmetric tops, including effects due to unpaired electrons and nuclear spin. The program is written to be as general as possible, and can handle many effects such as multiple interacting states, predissociation and multiphoton transitions. It is designed to be easy to use, with a flexible graphical user interface. PGOPHER has been released as an open source program, and can be freely downloaded from the website at http://pgopher.chm.bris.ac.uk. Recent additions include a mode which allows the calculation of vibrational energy levels starting from a harmonic model and the multidimensional Franck-Condon factors required to calculate intensities of vibronic transitions. PGOPHER takes account of both the displacement along normal co-ordinates and mixing between modes (the Duschinsky effect). I matrices produced from ab initio programs can be directly read by PGOPHER or the mode displacements and mixing can be fit to observed spectra.

In addition the effects of external electric and/or magnetic fields can now be calculated, including plots of energy level against electric field suitable for predicting Stark deceleration, focussing and trapping of molecules. The figure shows a typical plot, showing the electric field tuning of the M = 0 levels of 2\textsubscript{02}, 1\textsubscript{11} and 1\textsubscript{10} levels of (NO)\textsubscript{2}. Other new features include fits to combination differences, simulation of the Doppler split peak typical of Fourier transform microwave spectroscopy, specifying a nuclear spin temperature independent of rotational temperature and interactive adjustment of parameter values with the mouse in addition to typing values.
REVISITING THE AMMONIA HYPERFINE STRUCTURE WITH SPFIT

BRIAN J. DROUIN, SHANSHAN YU, JOHN C. PEARSON, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099.

The definitive ammonia maser measurements of Kukolich\textsuperscript{1,2} have proven to be vastly useful, with over 100 citations to date. A critical review of this work was published shortly afterwards by Hougen\textsuperscript{3}, who made a few corrections and showed that the hyperfine parameters, which were determined separately for each inversion-rotation transition, were internally consistent and useful for extrapolation. In the present work, the multiple-spin fitting routine, SPFIT, has been utilized to perform a global analysis of the available ammonia maser data. Within this framework many of the parameters given by Hougen become redundant, and the differences are introduced as centrifugal distortion corrections to the fundamental spin parameters. The global fit achieves experimental uncertainty for the relative line centers of the hyperfine-split features with 17 independent hyperfine parameters (15 of which are used for both inversion states simultaneously), the previous work had utilized 37 fitted parameters and 10 parameters fixed at assumed values.


ATTEMPTS AT USING IAMCALC TO ANALYZE LOW FREQUENCY ROTATIONAL SPECTRA OF MOLECULES WITH INTERNAL ROTATION AND NUCLEAR SPINS

CHRISTOPHER T. DEWBERRY AND STEPHEN A. COOKE, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH TEXAS, 1155 UNION CIRCLE #305070, DENTON, TX 76203-5017, U.S.A.

Recent progress in the fitting and analyses of simple methyl rotors to simultaneously account for internal rotation and nuclear hyperfine terms will be presented. The analyses have been attempted using Herb Pickett’s IAMCALC program which acts as a “front end” for the powerful SPFIT/SPCAT software. Progress has been made by simply appending hyperfine parameters to an IAMCALC-prepared SPFIT input file. This work has been prompted by our recent high resolution spectral measurements in the 1 - 21 GHz region on species such as methanol and methyl nitrite. Data will be presented together with comments on the validity of the fitting approach.

A PROPOSAL FOR A GENERAL METHOD FOR DETERMINING SEMI-EXPERIMENTAL EQUILIBRIUM STRUCTURES OF CARBON ATOM BACKBONES

NORMAN C. CRAIG, Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH 44074.

Semi-experimental equilibrium structures are determined from ground state rotational constants derived from the analysis of rotational transitions in high-resolution spectra and from the quantum chemical calculation of spectroscopic alphas. In the full application of this method, spectra of numerous isotopic species must be investigated. Most of these isotopic species require specialized synthesis. We now propose focusing on the carbon atoms, for which microwave spectroscopy routinely yields spectra for polar molecules with $^{13}$C substitution in natural abundance. Needed spectroscopic alphas can be computed with Gaussian software. Application of the Kraitchman substitution relationships gives Cartesian coordinates for the carbon atoms and thence bond parameters for the carbon backbone. This method will be evaluated with ethylene, 1,1-difluoroethylene, 1,1-difluorocyclopropane, propene, and butadiene. The method will then be applied to cis-hexatriene\textsuperscript{a} and the two conformers of glycidol.\textsuperscript{b}

CONSTRUCTION AND DEVELOPMENT OF A NEW LOW-FREQUENCY FOURIER TRANSFORM SPECTROMETER FOR OPERATION IN THE 1-6 GHZ RANGE

LASZLO SARKOZY, STEPHEN G. KUKOLICH, Department of Chemistry and Biochemistry, The University of Arizona, Tucson, AZ 85721.

Pulsed-beam Fourier transform spectrometers normally operate in the 4-20 GHz range. In many cases for larger molecules it is desirable to measure lower-J transitions which occur below 4 GHz. To address the need for high resolution experimental measurements in the 1-4 GHz range, a new pulsed-beam Fourier transform spectrometer has been successfully constructed and tested. The lower frequency range resulted in impressive dimensions and new technical challenges. Interesting aspects of the development and the characteristics of the new instrument are presented along with some of the first experimental spectra.

Supported by THE NATIONAL SCIENCE FOUNDATION

DESIGN AND INITIAL OPTIMISATION OF A BROADBAND (6.5-18 GHz) CHIRPED-PULSE, FOURIER TRANSFORM MICROWAVE SPECTROMETER

N. R. WALKER AND S. L. STEPHENS, School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K.

A chirped-pulse, Fourier transform microwave spectrometer has been constructed to allow the measurement of broadband microwave spectra from 6.5 GHz to 18 GHz. The design of the new instrument, developed from the original model of Pate and co-workers, and the results of tests using different experimental conditions and a wide range of molecules will be described. The PGOPHER program has been applied to fit broadband microwave spectra and some illustrative examples which demonstrate the usefulness of this program will be presented.

Intermission

TWO-DIMENSIONAL CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTROSCOPY: INTRODUCTION TO TWO-DIMENSIONAL BROADBAND TECHNIQUES

AMANDA J. SHIRAR, KELLY M. HOTOPP, DAVID S. WILCOX, BRIAN C. DIAN, Department of Chemistry, Purdue University, West Lafayette, IN, 47907.

There is a gap in the electromagnetic spectrum where the microwave region is located when considering broadband two-dimensional spectroscopy. We introduce two-dimensional chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy as a way to directly identify coherences between coupled rotational levels. The theory and application of these experiments is a direct extension of traditional two-dimensional NMR techniques. Several different pulse sequences will be presented that allow for selective (narrowband) and non-selective (broadband) excitation. Data acquisition with broadband (10 GHz) detection enables several coupled transitions to be monitored simultaneously. Due to the extremely large amount of data acquired in each experiment, a new way of processing data is explained that allows a more straightforward analysis of the spectra. An autocorrelation study of 1-chloro-1-fluoroethylene is presented as a simple example of this application in the microwave region of the spectrum.
TWO-DIMENSIONAL CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTROSCOPY: MODELING COHERENCE TRANSFER

DAVID S. WILCOX, KELLY M. HOTOPP, AMANDA J. SHIRAR, BRIAN C. DIAN, Department of Chemistry, Purdue University, West Lafayette, IN, 47907.

Two-dimensional broadband techniques have been introduced into the microwave regime using chirped-pulse Fourier transform spectroscopy. Theoretical considerations of expanding the prototypical three-level model to an N-level system are presented. Representative Hamiltonian and density matrices were used to solve the Liouville-von Neumann equations of motion in order to describe the evolution of coherently prepared states. Several selective excitation pulse sequences were performed on 1-chloro-1-fluoroethylene and 3,3,3-trifluoropropyne to test the validity of the theory. Through modeling one-dimensional slices of a traditional 2D plot, peaks in the indirectly measured frequency dimension were identified and classified and phenomenological selection rules were obtained.

STRATEGIES FOR COMPLEX MIXTURE ANALYSIS IN BROADBAND MICROWAVE SPECTROSCOPY.

AMANDA L. STEBER, JUSTIN L. NEILL, MATTHEW T. MUCKLE, AND BROOKS H. PATE, Department of Chemistry, University of Virginia, McCormick Rd., P.O. Box 400319, Charlottesville, VA 22904; D.F. PLUSQUELLIC, Optical Technology Division, NIST, Gaithersburg, MD 20899-8441; V. LATTANZI, S. SPEZZANO, AND M.C. MCCARTHY, Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138, and School of Engineering & Applied Sciences, Harvard University, 29 Oxford St., Cambridge MA 02138.

Broadband microwave spectra often contain overlapping spectra from a large number of species in the sample mixture, whether in the study of conformational isomers, molecular complexes, reaction products from reactive molecular sources (e.g., electrical discharge), or analysis of chemical mixtures. In these experiments, the identification of individual spectra in the full spectrum through pattern recognition becomes difficult when there is a high density of transitions. Strategies for extracting individual spectra from broadband measurements are discussed. Two approaches for microwave-microwave double resonance spectroscopy have been evaluated. One uses a transition-by-transition screening in a narrowband cavity spectrometer to identify an unknown spectrum and has a time advantage from the increased sensitivity of cavity spectroscopy. The second double-resonance approach uses a broadband spectral editing approach that gives a multiplex advantage in the detection. Both of these experimental techniques are combined with computer-aided assignment algorithms to make the spectral assignment in a minimum of double-resonance observations. The performance of spectral analysis solely using computer-aided assignment is also evaluated. The potential for fully automated spectral decomposition of the broadband spectrum of a complex mixture will be described.
TC11 15 min 11:36

A K_A-BAND CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTROMETER.

DANIEL P. ZALESKI, JUSTIN L. NEILL, MATTHEW T. MUCKLE, AND BROOKS H. PATE, Department of Chemistry, University of Virginia, McCormick Rd., P.O. Box 400319, Charlottesville, VA 22904; P. BRANDON CARROLL AND SUSANNA L. WIDICUS WEAVER, Department of Chemistry, Emory University, 1515 Dickey Drive, Atlanta, GA 30322.

The design and performance of a new chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer operating from 25-40 GHz will be discussed. A 10.5-3 GHz linear frequency sweep, generated by a 24 GS/s arbitrary waveform generator, is upconverted by a 23.00 GHz phase-locked oscillator, then fed into an active doubler to create a 25-40 GHz chirped pulse. After amplification with a 60-80 W pulsed traveling wave tube amplifier, the pulse is broadcast across a molecular beam chamber where it interacts with a molecular sample. The molecular FID signal is downconverted with the 23 GHz oscillator so that it can be digitized on a 50 GS/s oscilloscope with 16 GHz hardware bandwidth. The sensitivity and phase stability of this spectrometer is comparable to that of the previously reported 6.5-18.5 CP-FTMW spectrometer. On propyne ($\mu = 0.78$ D), a single-shot signal to noise ratio of approximately 200:1 is observed on the $J = 2$ - 1 rotational transition at 34183 MHz when the full bandwidth is swept; optimal excitation is observed for this transition with a 250 MHz bandwidth sweep. The emission has a $T_2$ lifetime of 4 $\mu$s. Early results from this spectrometer, particularly in the study of species of astrochemical interest, will be presented.


TC12 15 min 11:53

TWO-DIMENSIONAL CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTROSCOPY: APPLICATIONS TO MULTI-LEVEL SYSTEMS

KELLY M. HOTOPP, DAVID S. WILCOX, AMANDA J. SHIRAR, BRIAN C. DIAN, Department of Chemistry, Purdue University, West Lafayette, IN, 47907.

Two-dimensional chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy has been used to study rotational energy level connectivity of 1,3-difluoroacetone and m-methylbenzaldehyde. In this series of experiments, non-selective polarizing pulse sequences were used to probe both progressively and regressively connected systems through coherences of coupled rotational energy levels. Coherence propagation among shared energy levels will be demonstrated on 1,3-difluoroacetone. Ab initio calculations predict that the methyl rotor barrier of m-methylbenzaldehyde is less than 35 cm$^{-1}$ therefore giving rise to large A-E splitting. Furthermore there are two conformers of m-methylbenzaldehyde making the assignment of the rotational spectrum extremely difficult. We will show how coherence propagation demonstrated by 1,3-difluoroacetone can be applied in a general way to assign complex ground state rotational spectra such as m-methylbenzaldehyde.
PULSED JET DISCHARGE MATRIX ISOLATION STUDIES OF RADICALS, IONS, AND WEAKLY BOUND RADICAL-MOLECULE COMPLEXES

AIMABLE KALUME, LISA GEORGE AND SCOTT A. REID, Department of Chemistry, Marquette University, Milwaukee, WI 53233.

We have recently implemented pulsed jet discharge matrix isolation spectroscopy, a versatile method for trapping and spectroscopic interrogation of reactive intermediates, which combines matrix isolation techniques with a pulsed DC discharge nozzle. This method was initially demonstrated by Bondybey and co-workers, who showed that a variety of transient species (radicals, carbocations, and carbanions) could be trapped. A primary advantage of the pulsed discharge method over continuous deposition is that the short (ms) pulses produce a self-annealing effect due to the instantaneous temperature rise in the surface layers during deposition, which gives rise to clear, highly transparent matrices. We will demonstrate another advantage, in that the dependence of the absorption intensity on discharge current varies dramatically for different species, which provides a convenient diagnostic for spectral identification. By working at discharge currents near threshold, one successfully avoids extensive atomization and fragmentation. Our initial studies of halomethyl radicals, halocarbenium ions, and weakly bound complexes involving the hydroxyl radical trapped in Ar and Ne matrices will be presented. Our results on the halocarbenium ions suggest that the primary mechanism for ion formation is ionization/fragmentation of the precursor induced by collision with metastable rare gas atoms. We will discuss planned modifications to the method that should further broaden its scope and utility.


MATRIX ISOLATION AND COMPUTATIONAL STUDIES OF THE PHOTOLYSIS OF DIHALOETHANES: PROBING THE PATHWAYS LEADING TO RADICAL AND MOLECULAR PRODUCTS

AIMABLE KALUME, LISA GEORGE AND SCOTT A. REID, Department of Chemistry, Marquette University, Milwaukee, WI 53233; PATRICK Z. EL-KHOURY AND ALEXANDER TARNOVSKY, Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, OH 43403.

The importance of haloalkanes in atmospheric chemistry is well appreciated. In this talk, we will report on matrix isolation and computational studies of the photolysis of dihaloethanes following selected wavelength laser irradiation. The photolysis products are characterized by matrix isolation infrared and UV/Visible spectroscopy, supported by ab initio calculations. Results will be reported for the dibromo- and diiodoethanes. In our initial experiments, pulsed deposition of 1,2-dibromoethane:Ar samples (1:1000) onto a KBr window at 5 K yielded almost exclusively the anti-conformer (30:1 anti:gauche). Irradiation of this conformer at 220 nm yielded infrared absorptions assigned to: a) the gauche-conformer, b) the 2-bromoethyl radical, and c) the ethylene-Br$_2$ complex, which was confirmed in separate experiments where the complex was formed by deposition of ethylene:Br$_2$:Ar (1:1:1000) samples. The observed infrared and UV/Visible absorptions of these species are in excellent agreement with computational predictions. We will report on related studies of 1,1-dibromoethane and the corresponding diiodoethanes, with emphasis on the search for the bridged C$_2$H$_4$I radical.
The photolysis products of dibromodifluoromethane following selected wavelength laser irradiation were characterized by matrix isolation infrared and UV/Visible spectroscopy, supported by ab initio calculations. Photolysis at wavelengths of 240 and 266 nm of CF$_2$Br$_2$:Ar samples (1:5000) held at 5 K yielded iso-CF$_2$Br$_2$ (F$_2$CBrBr), a weakly bound isomer of CF$_2$Br$_2$, which is characterized here for the first time. The observed infrared and UV/Visible absorptions of iso-CF$_2$Br$_2$ are in excellent agreement with computational predictions at the B3LYP/aug-cc-pVTZ level. Single point energy calculations at the CCSD(T)/aug-cc-pVDZ level on the B3LYP optimized geometries show that the iso-form is a minimum on the CF$_2$Br$_2$ potential energy surface, lying some 55 kcal/mol above the CF$_2$Br$_2$ ground state. The energies of various stationary points on the CF$_2$Br$_2$ PES were characterized computationally; taken with our experimental results, these show that iso-CF$_2$Br$_2$ is an intermediate in the Br + CF$_2$Br reaction leading to molecular products (CF$_2$ + Br$_2$). The photochemistry of the iso-form was also investigated; excitation into the intense 359 nm absorption band resulted in isomerization to CF$_2$Br$_2$.

Our results are discussed in view of the rich literature on the gas-phase photochemistry of CF$_2$Br$_2$, particularly with respect to the existence of a roaming atom pathway leading to molecular products.

Hydroxyl radical, 'the detergent of atmosphere', the title is acquired due to capability of transformation of trace component present in atmosphere mainly troposphere into water soluble forms and also plays vital role in chemistry of the interstellar medium. The infrared spectra of OH radical isolated in solid neon have been investigated by Fourier Transform infrared spectroscopy (FTIR). OH monomer was prepared by microwave discharge of a mixture of water and neon gas at different concentrations prior to deposition on the cold mirror at 5 K. The microwave discharge of H$_2$O/Ne system is remarkable due to its propensity to form OH radical and other species like H$_2$, HO$_2$, OH-HO$_2$, OH-H$_2$O and (OH)$_n$-H$_2$O and IR spectroscopy reveals a variety of phenomena far from being fully understood. OH concentration studies, D/H isotopic substitution, and subsequent annealing leads to the characterization of the different species trapped in the neon matrix. All vibrational mode of OH-H$_2$O complex have been detected. The presence of species such as H$_2$ and HO$_2$ after matrix deposition led us to carry subsequent UV photolysis of our samples where the complex OH-H$_2$O may also be formed by following reaction:

\[ \text{HO}_2\cdot\text{H}_2 + h\nu \rightarrow \text{OH-H}_2\text{O} \]
AN FTIR STUDY OF THE INFLUENCE OF ENVIRONMENT CONDITIONS ON THE SUCCESSIVE HYDROGENATIONS OF CO

C. PIRIM, L. KRIM, UPMC Univ Paris 06, UMR 7075, Laboratoire de Dynamique, Interactions et Réactivité (LADIR), F-75005, Paris, France.

In a preliminary study, the reaction of CO successive hydrogenation has been performed at 3 and 10 K using a co-injection technique. A H/H$_2$ mixture and CO molecules are codeposited on a cold mirror and hydrogen atoms are reacting step by step with CO as follows: CO → HCO → H$_2$CO → H$_3$CO → CH$_3$OH

At 3 K, CO hydrogenation is limited to the first step of the reaction. However, when the reaction is performed at 10 K, CO hydrogenation is total and all intermediates are observed in the IR spectra.

The aim of this present work is to understand the influence of the environment in which the reaction takes place, in order to determine the best conditions promoting CO hydrogenation. Indeed, the catalytic potential of water molecules on CO hydrogenation has been more specifically studied. In this experiment, mixtures of (CO,H$_2$O) and H/H$_2$ are co-injected at various concentrations and in a temperature range between 3 and 20 K. It is clear that water environments induce noticeable changes by increasing the chemical reaction rate and promoting HCO conversion into H$_2$CO.

---

NEAR-IR BAND STRENGTHS OF MOLECULES DILUTED IN N$_2$ AND H$_2$O ICES


In order to determine the column density of a component of an ice from its infrared absorption features, the strengths of these features must be known. The peak positions, widths, profiles, and strengths of a certain ice components infrared absorption features are affected by the overall composition of the ice (Quirico et al. 1999). Many satellites within the solar system have surfaces that are dominated by either N$_2$ or H$_2$O (Roush 2001). The experiments presented here focus on the near-infrared absorption features of CO, CO$_2$, CH$_4$, and NH$_3$ ($\mu=10,000-4,000$ cm$^{-1}$, $\lambda=1-2.5$ $\mu$m) and the effects of diluting these molecules in N$_2$ and H$_2$O ice (dilution of 5:1). This is a continuation of previous results published by the Astro- and Solar-System Program at UAB by Gerakines et al. (2005). These data may be used to determine ice abundances from observed near-IR spectra or to predict the sizes of near-IR features in astrophysical environments.

---

Intermission
This study on MnC$_3$ is part of an ongoing project investigation of the structures and vibrations of small metal-carbon clusters using Fourier transform infrared (FTIR) spectroscopy and density functional theory (DFT). These species are of interest as potential species in astronomical environments and for understanding the structure and bonding of larger metal-carbide molecules such as metallocarbohedrenes. MnC$_3$ was produced by trapping the products from the dual laser Nd:YAG lased ablation of carbon and manganese rods in solid Ar at $\sim$12 K. Fourier transform infrared measurements of frequencies and $^{13}$C isotopic shifts were compared with the predictions of density functional theory calculations performed for three possible structures: two cyclic isomers with transannular C-C or C-Mn bonds and an asymmetric linear form. Based on this analysis the asymmetric stretching fundamental $\nu_1(\sigma)$ has been identified at 1846.9 cm$^{-1}$. This is the first optical detection of any isomer of MnC$_3$. A previous study by photoelectron spectroscopy reported evidence for the cyclic isomer with transannular Mn-C stretch based on preliminary DFT calculations. The results of calculations performed in conjunction with the present work will also be reported.


In all previous experimental studies of the thermal decomposition of acetaldehyde (CH$_3$CHO), the products were presumed to be CH$_3$ + CHO. These species result from cracking of the weakest bond. Other routes are possible: (DH$_{298}$(CH$_3$−CHO) $= 84.8 \pm 0.2$ kcal mol$^{-1}$; DH$_{298}$(CH$_3$CO-H) $= 89.4 \pm 0.3$ kcal mol$^{-1}$; DH$_{298}$(H-CH$_2$CHO) $= 92 \pm 2$ kcal mol$^{-1}$. This work explores the possibility of other thermal decomposition pathways, that result via C-H bond scission. We have used a resistively heated SiC tubular reactor with a 65 µsec residence time to study the thermal cracking of acetaldehyde. The decomposition products are identified by two independent techniques: 118.2 nm (10.487 eV) VUV photoionization mass spectroscopy and infrared absorption spectroscopy in a cryogenic matrix. The observed dissociation channels seem to be:

CH$_3$CHO $\rightarrow$ CH$_3$CO + H
\rightarrow CH$_2$=CHO
\rightarrow CH$_2$=C=O
\rightarrow CH$_3$ + HCO
DIMINISHED CAGE EFFECT IN $p$-$H_2$: INFRARED SPECTRA OF CH$_3$S OBSERVED FROM PHOTOLYSIS OF CH$_3$SH, CH$_3$SCH$_3$, AND CH$_3$SSCH$_3$ ISOLATED IN $p$-$H_2$

YUAN-PERN LEE, Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan and Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan; MOHAMMED BAHOU, Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan.

We report infrared absorption spectrum of the methylthio (or thiomethoxy) radical, CH$_3$S, isolated in solid $p$-$H_2$. CH$_3$S was produced by in situ UV photodissociation of three precursors: CH$_3$SH, CH$_3$SCH$_3$, and CH$_3$SSCH$_3$ isolated in solid $p$-$H_2$. New absorption features commonly observed with similar intensity ratios in experiments using these precursors are assigned as absorption of CH$_3$S. In addition to the previously assigned transitions of $\nu_3$ ($a_1$) at 727.1 cm$^{-1}$, fundamental transitions $\nu_6$ ($a_1$) at 771.1, $\nu_5$ ($e$) at 1056.6, $\nu_5$ ($a_1$) at 1400.0, and $\nu_4$ ($a_1$) at 2898.0 cm$^{-1}$ were observed. The wavenumbers of these features agree satisfactorily with those predicted with a spin-vibronic Hamiltonian accounting for the anharmonic effects and the Jahn-Teller effects to the quartic term; the corresponding wavenumbers predicted from theory are $\nu_6$ ($a_1$) at 793, $\nu_6$ ($e$) at 1105, $\nu_5$ ($a_1$) at 1436, and $\nu_4$ ($a_1$) at 2938 cm$^{-1}$, with deviations of 1.4-4.6% from experiments. Previous attempts of UV photolysis of CH$_3$SCH$_3$ and CH$_3$SSCH$_3$ isolated in an Ar matrix failed to produce CH$_3$S. These results serve as an excellent example that the diminished cage effect of solid $p$-$H_2$ makes production of free radicals via photolysis in situ feasible. If time permits, other examples will be discussed.


LONG-WAVELENGTH PHOTOCHEMISTRY OF MATRIX-ISOLATED BIACRYL

NATHAN G. KUCHMAS and C. A. BAUMANN, Department of Chemistry, The University of Scranton, Scranton, PA 18510-4626.

Visible irradiation ($520 \text{ nm} > \lambda > 485 \text{ nm}$) of matrix-isolated biacetyl (C$_4$H$_6$O$_2$) results in the formation of a complex of cis-methylhydroxycarbene (CH$_3$C=O) and ketene (CH$_2$CO), as well as other products. The wavelengths used in this study are longer than those necessary for the $S_0$-$S_1$ ($\tilde{X}^1A_g - \tilde{A}^1A_u$) transition, indicating that the photolysis is the result of a multiphoton process. One such process is sequential, where the spin-forbidden $S_0$-$T_1$ ($\tilde{X}^1A_g - \tilde{a}^3A_u$) transition is followed by the allowed $T_1$-$T_2$ ($\tilde{a}^3A_u - b^5B_g$) transition, with photoproducts emerging from the higher triplet (or following a radiationless transition to another state). A simultaneous two-photon process is also possible through the symmetry-forbidden $S_0$-$S_2$ ($\tilde{X}^1A_g - \tilde{B}^1B_g$) transition. Photoproduct formation as a function of irradiation flux and wavelength was used to sort out the relative contributions of each of these processes.
SOFT X-RAY SPECTROSCOPY OF GLYCYL-GLYCINE ADSORBED ON Cu(110) SURFACE

V. FEYER, O. PLEKAN, V. LYAMAYEV, T. SKALA, K. C. PRINCE, Sincrotrone Trieste, Basovizza (Trieste), Italy; V. CHAB, Institute of Physics, Prague, Czech Republic; N. TSUD, V. MATOLIN, Charles University, Prague, Czech Republic; V. CARRAVETTA, CNR-Institute of Chemical Physical Processes, Pisa, Italy.

Studies of the interaction between organic compounds and surfaces are motivated by their application as bio sensors, and their relevance to biocompatibility of implants and the origin of life. In the present work interaction of the simplest peptide, glycyl-glycine, with the Cu surface has been studied. Multilayer, monolayer and sub-monolayer films of this dipeptide on the clean and oxygen modified Cu(110) surface were prepared by thermal evaporation in high vacuum. The techniques used were soft X-ray photoelectron spectroscopy, near edge X-ray absorption fine structure spectroscopy and density functional theory calculations. By comparing the experimental and theoretical spectra, detailed models of the electronic structure and adsorption geometry for each coverage have been proposed, which are in good agreement with the theoretical calculations. The carboxylic acid group of glycyl-glycine loses hydrogen and the molecule is coordinated via the carboxylate oxygen atoms to the surface. At low coverage the amino group bonds to the surface via a hydrogen atom, while at higher coverage the bonding is via the nitrogen lone pair. The peptide group is not involved in the bonding to the surface.

IONS AS PROBES OF SUB-PS WATER NETWORK DYNAMICS.

G. W. SCHWAAB, D. A. SCHMIDT, S. FUNKNER, B. BORN, M. HAVENITH a, Department of Physical Chemistry II, Ruhr-University Bochum, D-44780 Bochum, Germany; O. BIRER, Department of Chemistry, Koç University, 34450 Istanbul, Turkey; R. GNANASEKARAN, and D. M. LEITNER, Department of Chemistry, University of Nevada, 89557 Reno, Nevada, USA.

We present THz measurements of salt solutions which shed new light on the controversy of salts as kosmotropes (structure makers) or chaotropes (structure breakers). We performed concentration dependent narrow-band THz-absorption spectroscopy on fifteen alkali-halide salt solutions around 85 cm$^{-1}$ (2.5 THz) and wide-band (30-300 cm$^{-1}$) THz Fourier transform measurements on six alkali halide salt solutions. All solutions show an increased THz-absorption compared to pure water with a linear concentration dependence. Our comprehensive data set is well-described by a model including damped harmonic oscillations (rattling modes) of both anions and cations within the water network. This model well-predicts key features of THz spectra for a variety of salt solutions. Complementary molecular dynamics simulations using the TIP3P water model support experiments and show that the fast sub-ps ionic motions and their surroundings are almost decoupled. These findings provide a complete description of the solute-induced changes in the THz solvation dynamics for the investigated salts and suggests a treatment of the ions as simple defects in an H-bond network. Our results show that THz spectroscopy is a powerful experimental tool to establish a new insights on contributions to the structuring of water by anions and cations.

aThe authors acknowledge financial support by the VW Stiftung Az I/84 302, the BMBF (grant 05 KS7PC2), FOR 618 and NSF (grant CHE-0910669).
TE. ATMOSPHERIC SPECIES  
TUESDAY, JUNE 22, 2010 – 8:30 am  
Room: 2015 McPHERSON LAB

Chair: CURTIS RINSLAND, NASA Langley Research Center, Hampton, Virginia

TE01 15 min 8:30
HIGH SENSITIVITY CRDS OF THE $a^1 \Delta_g \rightarrow X^3 \Sigma_g^-$ BAND OF OXYGEN NEAR 1.27 $\mu$m: MAGNETIC DIPOLE AND ELECTRIC QUADRUPOLE TRANSITIONS IN SPECTRA OF FIVE ISOTOPOLOGUES

O. M. LESHCHISHINA, S. KASSI, L. WANG, Université Joseph Fourier/CNRS, Laboratoire de Spectrométrie Physique, 38402 Saint Martin d’Hères, FRANCE; L.E. GORDON, L. S. ROTHMAN, Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge MA 02138-1516, USA; A. CAMPARGUE, Université Joseph Fourier/CNRS, Laboratoire de Spectrométrie Physique, 38402 Saint Martin d’Hères, FRANCE.

The knowledge of accurate spectroscopic parameters for the $a^1 \Delta_g \rightarrow X^3 \Sigma_g^-$ band of molecular oxygen near 1.27 $\mu$m is very important in the field of remote sensing. Although this band was studied by spectroscopists for over a century a lot of discrepancies still remain in the previously reported line positions and intensities. In this work the Continuous Wave-Cavity Ring Down Spectroscopy (CW-CRDS) technique has been used to record with high sensitivity the absorption spectrum of this band. The spectra were obtained between 7640 and 7917 cm$^{-1}$ with “natural” oxygen and with a sample highly enriched in $^{18}$O. The absolute intensities of 377 and 652 oxygen transitions were measured in the two spectra, respectively. They include the $a^1 \Delta_g \rightarrow X^3 \Sigma_g^-$ (0-0) bands of $^{16}$O$_2$, $^{16}$O$^{18}$O, $^{16}$O$^{17}$O, $^{17}$O$^{18}$O and $^{18}$O$_2$. The (0-0) bands of $^{16}$O$_2$ and $^{18}$O$_2$ show (previously undetected) electric quadrupole transitions with line intensities ranging from $1 \times 10^{-30}$ to $1.9 \times 10^{-28}$ cm/molecule. They are accompanied by the $a^1 \Delta_g \rightarrow X^3 \Sigma_g^-$ (1-1) hot bands which are also reported for the first time. Accurate spectroscopic parameters for the observed bands were derived from a global fit of the experimental line positions, combined with microwave and Raman measurements available in the literature.

TE02 15 min 8:47
PRESSURE BROADENING AND SPECTRAL OVERLAP IN THE MILLIMETER WAVE SPECTRUM OF OZONE

COREY CASTO AND FRANK C. DE LUCIA, Department of Physics, The Ohio State University, Columbus, OH 43210-1106.

Our understanding of propagation and remote sensing in the atmosphere is typically based on pressure broadening and line frequency measurements made at relatively low pressures, extended to atmospheric pressure theoretically. This is especially true for reactive species such as ozone. We will report on a series of measurements made over a range of pressures typical of the atmosphere. These measurements were made with a FASSST cavity ring down system that measures the absolute absorption of broad and continua effects across the 170 – 260 GHz window on a time scale that minimizes time variations that might be caused by the reactive ozone. Pressure broadening parameters will be presented and the remaining residuals discussed.
TEMPERATURE DEPENDENT OZONE ABSORPTION CROSS SECTIONS FOR SATELLITE SPECTROMETERS: NEW LABORATORY MEASUREMENTS

ANNA SERDYUCHENKO, VICTOR GORSHELEV, MARK WEBER, JOHN P. BURROWS,
INSTITUTE FOR ENVIRONMENTAL PHYSICS, UNIVERSITY OF BREMEN, OTTO-HAHN ALLEE 1, D-28359 BREMEN, GERMANY.

We report on the work devoted to the up-to-date measurements of the ozone absorption cross-sections. The main goal of the project is to produce a consolidated and consistent set of high resolution cross-sections for satellite spectrometers series that allows a derivation of the harmonized long term data set. It is expected that five atmospheric chemistry instruments will provide two or more decades (1995 - 2020) of ozone observations. Information from different sensors has to be combined for a consistent long-term data record, since the lifetime of individual satellite missions is limited. The harmonization of cross-sections is strongly supported by new experimental work. New laboratory measurements of ozone cross-section are underway that will improve a) absolute scaling of cross-sections, b) temperature dependence of cross-sections and c) wavelength calibration. We take advantage of a Fourier transform spectrometer and Echelle spectrophotometer to extend the dynamic range of the system (covering several orders of magnitude in cross-sections from UV up to the near IR). Measurements cover the spectral range 220 - 1000 nm at a spectral resolution of 0.02 nm in UV/VIS with absolute intensity accuracy of at least 2 percents, and wavelength accuracy better than 0.001 nm in the temperature range 193-293 K in 10 K steps. A lot of attention is paid to the accuracy of determining the temperature of the ozone flow and new methods for absolute calibration of relative spectra. New cross-sections dataset will improve significantly the ozone data quality and time series as required for climate, air quality, and stratospheric ozone trend studies. Updated ozone cross-sections will be available for reprocessing with satellite spectrometers and to the scientific community as well.

FAR-INFRARED EMISSION SPECTROSCOPY OF ROVIBRATIONALY EXCITED WATER VAPOR


Water vapor transitions involving excited rovibrational levels have been identified in many high temperature space sources. Extensive experimental and theoretical efforts are still needed to provide more accurate databases concerning highly excited rovibrational levels. In this context, the high resolution emission spectrum of water vapor has been recorded between 50 and 600 cm⁻¹ using a Bruker IFS 125HR Fourier transform interferometer and a continuous flow of water vapor rovibrationaly excited by an electroless radio-frequency discharge. More than 1500 pure rotational lines were assigned within the fundamental (000) and first excited (010) vibrational states up to \( J = 35 \). Rotational as well as rovibrational lines were identified for the higher lying states up to the first hexad. About 1000 pure rotational transitions within the vibrational states of the first hexad were assigned for the first time.

The new data, along with a large body of high-resolution data, was fitted using the bending-rotation theoretical approach to compute line positions. In a preliminary analysis, the wavenumbers of 1511 new transitions involving the ground and (010) states were accounted for up to \( J = 27 \) with a root mean square value of \( 0.8 \times 10^{-3} \text{ cm}^{-1} \). Work is still in progress and we are hoping to account for the new data at least up to the second triad.

In the paper the new data will be presented and the results of the line position analysis will be given.

\[ ^c \text{Coudert, J. Mol. Spec. 181 (1997) 246.} \]
THEORETICAL CALCULATION OF THE N₂ BROADENED HALF-WIDTHS OF H₂O

R. H. TIPPING, Department of Physics and Astronomy, University of Alabama, Tuscaloosa, AL 35487; Q. MA, NASA/Goddard Institute for Space Studies and Department of Applied Physics and Applied Mathematics, Columbia University, 2880 Broadway, New York, NY 10025.

For many applications, in addition to accurate spectral line frequencies and intensities one needs accurate Lorentzian parameters (half-widths, pressure shifts, and their temperature dependencies). Because of the importance of H₂O in the Earth’s atmosphere, extensive compilations of these data are available in the HITRAN database. Recently, ab initio calculations have been carried out and databases containing tens of millions of line frequencies and intensities are available. Obviously, it is not possible to measure their Lorentzian parameters, and one must rely on theoretical calculations. For many years researchers have used the Robert-Bonamy (RB) formalism; however, we recently discovered a subtle error was made in their original derivation, and this modification is not negligible for certain systems. In this theory the internal motions are treated quantum mechanically, while the translational motion is treated classically. In order to achieve the desired accuracy, one needs to use a realistic interaction potential, and a realistic trajectory model for the translational motion. Because of the large number of potential matrix elements appearing in the standard application of the RB theory, one is forced to introduce cut-offs that may limit the accuracy attainable. To obviate the necessity of low-order cut-offs and achieve results for half-widths to the accuracy of the interaction potential, we recently reformulated the theory using the coordinate representation. In the present paper, we present results to study the effects of using different experimental half-width data to obtain the parameters in several models for the interaction potential, and the effects of different trajectory models for treating the relative motion. From our detailed analysis, we are able to draw several conclusions that should help theorists to make choices in order to achieve realistic theoretical half-widths and to assess their accuracy.

NEW MEASUREMENTS OF H₂¹⁶O LINE INTENSITIES AROUND 8800 CM⁻¹ AND 1300 CM⁻¹

C. OUDOT, L. REGALIA, LE WANG, L. DAUMONT, X. THOMAS, P. VON DER HEYDEN, D. DECA-TOIRE, Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR 6089, Faculté des sciences, BP 1039, 51687 REIMS CEDEX 2 - FRANCE.

A precise knowledge of spectroscopic parameters for atmospheric molecules is necessary for the control and the modelling of the Earth’s atmosphere. The water vapor take a special key as it participate to the global radiative balance of the atmosphere. Our laboratory is engaged since many years in the study of H₂¹⁶O vapor and its isotopologues [1, 2, 3]. An important work has been already made in the spectral region of 4000 to 6600 cm⁻¹ [3] and it continues now in the following spectral window : 6600-9000 cm⁻¹. We have focused on the lines around 8800 cm⁻¹, as the latest version of HITRAN database still relies on the work of Mandin et al. performed in 1988 [4, 5]. We have recorded several spectra of water vapor with our step-by-step Fourier Transform Spectrometer built in our laboratory [6, 7]. We present here our intensity measurements compared to recent literature data [8] and HITRAN2008 database. Also we have performed a study around 1300 cm⁻¹. The precise knowledge of water vapor for this spectral range is very useful for inversion of IASI spectra. We show some comparisons between our new intensity measurements and LISA database, HITRAN2004, and recent literature data [9].

Intermission

TE07  15 min  10:30

EMPIRICAL LOWER STATE ENERGIES OF $^{13}$CH$_4$ AT 1.66 µm USING 296 K AND 81 K SPECTRA

O. M. LYULIN, Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, 1, Akademicheskii av., 634055 Tomsk; S. KASSI, A. CAMPARGUE, Laboratoire de Spectrométrie Physique (associated with CNRS, UMR 5588), Université Joseph Fourier de Grenoble, B.P. 87, 38402 Saint-Martin-d’Hères Cedex, France; K. SUNG, L.R. BROWN, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109, U.S.A.

The high resolution absorption spectra of $^{13}$CH$_4$ were recorded at 81 K by differential absorption spectroscopy using a cryogenic cell and a series of Distributed Feed Back (DFB) diode lasers at room temperature by Fourier transform spectroscopy (a Bruker IFS-125HR at JPL). Empirical line lists were constructed containing, respectively, 1629 $^{13}$CH$_4$ transitions detected at 81 K (5852 - 6124 cm$^{-1}$) and 3481 features measured at room temperature (5850 - 6150 cm$^{-1}$); the minimum observed intensities were, respectively, $3 \times 10^{-26}$ and $4 \times 10^{-25}$ cm/molecule at 81 K and 296 K. From the variation of the cold and room temperature line intensities, empirical lower state energies were derived for 1196 $^{13}$CH$_4$ transitions. Over 400 additional weak features, detected at 81 K, could not be matched to lines observed at room temperature. The observed intensities represent 99.2% and 84.6% of the total absorbance at 81 K and 296 K, respectively. The quality of the resulting empirical low energy values is demonstrated by the excellent agreement with the already-assigned transitions and the clear propensity of the empirical low J values to be close to integers.

*Part of the research described in this paper was performed at Jet Propulsion Laboratory, California Institute of Technology, under contracts and cooperative agreements with the National Aeronautics and Space Administration.

TE08  15 min  10:47

REAL TIME DIAGNOSTICS OF JET ENGINE EXHAUST PLUMES USING A CHIRPED QC LASER SPECTROMETER

K. G. HAY, G. DUXBURY and N. LANGFORD, Department of Physics, SUPA, John Anderson Building, University of Strathclyde, 107 Rottenrow, Glasgow G4 0NG, Scotland, UK.

Quantitative measurements of real-time variations of the chemical composition of a jet engine exhaust plume is demonstrated using a 4.86 µm intra-pulse quantum cascade laser spectrometer. The measurements of the gas turbine exhaust were carried out in collaboration with John Black and Mark Johnson at Rolls Royce. The recording of five sets of averaged spectra a second has allowed us to follow the build up of the combustion products within the exhaust, and to demonstrate the large variation of the integrated absorption of these absorption lines with temperature. The absorption cross sections of the lines of both carbon monoxide and water increase with temperature, whereas those of the three main absorption lines of carbon dioxide decrease. At the steady state limit the absorption lines of carbon dioxide are barely visible, and the spectrum is dominated by absorption lines of carbon monoxide and water.
MULTI-WAVELENGTH MEASUREMENT OF BUS EXHAUSTS USING A FOUR QC LASER SPECTROMETER

K. G. HAY, D. WILSON, G. DUXBURY and N. LANGFORD, Department of Physics, SUPA, John Anderson Building, University of Strathclyde, 107 Rottenrow, Glasgow G4 0NG, Scotland, UK.

Using a portable, lightweight, four laser intra-pulse quantum cascade laser spectrometer we have measured the variation of the composition of exhaust gases emitted by diesel engined buses which are representative of the decades from the 1930’s until the 1990’s. The lasers and the fast detector used in the spectrometer are Peltier cooled, and the spectra are recorded using each laser in turn, in a repeated four laser cycle. The instrument is controlled via a ruggedised laptop computer. The wavelengths of the lasers used were 7.84 microns (methane, nitrous oxide and formaldehyde), 6.13 microns (nitrogen dioxide) 5.25 microns (nitric oxide and water) and 4.88 microns (carbon monoxide and carbon dioxide). The path length of the multiple pass absorption cell used was 77 m. The results we will present demonstrate the possibility of deploying this type of instrument for investigating gas emissions from a variety of sources.

THE COF$_2$ ROTATIONAL SPECTRUM NEAR 1 THz; IMPROVED MOLECULAR CONSTANTS FOR THE GROUND AND FIRST EXCITED STATES OF $\nu_2$, $\nu_3$, $\nu_5$, and $\nu_6$

E. A. COHEN, and B. J. DROUIN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099.

The rotational spectrum of COF$_2$ has been observed near 1 THz as part of a continuing program to precisely characterize the spectra of atmospheric molecules. Spectra of the ground, $\nu_2$, $\nu_3$, $\nu_5$, and $\nu_6$ states have been assigned, combined with other available data, and fit up to $J \approx 90$ for a wide range of $K_c$. The spectrum of naturally abundant $^{13}$COF$_2$ in its ground vibrational state has also been observed and fit, although the range of quantum states is smaller due to interference from the nearby normal species. These results allow more accurate prediction of high $J$ infrared spectra of the fundamental vibrations below 1000 cm$^{-1}$. The fits will be described and some examples of rotational and infrared spectra will be shown.

A SUBMILLIMETER CHEMICAL SENSOR

CHRISTOPHER F. NEESE, IVAN R. MEDVEDEV, FRANK C. DE LUCIA, Department of Physics, 191 W. Woodruff Ave., Ohio State University, Columbus, OH 43210 USA; GRANT M. PLUMMER, Enthalpy Analytical, Inc., 2202 Ellis Rd., Durham, NC 27703 USA; CHRISTOPHER D. BALL, AARON J. FRANK, Battelle Memorial Institute, 505 King Ave., Columbus, OH 43201 USA.

Rotational spectroscopy has been recognized a potentially powerful tool for chemical analysis since the very beginnings of the field. A typical rotational fingerprint consists of $10^5$ resolvable spectral channels, leading to ‘absolute’ specificity, even in complex mixtures. Furthermore, rotational spectroscopy requires very small amounts of sample with detection limits as low as picograms. Nevertheless, this technique has not yet been widely applied to analytical science because of the size, cost, and complexity of traditional spectrometers.

A resurgence of interest in spectroscopic sensors has been fueled by increases in performance made possible by advances in laser systems and applications in medicine, environmental monitoring, and national security. Most of these new approaches make use of the optical/infrared spectral regions and their well established, but still rapidly evolving technology base. The submillimeter (SMM) spectral region, while much less well known, has also seen significant technological advances, allowing the design of powerful spectroscopic sensors.

Using modern solid-state multiplier technology we have built a small bench top SMM spectrometer designed for use as a chemical sensor. This spectrometer includes a sample acquisition system including the vacuum equipment to provide the ideal pressures (1–10 mtorr) for SMM spectroscopy and a sorbent tube for analyte collection and preconcentration. The entire spectrometer, including power supplies, frequency synthesizers, a 1.2 m folded sample cell, and a computer for data analysis fits into a cubic foot box.
TF MINI-SYMPOSIUM: METAL CONTAINING MOLECULES
TUESDAY, JUNE 22, 2010 – 1:30 pm
Room: 160 MATH ANNEX

Chair: NICHOLAS WALKER, University of Bristol, Bristol, United Kingdom

TF01  INVITED TALK  30 min  1:30
SIZE SELECTIVE FAR-INFRARED SPECTROSCOPY OF TRANSITION METAL CLUSTERS IN A MOLECULAR BEAM

ANDRÉ FIELICKE, Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin, Germany.

Transition metal clusters are frequently used as model systems for low coordinated sites of extended surfaces and their study can provide valuable insights into the mechanisms of heterogeneous catalytic reactions. In many cases, however, there is still a lack of information on their structures and the relationship between structure and chemical behavior. Size selective spectra of neutral and charged clusters in the gas-phase can be obtained by combining resonant photodissociation with mass spectrometric detection. This principle is used here in the far-infrared using the Free Electron Laser for Infrared eXperiments (FELIX) as an intense and widely tunable radiation source to induce multiple photon dissociation (MPD) of weakly bound complexes between the metal clusters and rare gas atoms. The far-IR spectra obtained are unique for each cluster size and are true fingerprints of the cluster’s structure. The comparison with IR spectra calculated using density functional theory allows determination of their structures and to obtain insights into the growth mechanism. The capabilities of structure determination via far-IR MPD spectroscopy are demonstrated for cationic rhodium and neutral gold clusters.

TF02  15 min  2:05
INFRARED SPECTROSCOPY OF METAL LIGAND AND METAL OXIDE LIGAND COMPLEXES

ALLEN M. RICKS and MICHAEL A. DUNCAN, Department of Chemistry, University of Georgia, Athens, GA.

Metal ligand and metal oxide ligand complexes are generated in a laser vaporization/supersonic expansion cluster source and are mass selected and studied using infrared spectroscopy in the 600-4000 cm\(^{-1}\) region using a tunable infrared OPO. Several different systems are investigated and some show evidence for intracluster reactions to form metal oxide species or coupling of coordinating ligands. In particular the V(CO\(_2\))\(_n^+\) system shows evidence for the onset of an intracluster reaction at \(n=7\) as evidenced by the sudden appearance of a band at 1800 cm\(^{-1}\). DFT calculations are performed in support of this work and several possible interpretations of the experimental data will be presented.

TF03  15 min  2:22
INFRARED SPECTROSCOPY OF DOUBLY-CHARGED METAL-WATER COMPLEXES

B. BANDYOPADHYAY and M. A. DUNCAN, Department of Chemistry, University of Georgia, Athens, GA 30602-2556.

Rare gas tagged, cold doubly charged vanadium-water complexes are produced in the supersonic expansion cluster source via laser vaporization technique. Often the doubly charged metal-water complexes are asymptotically unstable because of the charge transfer from the M\(^{2+}\) to H\(_2\)O if the second ionization energy of the metal is greater than the ionization energy of water (12.6eV). Therefore, the ion density of these species usually much lower than the cationwater complexes in the cluster source. We have investigated the V\(^{2+}\)(H\(_2\)O)Ar\(_n\) complexes via Infrared photodissociation spectroscopy in the O-H stretch region of the water. The O-H stretch of the water is shifted to the lower frequency than that of metal cation water complex due to the higher charge on the metal. Theoretical calculations were also done to support our experiment and to get the structures of these complexes as well.
THE OPTICAL STARK SPECTRUM OF THE $A^3\Phi_4 - X^3\Phi_4$ BAND SYSTEM OF IRIDIUM MONOFLUORIDE, IrF

XIUJUAN ZHUANG AND TIMOTHY C. STEIMLE, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287; COLAN LINTON, Center for Lasers, Atomic and Molecular Sciences and Physics Department, University of New Brunswick, Fredericton, NB Canada E3B 5A3.

Recently the New Brunswick group\textsuperscript{a} reported on the field-free detection and analysis of the $A^3\Phi_4 - X^3\Phi_4$ band system of IrF. Here we report on the analysis $Q(4)(15922\text{ cm}^{-1})$ branch feature of the (1,0) band of the $^{191}\text{IrF}$ isotopologue of that system recorded at field strengths of up to 3000 V/cm. The spectra are surprisingly complex at the achieved resolution of 40 MHz due to the presence of both the $^{191}\text{Ir}(I=3/2)$ and $^{19}\text{F}(I=1/2)$ magnetic hyperfine splitting. The determined permanent electric dipole moment, $\mu_{el}$, for the $X^3\Phi_4$ state is compared with that recently determined\textsuperscript{b} for the $X^3\Phi_4$ state of isovalent CoF. The trend in $\mu_{el}$ amongst the ground states of IrF, IrC and IrN\textsuperscript{c} will be discussed. Finally, a simple molecular orbital correlation diagram will be used to rationalize the change in $\mu_{el}$ upon excitation from the $X^3\Phi_4$ to $A^3\Phi_4$ state.

\textsuperscript{c}A.J.Marr; M.E. Flores; and T.C. Steimle J. Chem. Phys. 104 8183, 1996.

THE VISBILE SPECTRUM OF TITANUM DIOXIDE

XIUJUAN ZHUANG AND TIMOTHY C. STEIMLE, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287; RAMY NAGARAJ ANN AND JOHN P. MAIER, Department of Chemistry, University of Basel, Basel Switzerland.

Bulk TiO\textsubscript{2} is a widely used photo-activated catalytic material, yet poorly understood. Much of the motivation for studies of molecular TiO\textsubscript{2} is the observation\textsuperscript{a} that there is a smooth correlation of the molecular electronic states to the band gap of the bulk. The field-free energy levels of the ground state of the monomer have been fully characterized by microwave spectroscopy.\textsuperscript{b} Here we report on the visible spectrum in the region between 18200 cm$^{-1}$ to 18750 cm$^{-1}$ of a cold molecular beam sample of TiO\textsubscript{2} using laser induced fluorescence detection and mass-selected REMPI. Bands at 18240 cm$^{-1}$, 18411 cm$^{-1}$ and 18470 cm$^{-1}$ were recorded at a resolution of 40 MHz and rotationally analyzed. The dispersed fluorescence of 18411 cm$^{-1}$ and 18470 cm$^{-1}$ bands were analyzed to produce a set of vibrational parameters for the ground state. The optical Stark spectra of the 18411 cm$^{-1}$ and 18470 cm$^{-1}$ bands were recorded and analyzed to determine permanent electric dipole moments and compared with the results for the band at 18655 cm$^{-1}$\textsuperscript{c}

\textsuperscript{c}H.Wang; T.C. Steimle; C. Apetrei and J.P. Maier PCCP 11 2649, 2008.

SEARCH FOR THE LOW-LYING ELECTRONICALLY EXCITED STATES OF UO\textsubscript{2}

I. O. ANTONOV, M. C. HEAVEN, Department of Chemistry, Emory University, Atlanta, GA 30322.

Low-lying electronically excited states of UO\textsubscript{2} were studied by laser excitation and dispersed fluorescence spectroscopy. Excitation of UO\textsubscript{2} in 31300-31800 cm$^{-1}$ and 27100 cm$^{-1}$ region produced highly congested emission spectrum. A search for the low-lying absorption bands was performed in the region of 10000-15000 cm$^{-1}$ using two-color REMPI spectroscopy. Several band systems were found near 11500, 12300, 13100 and 13700 cm$^{-1}$.

Intermission
STUDY OF THE ZEEMAN EFFECT IN THE [17.6]7.5 X18.5 TRANSITION IN HOLMIUM MONOXIDE (HoO)

COLAN LINTON, Center for Lasers, Atomic and Molecular Sciences and Physics Department, University of New Brunswick, Fredericton, NB Canada E3B 5A3; HAILING WANG AND TIMOTHY C. STEIMLE, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287.

The diatomic oxides of the lanthanides and actinides have many low-lying electronic states due to the presence of open f and d orbitals on the metal. The magnetic and electric tuning of the fine structure is an effective means of identifying the dominant configuration of a particular electronic state and of testing theoretical predictions of the configurational composition of the eigenfunctions. Here we report on the first high-resolution molecular beam measurements of the Zeeman effect in electronic transitions of holmium monoxide, HoO. Several branch features in the previously detected [17.6](Ω = 7.5) - X1(Ω = 8.5) electronic transition were recorded at near natural linewidth limit (FWHM 35MHz) field free and in the presence of a tunable static magnetic field. The Zeeman splittings and shifts were used to extract values for the magnitudes of the magnetic g-factors respectively of the two electronic states. These are compared with theoretical predictions.

INTRACAVITY LASER ABSORPTION SPECTROSCOPY OF PLATINUM FLUORIDE IN THE NEAR INFRARED

LEAH C. O’BRIEN, KIMBERLY HANDLER, RACHEL A. HARRIS, Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026-1652; JAMES J. O’BRIEN, MEREDITH REDICK, BECCA STEINBERG, Department of Chemistry and Biochemistry and Center for Nanoscience, University of Missouri, St Louis, MO 63121-4499.

Several new bands of PtF has been recorded in the near-infrared with rotational resolution using intracavity laser absorption spectroscopy. The results of the analysis will be presented. The gas phase PtF molecules were produced using a platinum-lined hollow cathode in an argon-based electric discharge with a small amount of SF6.

INTRACAVITY LASER ABSORPTION SPECTROSCOPY OF PLATINUM SULFIDE IN THE NEAR INFRARED

JAMES J. O’BRIEN, Department of Chemistry and Biochemistry and Center for Nanoscience, University of Missouri, St Louis, MO 63121-4499; LEAH C. O’BRIEN, KIMBERLY HANDLER, Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026-1652.

A new electronic transition of PtS has been recorded using intracavity laser absorption spectroscopy. Two branches associated with a red-degraded bandhead at 12460cm⁻¹ are identified as the (0,0) band of a new [12.5]¹Σ⁺ - X¹Σ⁺ transition. The results of the analysis will be presented.
HOW CATION-PI INTERACTIONS ENHANCE AND STRUCTURE THE BINDING OF METAL IONS TO AMINO ACIDS AND PEPTIDES. DIALANINE PROBED BY IRMPD SPECTROSCOPY AS A PRIME EXAMPLE

ROBERT C. DUNBAR, Chemistry Department, Case Western Reserve Univ., Cleveland, OH 44106; JEFFREY STEILL, FOM Institute for Plasma Physics, Nieuwegein, Netherlands; JOS OOMENS, FOM Institute for Plasma Physics, Nieuwegein, and University of Amsterdam, Netherlands.

Spectroscopic examination of metalated amino acids and model peptides in the infrared region gives incisive conformational information. The role of cation-pi interactions of the metal ions with aromatic amino acids in structuring the complexes and enforcing particular architectures is being clarified by such experiments using IRMPD action spectroscopy as the experimental probe. The presence of multiple aromatic groups as in dialanine gives particularly stringent conformational stabilization. Comparing spectroscopic peak shifts across a range of alkali and alkaline earth metal ions, ranging from lithium to cesium, and from calcium to barium, allows us to view the systematic relations between normal mode frequencies and ion/peptide interactions. The spectra of the ions were acquired by irradiating the cell of the Fourier-transform ion cyclotron resonance mass spectrometer with infrared light from the FELIX free electron laser at wavelengths in the approximate range 500 to 1900 cm$^{-1}$.

ANION PHOTOELECTRON SPECTROSCOPY OF Mo-V BINARY TRANSITION METAL SUBOXIDE CLUSTERS

CAROLINE CHICK JARROLD, JENNIFER E. MANN, SARAH E. WALLER, and DAVID W. ROTHGEB, Department of Chemistry, Indiana University, 800 E. Kirkwood Avenue, Bloomington, IN 47405.

Vibrationally-resolved photoelectron spectra of molybdenum vanadium oxo cluster anions with 2 to 5 oxygen atoms and measured using 2.33 eV, 3.49 eV and 4.66 eV photon energies generally exhibit broad and overlapping electronic states. The adiabatic electron affinities for the series are 1.68(3) eV, 1.73(3) eV, 2.89(1) eV, and 3.4(1) eV for two through five oxygen atoms, respectively. Vibrational structure observed in the spectra can be reconciled with the lowest energy structural isomers of the anions determined in DFT calculations: The lowest energy isomers have low symmetry, with the Mo center in a higher oxidation state than the V center, and high spin states are favored.

MICROSOLVATION OF Ni$^{2+}$ AND Co$^{2+}$ BY ACETONITRILE AND WATER: PHOTODISSOCIA TION DYNAMICS OF M$^{2+}$($\text{CH}_3\text{CN}$)$_n$(H$_2$O)$_m$

MANORI PERERA, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801; RICARDO B. METZ, Department of Chemistry, University of Massachusetts, Amherst, MA 01002.

The microsolvation of metal dications by acetonitrile and water study is important in understanding the interaction of solvents with the metal center and how the nature of the solvent, protic water and aprotic acetonitrile, affect binding and charge transfer dynamics. The clusters were produced by electrospray and characterized by photofragment spectroscopy in an ion trap dual time-of-flight mass spectrometer.

The homogeneous clusters with acetonitrile, n=4 and 3 dissociated by simple solvent loss and only n=2 showed electron transfer as a dissociation pathway. Mixed clusters with water and acetonitrile reveal more interesting dissociation dynamics. In larger mixed clusters (n=4 and 3), the water loss was favored over acetonitrile loss by a significant yield which is understandable because acetonitrile is a better solvent in the gas phase due to its higher dipole moment and polarizability. Proton transfer was observed as a minor channel for M$^{2+}$($\text{CH}_3\text{CN}$)$_2$(H$_2$O)$_2$ and M$^{2+}$($\text{CH}_3\text{CN}$)$_2$(H$_2$O) but was not seen in M$^{2+}$($\text{CH}_3\text{CN}$)$_3$(H$_2$O). In our lab, we previously observed proton loss as the major channel for M$^{2+}$(H$_2$O)$_4$. Studies of deuterated clusters confirm that water acts as the proton donor. Considering the photodissociation yield it was clear that four coordinate clusters of cobalt dissociated more readily than nickel clusters whereas for the three coordinate clusters, dissociation was more efficient for nickel clusters over cobalt. For the two coordinate clusters, dissociation is via electron transfer but the yield is low for both metals. Our calculations of reaction energetics, dissociation barriers, and the positions of excited electronic states complemented the experimental work.
ELECTRONIC SPECTROSCOPY AND VIBRATIONALLY MEDIATED PHOTODISSOCIATION OF Co$^+$($\text{H}_2\text{O}$), Co$^+$($\text{D}_2\text{O}$) and Co$^+$($\text{HOD}$)

ABDULKADIR KOCAK, G. AUSTEIN-MILLER and R. B. METZ, Department of Chemistry, University of Massachusetts, Amherst, MA 01003.

Electronic spectra of gas phase clusters, Co$^+$($\text{H}_2\text{O}$), Co$^+$($\text{D}_2\text{O}$) and Co$^+$($\text{HOD}$), produced in a laser ablation ionization source, have been studied in the visible region, from 540 to 740 nm. The metal-ligand bond strength is determined from the dissociation onset. The photodissociation spectra show transitions to several excited electronic states. The resolved vibrational and partially resolved rotational structure are analyzed to give excited state vibrational frequencies and geometries. The O-H stretch frequencies in the ground electronic state are measured using vibrationally mediated photodissociation, in which IR excitation is combined with visible photodissociation.

QUADRUPLY BONDED M$_2$ COMPLEXES INCORPORATING THIENYLETHYNYL AND THIENYLVINYL CARBOXYLATES

CARLY R. REED, MALCOLM H. CHISHOLM, and CLAUDIA TURRO, Ohio State University, Department of Chemistry, Columbus, Ohio 43210.

Quadruply bonded metal complexes, where M = Mo, W, that incorporate thienylethynyl and thienyvinyl carboxylates are being synthesized. Varying the bond order of the C$_2$ unit between the thienyl group and the carboxylate tether provides a series of complexes in which a comparative study on the electronic delocalization in the ground and excited states can be conducted. The properties of these complexes will be predicted by DFT calculations and probed by steady-state absorbance, emission, electrochemistry, and ns- and fs-transient absorption.

USING ELECTROABSORPTION SPECTROSCOPY TO GAIN INSIGHT INTO THE GROUND- AND EXCITED-STATE MIXED VALENCE PROPERTIES OF A SERIES OF DIMERS FORMED FROM METAL-METAL QUADRUPLY BONDED UNITS

BENJAMIN J. LEAR, PHIL C. BUNTING, and MALCOLM H. CHISHOLM, The Ohio State University, Columbus, OH 43210.

A series of complexes of the type [(MM)(piv)$_3$]$_2$µ$_2$-BL, where M= Mo or W, piv= pivalate, and BL= oxalate or terephthalate, were synthesized. These complexes are known to form strongly coupled mixed valence species in their +1 (singly oxidized) state. Here, we report the properties of the neutral complexes, which are of appropriate symmetry to form mixed valence species in their metal-to-ligand charge transfer (MLCT) excited states. In particular, we discuss the steady state, electroabsorption, and time resolved spectroscopy associated with MLCT excitation. We also consider the inter-relation (if any) of the properties of ground- and excited-state mixed valency.
TG01 15 min 1:30

DIRECT OBSERVATION OF RYDBERG–RYDBERG TRANSITIONS IN CALCUIUM ATOMS


Chirped Pulse millimeter-Wave (CPmmW) spectroscopy, an extension of Brooks Pate’s Chirped Pulse Fourier Transform Microwave (CP-FTMW) technique, has been adapted to observe electronic transitions between Rydberg states. The feasibility of this method has been demonstrated on calcium atoms of effective principal quantum number $n^*$ of 40 and at frequencies of 70–84 GHz. Whereas Rydberg states are generally detected by ionization, we directly observe the free induction decay that they emit after polarization by the chirped pulse. Spectra with a bandwidth of 10 GHz and resolution of 1 MHz or better may be acquired in several shots, which could enable high-resolution “pure electronic” spectroscopy of molecules in core-nonpenetrating Rydberg states. The available millimeter-wave power is not a limitation in this experiment because the transition dipole moments are large ($\sim 5,000$ Debye). Furthermore, the ability to quickly and arbitrarily polarize the sample opens avenues for optical plus millimeter-wave coherent experiments. Schemes to extend this technique to molecules are under development.

TG02 15 min 1:47

RYDBERG STATES OF XENON COLLISION DIMERS IN THE VUV ENERGY REGION

WAN-CHUN PAN, I-CHIA CHEN, Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan; TZU-PING HUANG, and YIN-YU LEE, National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan.

The highly excited xenon dimers were prepared by colliding excited xenon atoms with ground-state xenon atoms. The excited xenon was produced by VUV light of synchrotron radiation for energy greater than 90000 cm$^{-1}$ to form states in $nd[3/2]_1$, $ns[3/2]_1$, $nd[1/2]_1$, and $ns[1/2]_1$, separately. Then the collision pairs, xenon dimers were ionized by an infrared light in the energy range of 11800–13400 cm$^{-1}$. This cw IR laser has a resolution of 0.2 cm$^{-1}$. Xenon ion produced from dissociative ionization was detected using a quadruple mass spectrometer in these experiments. The observed positions of spectral lines depend on the energy of the IR laser only, independent of the Rydberg states of xenon atoms. The line intensities significantly vary with the Rydberg states prepared of xenon atoms, indicating that the collision pairs Xe$_2$ were relaxed to some highly excited Rydberg states before ionization. Hence from the position of xenon dimer ion state B(1/2g) and energy restriction we assign the observed spectral lines corresponding to the Rydberg states of Xe$_2$ in the energy range of 84000-86000 cm$^{-1}$. Some tentative assignments will be reported.
We present the first sequential excitation of atom-doped helium nanodroplets. Rubidium atoms on the surface of a helium nanodroplet are selectively excited to the $^5\text{P}_\frac{1}{2}$ state so as not to desorb from the droplet. From there they are excited by a laser pulse to the $^5\text{D}$ state; a laser-induced fluorescence (LIF) spectrum is recorded by monitoring the $^6\text{P}_\frac{1}{2} \rightarrow ^5\text{S}_\frac{1}{2}$ emission. We find some difference in the LIF spectrum as compared to that of the two-photon one-color direct excitation spectrum $^5\text{D} \rightarrow ^5\text{S}_\frac{1}{2}$. This indicates that the system does relax vibrationally during the lifetime of the $^5\text{P}_\frac{1}{2}$ state. To model the LIF spectra we calculate the energy levels of the Rb atom as a function of its distance $R$ from the center of the droplet. The Franck-Condon factors of the resulting potential energy curves agree with the experimental findings. A similar behavior has been found for cesium. New measurements predict that it also stays bound on the surface of the droplet in its $^6\text{P}_\frac{1}{2}$ state. From there we further excited Cs monomers into their $^6\text{D}$ state, where also the LIF spectrum is recorded by watching the $^7\text{P} \rightarrow ^6\text{S}_\frac{1}{2}$ emission.

In the future these states can be used as a springboard to reach high-lying $^2\text{S}$ and $^2\text{D}$ states, and possibly create an artificial super-atom.

---

**TG04 15 min 2:21**

LASER-INDUCED FLUORESCENCE OF RUBIDIUM DIMER: OBSERVATION OF TWO NEW VIBRONIC BAND SYSTEMS

JIANDE HAN and MICHAEL C. HEAVEN, Department of Chemistry, Emory University, Atlanta, GA 30322.

Rubidium dimers were formed by thermal vaporization of the metal followed by continuous co-expansion with helium or argon through a small pinhole into a vacuum chamber. The dimers were detected by laser-induced fluorescence. vibrationally resolved excitation spectra were recorded for the D-X system near 430 nm and for new band systems in the wavelength regions of 386 nm - 401.5 nm and 347.2 nm - 358.4 nm. Long vibrational progressions were observed for all three band systems, indicative of substantial changes in the equilibrium bond lengths on electronic excitation. Isotope splittings between $^{85,85}\text{Rb}_2$ and $^{85,87}\text{Rb}_2$ were observable for one of the new band systems, facilitating the determination of the absolute vibrational numbering. Upper state vibrational constants were obtained, and the changes in the bond lengths were estimated from Franck-Condon modeling of the intensity distributions. A summary of the results and possible assignments of the excited electronic states will be presented.
COUPLED-CHANNEL ANALYSIS OF THE $D^{1}\Pi \rightarrow d^{3}\Pi$ COMPLEX IN NaK; POTENTIAL ENERGY CURVES AND SPIN-ORBIT FUNCTIONS

ANASTASIA DROZDOVA and AMANDA J. ROSS, LASIM, Université Lyon 1 & CNRS, 43 Bd du 11 novembre 1918, F-69622 Villeurbanne, France; ANDREY V. STOLYAROV, Department of Chemistry, Moscow State University, 119992 Moscow, Russia; WALDZIMIERZ JASTRZĘBSKI, Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland; and PAWEŁ KOWALCZYK, Institute of Experimental Physics, Warsaw University, ul. Hoża 69, 00-681 Warsaw, Poland.

Two-colour polarization labeling experiments measuring the $D \leftarrow X$ system of NaK have characterised more than 99 % of the potential well of the $D^{1}\Pi$ state of NaK, the last observed level being located 7 cm$^{-1}$ below the Na(3p $^2P_{3/2}$) + K(4s) atomic asymptote. The vibrational progressions all exhibit irregular intervals, because of strong interactions with the nearby $d^{3}\Pi$ state. A comprehensive analysis has now been made of all available data concerning the $D^{1}\Pi$ and $d^{3}\Pi^b$ states. The potential curves are represented by Morse/Lennard Jones analytical functions, with \textit{ab initio} constraints on the long-range part of V(R). Morse functions are also used to represent the R-dependent diagonal and off-diagonal spin-orbit terms. Initial values for the spin-orbit coupling matrix elements were extracted from quasi-relativistic \textit{ab initio} calculations. In total, 29 parameters were required to recalculate 95 % of the 1400 observed term energies to within experimental uncertainty, giving an unweighted standard deviation 0.03 cm$^{-1}$.

\[\text{[A Adohi-Krou et al. J. Mol. Spectrosc. 250 27 (2008)}\]
\[\text{[b P. Kowalczyk J. Mol. Spectrosc. 136 1 (1989)]}\]

CaF: ALL SPECTRA AND ALL DYNAMICS

R. W. FIELD, J. J. KAY, S. L. COY, V. S. PETROVIĆ, S. N. ALTUNATA, and B. M. WONG, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139; Ch. JUNGEN, Laboratoire Aim Cotton du CNRS, Université de Paris Sud, F-91405 Orsay, France.

More than 1,000 CaF rovibronic levels, spanning the range $n^* = 5$, $v = 0$ (42,500 cm$^{-1}$) to $n^* = 20$, $v = 1$ (47,500 cm$^{-1}$), and sampling $\ell = 0(s) - 5(h)$ are fitted to a quantum defect model. This model consists of two currently separate pieces: the core-penetrating $s$, $p$, $d$, $f$ series are fitted to the elements of an internuclear distance ($R$) and energy ($E$) dependent quantum defect matrix, $\mu(R,E)$; the core-nonpenetrating series are described by multipole ($\mu$, $Q$, $O$) moments and polarizabilities ($\alpha$, $\gamma$). The values of the fitted parameters agree well with \textit{ab initio} computed values. Although the fitted parameters permit calculation of all spectra and all dynamics of CaF, the physical meanings of the parameters remain obscure.
**TG07** 15 min 3:20

LASER-INDUCED FLUORESCENCE STUDIES OF THE JET-COOLED CARBON DIOXIDE AND NITROUS OXIDE CATIONS

MOHAMMED A. GHARAIBEH and DENNIS J. CLOUTHIER, Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.

Laser-induced fluorescence (LIF) and single vibronic level (SVL) emission spectra of the $\tilde{A}^2\Pi_u - \tilde{X}^2\Pi_g$ system of $^{12}\text{CO}_2^+$ and $^{13}\text{CO}_2^+$ and the $\tilde{A}^2\Sigma^+ - \tilde{X}^2\Pi$ system of $\text{N}_2\text{O}^+$ have been observed. The cations were produced in a pulsed electric discharge jet with a precursor mixture of the corresponding neutral molecule in high pressure argon. The LIF bands of $^{12}\text{CO}_2^+$ and $^{13}\text{CO}_2^+$ were partially rotationally analyzed to obtain band origins which yielded an accurate measure of the excited state vibronic energy levels. The energy levels of both isotopologues were fitted with a Renner-Teller model that included spin-orbit coupling, Fermi resonance and anharmonic terms. SVL emission spectra were also recorded for the $^{13}\text{CO}_2^+$ ion and the ground state energy levels fitted using the same Renner-Teller model. Due to excited state predissociation, only the low lying vibrational levels have been observed in the LIF spectrum of $\text{N}_2\text{O}^+$. Nitrous oxide cation SVL emission spectra were collected and a complete vibronic analysis of the $\tilde{X}^2\Pi$ electronic state has been carried out using the Renner-Teller model. Our experimental data provide rigorous tests for future ab initio potential energy surfaces of these important cations.

**TG08** 15 min 3:37

ELECTRONIC SPECTRA OF LiNH$_3$ AND YbNH$_3$

N. BHALLA, L. VARRIALE, N. M. TONGE AND A. M. ELLIS, Department of Chemistry, University of Leicester, Leicester, LE1 7RH, United Kingdom.

Alkalis and several rare earth elements dissolve in liquid ammonia and yield solvated electrons. Despite efforts to understand the electronic structure of these solutions, they are still poorly understood. We are trying to tackle this issue by providing electronic structure information on basic entities that might be found in such solutions, using isolated metal-ammonia clusters in the gas phase as model systems. Here we report on two of the simplest clusters, LiNH$_3$ and YbNH$_3$, and present their electronic spectra for the first time. These spectra have been recorded via two-colour REMPI and/or photodepletion spectroscopy. The spectrum of LiNH$_3$, with $\tilde{A} - \tilde{X}$ origin near 11,500 cm$^{-1}$, is quite complex, with both vibrational structure and evidence of $\tilde{B} - \tilde{X}$ excitation nearby. A possible assignment will be presented. YbNH$_3$ has a simpler spectrum with origin near to 14,000 cm$^{-1}$. Nevertheless, as will be shown, the assignment for this cluster is also non-trivial.

**TG09** 15 min 3:54

THE OPTICAL SPECTRUM OF ATOMIC CLUSTERS Si$_3$ and S$_3$

DAMIAN L. KOKKIN, NEIL J. REILLY, MICHAEL C. McCARTHY, and PATRICK THADDEUS, Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138, and School of Engineering & Applied Sciences, Harvard University, 29 Oxford St., Cambridge, MA 02138; JOHN F. STANTON, Department of Chemistry & Biochemistry, The University of Texas at Austin, 1 University Station A5300 Austin, TX 78712.

The optical spectra of the atomic clusters Si$_3$ and S$_3$ will be discussed in detail. The jet-cooled 2-colour resonant-2-photon ionisation spectrum of Si$_3$ has now been detected for the first time in the 530 nm region. For Si$_3$ a progression in the excited state bending and stretching modes are seen built onto the origin. Lower state frequencies derived from sequence band structure agree with those previously measured for the D$_{3h}$ low lying electronic state. For thiozone additional experiments were undertaken and progressions in the excited state bending and stretching modes are seen with frequencies of 350 cm$^{-1}$ and 420 cm$^{-1}$ built onto the origin band at 23053.5 cm$^{-1}$ respectively. In this talk our results are compared to theoretical results on both the C$_{2v}$ and D$_{3h}$ forms.
OPTICAL SPECTROSCOPY OF SILICON-CARBON CLUSTERS: Si$_2$C and Si$_3$C

NEIL J. REILLY, DAMIAN L. KOKKIN, MICHAEL C. McCARTHY, and PATRICK THADDEUS, Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138, and School of Engineering & Applied Sciences, Harvard University, 29 Oxford St., Cambridge, MA 02138.

We report the first measurement of an electronic spectrum of Si$_2$C, observed in a jet-cooled discharge through silane, acetylene and argon, in the 380 – 410 nm wavelength range. While Si$_2$C is a highly plausible astronomical molecule, searches for its rotational transitions in the laboratory and in space are impractical at present - ab initio predictions of the rotational constants of this slightly bent species have yet to performed to within the required accuracy. By analogy with SiC$_2$, the carrier of the well-known Merrill-Sanford bands, electronic spectroscopy may provide estimates of its rotational constants and structure, thereby constraining searches for its millimeter-wave transitions. Our experiments suggest that the electronic transition has a large oscillator strength and a significant fluorescence quantum yield, making it a good candidate for optical detection in space, particularly in those carbon stars where SiC$_2$ is known to be abundant. As part of a more general effort to measure the electronic spectra of small silicon-carbon clusters, several examples of which have been identified in space by radio-astronomy, we present a spectrum of Si$_3$C with a much higher S/N ratio than has been previously reported, and which is now in excellent agreement with theory.

LASER INDUCED FLUORESCENCE SPECTROSCOPY OF THE SiNSi RADICAL I: THE $\tilde{C}^2\Delta_u - \tilde{X}^2\Pi_g$ TRANSITION

MASARU FUKUSHIMA, TAKASHI ISHIWATA, Faculty of Information Sciences, Hiroshima City University, Hiroshima 731-3194, Japan; CHIHAYA MOTOTOYOSHI, YOSHIHIRO SUMIYOSHI, and YASUKI ENDO, Department of Basic Science, The University of Tokyo, Meguro 153-8902, Japan.

We have generated SiNSi in a supersonic free jet expansion, and measured the laser induced fluorescence (LIF) spectrum in the ultraviolet (UV) region. Dispersed fluorescence (DF) spectra from the single vibronic levels (SVL) have also been recorded by exciting each observed vibronic band. On the basis of the rotational analyses of the observed vibronic bands and the appearance the vibrational structure in the DF spectra, several bands were attributed to the $\tilde{C}^2\Delta_u - \tilde{X}^2\Pi_g$ system of SiNSi. From the analysis of the $0^0_0$ band with an origin of 29,261.61 cm$^{-1}$, the effective spin-orbit constants were determined to be 140.59 and 2.623 cm$^{-1}$ for the $\tilde{X}^2\Pi_g$ and $\tilde{C}^2\Delta_u$ states, respectively. In total, ten vibronic levels including the zero vibrational level were assigned to the $\tilde{C}^2\Delta_u$ state, and the vibonic structure was analyzed considering the Renner-Teller interaction.

LASER INDUCED FLUORESCENCE SPECTROSCOPY OF THE SiNSi RADICAL II: IDENTIFICATIONS OF THE $\tilde{A}^2\Sigma^+_1$ AND $\tilde{D}^2\Sigma^+_g$ STATES

CHIHAYA MOTOTOYOSHI, YOSHIHIRO SUMIYOSHI, YASUKI ENDO, Department of Basic Science, The University of Tokyo, Tokyo 153-8902, Japan; MASARU FUKUSHIMA and TAKASHI ISHIWATA, Faculty of Information Sciences, Hiroshima City University, Hiroshima 731-3194, Japan.

Among the LIF spectra of SiNSi observed in the near UV region, another band system with fluorescence lifetimes of 30 ns was identified. From detailed analyses of the rotational structures of the observed vibronic bands, they were assigned to the $\tilde{D}^2\Sigma^+_g - \tilde{X}^2\Pi_g$ band system of SiNSi, which is a symmetry forbidden transition borrowing intensity from vibronic mixings. Dispersed fluorescence spectra from SVL levels of the $\tilde{D}$ state show distinct features around 13,000 cm$^{-1}$ above the ground vibronic state, which were assigned to transitions to two electronic states $\tilde{A}^2\Sigma^+_1$ and $\tilde{B}^2\Pi_1$, correlated to a $^2\Pi_g$ state at the limit of linearity. LIF spectra were observed in the corresponding region from 13,000 to 14,000 cm$^{-1}$ to confirm the assignment. Dispersed fluorescence spectra from the visible transitions gave vibrational term energies for high lying bending vibrational levels in the ground state, showing that they are bent—linear transitions.
SUB-DOPPLER SPECTROSCOPY OF THE $\tilde{A}^1B_1 - \tilde{X}^1A_1$ ELECTRONIC TRANSITION OF CBr$_2$

EYAD H AL-SAMRA and COLIN WESTERN, School of Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS, UK.

Sub-Doppler spectra of selected bands of the $\tilde{A}^1B_1 - \tilde{X}^1A_1$ transition of CBr$_2$ are presented allowing all three rotational constants to be determined for the zero point level of the ground state for the first time. Refined rotational constants are presented for various $\tilde{A}$ state vibrational levels, and an additional progression is identified in the $\tilde{A}-\tilde{X}$ absorption spectrum. The assignment of this progression was assisted by modelling Franck-Condon factors with the PGOPHER$^b$ program.

$^b$PGOPHER, a Program for Simulating Rotational Structure, C. M. Western, University of Bristol, http://pgopher.chm.bris.ac.uk

ROTATIONALLY RESOLVED $\tilde{B} \leftarrow \tilde{X}$ ELECTRONIC SPECTRA OF THE ISO-PROPOXY RADICAL AND OTHER SECONDARY ALKOXY RADICALS

J. LIU and T. A. MILLER, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, OH 43210, USA.

The $\tilde{B} - \tilde{X}$ laser-induced-fluorescence (LIF) spectrum of jet-cooled iso-propoxy radical ($i$-C$_3$H$_7$O·) has been recorded. The observed rotational and fine structure of the origin band has been well simulated with rotational constants for both the $\tilde{X}$ and $\tilde{B}$ states and the electron spin-rotation constants of the $\tilde{X}$ state. The line intensities are well simulated with a parallel transition type, requiring the same symmetry for the $\tilde{X}$ as for the $\tilde{B}$ state ($A'$), which confirms the previous suggestion$^a$ that going from ethoxy (C$_2$H$_5$O·) to iso-propoxy, the energy ordering of the in- and the out-of-plane half-filled $p$-orbitals is reversed and the ground state symmetry changes from $A''$ to $A'$. The fit rotational constants are consistent with those obtained from the quantum chemistry calculations. However, the fit spin-rotation constants, particularly the nonzero $e_{aa}$ with $a$-axis perpendicular to the $C_s$ plane, can not be explained by second-order perturbation theory. Nevertheless they can be semi-quantitatively explained based on the transferability of the electron spin-molecular rotation tensor$^b$ in the axis system defined by the half-filled $p$-orbital and the $p \pi$-orbital using ethoxy as the reference molecule. The failure of the second-order perturbation theory, as well as that of the pure precession approximation, is due to the strong vibronic interaction between the near-degenerate $\tilde{X}$ and $\tilde{A}$ states. The vibrationless levels of these two states are separated by only 68 cm$^{-1}$ as determined in previous disperse-fluorescence study.$^c$ The near degeneracy of the $\tilde{X}$ and $\tilde{A}$ states of iso-propoxy and reversal of the energy ordering going from ethoxy to iso-propoxy have also been demonstrated in quantum chemistry calculations. Based on the result of iso-propoxy, spin-rotation constants of other secondary alkoxy radicals can be predicted and used for the simulation of the $\tilde{B} - \tilde{X}$ rovibronic spectra of these radicals. Specifically, analysis of the high-resolution LIF spectrum of cyclohexoxy ($c$-C$_6$H$_{11}$O·)$^d$ is ongoing.

LASER INDUCED FLUORESCENCE SPECTROSCOPY OF THE JET-COOLED TRANSIENT SPECIES AsD$_2$ AND AsHD

ROBERT A. GRIMMINGER and DENNIS J. CLOUTHIER, Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.

The $\tilde{A}^2A_1 - \tilde{X}^2B_1$ electronic band system of the AsD$_2$ and AsHD free radicals has been observed by laser induced fluorescence (LIF) spectroscopy. AsD$_2$ (or AsHD) was produced in a pulsed supersonic expansion by electric discharge dissociation of a mixture of 5% AsD$_3$ (or AsH$_x$D$_{3-x}$ mixture) seeded in argon. Single vibronic level emission spectra have been obtained for both AsD$_2$ and AsHD. The observed LIF transitions of AsD$_2$ in the 411 - 505 nm region exhibit a long progression in the excited state bending vibration. High-resolution rotationally resolved spectra of the $0^0_0$ band of AsD$_2$ were also recorded. This c-type band shows prominent $\Delta K_a = \pm 3$ transitions due to the large change in the asymmetry parameter upon electronic excitation. Extensive hyperfine splittings were resolved which allowed the determination of the excited state Fermi contact parameter. The data have been used to refine the molecular structure of the AsH$_2$ radical.

OH LASER-INDUCED FLUORESCENCE MEASUREMENTS in NANosecond PULSE DIScharge Plasmas

INCHUL CHOI, IGOR V. ADAMOVICH and WALTER R. LEMPERT, Michael A. Chaszeyka Nonequilibrium Thermodynamics Laboratory, Department of Mechanical Engineering, The Ohio State University, Columbus, OH 43210.

We present recent results of laser-induced fluorescence measurements of hydroxyl radical density in repetitively pulsed nanosecond plasmas, created using 10-20 nsec duration, high (up to 20 kV) voltage pulsers, capable of operation at repetition rates as high as 40-50 kHz. OH mole fraction as a function of time with respect to discharge creation is determined, with absolute calibration performed using a Hencken flat flame burner. This paper will focus on a series of low temperature, non-equilibrium kinetics measurements in hydrogen and hydrocarbon-air mixtures, with results compared to predictions of a recently developed plasma chemical oxidation model.
TH. MICROWAVE (ROTATIONAL)
TUESDAY, JUNE 22, 2010 – 1:30 pm
Room: 1000 McPHERSON LAB

Chair: JENNIFER VAN WIJNGAARDEN, University of Manitoba, Winnipeg, Canada

TH01 15 min 1:30
MICROWAVE SPECTRA AND STRUCTURE OF N\textsubscript{2}-CO\textsubscript{2}

DANIEL J. FROHMAN, EDWIN S. CONTRERAS, ROSS S. FIRESTONE, STEWART E. NOVICK, Department of Chemistry, Wesleyan University, Middletown, CT 06459; WILLIAM KLEMPERER, Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138.

We present here the FTMW spectra of the various isotopologues of the weakly-bound complex of carbon dioxide with the most abundant molecule in the atmosphere, nitrogen. The structure of the complex along with the inversion of the N\textsubscript{2} (or lack of it) will be discussed. The molecule is T-shaped, with the OCO forming the cross of the T, a structure deduced from a previous rotationally-resolved infrared experiment.\textsuperscript{a} A significant wide-amplitude bending motion of the N\textsubscript{2} is deduced from the values of the (nearly identical) nuclear quadrupole coupling constants of the nitrogen nuclei. The spectroscopic results will be compared with ab-initio calculations. We will examine the consequences of N\textsubscript{2}-CO\textsubscript{2} formation upon atmospheric opacity.


TH02 15 min 1:47
MILLIMETER-WAVE SPECTROSCOPY OF THE vdW BANDS OF He-HCN NEAR THE DISSOCIATION LIMIT.

KENSUKE HARADA and KEIICHI TANAKA, Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashiku, Fukuoka, 812-8581 Japan.

The He-HCN complex is a weakly bound complex with binding energy of about 9 cm\textsuperscript{-1}. We have measured the internal rotation bands (to the \(j = 1\) and \(2\) states) and intermolecular stretching bands of the He-HCN complex by millimeter-wave absorption spectroscopy combined with a pulsed-jet expansion technique, and reported the potential energy surface (PES) to reproduce the observed transition frequencies.\textsuperscript{a} The PES obtained has a global minimum in the linear configuration with a depth of 30.3 cm\textsuperscript{-1} and has a saddle point at the anti-linear configuration with a depth of 20.3 cm\textsuperscript{-1}. The intermolecular stretching level and the second excited (\(j = 2\)) level of the internal rotation state are determined to be located 9.1407 and 9.0529 cm\textsuperscript{-1}, respectively, above the ground state, very close to the calculated dissociation limit (\(D_0\)) of 9.33 cm\textsuperscript{-1}.

In the present study, we have extended the measurement to the transitions to the bound states above the "dissociation limit" (\(D_0\)) and observed several such transitions for the first time in the ground state of the molecular complex. The rovibrational levels of He-HCN with \(e\) label dissociate to the HCN molecule with \(J = 0\) and the He atom (\(D_0\)), while those with \(f\) label, due to the parity conservation, to the HCN molecule with \(J = 1\) and the He atom which is higher in energy by about \(2B_{\text{HCN}} \sim 2.96 \text{ cm}^{-1}\) than \(D_0\), as discussed in the infrared study of He-HF.\textsuperscript{b} The PES obtained in the present analysis indicates that four \(f\) levels in the \(j = 1\) and \(2\) excited states are bound above the "dissociation limit" (\(D_0\)) due to the parity conservation. In addition five levels (both of \(e\) and \(f\) labels) are predicted to be bound by centrifugal barrier with finite life times but not yet observed.

OBSERVATION OF THE WEAKLY BOUND (HCl)$_2$H$_2$O CLUSTER BY CHIRPED-PULSE FTMW SPECTROSCOPY

ZBIGNIEW KISIEL, Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland; ALBERTO LESARRI, Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47011 Valladolid, Spain; JUSTIN NEILL, MATT MUCKLE, BROOKS PATE, Department of Chemistry, University of Virginia, McCormick Rd., Charlottesville, VA 22904-4319.

Investigation of small cluster formation in the H$_2$O + HCl binary system is expected to provide stepwise insight into the chemically fundamental process of ionization of the HCl molecule towards hydrochloric acid. Previous studies of the rotational spectra of this system in supersonic expansion resulted in detailed characterization of H$_2$O···HCl$^a$ and (H$_2$O)$_2$HCl$^b$ clusters, and in identification of the (H$_2$O···HCl)···Ar cluster.$^c$ Many unassigned weak lines were observed but further progress was hindered by the multiple alternatives to assignment, particularly in the case of the deuterated mixture.

Application of the broadband, chirped-pulse FTMW technique reinvigorated the investigation of this system. The assignment of (H$_2$O···HCl)···Ar was completed and it was found that the strongest unassigned cluster was (HCl)$_2$H$_2$O. Identification of this cluster is confirmed by successfully fitted nuclear quadrupole hyperfine structure from the two chlorine nuclei, and observation of spectra for several isotopic species. Detailed results concerning the spectroscopy and properties of (HCl)$_2$H$_2$O are presented.

---

THE HCCIF$_2$–HCCH COMPLEX: MICROWAVE SPECTRUM, STRUCTURE AND C–H···π INTERACTIONS

REBECCA A. PEEBLES, JOHN M. SEXTON, ASHLEY A. ELLIOTT, AMANDA L. STEBER and SEAN A. PEEBLES, Department of Chemistry, Eastern Illinois University, 600 Lincoln Ave., Charleston, IL 61920; JUSTIN L. NEILL, MATT T. MUCKLE and BROOKS H. PATE, Department of Chemistry, University of Virginia, McCormick Rd., PO Box 400319, Charlottesville, VA 22904.

The HCF$_3$–HCCH complex was recently found to have a weak C–H···π interaction between the fluoroform and acetylene, as well as having a secondary interaction between the fluorine atoms and one of the acetylene hydrogen atoms; however, extensive splittings due to large amplitude motions within the complex have complicated our efforts at making a full assignment of the HCF$_3$–HCCH spectrum. In an attempt to remove some of the ambiguity in the HCF$_3$–HCCH study, we have substituted a chlorine atom for one fluorine atom and undertaken an investigation of the HCCIF$_2$–HCCH complex. This eliminates the possibility of internal rotation of the methane subunit, while still maintaining a C–H···π interaction.

Using the chirped-pulse Fourier-transform microwave (CP-FTMW) spectrometer at the University of Virginia and the Balle-Flygare FTMW spectrometer at Eastern Illinois University, the spectra of four isotopologues of HCCIF$_2$–HCCH have been assigned, with no indication of internal motions within the complex. The structure has been determined from the experimental moments of inertia, confirming that this dimer has the expected weak C–H···π interaction. In addition, the off-diagonal $\chi_{ab}$ quadrupole coupling constant has been used to determine the angle between the C–Cl bond and the $a$-axis of the complex. This, and Kraitchman coordinates for the chlorine atom, help confirm the structural details from the inertial fit. The structural results will be compared with other complexes showing C–H···π and C–H···O interactions.

---


---

TH05 15 min 2:38
THE FT MICROWAVE SPECTRA AND STRUCTURE OF THE ARGON AND NEON VAN DER WAALS COMPLEXES OF CYANOCYCLOBUTANE

WALLACE C. PRINGLE, DANIEL J. FROHMAN, WILLIAM NDUGIRE, STEWART E. NOVICK, Department of Chemistry, Wesleyan University, Middletown, CT 06459.

The Fourier transform pulsed jet microwave spectra of the argon and neon van der Waals complexes of cyanocyclobutane have been observed and assigned from 5 to 26 GHz. The position of the rare gas is analogous to that of the argon-chlorocyclobutane complex in that the rare gas is on the same side of the ring as the cyanide group and several Angstroms to the side of the ring away from the C₄ plane of the cyanocyclobutane monomer. Isotopologues and the nuclear quadrupole coupling constants will be discussed.

TH06 15 min 2:55
FOURIER TRANSFORM MICROWAVE SPECTRA OF CO₂-ETHYLENE SULFIDE, CO₂-ETHYLENE OXIDE AND CO₂-PROPYLENE OXIDE COMPLEXES

YUKARI ORITA, YOSHIYUKI KAWASHIMA, Department of Applied Chemistry, Faculty of Engineering, Kanagawa Institute of Technology, Atsugi, Kanagawa 243-0292, JAPAN; and EIZI HIROTÅ, The Graduate University for Advanced Studies, Hayama, Kanagawa 240-0193, JAPAN.

We have previously examined the difference in roles of O and S in structure and dynamics of the CO-ethylene oxide (EO) and CO-ethylene sulfide (ES) complexes. We have extended the investigation to CO₂-EO and CO₂-ES for comparison. We have also observed the CO₂-propylene oxide (PO) complex, which is an important intermediate in the reaction of PO with CO₂ leading to polycarbonate. Both a-type and b-type transitions were observed for the CO₂-EO and CO₂-ES, but no c-type transitions were observed at all. We also detected the ³⁴S and ¹³C isotopic species in natural abundance and the species containing ¹⁸OCO and C¹⁸O₂, which were synthesized by burning paper in an ¹⁸O₂ and ¹⁶O₂ mixture. By analyzing the observed spectra we concluded the CO₂ moiety of CO₂-EO and CO₂-ES located in a plane perpendicular to the three-membered ring and bisecting the COC or CSC angle of EO or ES, respectively, as in the case of CO-EO and CO-ES complexes. An ab initio MO calculation at the level of MP2/6-311G(d, p) yielded an optimized structure in good agreement with the experimental result. We have derived from the observed spectra the distance, the stretching force constant, and the binding energy of the bonds between the constituents of the CO₂-EO and CO₂-ES complexes and have found that the distances of the two complexes were shorter by 0.2Å than those in CO-EO and CO-ES, respectively, and that the intermolecular bonds were two times stronger in the CO₂ complexes than in the corresponding CO complexes. We have concluded from the observed spectra that the CO₂ moiety in CO₂-PO is located on the PO three-membered ring plane opposite to the methyl group. The constituents in CO₂-PO were more weakly bound than those in CO₂-EO and CO₂-ES.

ROTATIONAL SPECTROSCOPIC INVESTIGATIONS OF \( CH_4 - H_2S \) COMPLEX

AISWARYA LAKSHMI P. and E. ARUNAN, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India.

Recently, Raghavendra and Arunan [1] have shown that methane can form a hydrogen bonded complex with \( HX \) \( (X = F, Cl, OH, SH) \), in which \( H - X \) points towards the carbon of methane. Microwave spectroscopy has confirmed the structure of \( CH_4 - HF/HCl/H_2O \) complexes. No experimental data is available for \( CH_4 - H_2S \) complex to the best of our knowledge. Pulsed Nozzle Fourier Transform Microwave Spectrometer has been used to study the rotational spectrum of \( CH_4 - H_2S \) complex. Two progressions were observed. Both could be fitted independently to a linear top. The ground state rotational constant is determined to be \( B = 2683.100(1) \text{MHz} \) and the distortion constant to be \( D_J = 0.09413(9) \text{MHz} \). Based on this rotational constant, the intermolecular separation is determined to be 4.136 Å. The other state has a rotational constant \( B = 2593.05(1) \text{MHz} \) and a negative distortion constant, \( D_J = -0.0089(7) \text{MHz} \). The negative distortion constant implies rotational - vibrational coupling and the progression arises from some excited internal rotor/torsional state. Experiments are in progress to look for more states and isotopologues of this complex. Details will be presented in the talk.


Intermission

MICROWAVE SPECTRUM AND PARTIAL GAS PHASE STRUCTURE OF A FORMIC ACID-FORMAMIDE COMPLEX

ADAM M. DALY, STEPHEN G. KUKOLICH, Department of Chemistry and Biochemistry, 1306 E. University, Tucson, Arizona 85721; BRYAN SARGUS, Catalina Foothills High School Teacher, Tucson, Arizona 85718.

The rotational spectrum of 5 isotopomers of the complex formed between formic acid and formamide have been measured and analyzed using a pulsed beam fourier transform microwave spectrometer. The rotational constants and nitrogen’s quadrupole coupling strength for \( HC^{12}OOH - H_2N^{14}COH \) are \( A=5889.51(9) \), \( B=2148.734(2) \), \( 1575.127(1) \), \( eQ_{qaa} = 1.020(8) \), \( eQ_{qbb} = 1.98(1) \) and \( eQ_{qcc} = -2.998(9) \) MHz. Using the 15 rotational constants obtained with \( HC^{13}OOH \), HCOOD, DCOOH and \( H_2N^{15}CHO \) isotopologues, key structural information was obtained from a least squares fit. R(CO-HN) distance of 1.77 Å and R(OH-OC) distance of 1.81 Å and an (COH) angle of formic acid of 121° was obtained that was very different from the monomer value of 106.9°. Density functional theory using B3PW91, HCTH407 and TPSS and MP2 calculations were performed using 6-311++G(d,p) and compared to experimentally determined values.

\(^a\)Supported by THE NATIONAL SCIENCE FOUNDATION
MICROWAVE SPECTRUM OF THE HYDROGEN BONDED COMPLEX BETWEEN PROPIOLIC AND FORMIC ACID

ADAM M. DALY, STEPHEN G. KUKOLICH, Department of Chemistry and Biochemistry, 1306 E. University, Tucson, Arizona 85721.

The microwave spectrum of the gas phase complex formed between propiolic acid (HCCCOOH) and formic acid (HCOOH) along with 5 other isotopomers were obtained using a pulsed beam fourier transform microwave spectrometer. The spectra of the $\text{H}^{12}\text{C}_2\text{O}2\text{H}$ and $\text{H}^{13}\text{C}_2\text{O}2\text{H}$ isotopomers were each fit to two sets of rotational constants. The parent rotational constants were 5988.7(8), 927.782(7), 803.720(7) and 5988(1), 927.779(9) 804.058(9) MHz respectively. Isotomers containing deuterium in the OH bonds, HCOOD and HCCCOOD, do not show this feature. We tentatively assign the two sets of rotational constants to the two different inversion states for the concerted proton tunnelling in the hydrogen bonds.

*Supported by THE NATIONAL SCIENCE FOUNDATION

MICROSOLVATION OF $\beta$-PROPIOLACTONE AS REVEALED BY CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTROSCOPY.

JUSTIN L. NEILL, MATT T. MUCKLE, AND BROOKS H. PATE, Department of Chemistry, University of Virginia, McCormick Rd., P.O. Box 400319, Charlottesville, VA 22904; I. PENA, C. PEREZ, AND J.L. ALONSO, Grupo de Espectroscopía Molecular (GEM), Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47005 Valladolid, Spain.

Microwave spectra of water clusters of $\beta$-propiolactone with up to five water molecules attached are presented. Helium or neon carrier gas with 3 atm of backing pressure is flowed over a room-temperature water reservoir, then over a room-temperature sample of $\beta$-propiolactone before being expanded into a chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer operating between 6.5 and 18.5 GHz. A very dense spectrum, with approximately 2000 lines with a signal to noise ratio of at least 3:1, was observed, of which 800 have been assigned to a total of 20 species, including isotopomers in natural abundance and clusters with the carrier gas. Due to the complexity of the spectrum, after the first few, all other spectra were assigned with the aid of microwave-microwave double resonance experiments, either performed on the CP-FTMW spectrometer or in a Balle-Flygare-type cavity FTMW spectrometer. In the case of an extremely dense spectrum like this in which many species are present, these double resonance measurements are required to successfully analyze the spectrum. Stark effect measurements and assignments of isotopically substituted species are used to determine the structures of these microsolvated complexes.
THE EFFECT OF VINCINAL VERSUS GEMINAL SUBSTITUTION OF HYDROGEN BY CHLORINE: MICROWAVE SPECTRA AND MOLECULAR STRUCTURES OF THE COMPLEXES OF 1-CHLORO-1-FLUOROETHYLENE AND (E)-1-CHLORO-2-FLUOROETHYLENE WITH HYDROGEN FLUORIDE

HELEN O. LEUNG, MARK D. MARSHALL, ALEX J. LEE, AARON T. BOZZI, PAUL M. COHEN, and MABLE LAM, Department of Chemistry, Amherst College, P.O. Box 5000, Amherst, MA 01002-5000.

Previous work in our laboratory has demonstrated that increasing the degree of fluorine substitution in complexes of fluorooethylenes with protic acids results in a weaker primary hydrogen-bonding interaction. This has been interpreted as arising from a decrease in the nucleophilicity of the hydrogen bond-accepting fluorine atom as a consequence of the inductive, electron-withdrawing nature of the additional fluorine atoms. We have recently extended these studies to investigate the effects of substitution with the less electronegative, but more polarizable chlorine atom. Through analysis of their 6-21 GHz Fourier transform microwave spectra, molecular structures are obtained for the complexes of 1-chloro-1-fluoroethylene and the (E) isomer of 1-chloro-2-fluoroethylene with hydrogen fluoride. The structures are compared with each other and with their difluoroethylene counterparts.

THE STRUCTURE OF THE 1-CHLORO-1-FLUOROETHYLENE–ACETYLENE COMPLEX

HELEN O. LEUNG, MARK D. MARSHALL, AND DAVID D. GRIMES, Department of Chemistry, Amherst College, P.O. Box 5000, Amherst, MA 01002-5000.

The insensitivity of the moments of inertia to certain geometric parameters for the limited set of isotopologues studied led to unexpected results for a preliminary structure of the complex formed between 1-chloro-1-fluoroethylene and acetylene presented three years ago. The availability of this chlorofluoroethylene with a single deuterium substitution in both (E) and (Z) isomeric forms allows us to supplement the original data set with microwave spectra of (E)-CHDC\textsuperscript{35}ClF–HCCH and (Z)-CHDC\textsuperscript{35}ClF–HCCH. Supported by the results of ab initio calculations, a planar, chemically reasonable structure is obtained for this complex, in which the acetylene forms a hydrogen bond with the fluorine atom of 1-chloro-1-fluoroethylene. The hydrogen bond bends to allow a secondary interaction with the hydrogen atom cis to this fluorine atom. Comparisons with the structure of the analogous complexes formed with vinyl fluoride and 1,1-difluoroethylene reveal the effects of chlorine substitution geminal to the acceptor atom of the hydrogen bond.

\textsuperscript{b}Kindly provided by Prof. Norman Craig, Oberlin College
TH13 15 min 5:05
DETERMINING THE GROUND STATE GEOMETRY OF THE \((E)\)-1-CHLORO-1,2-DIFLUOROETHYLENE–HYDROGEN FLUORIDE COMPLEX USING MICROWAVE SPECTROSCOPY

AARON T. BOZZI, HELEN O. LEUNG and MARK D. MARSHALL, Department of Chemistry, Amherst College, P.O. Box 5000, Amherst, MA 01002-5000.

To better understand the effects of chlorine substitution on the intermolecular interactions between fluorinated ethylenes and linear, protic acids, the structure of the \((E)\)-1-chloro-1,2-difluoroethylene–hydrogen fluoride complex has been investigated via \textit{ab initio} calculations and microwave spectroscopy. It was necessary first to determine an improved experimental structure of \((E)\)-1-chloro-1,2-difluoroethylene itself, and the rotational spectra of four isotopologues of this monomer have been obtained in the 6-21 GHz range using Fourier transform microwave spectroscopy for this purpose. \textit{Ab initio} calculations for the van der Waals complex with hydrogen fluoride, performed at the MP2 level of theory, predict that the lowest energy conformation is similar to that observed for the trifluoroethylene–HF dimer. Based on these predictions, rotational spectra of three isotopologues of the \((E)\)-1-chloro-1,2-difluoroethylene–hydrogen fluoride complex spanning 7-19 GHz are collected. Rotational constants, centrifugal distortion constants, and chlorine quadrupole coupling constants are determined using a least-squares fitting program. The data obtained so far are consistent with a planar ground-state structure in which the HF molecule binds to the side of the substituted ethylene by forming a hydrogen bond to fluorine and a secondary interaction with the geminal hydrogen.


TH14 15 min 5:22
FTMW STUDY OF THE CHIRALITY RECOGNITION BETWEEN TWO DIFFERENT CHIRAL MOLECULES: THE GLYCIDOL-PROPYLENE OXIDE COMPLEX

JAVIX THOMAS, FUMIE X. SUNAHORI, NICOLE BORHO, and YUNJIE XU, Department of Chemistry, University of Alberta, Edmonton, AB, T6G 2G2, Canada.

The chirality recognition effect between the prototype chiral molecular systems, i.e. glycidol and propylene oxide has been studied using rotational spectroscopy and high level \textit{ab initio} calculations. Extensive \textit{ab initio} calculations have been performed to locate all possible low energy conformers of the diastereomeric pair and \textit{twenty eight} minima have been found. The four most sable hetero and four homo chiral dimers, formed from the two lowest energy monomer conformations G-g- and G-g+ of the glycidol, were predicted to be close in their stability. Jet-cooled rotational spectra of some of them have been detected using a pulsed molecular beam Fourier transform microwave spectrometer and been assigned for the first time. All the low energy binary conformers observed show one primary intermolecular OH- - -O hydrogen bond and two secondary intermolecular CH- - -O hydrogen bonds. The induced fit phenomenon detected will be discussed.

TH15 15 min 5:39
MICROWAVE SPECTROSCOPY OF TRANS-ETHYL METHYL ETHER IN THE TORSIONALLY EXCITED STATE 3

KAORI KOBAYASHI, KEIGO MURATA, SHOZO TSUNEKAWA, Department of Physics, University of Toyama, 3190 Gofuku, Toyama, 930-8555 Japan; and NOBUKIMI OHASHI, Kanazawa University, Japan.

The \textit{trans}\textendash ethyl methyl ether molecule (CH\textsubscript{3}CH\textsubscript{2}OCH\textsubscript{3}) has two methyl group internal rotors which are equivalent to the two vibrational motions, \(\nu_{28}\) and \(\nu_{29}\). There is another low-lying torsional motion which is a skeletal torsion (\(\nu_{30}\)) and does not cause splitting. The microwave spectra of the \textit{trans}-ethyl methyl ether molecule in the \(\nu_{28} = 1, \nu_{29} = 1, \) and \(\nu_{30} = 1\) have been studied and interactions between these states were discussed. In this paper we report results on the \(\nu_{28} = 2, \nu_{29} = 1, \) and \(\nu_{30} = 3\) state. The analysis based on Hougen’s tunneling matrix formulation considering two methyl groups are used. We try to interpret tunneling parameters obtained in the present analysis quantitatively from the viewpoint of torsion-torsion interaction.
TI. THEORY
TUESDAY, JUNE 22, 2010 – 1:30 pm
Room: 1015 McPHERSON LAB

Chair: RUSSELL PITZER, The Ohio State University, Columbus, Ohio

T01 15 min 1:30
MODELING SIMULTANEOUS STARK AND ZEEMAN EFFECTS

WILTON L. VIRGO, KATHY J. CHEN and SARAH A. HYDE, Department of Chemistry, Wellesley College, Wellesley, MA 02481.

Theoretical calculations of shifts and splitting of atomic energy levels in simultaneously applied electric and magnetic fields are crucial for interpretation of experimental results relevant to plasma chemistry diagnostics. In this work, a theoretical method of calculating the combined Stark and Zeeman effects from simultaneously applied electric and magnetic fields will be presented. The research focus is on atoms with hyperfine structure such as Cs and Rb. Theoretical calculations have been developed using free, open-source software built on the Python programming language to model the hyperfine structure of free atoms in uniform electric and magnetic fields. Matrix representations of the Stark, Zeeman and Hyperfine operators have been constructed in spherical tensor form, and matrix elements have been evaluated in order to determine the energy level dependence on simultaneously applied electric and magnetic fields.

T02 15 min 1:47
CHARACTERIZATION AND FORMATION PROCESSES OF $C_4^-$, $C_4H$ and $C_4H^-$

M.L. SENENT, Departamento de Astrofísica Molecular e Infrarrojo, Instituto de Estructura de la Materia, C.S.I.C., Serrano 121, Madrid 28006, SPAIN; V. BRITES, M. HOCHLAF, Université Paris-Est, Laboratoire de Modélisation et Simulation Multi Échelle, MSME FRE 3160 CNRS, 5 boulevard Descartes, 77454 Marne-la-Vallée, FRANCE.

Using state-of-the-art theoretical methods, we investigate the stable isomers of $C_4^-$, $C_4H$ and $C_4H^-$. Three of them are relevant for astrophysics and astrochemistry. These computations are performed using interaction configuration ab initio methods and the aug-cc-pVXZ (X=T,Q) basis sets. In addition to the linear isomers, we predict the existence of several cyclic and branched forms for these molecules. For all the molecular species of interest here, sets of spectroscopic parameters are determined with perturbation theory, which compare quite well with experiment. For $l = C_4H^- (X^1\Sigma^+)$, the quartic force field is computed at the coupled cluster level of theory. This force field is derived from full nine-dimensional potential energy surface generated close to the equilibrium geometry of this anion. Finally, we treat the photochemistry processes of the hydrogen attachment and the electron attachment reactions that may lead to the formation of the $C_4H^-$ from either $C_4^-$ or $C_4H$.

T03 15 min 2:04
CHARACTERIZATION OF $C_3HSi^-$

N. INOSTROZA, Departamento de Astrofísica Molecular e Infrarrojo, Instituto de Estructura de la Materia, C.S.I.C., Serrano 121, Madrid 28006, SPAIN; M.L. SENENT, Departamento de Astrofísica Molecular e Infrarrojo, Instituto de Estructura de la Materia, C.S.I.C., Serrano 121, Madrid 28006, SPAIN.

Structural and spectroscopic properties of the astrophysically relevant $SiC_3H^-\ anion are investigated at the RCCSD(T) and CASSCF levels of theory. The molecule presents a total of 12 isomers (4 lineal and 8 cyclic), all of them showing singlet ground electronic states. The stability of the linear isomer $l = SiC_3H^- (X^1\Sigma^-)$ is notorious. The B0 rotational constant of $l = Si^{12}C_3H^-\ and\ l = Si^{12}C_3D^-$, the dipole moment, excitation energies to the lowest electronic states and electron affinities have been estimated.
AB INITIO INVESTIGATION OF NH$_3$-O$_2$ EXCIPLEX

L. M. HAUPERT, G. SIMPSON, AND L. V. SLIPCHENKO, Department of Chemistry, Purdue University, West Lafayette, IN 47907.

In their recent investigation of fluorescence from poly(amide amine) (PAMAM) dendrimers, Chu and Imae suggested an exciplex composed of tertiary amine and oxygen molecules might be responsible for fluorescence in PAMAM dendrimers.$^a$

In this work, we present an ab initio investigation of the electronic structure of a possible ammonia-oxygen exciplex model system using equation-of-motion coupled cluster techniques. Geometry optimization of the triplet ground state produced a weakly bound state with an equilibrium separation of $\sim 3.5$ Å, and an excited state geometry scan revealed a bound, excited triplet state with an equilibrium separation of 2.02 Å, consistent with results of earlier PM3 work by Juranic et al.$^b$

The energy gap between the triplet ground state and first triplet excited state of the exciplex at 2.02 Å is 412.8 nm, lending support to the exciplex hypothesis.

---

EQUILIBRIUM STRUCTURES OF MOLECULES FEATURING BONDS BETWEEN SECOND-ROW ELEMENTS

SVEN THORWIRTH, I. Physikalisches Institut, Universität zu Köln, Germany and Max-Planck-Institut für Radioastronomie, Bonn, Germany; MICHAEL E. HARDING, Institute for Theoretical Chemistry, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712, USA.

Equilibrium geometries of a set of molecules containing chemical bonds between second-row elements (Al, Si, P, S, Cl) have been evaluated at the CCSD(T) level of theory in combination with large basis sets. The results of these calculations are compared against equilibrium values from experiment. Purely experimental equilibrium structures are only available for very few molecules of this kind. Consequently, empirical equilibrium structural parameters for the majority of members of the set had to be determined using ground-state rotational constants corrected for zero-point vibrational effects. The latter were obtained by second-order vibrational perturbation theory employing coupled-cluster calculations of anharmonic force fields.

---

CALCULATION OF VIBRATIONAL ENERGY LEVELS: VPT2 VS. A VARIATIONAL APPROACH

M. E. HARDING, J. VÁZQUEZ, J. F. STANTON, Institute for Theoretical Chemistry, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712, USA.

For several potentials a detailed comparison of vibrational energy levels obtained via variational calculations employing the complete vibrational Hamiltonian$^a$ and second-order vibrational perturbation theory (VPT2) is carried out.

---


BOND-STRETCH ISOMERISM IN SFCl AND OTHER SULFUR HALIDES

JEFF LEIDING, DAVID E. WOON and THOM H. DUNNING, JR., Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana IL, 61801.

We have identified bond-stretch isomers in $^3A''$ excited states of SFCl and other triatomic sulfur halides using high-level ab initio techniques [RCCSD(T)/aug-cc-pVQZ]. These bond-stretch isomers are true minima on their potential energy surfaces, and they are manifested by alternation in bond type: There is a shorter (covalent) bond, and longer (recoupled pair) bond in all cases, while the bond angle is nearly constant for the isomers ($\sim 90^\circ$). The SFCl isomers are $\sim 15$ kcal/mol above a third nearly linear isomer on the PES for which both bonds are recoupled pair bonds. The recoupled pair bond is one in which the $p^2$ pair of singlet coupled electrons on the sulfur has been decoupled so that one of the electrons is recoupled to form a bond with a halogen and is typically $\sim 0.3$ Å longer than a covalent bond. The bond-stretch isomers are interesting because the potential in the direction of bond alternation is very flat, and the barrier between the isomers is very low ($< 1.0$ kcal/mol for SFCl, for example). Harmonic frequencies of these minima and the transition states between them have been calculated. Potential energy surfaces are being calculated in order to obtain a numerical solution to the nuclear Schrödinger equation.

Intermission

NEW METHODS FOR EXPLORING QM:MM POTENTIAL ENERGY LANDSCAPES

HRANT P. HRATCHIAN, Gaussian, Inc., Wallingford, CT 06492, USA.

In recent years, the applicability of quantum chemical methods for large system studies has been greatly enhanced by the development of hybrid QM:MM techniques. Despite these advancements, exploring the associated potential energy surfaces continues to present two key challenges. First, the QM energy and derivative evaluations may be too costly for simulations; and second, the system size for many QM:MM cases are too large to effectively store or use second-order information, an approach often used in QM studies to allow for larger integration steps and fewer QM evaluations of the potential energy surface. Our most recent work is focused on overcoming both computational bottlenecks. Using surface fitting models together with direct Hessian-vector and diagonalization algorithms, we are developing models that can accurately and efficiently explore QM:MM potential energy landscapes for very large systems. Our current development status and results from initial applications will be described.

DESCRIBING THE HYDRATED ELECTRON WITH A POLARIZABLE ELECTRON-WATER PSEUDOPOTENTIAL

LEIF D. JACOBSON, JOHN M. HERBERT, Department of Chemistry, The Ohio State University, Columbus, OH 43210.

We have constructed a one-electron pseudopotential that treats the mutual polarization of an excess electron with a water bath in a self-consistent fashion. This potential is able to reproduce MP2-quality vertical binding energies of anionic water clusters with an average error of less than 0.1 eV. We are also able to reproduce the bulk optical absorption spectrum of the aqueous electron where we find that the many-electron response of the water bath is important in describing the lineshape of this spectrum. The binding energy and absorption spectrum maximum have been important experimental observables in studies of anionic water clusters and so our potential is well suited to address the structural complexity of these systems. We reconstruct a diagram of vertical binding energy versus inverse cluster size in order to investigate the extent to which our model is able to reproduce photoelectron experimental data for anionic water clusters for n=20-200, as well as provide insight into the binding motifs of these clusters.
INSIGHTS INTO THE PA NEUTRAL ATOM: FROM AN EVALUATION OF PA$^{2+}$ OUTER-CORE CORRELATION ENERGY CALCULATIONS

MICHAEL K. MROZIK, RUSSELL M. PITZER, DEPT. OF CHEMISTRY, THE OHIO STATE UNIVERSITY; BRUCE E. BURSTEN, UNIVERSITY OF TENNESSEE-KNOXVILLE.

Since the identification of f-orbital contribution to the bonding in PaO$^+$, investigations into Pa cations have hoped to characterize as many of the electronic states possible. Electronic states of the Pa$^{n+}$ (n=0-4) ions have been investigated using multi-reference spin-orbit configuration interaction ($MR – SOCI$). Initial investigations using Dunning style correlation consistent double-$\zeta$ basis sets are re-examined with a larger triple-$\zeta$ basis, with the hope of supporting the order of electronic states. Calculations using Hartree-Fock and CI calculations on the neutral atom did not produce the known order of states. A case study was deemed necessary on similar electron configurations present in the low energy states of Pa$^{2+}$ more specifically those generated from the $5f^26d^1$ and $5f^16d^2$ configurations. Comparison in the Pa$^{2+}$ ion is complicated by the lack of experimental results, but the states are presumed to be similar sequence as those in the neutral atom, with the addition of two electrons in the 7s shell. In evaluating the impact of inclusion of the outer core, calculations including valence-outer core correlation were completed for the 5d, 6s, and 6p shells of the Pa$^{2+}$ ion. The magnitude of these individual shell correlation calculations will allow for identification of the energy level shifts associated with even and odd configurations, better describing the energy order in both the Pa$^{2+}$ ion case study and for the neutral Pa atom. Upon completion of this aspect of the Pa neutral atom study, the knowledge of the energy levels in the Pa$^{n+}$ (n=0-4) family of ions will be greatly expanded, and may yield a model for future studies of atomic actinide systems.


CONNECTIONS BETWEEN THE RAYLEIGH-SCHRÖDINGER AND VAN VLECK PERTURBATION THEORIES AND THEIR APPLICATION TO RESONANCES IN MOLECULAR VIBRATIONS

D. A. MATTHEWS, J. VÁZQUEZ, AND J. F. STANTON, Institute for Theoretical Chemistry, The University of Texas at Austin, Austin, Texas 78712.

The similarities of Rayleigh-Schrödinger (RSPT) and Van Vleck (VVPT) perturbation theories are discussed. It is shown that a straightforward application of RSPT produces the VVPT Hamiltonian at the highest order of the contact transformations applied, which is always a diagonal matrix. VVPT Hamiltonians at an order higher than this are non-diagonal, but it is shown that a careful application of RSPT can produce the same matrices. The usefulness of these higher-order “dressed” Hamiltonians in treating resonance is discussed, as well as specific discussions of first-order Fermi, second-order Darlington-Dennison, and higher-order resonances. Lastly, VVPT is discussed in a wavefunction-based context and RSPT in a Hamiltonian-based context, and the approaches are contrasted.

NEW PERSPECTIVE ON PF$_n$ (n=1–5) FROM THE RECOUPLED PAIR BONDING MODEL: A QUANTUM CHEMICAL STUDY

D. E. WOON and T. H. DUNNING, JR., Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

Structures of the PF$_n$ family (n=1–5) were characterized with high level RCCSD(T) coupled cluster theory calculations using triple and quadruple zeta quality correlation consistent basis sets. In addition to accounting for the well-known ground states of PF through PF$_3$, insight from the recoupled pair bonding model also led to locating a previously unknown $^3B_1$ state of PF$_3$, which lies about 90 kcal/mol above PF$_3(1A_1)$ but is still bound with respect to PF$_3(2B_1)+F(2P)$ by about 40 kcal/mol. We also revisited the less-studied C$_{3v}$ local minimum on the PF$_4$ doublet surface and characterized the transition state for interconversion to the C$_{2v}$ global minimum. The energetics suggest that both PF$_3(3B_1)$ and C$_{3v}$ PF$_4(2A_1)$ are potentially observable in the laboratory. The trends in the bond dissociation energies and relative energy differences of the PF$_n$ family are very consistent with predictions from the recoupled pair bonding model.
A QUANTUM CHEMICAL STUDY OF FAMILIAR AND EXOTIC LOW-LYING SINGLET AND TRIPLET STATES OF CH₂, CF₂, AND CHF

LU XU, D. E. WOON, and T. H. DUNNING, JR., Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

High level MRCl and RCCSD(T) calculations using triple and quadruple zeta quality correlation consistent basis sets were used to study the low-lying singlet and triplet states of CH₂, CF₂, and CHF. The bonding in carbon was found to be very similar to that of sulfur, where there is also a competition between states that form through normal covalent bonding and recoupled pair bonding. The recoupled pair bonding model was used to investigate these states systematically to see how closely they resemble the behavior of SF₂, which has a 1A¹ ground state and 3B¹ and 3A₂ excited states. In addition to accounting for the separations and ordering of the lowest singlet and triplet states of each species, the less-studied 3A₂ states of CH₂ and CF₂ and the 3A'' state of CHF were investigated and compared to gain insight into the underlying reasons for the energetic and bonding differences between these species. Interestingly, the 3A₂ state of CH₂ is a cyclic structure, the 3A₂ state of CF₂ is bent but not cyclic (resembling the same state of SF₂), and the analogous minimum structure on the 3A'' surface of CHF is a C—HF complex.

APPLICATION OF THE RECOUPLED PAIR BONDING MODEL TO BOUND DOUBLET AND QUARTET STATES OF HSO, SOH, OSF AND SOF

TYLER Y. TAKESHITA, D. E. WOON, and T. H. DUNNING, JR., Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

The recoupled pair bonding model and high level ab initio calculations [MRCl, RCCSD(T)] with correlation consistent basis sets were used to examine the optimized structures, bonding behavior and bond energies of bound HSO, SOH, OSF and SOF doublet and quartet states. This was done by the systematic addition of H or F to the 3Σ⁻, 1Δ and 3Π states of SO or by adding O(3P,1D) to the 2Π and 4Σ⁻ states of SF. Of particular interest are those states that are either formed as a result of decoupling a pair of electrons or by further addition to a molecule that has already undergone the decoupling process. One of the goals of these studies is to explore the effect of ligand properties such as electronegativity or electron affinity in order to anticipate their impact on trends in bond energy and other properties similar to those observed in previous SFₙ (n=1–6) recoupled pair bonding studies. This study marks the first exploration of the behavior of a divalent ligand in hypervalent bonding under the recoupled pair bonding model.

THE SWITCHING/GAUSSIAN METHOD FOR POLARIZABLE CONTINUUM MODELS WITH APPLICATIONS TO AQUEOUS MOLECULAR DYNAMICS AND VIBRATIONAL SPECTRA

ADRIAN W. G. LANGE, JOHN M. HERBERT, 100 W. 18th Ave, Columbus, OH 43210.

We describe the recently-developed Switching/Gaussian (SWIG) formalism for polarizable continuum models (PCMs) in electronic structure theory and QM/MM calculations. Existing PCM implementations are well-established, yet still exhibit Coulomb singularities and/or discontinuities in potential energy surfaces, which result from the finite-element discretization of the solute–continuum interface. Our revised implementation eliminates these problems. We illustrate the robustness this approach using ab initio molecular dynamics and vibrational spectra calculations, for which existing PCM implementations fail. Furthermore, we present the extension of SWIG to unprecedentedly large systems, making it a viable implicit solvation method even for molecular mechanics calculations of biological macromolecules.
In our present work, we are interested in the excited state dynamics of four explicit solutes, all of which are polyadenine B-DNA derivatives, which range in size from two to four adenine bases. Of all the excited state properties these systems possess, we have specific interest in determining the exciton length as this has been an area of debate in the literature. In order to accurately calculate the exciton length, we explore the use of both implicit and explicit solvation on the system by means of a polarizable continuum model (PCM) and a combined quantum mechanical/molecular mechanical model (QM/MM). For both solvation models the solute particles are treated with LRC-TDDFT, specifically we make use of two “long-range corrected” (LRC) density functionals developed previously in our group, LRC-ωPBE and LRC-ωPBEh. Previous comparisons to ab initio benchmarks have shown that these functionals provide a consistent treatment of both localized and charge-transfer excited states within TDDFT.
TJ. ASTRONOMICAL SPECIES AND PROCESSES
TUESDAY, JUNE 22, 2010 – 1:30 pm
Room: 2015 McPHERSON

Chair: DeWAYNE HALFEN, University of Arizona, Tucson, Arizona

TJ01 15 min 1:30
NEW MICROWAVE SPECTRUM AND GLOBAL FIT OF METHYL ACETATE GROUND STATE

J. KLEINER, M. TUDORIE, Laboratoire Interuniversitaire des Systèmes Atmosphériques, CNRS et Universités Paris 7 et Paris 12, 61 av. Général de Gaulle, Créteil, France; J. T. HOUGEN, Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441, USA; S. MELANDRI, Dipartimento di Chimica “G. Ciamiciani”, via Selmi 2, 40126 Bologna, Italy; W. STAHL, L. SUTIKDJIA, Institut für Physikalische Chemie, Raum 234, RWTH Aachen, Landoltweg 2 52062 Aachen.

Last year, we presented a newly written program to calculate and fit torsion-rotation transitions in molecules containing two inequivalent $C_3v$ methyl tops and a plane of symmetry, based on the Hamiltonian described by Ohashi et al.\textsuperscript{a}, which in turn was based on earlier theoretical models cited in their references. We applied this code to refit microwave data for the methyl acetate molecule published in 1980\textsuperscript{b}. Two sets of new measurements for this molecule were obtained, one using the Fourier transform microwave (FTMW) instrument in Aachen (4-18 GHz) with a measurement uncertainty of 5 kHz, the other using the millimeter wave (MMW) instrument in Bologna, (60-150 GHz) with a measurement uncertainty of 50 kHz. In the absence of top-top interactions, each asymmetric-top energy level splits into AA, AE, EA and EE components where the individual letters A and E indicate the symmetry species of the wave function with respect to internal rotation of one of the methyl tops. The new data for methyl acetate were assigned up to $J=10$ and put in the program. For the moment, almost all the 50 kHz measurements fit to experimental error, but we are still having trouble with the FTMW lines, which only fit to 7 kHz. By the time of the conference we hope to have found a better set of parameters, i.e., a set that describes more precisely the physical couplings occurring in this molecule\textsuperscript{c}.

\textsuperscript{b}J. Sheridan, W. Bossert and A. Bauer, J. Mol. Spectrosc., 80, 1-11 (1980)
\textsuperscript{c}Project partly supported by the ANR-08-BLAN-0054 contract (France)

TJ02 15 min 1:47
3-D SUBMILLIMETER SPECTROSCOPY OF ASTRONOMICAL ‘WEEDS’ — EXPERIMENTAL AND THEORETICAL ASPECTS OF DATA PROCESSING AND CATALOGING

IVAN R. MEDVEDEV, SARAH M. FORTMAN, CHRISTOPHER F. NEESE, and FRANK C. DE LUCIA, Department of Physics, 191 W. Woodruff Ave., Ohio State University, Columbus, OH 43210 USA.

In this presentation we report on the latest enhancements and improvements of the temperature resolved 3-dimensional spectroscopic technique as applied to the astronomical ‘weed’ problem. Experimental determination of the lower state energy and transition strength for every transition in a molecular spectrum provides the ability to predict spectra over a wide range of temperatures.

We have extended the spectral range of our experiment to 210–270 GHz. A heterodyne receiver has been employed in this range to enhance sensitivity and suppress undesirable harmonics in the output of the multiplier chain. The previously reported analysis of the ethyl cyanide spectrum in the 575–645 GHz spectral range\textsuperscript{a} has been successfully integrated into the Splatalogue database (www.splatalogue.net). In addition to cataloging frequencies, lower state energies and transition strengths we provide the end-users with the complete experimental dataset. We also have developed algorithms to calculate complete experimental spectra at an arbitrary user-specified temperature.

3-D SUBMILLIMETER SPECTROSCOPY OF ASTRONOMICAL ‘WEEDS’ – LATEST RESULTS

SARAH M. FORTMAN, IVAN R. MEDVEDEV, CHRISTOPHER F. NEESE, and FRANK C. DE LUCIA,
Department of Physics, 191 W. Woodruff Ave., Ohio State University, Columbus, OH 43210 USA.

We have previously reported on an experimental spectroscopic approach that makes possible the calculation of lower state energy levels and transition strengths without the need for spectral assignment. This approach provides results in the standard astronomical catalog form (frequency, line strength, lower state energy) as well as experimental temperature dependent spectra. Here we report our latest spectroscopic results and analyses for a number of astronomical weeds in the 575–645 GHz and 210–270 GHz spectral ranges. The latest improvements of the spectrometer result in more accurate power calibration of the experimental spectra. Additionally we have developed new approaches to data analysis which allow us to process this data in timely fashion providing rapid availability for the astronomical community.

THE MICROWAVE SPECTRUM OF THE HCOOCD$_2$H SPECIES OF METHYL FORMATE

L. H. COUDERT, LISA, CNRS/Universités Paris Est et Paris Diderot, 61 Avenue du Général de Gaulle, 94010 Créteil, France; T. R. HUET, L. MARGULÈS, R. MOTIYENKO, Laboratoire PhLAM, UMR 8523 CNRS, Bât. P5, Université des Sciences et Technologies de Lille 1, 59655 Villeneuve d’Ascq Cedex, France; and H. MOLLENDAL, Centre for Theoretical and Computational Chemistry (CTCC), University of Oslo, P. O. Box 1033, Blindern, 0315 Oslo, Norway.

Methyl formate is a non-rigid molecule displaying internal rotation of its methyl group. The microwave spectra of its normal$^b$ and mono deuterated HCOOCH$_2$D$^c$ species have already been studied and values for the tunneling splitting due to the internal rotation were determined. The normal species displays a 405 MHz $A'/E$ splitting, the mono deuterated one, a smaller 84.76 MHz $A''/A'$ splitting. For the bideuterated species HCOOCD$_2$H, the value of this splitting is not known as its microwave spectrum has not been studied yet.

In this paper experimental and theoretical investigations of the microwave spectrum of HCOOCD$_2$H are presented. More than 9000 transitions were measured with a submillimeter wave spectrometer. About 20 lines were recorded with a molecular beam spectrometer. Like for the mono deuterated species,$^c$ depending on the location of the only hydrogen atom of the methyl group, two configurations arise. The $C_s$-symmetry H-in plane configuration displays a rigid rotator spectrum and its data was analyzed using a Watson-type Hamiltonian. The $C_1$-symmetry H-out of plane configuration undergoes the large amplitude internal rotation. Its data was analyzed using the so called water dimer formalism$^d$ which allowed us to accurately reproduce the observed frequencies and to obtain the value of the tunneling splitting as well as the parameters involved in its rotational dependence. The hyperfine structure due to quadrupole coupling at the two deuterium atoms was also analyzed. Unexpectedly, for the H-out of plane configuration, the observed hyperfine patterns are neither those expected for two equivalent deuterium atoms nor those of a rigid molecule.

---

$^a$This work is supported by the ANR-08-BLAN-0054 and ANR-08-BLAN-0225 contracts.
Due to the asymmetry of the CH$_2$D group, the internal rotation problem in the partially deuterated species of methanol CH$_2$DOH is a complicated one as, unlike in the normal species CH$_3$OH, the inertia tensor depends on the angle of internal rotation. The CH$_2$DOH species also displays a dense far infrared torsional spectrum difficult to assign. Recently 38 torsional subbands of CH$_2$DOH have been identified, but for most of them there is neither an assignment nor an analysis of their rotational structure.

In this paper, an analysis of the rotation-torsion spectrum of CH$_2$DOH will be presented. The rotational structure of 23 torsional subbands have been assigned. These subbands are $\Delta v_t \geq 1$ perpendicular subbands with a value of $v'_t$ up to 10 and values of $K'$ and $K''$ ranging from 0 to 9. For all subbands, the $Q$-branch was assigned, for 3 subbands, the $R$- and $P$-branches could also be found. The results of the rotational analysis with an expansion in $J(J+1)$ of the new subbands and of already observed ones will be presented. When available, microwave lines within the lower torsional level, recorded in this work or already measured, were added to the data set.

A theoretical approach aimed at calculating the rotation-torsion energy levels has also been developed. It is based on an expansion in terms of rotation-torsion operators with $C_s$ symmetry and accounts for the dependence of the inertia tensor on the angle of internal rotation. This approach will be used to carry out a preliminary global analyses of the wavenumbers and of the frequencies.

Contrary to the isotopic specie of methanol with a symmetrical CH$_3$ or CD$_3$ methyl group, in the mono-deuterated species CH$_2$DOH the hindering potential no longer displays 3-fold symmetry and all moments of inertia depend on the angle of internal rotation. For this reason, this mono-deuterated species displays a fairly dense torsional spectrum difficult to compute and to assign.

In this paper, an analysis of the torsional spectrum of mono-deuterated methanol is presented. More than 40 torsional subbands have been assigned in the 20 to 800 cm$^{-1}$ region. The body of data available for CH$_2$DOH consists of these newly assigned subbands and of the already available ones. The observed torsional subbands are characterized by $K \leq 10$ and $v_t \leq 10$. For 23 subbands, the rotational structure could be analyzed and this provides us with a mean to check their torsional assignment. The positions of the subband centers were analyzed with a theoretical approach accounting for the dependence of the inertia tensor on the angle of internal rotation. This allowed us to reproduce 58 experimental wavenumbers with an RMS value of 0.12 cm$^{-1}$. The spectroscopic parameters corresponding to the hindering potential and to the inertia tensor were also retrieved.

---

Intermission
In interstellar carbon chemistry, CH$_3^+$ is thought to be an important and abundant molecular ion. However, as it is a symmetric planar molecule and, as a result, it has no permanent dipole moment, it is almost impossible to detect this species by radio astronomical observations. Its deuterated species, CH$_2$D$^+$ and CHD$_2^+$, possess the dipole moment, so the rotational lines should be observable. Rösslein et al.$^a$ and Jagod et al.$^b$ observed the infrared spectra of these deuterated species. Demuyck and coworkers$^c$ tried to observe CH$_2$D$^+$ rotational lines in an extended negative glow discharge with no success. More recently Lis et al.$^d$ reported tentative identification of CH$_2$D$^+$ toward Ori IRc2. The molecular constants and the predicted rotational transition frequencies given by Rösslein et al.$^a$ were a good starting point in searching for the rotational lines. A very weak feature was found almost exactly at the calculated frequency for the $2_{12} - 1_{11}$ transition. Eventually the line appeared stronger enough for precise frequency measurements, after adjusting the reaction conditions. The optimum gas mixture was found to be CH$_4$ ($\sim$ 3 mTorr), CD$_4$ ($\sim$ 1 mTorr), H$_2$ ($\sim$ 2 mTorr), and He ($\sim$ 35 mTorr). It is interesting to note that helium is essential to produce CH$_2$D$^+$. No signals were detectable with Ar buffer. Although the signal was seen without H$_2$, it appears to play a subtle role in the formation, resulting in about a factor 2 increase in intensity. Adding D$_2$ instead of CD$_4$ resulted in no signal. The observations were made with about 16 mA discharge current with liquid nitrogen cooling. As this ion is a light molecule and the signal was only weakly observed, four transitions were detected so far in the 280-890 GHz region. All observed transition frequencies agree within 1 MHz of the predicted frequencies. These laboratory transition frequencies strongly support the tentative astronomical identification by Lis et al.$^d$

$^b$M.-F. Jagod et al., J. Mol. Spectrosc. 153, 666 (1992)
$^d$D. C. Lis et al., in Submillimeter Astrophysics and Technology, ASP Conference Series, 417, 23 (2009)
THE \( J = 1 \leftrightarrow 0 \) ROTATIONAL TRANSITIONS OF \( ^{12}\text{CH}^+ \), \( ^{13}\text{CH}^+ \) and \( ^{12}\text{CD}^+ \)

T. AMANO, Department of Chemistry and Department of Physics and Astronomy, University of Waterloo, Waterloo, ON, Canada N2L 3G1.

The \( \text{CH}^+ \) ion is the first molecular ion identified in interstellar space. Dunham\textsuperscript{a} detected a couple of unidentified lines in near-UV, and later Douglas and Herzberg\textsuperscript{b} identified them based on their laboratory observations. The electronic spectra have been investigated extensively. On the other hand, the pure rotational transitions are less extensively studied. Cernicharo \textit{et al.}\textsuperscript{c} reported the interstellar detection of the \( J=2-1, 3-2, \) and \( 4-3 \) transitions in NGC 7027. Pearson and Drouin\textsuperscript{d} reported the laboratory observation of the \( J=1-0 \) line of \( ^{12}\text{CH}^+ \) at 835078.950 MHz and, based on this frequency, predicted the frequencies for \( ^{13}\text{CH}^+ \) and \( \text{CD}^+ \). The predicted \( ^{13}\text{CH}^+ \) frequency led to identification of the interstellar line\textsuperscript{e}. In this talk, we present a new set of measurements of the \( J=1-0 \) lines for the normal species together with the \( ^{13}\text{C} \) and \( \text{D} \) isotopic species. The overwhelming evidences obtained in our experiments support the new identifications.

An extended negative glow discharge in a gas mixture of \( \text{CH}_4 \) (\( \sim \) 0.5 mTorr) diluted in \( \text{He} \) (\( \sim \) 60 mTorr) was used for production of \( \text{CH}^+ \) with the discharge current of about 15 mA. Axial magnetic filed up to 160 Gauss was applied. The normal species line exhibited a surprisingly large Zeeman splitting for a \( ^1\Sigma \) molecule. The \( ^{13}\text{CH}^+ \) line showed the spin-rotation hyperfine splitting, and at higher field of 150 Gauss an unresolved lineshape was exhibited due to combined hfs and Zeeman splittings. The spin-rotation splitting in the normal species was negligibly small. The \( \text{CD}^+ \) line showed much smaller Zeeman and spin-rotation splittings, as expected. Details of the mechanism to induce such Zeeman effect and the spin-rotation interaction will be presented. The transition frequencies for these \( J = 1 - 0 \) lines are: 835137.498(20) MHz and 453521.847(20) MHz for \( ^{12}\text{CH}^+ \) and \( \text{CD}^+ \), respectively. The transition frequencies for \( ^{13}\text{CH}^+ \) are 830216.680(50) MHz (\( F = 3/2 - 1/2 \)) and 830214.961(50) MHz (\( F = 1/2 - 1/2 \)). The uncertainties reflect possible errors in correcting the Zeeman shifts.

\textsuperscript{a} T. Dunham, \textit{Publ. Astron. Soc. Pac.}, \textbf{49}, 26 (1937)
\textsuperscript{b} A. E. Douglas and G. Herzberg, \textit{Astrophys. J.} \textbf{94}, 381 (1941)
\textsuperscript{c} J. Cernicharo \textit{et al.}, \textit{Astrophys. J.}, \textbf{483}, L65 (1997)
\textsuperscript{e} E. Falgarone \textit{et al.}, \textit{Astrophys. J.}, \textbf{634}, L49 (2005)

QUANTUM CHEMICAL PREDICTIONS OF THE DIPOLE MOMENTS AND DIPOLE POLARIZABILITIES FOR 200+ KNOWN AND POSTULATED NEUTRAL ASTROMOLECULES

D. E. WOON, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801; E. HERBST, Departments of Physics, Chemistry, and Astronomy, The Ohio State University, Columbus, OH 43210.

Quantum chemical calculations of dipole moments and dipole polarizabilities were carried out for about 200 neutral molecules with up to 12 atoms that are known or postulated to be present in interstellar or circumstellar sources in order to make new predictions of chemical rate coefficients for ion-molecule reactions. Optimized structures and the response properties were computed at the RCCSD(T) level of coupled cluster theory with basis sets as large as aug-cc-pVTZ, depending on the size of the molecule. The accuracy of the predictions was assessed against existing experimental data, which is particularly limited in the case of dipole polarizabilities. In addition to appearing in publication form, the predictions are available online at http://www.astrochymist.org/properties.
The observation and characterization of water spectra have been intensely pursued in the astrophysical community. Its rotational transitions in the ground, (010) ($v_2 = 1$), (020), (100), and (001) states are primary targets of the ongoing Herschel mission. In this study, laboratory terahertz spectroscopy of water was carried out at JPL and Cologne, with the goals to measure all transitions HIFI might see and critically review and fit the lowest 5 vibrational states. DC discharge, radio frequency discharge and heating tapes were used to generate highly excited water. A total of 145 pure rotational transitions in the (000), (010), (020), (100), and (001) states of water were observed in the 293−1969 GHz region. Of these, 86 have been detected for the first time with MW accuracy. So far, the $1(1,0) - 1(0,1)$ transition was observed for all five states; the $2(1,2) - 1(0,1)$ transition was observed for (000), (100), and (001) but is missing for (010) (1753914 GHz) and (020) (1872972 GHz); the $1(1,1) - 0(0,0)$ transition was observed for all states but (020) (1332967 GHz). The analysis is still in progress, and we will present the most recent fitting results to date. There are difficulties in fitting water spectra, such as the strong centrifugal distortion, which gives a non-convergent Watson Hamiltonian. In addition, the first triad states (100, 020, and 001) are strongly coupled. The latest attempt at a global fit of these 5 states using Euler series achieved a reduced RMS of 8.4 (Pickett et al. 2005, J. Mol. Spectrosc. 233, 174).

Complex organic molecules are relatively heavy, their maximum absorption is in the millimetric domain at about 300 GHz. But the most abundant, like methyl formate, could be detected in the ISM up to 900 GHz. We will present here the last results obtained about the two $^{18}$O and the doubly-deuterated species of methyl formate. This concludes the systematic investigation up to 660 GHz for the mono-substituted isotopic species with either $^{13}$C, $^{18}$O, or D, which began in 2006. The lines from these isotopic species will certainly be present in the spectra which will be recorded in the next years with the very sensitive telescope ALMA, HERSHEL and SOFIA. The detection of isotopic species is very important for the astrophysical community to improve the interstellar chemical modeling and to understand the formation mechanism of these complex organic molecules.

Our interest was also on the theoretical aspects. Like other complex organic molecules, methyl formate displays a large amplitude motion. Here it is the rotation of the methyl group with respect to the rest of the molecule. Theoretical models were developed to reproduce accurately the observed frequencies for large quantum numbers values as $J$-values as high as 70 could be reached. Similarly the investigation of the doubly-deuterated HCOOCHD$_2$ was undertaken to test the model developed for mono-deuterated HCOOCH$_2$D.$^b$ This work is supported by ANR-08-BLAN-0054 and ANR-08-BLAN-0225.

---

The detection of chiral compounds in the interstellar medium is a great challenge and could tell us the connection between the chemistry of the ISM and the origin of life on the primitive Earth. Chiral C-3 sugar, α-aminonitriles and cyanohydrins or the corresponding chloro-derivatives are intuitively the simplest chiral candidates consistent with the nature of the heteroatoms observed in the ISM. The aminoacetonitrile being observed in Sgr B2(N) but not the simplest cyanohydrins and chloacetonitrile, our study was devoted to the 2-aminopropanenitrile, the methyl derivative of aminoacetonitrile and the precursor of alanine (an amino acid) by hydrolysis.

The measurements were made in Oslo and in Lille from 7 to 660 GHz. More than 2000 lines were assigned. The search in Sgr B2(N) has been unsuccessful so far. The upper limit currently derived on the column density is comparable to the column density of aminoacetonitrile.

This work is supported by the French Programme National de Physique Chimie du Milieu Interstellaire

---

Methyl mercaptan, CH₃SH, is an abundant molecule e.g. in the high-mass star-forming region Sagittarius B2. It is the sulfur analog of methanol and features also threefold internal rotation of the methyl group. The most recent analysis consisted mostly of a-type transitions, treated A and E torsional species separately, and does not yield predictions of sufficient accuracy for the needs of the recently launched Herschel mission or the upcoming SOFIA and ALMA. New terahertz spectra have been recorded with microwave accuracy at the Universität zu Köln which cover thus far large portions of the 1.1−1.5 THz region as well as a section near 1.9 THz. Numerous νₓ = 0, 1 and 2 pure rotational transitions have been assigned. FIR synchrotron spectra have recently been measured at the Canadian Light Source (CLS) between 55 and 550 cm⁻¹ at 0.001 cm⁻¹ resolution. 53, 15, and 2 subbands have been assigned thus far for the νₓ = 1−0, 2−1 and 2−0 torsional bands along with further pure rotational transitions. We will present up-to-date results from our analysis which has been started.

---

Linke et al., Astrophys. J. 234 (1979) L139
THE SUBMILLIMETER SPECTRUM OF GLYCOLALDEHYDE FROM 500 GHz TO 1.2 THz

P. BRANDON CARROLL, Department of Chemistry, Emory University, Atlanta, GA 30322; BRIAN J. DROUIN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, 91109; and SUSAANNA L. WIDICUS WEAVER, Department of Chemistry, Emory University, Atlanta, GA 30322.

Glycolaldehyde is the simplest $\alpha$-hydroxy aldehyde and the only sugar-related molecule definitively detected in the interstellar medium to date. Previous spectral studies\textsuperscript{a,b} have reported its rotational spectrum up to $\sim$350 GHz. With the advent of several new submillimeter and THz astronomy facilities equipped with high-resolution spectrometers, it is important to begin collecting and analyzing higher frequency spectra for all known interstellar molecules. We have acquired the submillimeter/THz direct absorption spectrum of glycolaldehyde from 520 – 600 GHz and from 1.1 – 1.2 THz. The spectra were measured at JPL using a 3-meter static cell in double-pass configuration. The submillimeter radiation was generated using a standard microwave frequency synthesizer coupled with cascaded frequency multipliers. A Schottky diode detector was used during acquisition of the lower frequency spectra, and an Si hot electron bolometer detector was used for scans above 1 THz. The analysis of these spectra is underway, and new line assignments are being combined with the assignments from previous studies to determine a global spectral fit. The details of the experiment and progress on the spectral analysis will be reported.


LABORATORY DETECTION OF THE TRANS-GAUCHE CONFORMER OF ETHYL FORMATE.

JUSTIN L. NEILL, MATT T. MUCKLE, DANIEL P. ZALESKI, AND BROOKS H. PATE, Department of Chemistry, University of Virginia, McCormick Rd., P.O. Box 400319, Charlottesville, VA 22904; V. LATANZI, S. SPEZZANO, AND M.C. MCCARTHY, Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138, and School of Engineering & Applied Sciences, Harvard University, 29 Oxford St., Cambridge MA 02138.

Ethyl formate has two coordinates of conformational flexibility, in the ester (O=C-O-C) and ethyl (C-O-C-C) dihedral angles. Two conformers, one with a cis ester and trans ethyl orientation, the other with a cis ester and gauche ethyl orientation, have been previously detected by rotational spectroscopy.\textsuperscript{a} In addition, the cis-trans isomer, the lowest-energy conformer, has recently been detected in the SgrB2(N) hot core.\textsuperscript{b} The third conformer of ethyl formate, with a trans ester orientation and gauche ethyl orientation, is significantly higher in energy than the cis-trans conformer according to electronic structure calculations (1900 cm$^{-1}$, or 1330 K), but there is a barrier of 2870 cm$^{-1}$ (2000 K) for this conformer to relax into the more stable cis ester potential well, and so local thermodynamic equilibrium between these conformers is not expected in the interstellar medium. Similar behavior is found for the trans ester conformer of methyl formate, for which a tentative detection in SgrB2(N) was presented at this meeting last year, with a column density roughly 1% of that of the more stable cis isomer.\textsuperscript{c} Here we report the laboratory detection of trans-gauche ethyl formate using Fourier transform microwave spectroscopy; its low population at room temperature equilibrium has been enhanced by the use of a pulsed discharge nozzle. The spectrum is complicated by a low barrier (140 cm$^{-1}$) to tunneling between equivalent structures.

\textsuperscript{c}M.T. Muckle et al., RH15, 64th International Symposium on Molecular Spectroscopy (2009).
HIGH RESOLUTION SPECTROSCOPY AND DYNAMICS: FROM JET COOLED RADICALS TO GAS-LIQUID INTERFACES

E. SHARP-WILLIAMS, M. A. ROBERTS, J. R. ROSCIOLI, A. W. GISLER, M. ZIEMKIEWICZ, D. J. NESBITT, JILA, University of Colorado and National Institute of Standards and Technology, Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0440; F. DONG, Los Gatos Research, 67 E. Evelyn Ave. Suite 3, Mountain View, CA 94041; B. G. PERKINS, JR., Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Ave Building 6-026, Cambridge, MA 02139.

This talk will attempt to reflect recent work in our group involving two quite different but complementary applications of high resolution molecular spectroscopy for detailed study of intramolecular as well as intermolecular dynamics in small molecules. The first is based on direct infrared absorption spectroscopy in a 100 KHz slit supersonic discharge, which provides a remarkably versatile and yet highly sensitive probe for study of important chemical transients such as open shell combustion species and molecular ions under jet cooled (10-20K), sub-Doppler conditions. For this talk will focus on gas phase spectroscopic results for a series of unsaturated hydrocarbon radical species (ethynyl, vinyl, and phenyl) reputed to be critical intermediates in soot formation. Secondly, we will discuss recent applications of high resolution IR and velocity map imaging spectroscopy toward quantum state resolved collision dynamics of jet cooled molecules from gas-room temperature ionic liquid (RTIL) and gas-self assembled monolayer (SAM) interfaces. Time permitting, we will also present new results on hyperthermal scattering of jet cooled NO radical from liquid Ga, which offer a novel window into non-adiabatic energy transfer and electron-hole pair dynamics at the gas-molten metal interface.
GLOBAL CALCULATIONS USING POTENTIAL FUNCTIONS AND EFFECTIVE HAMILTONIAN MODELS FOR VIBRATION-ROTATION SPECTROSCOPY AND DYNAMICS OF SMALL POLYATOMIC MOLECULES

VLADIMIR TUYTEREV, Groupe de Spectrométrie Moléculaire et Atmosphérique, U.M.R. CNRS 6089, Université de REIMS, Moulin de la Housse, B.P. 1039, 51687 REIMS cedex 2, FRANCE.

It has become increasingly common to use accurate potential energy surfaces and dipole moment surfaces for predictions and assignment of high-resolution vibration-rotation molecular spectra. These surfaces are obtained either from high-level ab initio electronic structure calculations or from a direct fit to experimental spectroscopic data. The talk will continue a discussion of some recent advances in the domain of the "potentiology". The role of basis extrapolations, of the Born-Oppenheimer breakdown corrections, in particular for very highly excited vibration states will be considered. As effective polyad Hamiltonians and band transition moment operators are still widely used for data reductions in high-resolutions molecular spectroscopy, experimental spectra analyses invoke a need for accurate methods of building physically meaningful effective models from ab initio surfaces. This involves predictions for various spectroscopic constants, including vibration dependence of rotational and centrifugal distortion and resonance coupling parameters. Topics planned for discussion include: high-order Contact Transformations of rovibrational Hamiltonians and of the dipole moment for small polyatomic molecules; convergence issues; the role of the anharmonicity in a potential energy function and of resonance couplings on the normal mode mixing and on vib-rot assignments with application to high energy vibration levels of SO₂ and to ozone near the dissociation limit; intensity anomalies in H₂S / HD₅ / D₂S spectra, relation of the shape of ab initio dipole moment surfaces with a "mystery" of nearly vanishing symmetry allowed bands. A full account for symmetry properties requires efficient theoretical tools for transformations of molecular Hamiltonians such as irreducible tensor formalism, applications using phosphine and methane potentials will be discussed. Both potential functions and effective polyad Hamiltonians allow studying changes in quasi-classical vibration periodic orbits and in of the nodal structure of wavefunctions with mass variations. An investigation of the consequences of symmetry breaking by isotopic substitution, in the classical and quantum dynamics is particularly instructive. This helps understanding the fingerprints of bifurcations effects in the quantum states of isotopologues and their assignment. The work of our research team with collaborators in these areas will be described.

Intermission

PROBING FUNDAMENTAL PHYSICS WITH COLD AND ULTRACOLD MOLECULES

E.A. HINDS, B.E. SAUER, J.J. HUDSON, M.R. TARBUTT, D.M. KARA, Centre for Cold Matter, Imperial College London, SW7 2AZ.

The search for an electron EDM is a search for new particle physics. We are measuring the electron EDM using a beam of cold YbF. The present version of our experiment has the statistical sensitivity to make a measurement at the level of a few times 10⁻²⁸ e.cm. and this is in progress. Several upgrades now in preparation, will give a further tenfold improvement in sensitivity. I will discuss the present status of this programme and future prospects.

There is now a strong prospect of greatly improving sources of cold molecules towards much higher intensity and also towards much lower temperature. I will describe some of these methods and the new physics that is starting to become accessible as a result.

COBLENTZ AWARD

Presentation of Award by Ian Lewis, Kaiser Optical Systems
INTERROGATING HYDROCARBON RADICALS

TIMOTHY W. SCHMIDT, School of Chemistry, The University of Sydney, NSW 2006, Australia.

Motivated by astrophysical problems (and a sense of fun) for some years my research group has been obtaining new spectra of hitherto unobserved hydrocarbon radicals. We employ the complementary techniques of resonant ionization and laser induced fluorescence to rigorously identify radicals by matching their ground state vibrational frequencies to those obtained using density functional theory (DFT).

While some radicals were made to order in our pulsed electrical discharge source, others of particular chemical importance have been found lurking in the congested forest of dicarbon and tricarbon fluorescence. Using a 2-dimensional fluorescence (2df) map, we have extracted pure spectra, unpolluted by C₂ and C₃, from a benzene discharge. One spectrum was first presented at this symposium in 2006, but at that stage was not identified. Subsequent measurement of a matching resonant ionization spectrum revealed a mass of 115, much higher than the benzene precursor. With the aid of DFT calculations, the species was positively identified, giving clues to hydrocarbon-building chemistry of relevance to combustion; planetary atmospheres; and the interstellar and circumstellar space. Further experiments revealed other surprising additions to the radical zoo, also identified with the help of 2df.

Along the way we have also identified two new band systems of C₂, the first involving the hidden e³Σ⁺ state, and have ventured into the world of larger molecules, such as hexabenzocoronene, C₄₂H₁₈.
INCORPORATING DAMPING FUNCTIONS INTO THE MORSE/LONG-RANGE POTENTIAL FUNCTION FORM IMPROVES BOTH LONG-RANGE AND VERY SHORT-RANGE BEHAVIOUR

ROBERT J. LE ROY, CARL HAUGEN and JASON TAO, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

In recent years it has become increasingly common to analyze diatomic molecule spectroscopic data by using fully quantum mechanical direct potential fits (DPFs) to determine the potential energy function(s) of the state(s) in question. However, the efficacy of this approach is strongly dependent on the quality of the analytic model used for the potential function. The best global analytic model introduced to date is (arguably) the ‘Morse/Long-Range’ (MLR) function, which provides particularly compact flexible functions which explicitly incorporate correct long-range. To date, applications of this form have mainly used a simple sum of inverse-power terms to represent the long-range behaviour. However, that neglects the fact that dispersion and other inverse-power terms change character at shorter distances where the electron distributions on the two moieties begin to overlap. With illustrative applications to MgH, Ca$_2$ and NaRb, we show that in addition to yielding more physically realistic long-range behaviour, including appropriately designed ‘damping functions’ with these inverse-power terms also gives potential functions with more realistic short-range behaviour.


ELECTRONIC TRANSITIONS OF IRIDIUM MONOBORIDE

A. S-C. CHEUNG, H.F. PANG, Y.W. NG, AND G. CHEN, Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong.

Laser induced fluorescence spectrum of iridium monoboride (IrB) in the spectral region between 420 and 480nm has been studied. New electronic transition system observed at 435nm has been assigned to be the [22.3] $^3\Phi_3$ - $X^3\Delta_3$ transition. Isotopic relationship confirmed the vibrational numbering. Molecular constants obtained will be reported. Resolved fluorescence spectrum of the [22.3] $^3\Phi_3$ - $X^3\Delta_3$ transition showed that the $\Delta G_{1/2}$ of the $X^3\Delta_3$ state is 917 cm$^{-1}$. Theoretical study using complete active space self-consistent field (CASSCF) calculations followed by MS-CASPT2 including scalar relativistic effect has been performed to the IrB molecule; molecular bond length, electronic configurations and relative energies of the ground and low-lying electronic states have been obtained. Our computed results indicated that the ground state of IrB is an inverted $X^3\Delta$ state with a bond length, $r_0$, equal to 1.767 Å, which is in very good agreement with our experimental determination earlier. The electronic configuration giving rises to the ground state is $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^1 1\delta^3$. Our calculations also showed that the earlier observed [16.5] $^3\Pi$ state and the [22.3] $^3\Phi$ state in this work are the $(2)^3\Pi$ and the $(2)^3\Phi$ states, respectively. The molecular properties obtained in our calculations agree reasonably well with those determined.

Financial support from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. HKU 701008P) is gratefully acknowledged.
Electric quadrupole transitions in the $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ band of $^{16}\text{O}_2$ are reported for the first time. They were first detected in atmospheric solar spectra acquired with a ground based Fourier transform spectrometer (FTS) in Park Falls, WI. Subsequently high-sensitivity Continuous Wave-Cavity Ring Down Spectroscopy (CW-CRDS) experiments were carried out at Grenoble University in the 7717-7917 cm$^{-1}$ region in order to provide quantitative intensity information for these transitions. Experimental intensities of the $\Delta J = \pm 2$ transition were used as input data for calculation of the complete list of electric quadrupole transitions with $\Delta J = \pm 2$, $\pm 1$ and 0. The calculation was carried out for the intermediate coupling case and assuming that these transitions are possible only through mixing of the $\Omega=0$ component of the ground electronic state and $b^1\Sigma^+_g$ state induced by spin-orbit coupling. The calculated line list agrees well with experimental measurements and was used to improve the residuals of the fitted atmospheric spectrum. Emission probability for the electric quadrupole band was determined to be $(1.02 \pm 0.10) \times 10^{-6}$ s$^{-1}$.

OSCILLATOR STRENGTHS IN THE VISIBLE ABSORPTION SPECTRUM OF I$_2$

The $B \leftarrow X$ transition in I$_2$ stands as one of the most precisely characterized diatomic electronic systems, with thousands of lines having been measured with precision sufficient to serve as frequency standards across the 500-700-nm spectral region. Accordingly the molecular constants of the $B \leftarrow X$ system permit recalculation of those line positions with similar precision (0.001 cm$^{-1}$). Yet the $B \leftarrow X$ electronic transition strength remains a 10-percent quantity, in part from the difficulty of dealing with two overlapping continuous 1u- $X$ transitions, $A \leftarrow X$ and $C \leftarrow X$. In this work, oscillator strengths are estimated from a long-known but little used method – integration of absorption cross sections over single rotational lines – using measurements obtained for lines near 650 nm with a diode laser. The results are combined with new, precise low-resolution (1 nm) absorption data to obtain a refined assessment of electronic transition strengths in the I$_2$ visible absorption spectrum.

ULTRAFAST PHOTOCHEMISTRY OF BROMOFORM IN SOLUTION PROBED IN THE DEEP-UV- TO NEAR-IR SPECTRAL RANGE

The photochemical pathways of bromoform (CHBr$_3$) in dilute (10 mM) and concentrated (500 mM) acetonitrile and methylcyclohexane solutions following excitation with ultrafast (100 fs) 255-nm laser pulses were investigated. Ultrafast transient absorption spectra manifest the formation of a CHBr$_2$ radical species within the apparatus response function through its intense deep-UV ($\sim$ 250-nm) absorption band. The formation of $\text{iso}$-bromoform ($\text{iso}$-CHBr$_2$-Br) occurs within few hundreds of femtoseconds after photoexcitation and do not correlate with the dynamics of CHBr$_2$ radical. The $\text{iso}$-CHBr$_2$-Br isomer species decays single exponentially with a 290-ps time constant in acetonitrile. In methylcyclohexane, however, the intense absorption of the isomer in the visible spectral range dominates the transient spectra up to the longest investigated time delays of 1.2 ns. $\text{Ab initio}$ and DFT calculations in conjunction with continuum solvation models strongly suggest that acetonitrile opens a pathway for the $\text{iso}$-CHBr$_2$-Br to CHBr$_3$ isomerization through a polar, cyclic transition state. This channel is not thermodynamically feasible in the non-polar solvent.
In conventional biomedical applications intense and broadband high energy X-rays are used in therapy and diagnostics (theranostics) to ensure sufficient tissue penetration for imaging or treatment. To avoid damages incurred by these, our proposed method, Resonant Theranostics, aims to find narrow energy regions that correspond to resonant absorption or emission. We show that such energy bands lie below the K-shell ionization energy, contrary to the research focus on the K-shell ionization energy itself. Targeting these energy bands, Auger processes can be initiated to produce a number of photons and electrons from each atomic/molecular species via photon fluorescence and electron ejections. We will report our study on the bromine compound bromodeoxyuridine (B UdR), widely used as radiological contrast agent in radiation imaging. The active system is Br−−Br+ combination, which can emit or absorb X-rays in the relative narrow energy range of 12 to 13.6 keV, through 1s−np transitions. We will present the oscillator strengths and transition probabilities for various Auger or K-shell 1s − np transitions. We will show that the corresponding cross sections and attenuation coefficients per unit mass, are orders of magnitude higher than the background and that at K-shell ionization energy. Employing these attenuation coefficients in the Monte Carlo simulation program Geant4, we study the intensities of photon and electron emission spectra.  

Acknowledgement: Partially support: Large Interdisciplinary Grant award of the Ohio State University and NASA (SNN). The computational work was carried out at the Ohio Supercomputer Center, Columbus Ohio.  


WF07  
Doubly Hydrogen Bonded Bis-(4-Hydroxyphenyl) Methane Dimers.  

CHIRANtha P. RODRIGO, WILLIAM H. JAMES III, TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN 47907-2084.

Single-conformation spectroscopic methods were used to investigate the jet-cooled dimers of the bichromophore bis-(4-hydroxyphenyl) methane (B4HPM). This study serves as an extension of our previous studies on the B4HPM monomer, which revealed two stable monomer conformations in the jet expansion. Here, resonant two-photon ionization, IR-UV holeburning, and resonant ion-dip infrared spectroscopy were used to record the conformation-specific IR and UV spectra of two distinguishable dimer conformations. The first conformer possessed a strong S0−S1 origin transition at 34899 cm−1 with little vibronic activity, whereas the second conformer exhibits long progressions in several low frequency modes without a clear origin band. The S0−S1 origin transitions of the dimer conformations are shifted −285 cm−1 from the monomer S0−S1 origins, similar to the shift observed between mthrmS0−S1 origins of para-cresol monomer and dimerd (−328 cm−1). Furthermore, single-conformation IR spectra show that both dimer conformers have two hydroxyl groups H-bonded. The dimer OH stretches are shifted from the B4HPM monomer values by (−11/−144) and (−17/−144) cm−1. These shifts are comparable to those of phenol dimer, relative to phenol monomer hydroxyl group stretching frequency.  

Finally, theoretical predictions provide evidence for two low energy structures. The lowest energy structure consists of monomers in which each molecule acts simultaneously as donor and acceptor. In the second lowest energy structure, however, the two monomers are distinguishable, with one acting as double-donor and the other as double acceptor. This talk will discuss the comparison of the experimental results with the predicted structures and their properties as flexible tetrachromophores.

NON-SYMMETRIC PUSH-PULL MOLECULES IN THE GAS PHASE: HIGH RESOLUTION STARK SPECTROSCOPY OF M-AMINOBENZOIC ACID.\textsuperscript{a}

ADAM J. FLEISHER, PHILIP J. MORGAN and DAVID W. PRATT, Department of Chemistry, University of Pittsburgh, 15260.

The permanent electric dipole moments of two conformers of \textit{m}-aminobenzoic acid (MABA) in their ground and electronically excited states have been experimentally determined by Stark-effect measurements in a molecular beam. The two conformers, differing by a rotation about the bond connecting the carboxylic acid group and aniline ring, have very similar rotational constants. However, the two conformers may be unambiguously assigned using their respective permanent dipole moment orientations. The possibility of excited state mixing in this non-symmetric biologically relevant push-pull molecule will be discussed.

\textsuperscript{a}Work supported by NSF (CHE-0911117).

GAS PHASE ELECTRONIC SPECTROSCOPY OF 5-FLUOROSALICYLIC ACID.\textsuperscript{a}

JUSTIN W. YOUNG, ADAM J. FLEISHER and DAVID W. PRATT, Department of Chemistry, University of Pittsburgh, Pa 15260.

Methyl salicylate and its derivatives have generated large amounts of interest due to the possibility of intramolecular proton transfer in their electronically excited states (ESPT). Here, the excited state dynamics of 5-fluorosalicylic acid and its dimer will be discussed within the context of their vibrationally and rotationally resolved electronic spectra. Stark effect studies of the latter permit identification of specific conformers of 5FSA. However, some species exhibit broadened spectra, whereas others do not, suggesting a species-specific ESPT reaction.

\textsuperscript{a}Work supported by NSF (CHE-0911117)

LASER INDUCED CHLOROPHYLL FLUORESCENCE SPECTRA OF CAJANUS CAJAN L PLANT GROWING UNDER CADMIUM STRESS

RAM GOPAL, Laser Spectroscopy and Nanomaterial Lab, Department of Physics (UGC-CAS) University of Allahabad, Allahabad-211002, INDIA.; and J. K. PANDEY, M.N.Saha Center of Space Studies, IIDS, Nehru Science Center, University of Allahabad, Allahabad-211002, INDIA.

Laser-induced Chlorophyll fluorescence (LICF) spectra of Cajanus cajan L leaves treated with different concentrations of Cd (0.05, 0.5 and 1 mM) are recorded at 10 and 20 days after first treatment of cadmium. LICF spectra are recorded in the region of 650-780 nm using violet diode laser (405 nm). LICF spectra of plant leaves show two maxima near 685 and 730 nm\textsuperscript{a}. Fluorescence induction kinetics (FIK) curve are recorded at 685 and 730 nm with red diode laser (635 nm) for excitation. The fluorescence intensity ratios (FIR) F685/F730 are calculated from LICF spectra and vitality index (Rfd) are determined from FIK curve. FIR and Rfd value are good stress indicator of plant health\textsuperscript{b,c}. These parameters along with chlorophyll content are used to analyze the effect of Cd on wheat plants. The result indicates that higher concentrations of Cd hazardous for photosynthetic activity and health of Arhar plants. The lower concentration of 0.05 mM shows stimulatory response up to 10 days while after 20 days this concentration also shows inhibitory response.

\textsuperscript{a}R. Gopal, K. B. Mishra, M. Zeeshan, S. M. Prasad, and M. M. Joshi Curr. Sci. 83, 880, 2002
\textsuperscript{b}K. B. Mishra and R. Gopal Int. J. Rem. Sen. 29, 157, 2008
OSCILLATOR STRENGTHS AND PREDISSOCIATION RATES FOR RYDBERG TRANSITIONS IN CO BETWEEN 930 AND 935 Å

S. R. FEDERMAN, Y. SHEFFER, Department of Physics and Astronomy, University of Toledo, Toledo, OH 43606; M. EIDELSBERG, J. L. LEMAIRE, F. ROSTAS, Observatoire de Paris Meudon and Université de Cergy-Pontoise; J. H. FILLION, Université UMPC, Paris VI.

CO is used as a probe of astronomical environments ranging from planetary atmospheres and comets to interstellar clouds and the envelopes surrounding stars near the end of their lives. One of the processes controlling the CO abundance and the ratio of its isotopologues is photodissociation. Accurate oscillator strengths and predissociation rates for Rydberg transitions are needed for modeling this process. We present initial results of a survey to obtain the necessary data for transitions in $^{12}$C$^{16}$O, $^{13}$C$^{16}$O, and $^{13}$C$^{18}$O. Data on a series of overlapping bands between 930 and 935 Å were acquired at the DESIRS beam-line on the SOLEIL synchrotron. A VUV Fourier Transform Spectrometer provided a resolving power of about 300,000; this resolution greatly aided our ability to disentangle absorption from the overlapping bands. Absorption bands were analyzed by synthesizing the profiles with codes developed independently in Meudon and Toledo. The synthetic spectra were based on tabulated spectroscopic data. Each synthetic spectrum was adjusted to match the experimental one in a non-linear least-squares fitting procedure with the band oscillator strength and the line width (instrumental, thermal, and predissociation) as free parameters. We will compare our results to previous ones and will describe future directions for this effort.

---

EXOTIC METAL MOLECULES IN OXYGEN-RICH ENVELOPES: DETECTION OF AlOH ($X^1\Sigma^+$) IN VY CANIS MAJORIS

E. D. TENENBAUM and L. M. ZIURYS, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.

A new interstellar molecule, AlOH, has been detected toward the envelope of VY Canis Majoris, an oxygen-rich red supergiant. Three rotational transitions of AlOH were observed using the facilities of the Arizona Radio Observatory (ARO). The $J = 9 \rightarrow 8$ and $J = 7 \rightarrow 6$ lines at 1 mm were measured with the ARO Submillimeter Telescope (SMT), while the $J = 5 \rightarrow 4$ transition at 2 mm was observed with the ARO 12 m antenna on Kitt Peak. The AlOH spectra exhibit quite narrow line widths, indicating that the emission arises from within the dust acceleration zone of the central circumstellar outflow. From a radiative transfer analysis, the abundance of AlOH relative to H$_2$ was found to be $1 \times 10^{-7}$ for a source size of 0.26″ or 22 R$_*$, AlOH is likely formed just beyond the photosphere via thermodynamic equilibrium chemistry, and then disappears due to dust condensation. The AlOH/AIO abundance ratio found in VY CMa is ~17. LTE calculations predict the monohydroxides should be the major carriers of Al, Ca, and Mg in O-rich envelopes, as opposed to the oxides or halides.
CONFIRMATION OF KCN IN THE CIRCUMSTELLAR ENVELOPE OF IRC+10216

R. L. PULLIAM, L. M. ZIURYS, Department of Chemistry and Biochemistry, Department of Astronomy, Steward Observatory, University of Arizona, Tucson, AZ 85721; C. SAVAGE, Applied Electromagnetics (IAT-2), Los Alamos National Laboratory, Los Alamos, NM 87545.

Over the past few years, there has been discussion about the presence of KCN in IRC+10216. To settle the issues on this matter, additional observations have been conducted for KCN and a definitive identification has been made. KCN is a T-shaped, closed shell asymmetric top. A total of ten rotational transitions have been searched for in the frequency range of 85-250 GHz using the Arizona Radio Observatory (ARO) 12m telescope on Kitt Peak and the Submillimeter Telescope (SMT) on Mt. Graham. Emission was detected at all transitions observed, with six blended features and four uncontaminated lines. Transitions for both the $K_a=0$ and $K_a=1$ levels were detected. Line intensities ranged from 0.6 mK to 2 mK. A few lines observed required integration times of 200 hours or more to achieve the necessary signal-to-noise ratio, demonstrating the stability of ALMA technology. KCN is the fifth metal cyanide/isocyanide identified in circumstellar gas, along with MgNC, MgCN, NaCN, and AlNC. Derived column densities and abundances will be reported and the significance of this detection will be discussed.

CS AND HCO$^+$ IN PLANETARY NEBULAE


Although the majority of stars in our Galaxy will end their lives as planetary nebulae (PNe), the molecular content of these sources is not well understood. At first glance, the high ultraviolet radiation field originating from the dying star as it becomes a white dwarf should photodissociate any molecules in the remnant AGB shell. However, molecular line studies of the Helix Nebula suggest that this picture is too simplistic. To further examine the question of molecular survival in PNe, molecular line observations are currently being carried out for CS and HCO$^+$ in a number of planetary nebulae using the Arizona Radio Observatory (ARO) telescopes. CS and HCO$^+$ have been detected so far in four PNe with some sources exhibiting interesting line profiles. A summary of current observations and an analysis of chemical complexity as a function of nebula age will be given.

COMPARING THE ORTHO-TO-PARA RATIOS OF H$_2$ AND H$_3^+$ IN DIFFUSE INTERSTELLAR CLOUDS

NICK INDRIOLO, Department of Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801; TAKESHI OKA, Department of Astronomy & Astrophysics and Department of Chemistry, University of Chicago, Chicago, IL 60637; THOMAS R. GEBALLE, Gemini Observatory, Hilo, HI 96720; KENNETH H. HINKLE, National Optical Astronomy Observatories, Tucson, AZ 85726; GEOFFREY A. BLAKE, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125; BENJAMIN J. McCALL, Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

The ratio between the populations of the two lowest rotational levels of H$_2$, $J = 0$ and $J = 1$, can be used to determine the temperature of interstellar gas (referred to as $T_{01}$). Likewise, a temperature can be inferred from the populations of the $(J, K) = (1, 0)$ and $(J, K) = (1, 1)$ states of H$_3^+$. However, the average temperatures derived from these methods ($T_{01} \approx 60$ K, $T(H_3^+) \approx 30$ K) do not agree. Theories predict that the deviation from a Boltzmann distribution in both species is due to collisions between H$_2$ and H$_3^+$ which can change the spin alignment. Recent laboratory results confirm this deviation from a thermal distribution, and provide a relationship between the $(1,0)/(1,1)$ ratio of H$_3^+$ and the $(1)/(0)$ ratio of H$_2$. We have made observations searching for H$_3^+$ in several sight lines with measured H$_2$ abundances for the purpose of determining this relationship in interstellar clouds. With such a relationship, we then show that IR observations probing the $(1,0)$ and $(1,1)$ states of H$_3^+$ can be used to estimate the H$_2$ temperature in highly extinguished sight lines where UV spectroscopy is not possible.
THE NEARLY PERFECT CORRELATION BETWEEN THE DIFFUSE INTERSTELLAR BANDS $\lambda\lambda$ 6196.0 AND 6613.6

BENJAMIN J. MCCALL, University of Illinois at Urbana-Champaign, Urbana, IL 61801; MEREDITH M. DROSBACK, University of Virginia, Charlottesville, VA 22904; JULIE A. THORBURN, Carthage College, Kenosha, WI 53140; DONALD G. YORK, University of Chicago, Chicago, IL 60637; SCOTT D. FRIEDMAN, Space Telescope Science Institute, Baltimore, MD 21218; LEWIS M. HOBBS, University of Chicago, Yerkes Observatory, Williams Bay, WI 53191; BRIAN L. RACHFORD, Embry-Riddle Aeronautical University, Prescott, AZ 86301; THEODORE P. SNOW, University of Colorado, Boulder, CO 80309; PAULE SONNENTRUCKER, Johns Hopkins University, Baltimore, MD 21218; DANIEL E. WELTY, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

As part of our long-term survey of the diffuse interstellar bands (DIBs) at the Apache Point Observatory, we found that the equivalent widths of $\lambda\lambda$ 6196.0 and 6613.6 are extremely well correlated, with a correlation coefficient of 0.986 in a diverse sample of 114 diffuse cloud sightlines. The observations are statistically consistent with a perfect correlation if the observational errors have been underestimated by a factor of two. The quality of this correlation far exceeds other previously studied correlations, for example those between the $\lambda$ 5780.5 DIB and quantities such as the color excess or atomic hydrogen column density. The very tight correlation between these two DIBs strongly suggests that they may represent the first pair of DIBs known to be caused by the same molecular carrier. However, an explanation of how a single carrier can produce bands with such different linewidths and band shapes is still needed.

A NEW ATLAS OF THE DIFFUSE INTERSTELLAR BANDS: HD 183143

LEWIS M. HOBBS, University of Chicago, Yerkes Observatory, Williams Bay, WI 53191; DONALD G. YORK, University of Chicago, Chicago, IL 60637; JULIE A. THORBURN, Carthage College, Kenosha, WI 53140; THEODORE P. SNOW, University of Colorado, Boulder, CO 80309; MICHAEL BISHOF, University of Chicago, Chicago, IL 60637; SCOTT D. FRIEDMAN, Space Telescope Science Institute, Baltimore, MD 21218; BENJAMIN J. MCCALL, University of Illinois at Urbana-Champaign, Urbana, IL 61801; TAKESHI OKA, University of Chicago, Chicago, IL 60637; BRIAN L. RACHFORD, Embry-Riddle Aeronautical University, Prescott, AZ 86301; PAULE SONNENTRUCKER, Johns Hopkins University, Baltimore, MD 21218; DANIEL E. WELTY, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

We present our second catalog\(^a\) of the diffuse interstellar bands (DIBs), based on high signal-to-noise ratio echelle spectra of HD 183143 obtained at the Apache Point Observatory. This catalog complements our first catalog\(^b\), which was based on spectra of HD 204827. Unlike the sightline towards HD 204827, which hosts a high column density of C\(_2\) and C\(_3\), the sightline towards HD 183143 has no detectable amount of carbon chain molecules and therefore samples a somewhat chemically distinct environment.

Our catalog of HD 183143 contains 414 DIBs, of which 135 (or 33\%) were not reported in four previous modern DIB surveys. When combined with our catalog of HD 204827, the total number of distinct DIBs observed is $\sim$545. Our collaboration’s website at http://dibdata.org contains a complete listing of the properties of the observed DIBs in tabular format, PDF files containing the observed spectra, and an interactive spectral plotting tool that enables users to rescale the spectra. Our hope is that this dataset will facilitate the comparison of laboratory molecular spectra with the astronomical observations, and ultimately the identification of the molecular carriers of the DIBs.

\(^a\) L. M. Hobbs et al., Astrophysical Journal 705, 32-45 (2009)
**WG08**

NH AND CH IN THE ACE SATELLITE SOLAR SPECTRUM

P. F. BERNATH, Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK; R. S. RAM, Department of Chemistry, University of Arizona, Tucson, AZ 85721, USA; R. COLIN, Service de Chimie Quantique et Photophysique, Université Libre de Bruxelles (ULB), 50, av. F.D. Roosevelt, 1050 Brussels, Belgium.

The Canadian ACE (Atmospheric Chemistry Experiment) mission has a high resolution (0.02 cm\(^{-1}\)) Fourier transform spectrometer (FTS) in low earth orbit. The primary ACE mission goal is the study ozone chemistry in the stratosphere although it is making a wide range of other measurements, for example, of organic molecules in the troposphere. In the normal operating mode, the ACE-FTS measures a sequence of atmospheric absorption spectra during sunrise and sunset ("solar occultation"). As part of the measurement sequence about 16 high sun exoatmospheric spectra are recorded for each occultation to serve as reference spectra. We have co-added 224782 pure solar spectra to produce the ACE solar atlas in the 750–4400 cm\(^{-1}\) spectral region [Hase et al., JQSRT 111, 521 (2010), see http://www.ace.uwaterloo.ca/solaratlas.html]. The ACE solar spectrum displays prominent vibration-rotation bands of CO, OH, NH and CH, and pure rotational lines of OH and NH. An improved spectroscopic analysis for OH has already been published [Bernath and Colin, JMS 257, 20 (2009)] and we now report on similar work for NH and CH. The vibration-rotation spectra of NH have been re-investigated using laboratory spectra and infrared solar spectra recorded from orbit by the ACE and ATMOS instruments. In addition to identifying the previously unobserved 6 \(-\) 5 vibration-rotation band in the laboratory spectra, many additional high N rotational lines have been observed. By combining the new observations with the previously published data and recent far infrared data, an improved set of molecular constants and term values have been derived for the NH X\(^3\Sigma^-\) and A\(^3\Pi\) states.

Vibration-rotation spectra of the CH \(^1\Pi\) ground state have also been re-analyzed based on laboratory spectra, the ACE solar spectrum and published data. The previously unobserved 5 \(-\) 4 band has been measured and the other four bands (1 \(-\) 0 to 4 \(-\) 3) have been extended to higher J values.

**WG09**

THE GAS-PHASE SPECTRA OF RESONANCE-STABILIZED RADICALS AND THE RED RECTANGLE EMISSION

NAHID CHALYAVI, TYLER P. TROY, MASAKAZU NAKAJIMA, KLAAS NAUTA, SCOTT H. KABLE, and TIMOTHY W. SCHMIDT, School of Chemistry, The University of Sydney, NSW 2006, Australia.

Alpha aromatic radicals may explain some of the emission features of Red Rectangle (RR), a nearby protoplanetary nebulae. Erosion of amorphous hydrogenated carbon may lead to resonance-stabilized products by breaking aliphatic side-chains to aromatic “islands”. The resulting radicals may be excited by starlight to give rise to the characteristic emissions. As a part of the ongoing research \(^a\) \(^b\) and in order to investigate this hypothesis, the gas-phase excitation and emission spectra of some of these radicals have been identified in a molecular beam using laser induced fluorescence (LIF) spectroscopy. Resonance-stabilized 1-naphthylmethyl, 2-naphthylmethyl and acenaphthyl radicals were produced from the discharge of 1-methylnaphthalene, 2-methylphenyl and acenaphthene precursors in argon, respectively. In order to determine the ground state vibrational energies of these species, their fluorescence bands were dispersed. The results are consistent with the Density Functional Theory (DFT) calculated ground state frequencies. As a complementary experiment, and to further confirm the identity of the spectral carriers, resonant two color two photon ionization (R2C2PI) spectra were also recorded. The origin bands of all these three molecules show up in the 5790 - 5840 Å range of the spectrum, the well-known RR emission region.

MOLECULAR HYDROGEN FORMATION IN THE EARLY UNIVERSE: NEW IMPLICATIONS FROM LABORATORY MEASUREMENTS

HOLGER KRECKEL, HJALMAR BRUHNS, KENNETH A. MILLER, DANIEL W. SAVIN, Columbia Astrophysics Laboratory, Columbia University, New York, NY 10027, USA; MARTIN CIZEK, Charles University Prague, Faculty of Mathematics and Physics, Institute of Theoretical Physics, 180 00 Praha 8, Czech Republic; SIMON C.O. GLOVER, Zentrum für Astronomie der Universität Heidelberg, Institut für Theoretische Astrophysik, 69120 Heidelberg, Germany; XAVIER URBAIN, Department of Physics/PAMO, Université Catholique de Louvain, Louvain-la-Neuve B-1348, Belgium.

We have performed the first energy-resolved measurement of the associative detachment (AD) reaction $\text{H}^- + \text{H} \rightarrow \text{H}_2 + e^-$. This reaction is the dominant formation pathway for $\text{H}_2$ during the epoch of first star formation in the early universe. Despite being the most fundamental anion-neutral reaction in chemistry, experiment and theory have failed to converge in both magnitude and energy dependence for this process. The uncertainty in the rate coefficient of the AD reaction severely limits our understanding of the formation of the first stars and protogalaxies.

To address this issue we have developed a dedicated merged beams apparatus utilizing photodetachment to create a strong ground state H atom beam. Kinematical compression in a collinear beams arrangement allows us to cover the entire relevant collision energy range from 4 meV to 1 eV. We will give an overview of the technique and compare the experimental results to theoretical calculations. We will present a new experimentally confirmed thermal rate coefficient for the AD process and outline its implications for early universe cosmological models.

*Present address: Department of Chemistry, University of Illinois, Urbana, IL 61801, USA, Email: hkreckel@illinois.edu
WH. MICROWAVE (ROTATIONAL)
WEDNESDAY, JUNE 23, 2010 – 1:30 pm
Room: 1000 McPHERSON LAB

Chair: STEPHEN COOKE, University of North Texas, Denton, Texas

WH01  15 min  1:30
MICROWAVE STUDY OF A HYDROGEN-TRANSFER-TRIGGERED METHYL-GROUP INTERNAL ROTATION IN 5-METHYLTROPOLONE

VADIM V. ILYUSHIN, INSTITUTE OF RADIO ASTRONOMY OF NASU, CHERVONOPRAPORNA 4, 61002 KHARKOV, UKRAINE; EMILY A. CLOESSNER, DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY, COLLEGE OF CHARLESTON, CHARLESTON, SC 29424, USA; YUNG-CHING CHOU, DEPARTMENT OF NATURAL SCIENCE, TAIPEI MUNICIPAL UNIVERSITY OF EDUCATION, TAIPEI 10048, TAIWAN; LAURA B. PICRAUX, SUN CHEMICAL, CINCINNATI, OH 45232, USA; JON T. HOUGEN, OPTICAL TECHNOLOGY DIVISION, NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY, GAITHERSBURG, MD 20899-8441, USA; RICHARD LAVRICH, DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY, COLLEGE OF CHARLESTON, CHARLESTON, SC 29424, USA.

We present here the first experimental and theoretical study of the microwave spectrum of 5-methyltropolone, which can be visualized as a 7-membered aromatic carbon ring with a five-membered hydrogen-bonded cyclic structure at the top and a methyl group at the bottom. The molecule exhibits two large-amplitude motions, an intramolecular hydrogen transfer and a methyl torsion. The former motion is particularly interesting because transfer of the hydrogen atom from the hydroxyl to the carbonyl group induces a tautomerization in the molecule, which then triggers a 60° internal rotation of the methyl group. Measurements were carried out by Fourier-transform microwave spectroscopy in the 8 to 24 GHz frequency range. Theoretical analysis was carried out using a tunneling-rotational Hamiltonian based on a G12 extended-group-theory formalism. Our global fit of 1015 transitions to 20 molecular parameters gave a root-mean-square deviation of 1.5 kHz. The tunneling splitting of the two $J = 0$ levels arising from a hypothetical pure hydrogen transfer motion is calculated to be 1310 MHz. The tunneling splitting of the two $J = 0$ levels arising from a hypothetical pure methyl-top internal rotation motion is calculated to be 885 MHz. Some theoretical difficulties in interpreting the low-order tunneling parameters in this and the related molecule 2-methylmalonaldehyde will be discussed.

WH02  10 min  1:47
ROTATIONAL SPECTRA AND MOLECULAR CONFORMATION OF TWO CONFORMERS OF LEUCINAMIDE

ANDREW R. CONRAD and MICHAEL J. TUBERGEN, Department of Chemistry, Kent State University, Kent, Ohio 44242; RICHARD J. LAVRICH, Department of Chemistry and Biochemistry, College of Charleston, 66 George Street, Charleston, South Carolina 29424.

The rotational spectra of the parent species of two conformers of the amino acid derivative leucinamide have been recorded between 10.5 and 20 GHz using a Balle-Flygare Fourier-transform microwave spectrometer. 6 a- and b-type rotational transitions were recorded for conformer I and 23 a- and b-type rotational transitions were recorded for conformer II. The rotational constants are $A = 2274.94(9)$ MHz, $B = 1033.336(7)$ MHz, and $C = 911.732(3)$ MHz and $A = 2752.775(8)$ MHz, $B = 843.502(1)$ MHz, and $C = 796.721(1)$ MHz for conformers I and II respectively. The congested hyperfine patterns arising from the two $^{14}$N nuclei were not resolved. Comparison of the experimental moments of inertia to those derived from the lowest energy ab initio (MP2/6-311++G(d,p)) structures indicates gas-phase backbone structures that differ from both the crystal structures of leucinamide$^a$ and the gas-phase structures of the amino acid leucine$^b$.

WH03

MICROWAVE SPECTRUM, STRUCTURAL PARAMETERS AND QUADRUPOLE COUPLING FOR AZABORINE AND 1-ETHYL-AZABORINE

ADAM DALY, STEPHEN G. KUKOLICH, Department of Chemistry and Biochemistry, The University of Arizona, Tucson, Arizona 85721; CHAKREE TANJAROON, Department of Chemistry and Physics, Arkansas State University, Jonesboro, AR 72467; ADAM J. V. MARWITZ and SHIH-YUAN LIU, Department of Chemistry, University of Oregon, Eugene, OR 97403.

The first microwave spectra for the unusual and elusive aromatic molecules, 1,2-dihydro-1,2-azaborine (azaborine) and 1-ethyl-azaborine have been measured, in the 7-18 GHz range, providing accurate rotational constants, nitrogen and boron quadrupole coupling strengths, important bond lengths and other structural parameters. Azaborine (BNC\textsubscript{4}H\textsubscript{6}) is an aromatic, B-N substituted analog of benzene, the quintessential aromatic molecule. The experimental bond lengths determined for azaborine are: R(B-N) = 1.45(3) Å, R(B-C) = 1.51(1) Å, and R(N-C) = 1.37(3) Å. Accurate measurements of \textsuperscript{14}N, \textsuperscript{11}B, and \textsuperscript{10}B nuclear quadrupole coupling were obtained. The inertial defect $\Delta = 0.02$ amu Å\textsuperscript{2} indicating a planar structure. A Townes-Dailey population analysis of the B and N quadrupole coupling constants provided the valence p-electron occupancy.

"Supported by THE NATIONAL SCIENCE FOUNDATION"

WH04

ROTATIONAL INVESTIGATION OF TROPANE ALKALOIDS

EMILIO J. COCINERO, Departamento de Química Física, Universidad del País Vasco, 48080 Bilbao, Spain; ALBERTO LESARRI, Departamento de Química Física y Química Inorgánica, Universidad de Valladolid, 47011 Valladolid, Spain; PATRICIA ECÍJA, Departamento de Química Física, Universidad del País Vasco, 48080 Bilbao, Spain; JENS-UWE GRABOW, Institut für Physikalische Chemie und Elektrochemie, Gottfried-Wilhelm-Leibniz-Universität Hannover, Callinstraße 3A, 30167 Hannover, Germany; JOSE A. FERNÁNDEZ, FERNANDO CASTANO, Departamento de Química Física, Universidad del País Vasco, 48080 Bilbao, Spain.

We report an investigation of the rotational spectrum of several tropane alkaloids using the new Balle-Flygare-type FT-MW spectrometer\textsuperscript{a} built at the University of the Basque Country. The initial work focused on the azabicycles of tropinone, scopine and scopoline, vaporized using heating methods. For tropinone\textsuperscript{b} the spectrum confirmed the presence of equatorial and axial conformers originated by the inversion of the N-methyl group, with the tropane motif adopting a distorted chair configuration. The determination of substitution and effective structures for the two conformers included the \textsuperscript{13}C, \textsuperscript{15}N and \textsuperscript{18}O isotopomers observed in natural abundance. The structures revealed the flexibility and structural changes associated to the N-methyl inversion, mostly a flattening at the nitrogen atom and a simultaneous rising of the carbonyl group in the axial form. The investigation of scopine gave an intense spectrum, but it was inconsistent with the structural models expected for this molecule. The carrier of the new spectrum was later identified as scopoline, generated \textit{in situ} by an intramolecular reaction at the moderate temperatures of the nozzle. A single conformation was detected for scopoline, with an ether bridge seriously distorting the tropane motif.

\textsuperscript{a}E. J. Cocinero, A. Lesarri, P. Écija, J.-U. Grabow, J. A. Fernández, F. Castaño, in publication, 2010

WH05 10 min 2:33

CONFORMATIONAL LANDSCAPE OF NICOTINOIDs: SOLVING THE "CONFORMATIONAL DISPARITY" OF ANABASINE

ALBERTO LESARRI, Departamento de Química Física y Química Inorgánica. Universidad de Valladolid, 47011 Valladolid, Spain; EMILIO J. COCINERO, Departamento de Química Física, Universidad del País Vasco, 48080 Bilbao, Spain; LUCA EVANGELISTI, Dipartimento di Chimica "G. Ciamiciam", Università di Bologna, 40126 Bologna, Italy; RICHARD D. SUENRAM, Department of Chemistry, University of Virginia, Charlottesville, VA 22904, USA; WALTER CAMINATI, Dipartimento di Chimica "G. Ciamiciam", Università di Bologna, 40126 Bologna, Italy; JENS-UWE GRABOW, Institut für Physikalische Chemie und Elektrochemie, Gottfried-Wilhelm-Leibniz-Universität Hannover, Callinstrasse 3A, 30167 Hannover, Germany.

The conformational landscape of the alkaloid anabasine (neonicotine) has been investigated using rotational spectroscopy and ab initio calculations. The results allow a detailed comparison of the structural properties of the prototype piperidinic and pyrrolidinic nicotinoids (anabasine vs. nicotine\(^a\)). Anabasine adopts two most stable conformations in isolation conditions, for which we determined accurate rotational and nuclear quadrupole coupling parameters. The preferred conformations are characterized by an equatorial pyridine moiety and additional N-H equatorial stereochemistry at the piperidine ring (Eq-Eq). The two rings of anabasine are close to a bisecting arrangement, with the observed conformations differing in a ca. 180° rotation of the pyridine subunit, denoted either Syn or Anti. The preference of anabasine for the Eq-Eq-Syn conformation has been established by relative intensity measurements (\(\text{Syn}/\text{Anti} \sim 5(2)\)). The conformational preferences of free anabasine are directed by a N···H-C weak hydrogen bond interaction between the nitrogen lone pair at piperidine and the closest hydrogen bond in pyridine, with N···N distances ranging from 4.750 Å (Syn) to 4.233 Å (Anti).

\(^a\) R. J. Lavrich, R. D. Suenram, D. F. Plusquellic and S. Davis, 58th OSU Int. Symp. on Mol. Spectrosc., Columbus, OH, 2003, Comm. RH13

WH06 15 min 2:45

MICROWAVE SPECTROSCOPY OF ALKALOIDS: THE CONFORMATIONAL SHAPES OF NICOTINE


Nicotinoid alkaloids consist of two ring systems connected via a \(C – C\) \(\sigma\)-bond: Joining pyridine either with a (substituted) pyrrolidine or piperidine ring system, pyrrolidinic or piperidinic nicotinoids are formed. Nicotine itself, consisting of pyridine and N-methylpyrrolidine, is the prototype pyrrolidinic nicotinoid. Its coupled heteroaromatic and heteroaliphatic ring systems exhibit three sites that allow for conformational flexibility: (I) puckering of the pyrrolidine ring (Eq./Ax. positions of the pyridine), (II) inversion of the N-methyl group (Eq./Ax. positions of the hydrogen), and (III) relative orientation of the two rings (Syn-Anti).

Two conformations of nicotine have been observed using the In-phase/quadrature-phase-Modulation Passage-Acquired-Coherence Technique (IMPACT) Fourier Transform Microwave (FTMW) spectrometer in Valladolid. The preferred conformations\(^a\) are characterized by an equatorial (Eq.) pyridine moiety and equatorial (Eq.) \(N – CH_3\) stereochemistry. The planes of two rings are almost perpendicular with respect to each other while exhibiting two low energy conformations, Syn and Anti, that differ by a 180 rotation about the \(C – C\) \(\sigma\)-bond. The Eq.-Eq. conformational preference is likely due to a weak hydrogen bond interaction between the nitrogen lone pair at the N-methylpyrroline and the closest hydrogen in pyridine. Supporting quantum-chemical calculations are also provided.

\(^a\) Lavrich, R. J.; Suenram, R. D.; Plusquellic, D. F.; Davis, S. 58th International Symposium on Molecular Spectroscopy, Columbus, OH 2003, RH13.
LARGE AMPLITUDE MOTIONS AND INFORMATION TRANSFER ALONG CONJUGATED BONDS: THE CASE OF PARATOLUALDEHYDE

HILKKA SAAL, JENS-UWE GRABOW, Gottfried-Wilhelm-Universität, Institut für Physikalische Chemie und Elektrochemie, Lehrgebiet A, Callinstraße 3A, D-30167 Hannover, Germany; ANGELA R. HIGHT-WALKER, JON T. HOUGEN, Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441, USA; WALTHER CAMINATI, Universita di Bologna, Dipartimento di Chimica G. Cianci, via F. Selmi 2, 40126 Bologna, Italy; ISABELLE KLEINER, Laboratoire Interuniversitaire des Systèmes Atmosphériques, CNRS et Universités Paris 7 et Paris 12, 61 av. Général de Gaulle, 94010 Créteil, France.

Historically, barriers to large amplitude motions are often related, using steric hinderance arguments, to the local atom arrangement. More recently, large changes have been found in the barrier inhibiting methyl rotation, when electronic excitation or ionization of a substituted toluene occurs, suggesting molecular orbital occupancy as a dominant factor in aromatic molecules. Theoretically, the relation can also be made to the molecular orbital and electron density structure.

Experimentally, we examine the situation by comparing toluene with paratolualdehyde. In particular, the barrier in toluene, \( \text{CH}_3 - \text{C}_6\text{H}_5 \), is six-fold by symmetry. In paratolualdehyde, \( \text{CH}_3 - \text{C}_6\text{H}_4 - \text{CHO} \), the aldehyde group is far enough from the methyl rotor that direct through-space interactions should be rather small. Thus, a three-fold contribution to the barrier would leave electron orbital effects in the \( \pi \)-system as the primary causal agent.

Microwave spectroscopy is well suited for discriminating between \( V_3 \) and \( V_6 \) contributions - but only if torsionally exited states can be accessed which typically requires temperatures much higher that those encountered in pulsed-jet expansions. Thus, the supersonic-jet FT-MW spectrometers in Hannover and Gaithersburg as well as the free-jet CW mm-wave spectrometer in Bologna were needed to take the spectra. Analyzing 5 torsional species using the Belgi program, the barrier was found to vastly be dominated by the \( V_3 \) vs. a minor \( V_6 \) contribution, thus revealing the information transfer though conjugated \( \pi \)-electron systems.

---

DDS-BASED FAST SCAN SPECTROMETER

E. A. ALEKSEEV, Institute of Radio Astronomy of NASU, Chervonopravorna 4, 61002 Kharkov, Ukraine; R.A. MOTIYENKO, L. MARGULÈS, Laboratoire PhLAM, CNRS UMR 8523, Université de Lille 1, 59655 Villeneuve d’Ascq Cedex, France.

The technique of direct digital synthesis (DDS) has two important features which enable its application in microwave spectroscopy: micro-Hz tuning resolution and extremely fast frequency switching with continuous phase. We have applied a direct digital synthesizer in a PLL-spectrometer based on backward-wave oscillator (BWO). As result we have obtained an instrument that can cover a 100 GHz bandwidth in less than one hour with high spectral resolution and high precision of frequency measurement. The application of the spectrometer to sub-millimeter wave survey spectra records of several isotopic species of astrophysical molecules (methanol, formamide, methyl formate, aziridine) will be discussed.

The support of Université de Lille 1 and le Programme National de Physique Chimie du Milieu Interstellaire is gratefully acknowledged.
New opportunities are provided by the development of higher power THz frequency multiplier sources, the development of a broadband Chirped-Pulse FT MW spectroscopy technique at microwave and mmWave frequencies, and recently demonstrated heterodyne hot electron bolometer detection technology in the THz frequency region with near quantum noise-limited performance and high spectral resolution. Combining these three technologies and extending the chirped-pulse technique to 0.85 THz enables a host of new applications. NIST is currently pursuing applications as a point sensor for greenhouse gases, volatile organic compounds, and potentially human breath. The generation and detection of phase stable chirped pulses at 850 GHz will be demonstrated. A description of the experimental setup and preliminary data will be presented for nitrous oxide.


We have developed a radiometer-type spectrometer. The method is suitable for absolute spectral line measurement so that the information on the rotational partition function can be directly obtained. In our systems for 375-490 GHz band a spectral image of 600 MHz bandwidth can be obtained as 10000 spectral channel data, with being calibrated along frequency and intensity axis.

Well known interstellar molecule, methyl formate has a number of low-lying states and many transitions are left unassigned. We recorded rotational spectrum of this molecule in emission by our spectrometer, with changing pressure and temperature of the sample in order to facilitate the assignment. Our experimental results are compared to the ab initio MO calculations.
W1. MINI-SYMPOSIUM: METAL CONTAINING MOLECULES
WEDNESDAY, JUNE 23, 2010 – 1:30 pm
Room: 1015 McPHERSON LAB
Chair: J. MATHIAS WEBER, JILA, University of Colorado, Boulder, Colorado

W101 INVITED TALK 30 min 1:30
UNUSUAL BONDING MECHANISMS IN BERYLLIUM COMPOUNDS

IVAN O. ANTONOV, BEAU J. BARKER, VLADIMIR E. BONDYBEY, JEREMY M. MERRITT and MICHAEL C. HEAVEN, Department of Chemistry, Emory University, Atlanta, GA 30322.

Metal clusters and small molecules that involve Be exhibit unusual bonding characteristics. For example, the Be$_2$ dimer exhibits a weak bond, short equilibrium bond length and an atypical potential energy curve. Although the bond is weak, the dissociation energy of Be$_2$ exceeds that of Mg$_2$ by a factor of two. Be$_2$O is more strongly bound than would be expected on the basis of simple molecular orbital theory, and higher level theoretical calculations indicate that it has a highly multi-reference ground state. Indeed, calculations for many Be species indicate multi-reference character. To obtain results that are even qualitatively correct often requires the correlation of all electrons and the use of basis sets that include at least triple excitations. Consequently, spectroscopic data for these molecules provide a valuable set of benchmarks for the evaluation of highly correlated, multi-reference computational techniques.

We are currently exploring the characteristics of Be compounds using electronic spectroscopy and photoionization techniques. The species being investigated include Be$_2$O, BeC and BeOH. Experimental results and theoretical calculations for these molecules will be presented, along with a progress report for studies of larger Be clusters.

W102 15 min 2:05
PFI-ZEKE SPECTROSCOPY OF Be$_2$O

I. O. ANTONOV, M. C. HEAVEN, Department of Chemistry, Emory University, Atlanta, GA 30322.

The PFI-ZEKE spectrum of Be$_2$O$^+$ ion was recorded to obtain accurate ionization energy for Be$_2$O and vibrational frequency data for Be$_2$O$^+$. A short progression of the bending mode was observed, which included bands involving odd changes in the vibrational quanta. This observation indicates that the ion and/or the intermediate state used in the excitation process deviate from D$_{∞h}$ symmetry.

W103 15 min 2:22
VIBRATIONAL SPECTROSCOPY OF BINARY METAL OXIDE CLUSTERS

L. JIANG, T. WENDE, G. MEIJER, K. R. ASMIS, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany; P. CLAES, S. BHATTACHARYY, P. LIEVENS, Laboratorium voor Vaste-Stoffysica en Magnetisme, Katholieke Universiteit Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium.

Cerium oxide is one of the most reactive rare earth metal oxides and is commonly used as a support material for metals and metal oxides in heterogeneous catalysis. In many cases it is not chemically inert, but directly participates in the catalytic process. The well-known difficulty of quantum chemical approaches for f-element containing molecules remains unresolved. In order to investigate the electronic and geometric structure and deliver benchmark vibrational frequencies for testing the accuracy of density functional theory calculations, infrared photodissociation spectra of rare gas tagged binary (CeO$_2$)(VO$_2$)$_{2/3}$ and (Ce$_2$O$_3$)(VO$_2$)$_2^+$ clusters are measured in the 400 to 1200 wave number range. The first cluster contains no electron in either the Ce-f or V-d orbitals. As the number of valence electrons is increased, the question arises, which orbital the additional electrons prefers, i.e., which atom is preferentially reduced. The present results are compared to the previously determined structures of the respective monometal oxide clusters.
ELECTRONIC SPECTROSCOPY OF Li(NH$_3$)$_4$

N. BHALLA, L. VARRIALE, N. M. TONGE, A. M. ELLIS, Department of Chemistry, University of Leicester, Leicester, LE1 7RH, United Kingdom.

Li(NH$_3$)$_4$ has been proposed as a key entity in lithium-ammonia solutions, but its spectral signature has so far proved impossible to distinguish from other species in these solutions. Here we present the first electronic spectrum of Li(NH$_3$)$_4$ in the gas phase in an effort to understand the electronic structure of this important cluster. This spectrum was recorded using mass-selective depletion spectroscopy. Strong absorption is observed in the near-infrared and the band system is assigned to the $\tilde{A}^2T_2 - \tilde{X}^2A_1$ transition in a nominally tetrahedral complex. However, an extensive vibrational progression in a low frequency bending vibration is indicative of a substantial Jahn-Teller effect in the excited electronic state. Our observations confirm a recent theoretical prediction that the electronic spectrum of Li(NH$_3$)$_4$ will strongly overlap with the spectrum of the solvated electron in liquid ammonia.

ACCIDENTAL CONICAL INTERSECTIONS IN MIXED TRIMERS OF POTASSIUM AND RUBIDIUM: A VIBRONTIC ANALYSIS OF THE 4$^4$B$_2$ AND 3$^4$A$_1$ STATES

A. W. HAUSER, G. AUBÖCK, C. CALLEGARI$^a$ and W. E. ERNST, Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria.

We compare the 3$^4$A$_1$ and 4$^4$B$_2$ states of homonuclear and heteronuclear alkali trimers formed of potassium and rubidium. The Multireference Rayleigh Schrödinger Perturbation Theory of second order is applied to obtain the corresponding adiabatic potential energy surfaces. In the case of homonuclear trimers these pairs of states correspond to the two branches of the E$x$e Jahn-Teller distorted 2$^4$E$'$ state. For heteronuclear trimers, the vibrational modes $Q_x$ and $Q_y$ are no longer degenerate, but the two electronic states still show a conical intersection at obtuse (KRb$_2$) or acute (K$_2$Rb) isosceles geometries. Spectroscopic consequences of this situation are discussed, vibronic spectra are predicted and compared to LIF spectra obtained in helium droplet isolation spectroscopy experiments of our group$^{b,c}$.

FEMTOSECOND SPECTROSCOPY OF ALKALI TRIMERS ON HELIUM NANODROPLETS

C. GIESE, B. GRÜNER, L. FECHNER, M. MUDRICH, F. STIENKEMEIER, Physikalisches Institut, Universität Freiburg, Hermann-Herder-Strasse 3, 79104 Freiburg, Germany; A.W. HAUSER and W.E. ERNST, Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria.

Superfluid helium nanodroplets offer the opportunity to study dopant molecules in the sub-Kelvin range with only weak matrix perturbations. Femtosecond wave packet spectroscopy has been shown to be well suited to obtain high resolution vibrational spectra of cold alkali molecules in weakly bound high-spin states$^a$. In a pump-probe scheme a first laser pulse excites a vibrational wave packet that evolves on the molecular potential and is probed by a second ionizing pulse. We present spectroscopic data on Rb$_3$ and K$_3$ showing different vibronic progressions. These are assigned with the help of high level ab initio calculations of the electronic structure of the bare trimers$^b$.

---

$^a$present adress: Sincrotrone Trieste, Strada Statale 14 - km 163.5, 34149 Basovizza, Trieste, Italy


GROWING OF METAL-MOLECULE CLUSTERS IN HELIUM DROPLETS

EVGENY LOGINOV, LUIS GOMEZ and ANDREY VILESOV, Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482.

The utility of a continuous beam of helium droplets for assembly of composite metal-molecular clusters is studied. Clusters of silver having up to about $10^4$ atoms and molecules such as methane, ethane, ethylene and acetylene with up to $10^4$ were obtained via sequential pickup of molecules by He droplets with average sizes in the range of $10^5$ to $10^7$ atoms. The IR spectra of the formed clusters showed a splitting of the C-H band, which we ascribed to molecules in the first layer in immediate contact with the surface of the metal clusters and to molecules in subsequent layers. Applications of this technique to a broader range of metal-molecule composites and surface deposition of formed clusters are discussed.

IR SPECTRA OF LARGE TAILOR-MADE Ag-MOLECULE (METHANE, ETHANE, ETHYLENE, ACETYLENE) CLUSTERS PRODUCED IN HELIUM NANODROPLETS

EVGENY LOGINOV, LUIS GOMEZ and ANDREY VILESOV, Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482.

Clusters of silver having up to about $10^4$ atoms and molecules such as methane, ethane, ethylene and acetylene with up to $10^4$ were obtained via sequential pickup of molecules by He droplets with average sizes in the range of $10^5$ to $10^7$ atoms. The formed clusters have been studied via infrared spectra in the C-H stretching range of the molecules. The spectra show two distinct features due to molecules on the boundary with silver atoms and those in the volume of the neat molecular part of the clusters. The relative intensities of the peaks allow obtaining of the cluster size, in good agreement with the estimates based on the known binding energies of the clusters. Experiments also suggest that selection rules for infrared transitions for molecules adsorbed on metal surfaces are also valid for silver clusters as small as 100 atoms.
ROVIBRONIC INTERACTIONS IN NO$_3$: HISTORICAL OVERVIEW, PRESENT STATUS AND FUTURE PROSPECT OF HIGH-RESOLUTION SPECTROSCOPIC STUDIES

**EIZI HIROTA**, The Graduate University of Advanced Studies, Hayama, Kanagawa 240-0293, Japan; KEN-TAROU KAWAGUCHI, Department of Chemistry, Faculty of Science, Okayama University, 3-1-1, Tsushima-Naka, Okayama 700-8530, Japan; TAKASHI ISHIWATA, Graduate School of Information Sciences, Hiroshima City University, 3-4-1 Otsuka-Higashi, Hiroshima 731-3194, Japan.

The study started in 1985 with the observation and analysis of a band around 1492 cm$^{-1}$ by our group. Since then, more than ten and five bands were recorded, respectively, for $^{14}$NO$_3$ and $^{15}$NO$_3$ in the infrared. We have found that, although the ground vibronic state is free of any perturbations and conforms with a regular triangle structure of $D_{3h}$ symmetry, the upper states of almost all the infrared bands are more or less perturbed by vibration-rotation interactions and also by rovibrionic interactions with excited electronic states. Although most of the observed bands are by no means easy to analyze, they are well resolved in rotational structure, providing us with clues to assign them. Molecular constants such as rotational and 1-type doubling constants allow us to estimate cubic anharmonic potential constants, some of which obviously originate from excited electronic states through vibronic interactions, and may give us a global view on NO$_3$ in near future.

HIGH-ACCURACY DIABATIC TREATMENT OF NO$_3$ ENERGY LEVELS

**JOHN F. STANTON**, Department of Chemistry & Biochemistry, The University of Texas at Austin, 1 University Station A5300 Austin, TX 78712.

Recent developments in vibronic coupling theory and quantum chemistry now allow the parametrization of vibronic Hamiltonians that are capable of achieving semi-quantitative agreement with experimental energy levels for strongly coupled systems. First applied to the HCO$_2$ and BNB radicals, this sophisticated parametrization has been used for the nitrate radical. Results of calculations bearing on both all electronic states of NO$_3$ below 2 eV will be presented.

SOLVING THE PUZZLE OF TETRATOMIC, 23-VALENCE-ELECTRON MOLECULES

**MARILYN E. JACOX**, Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441.

Because of extensive electron correlation, the ground-state structures, infrared spectra, and chemical bonding properties of a number of tetratomic molecules which possess 23 valence electrons are anomalous. Approaches which have recently been helpful in understanding this phenomenon include ab initio calculations and spectroscopic observations of these species trapped in solid neon at temperatures near 4 K. Molecules for which infrared spectra have been obtained and which will be discussed include NO$_3$, NNO$_2$ anion, BF$_3$ cation, and O$_4$ cation.
The three energetically lowest electronic states \((\tilde{X} \, 2\, A''_2, \tilde{A} \, 2\, E''', \text{and} \tilde{B} \, 2\, E')\) of NO\(_3\) are strongly coupled by vibronic interactions and have been treated in considerable detail theoretically.\(^b\) Corresponding experimental characterization of the interaction is much less detailed. Previous experimental results primarily consist of IR measurements of vibrational transitions in the ground state.\(^c\) In addition, the electronically forbidden \(\tilde{A}-\tilde{X}\) transition has been observed in ambient temperature CRDS studies.\(^d\) A slit-jet nozzle with a high voltage pulsed discharge has been applied to produce the NO\(_3\) radical by dissociating the N-O bond of N\(_2\)O\(_5\), and the jet-cooled NO\(_3\) CRDS absorption spectrum has been successfully observed with a high-resolution laser source (\(\Delta \nu \approx 250\text{MHz}\), intrinsic resolution considering the instrumental linewidth and the residual Doppler broadening in the jet). The \(4^1\) band (parallel band) shows complex rotational structure which is presently being analyzed. The \(2^1\) band has also been measured as an example of a perpendicular band. Besides the \(\nu_2\) and \(\nu_4\) vibronic bands, the vibronically forbidden origin band (\(0^0\) band) has been recorded under the same experimental conditions. The weakly observed \(\tilde{A}-\tilde{X}\) origin band is likely either a magnetic dipole or an electric quadrupole transition.

\(^{ab}\)present address: Lawrence Berkeley National Laboratory, Lawrence Berkeley National Laboratory


The nitrate radical NO\(_3\) has been known as an important intermediate in chemical reaction in the night atmosphere. The \(B \, 2\, E' \rightarrow X \, 2\, A'_2\) transition has been known as an intense absorption in the visible region (\(T_0 \approx 15108\text{ cm}^{-1}\)). The rotational structure of the 0-0 band of \(B \, 2\, E' \rightarrow X \, 2\, A'_2\) transition has been reported by Carter \textit{et al.}\(^a\), but the rotational assignment is still remained because the spectrum is too complicated. In this work, we measured the rotationally resolved high-resolution fluorescence excitation spectra of the 0-0 band of NO\(_3\) \(B \, 2\, E' \rightarrow X \, 2\, A'_2\) transition by crossing a single-mode laser beam perpendicular to a collimated molecular beam in the range of 15080-15135 cm\(^{-1}\). In our spectrum, the typical linewidth was 25 MHz and the absolute wavenumber was calibrated with accuracy 0.0001 cm\(^{-1}\) by measurement of the Doppler-free saturation spectrum of iodine molecule and fringe pattern of the stabilized etalon. Additionally, we have observed the change of the spectra with magnetic field. We are trying to assign the observed rotational lines by using the observed Zeeman splitting and the combination difference in the ground state calculated from the molecular constants reported by Kawaguchi \textit{et al.} \(^b\)


INSIGHT INTO THE JAHN-TELLER EFFECT IN THE NITRATE RADICAL VIA THE A-X HOT BANDS

KANA TAKEMATSU, NATHAN EDDINGSAAS, and MITCHIO OKUMURA, Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125; JOHN STANTON, Department of Chemistry, University of Texas at Austin, Austin, TX 78712.

Elucidation of the electronic states of the nitrate radical NO$_3$ remains an interesting puzzle for experimentalists and theorists alike. The A$^2$E$^\prime$ state is Jahn-Teller active and is pseudo-Jahn-Teller coupled to the ground X$^2$A$_2^\prime$ and excited B$^2$E$^\prime$ states. Analysis of the vibronic-allowed A-X transition spectrum shows vibronic bands exhibiting both static and dynamic distortions depending on the vibrational level of the upper A state. In the E$^\prime$$\times$$e''=a_1^\prime$$+a_2^\prime$$+e^\prime$ manifold, only the a$_1^\prime$ levels are accessible under ambient temperature experiments. We have gained new insight into the A state by examining the hot bands of NO$_3$, as previously dark levels of the A state become accessible. We present analysis of our hot band spectrum along with calculations of the upper A state levels.

FTIR SPECTROSCOPY OF NO$_3$: OBSERVATION AND ANALYSIS OF THE 1127 cm$^{-1}$ BAND.

K. KAWAGUCHI, N. SHIMIZU, R. FUJIMORI, Department of Chemistry, Faculty of Science, Okayama University, 3-1-1, Tsushima-Naka, Okayama 700-8530, JAPAN; T. ISHIWATA, Graduate School of Information Sciences, Hiroshima City University, 3-4-1 Otsuka-Higashi, Hiroshima 731-3194, JAPAN; I. TANAKA, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro, Tokyo 152-8550, Japan; and E. HIROT A, The Graduate University for Advanced Studies, Hayama, Kanagawa 240-0193, JAPAN.

We report the infrared spectrum of NO$_3$ studied with a Bruker 120 HR. In the present experiment, the NO$_3$ production was monitored by using He-Ne laser absorption at 633 nm. The multi-path cell was also improved to attain 48 m effective path length, and a new HgCdTe detector was introduced. In the 1000-1900 cm$^{-1}$ region, the following 7 bands were observed at 1127, 1137, 1173, 1413, 1492, 1550, 1927 cm$^{-1}$. The 1127, 1137 and 1550 bands were not reported by matrix isolation, and these are thought to be due to hot bands from the $\nu_4$ state. The analysis of the 1127 band was carried out by fixing the upper state parameters to those of the 1492 band, and major molecular constants are determined as follows, B=0.459339(12), C=0.228848(20), $C\zeta_4$=-0.044279(29), $\nu_4$=365.4887(13) cm$^{-1}$. The two A-E type bands are also assigned in the 1133 and 1137 cm$^{-1}$ regions in addition to E-E type, indicating that the 1492 band is assignable to $\nu_3 + \nu_4$, in contrast to the previous $\nu_5$ assignment.

NUCLEAR SPIN DEPENDENCE OF THE REACTION OF H$_3^+$ WITH H$_2$

KYLE N. CRABTREE, BRIAN A. TOM, CARRIE A. KAUFFMAN, BENJAMIN J. McCALL, Department of Chemistry, University of Illinois, Urbana, IL 61801.

The chemical reaction H$_3^+$ + H$_2$ → H$_2$ + H$_3^+$ is the simplest bimolecular reaction involving a polyatomic, and is possibly the most common such process occurring in the universe. Recent measurements of interstellar clouds have shown that the temperatures derived from the lowest rotational levels of H$_2$ and H$_3^+$ do not agree, and it is expected that this reaction plays a key role in this deviation. To investigate this process, we have measured the ortho/para ratio of H$_3^+$ produced in this reaction by performing high resolution spectroscopy on its $\nu_2$ fundamental band in plasmas formed from various mixtures of ortho and para H$_2$. These measurements have been performed in a supersonic expansion discharge source and in a cooled hollow cathode cell to probe the reaction at a variety of temperatures at and below 300 K. Our results provide experimental evidence that the population distribution of the lowest levels of H$_3^+$ is governed by the steady state of the H$_3^+$ + H$_2$ → H$_2$ + H$_3^+$ reaction, not by thermalization.

$^a$Current Address: Department of Chemistry, United States Air Force Academy, CO 80840
FOURIER TRANSFORM INFRARED EMISSION SPECTROSCOPY AND AB INITIO STUDY OF HBO AND BO

G. LI, R. J. HARGREAVES, and P. F. BERNATH, Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK.

The Fourier-transform infrared emission spectra of HBO and BO were recorded using a Bruker IFS-125HR Fourier transform spectrometer. HBO molecules were synthesized using a high temperature tube furnace at 1450°C. Our spectra of the HBO molecule in the 1200 – 4000 cm⁻¹ region contain the $v_1$ and $v_3$ fundamental vibrational modes plus numerous hot bands. An accurate potential energy surface using the MRCI method with correlation consistent core-valence basis sets aug-cc-PCVnZ (n=3, 4, 5) is being calculated and a vibrational configuration interaction (VCI) calculation based on this surface will be performed to assist in the assignment of the HBO hot bands. BO molecules were produced by applying a DC discharge to the furnace containing HBO. Our spectrum of BO in the 1200 – 2100 cm⁻¹ region contains the fundamental bands of both isotopic species, $^{11}$BO, $^{10}$BO, and one hot band of the main isotopologue $^{11}$BO. The fundamental band of $^{11}$BO contains 95 lines roughly equally distributed between the P and R branches. A combined least-squares fit with ground state microwave data was performed to determine the spectroscopic constants. Further results on this ongoing project will be presented.

INFRARED PHOTODISSOCIATION SPECTROSCOPY OF HYDROGEN CLUSTERS

T. C. CHENG, B. BANDYOPADHYAY, M.A. DUNCAN, Department of Chemistry, University of Georgia, Athens, GA 30602-2556; Y. WANG, S. CARTER, B.J. BASTIAANJ.M. BOWMAN, Department of Chemistry, Emory University, Atlanta, GA 30322.

Highly fluxional H$_5^+$ and D$_5^+$ ions are generated via arc discharge in a pulsed supersonic expansion source and analyzed by infrared photodissociation spectroscopy. A breakdown in the harmonic approximation because of the delocalized and highly anharmonic shared-proton stretch mode has caused uncertainty with previous attempts by Lee and coworkers to assign the peaks. An improvement in quality of the spectra along with good agreement with frequencies from a new fixed-node diffusive Monte Carlo calculation method help assign the peaks to their corresponding vibrational modes.
WK. COMMEMORATIVE SESSION
JUNE 23, 2010 – 5:00 pm
Room: FAWCETT CENTER AUDITORIUM

Chair: FRANK DE LUCIA, The Ohio State University, Columbus, Ohio

Greeting 5:00
Gordon Gee, President
The Ohio State University

WK01 20 min 5:05
65 SCARLET AND GRAY BOOKLETS

BRENDA P. WINNEWISER, Department of Physics, The Ohio State University, Columbus, Ohio 43210.

Delving into the archives, and drawing on the experiences of various spectroscopists, several questions will be addressed, including: What has changed since the first meeting? What has not changed since the first meeting? How did this meeting spawn not only one, but two similar meetings in Europe? How has international participation evolved over the years? How has female participation evolved? And why do we keep coming back?

WK02 20 min 5:30
THE SYMPOSIUM: A PERSONAL PERSPECTIVE

ROBERT CURL, Department of Chemistry and Rice Quantum Institute, Rice University, Houston, TX 77005, USA.

The International Symposium on Molecular Spectroscopy at Ohio State University has been serving the spectroscopic community magnificently for sixty-five years. Many spectroscopists, myself included, made their very first meeting presentation here. In my case, that was a mere fifty-two years ago. Looking back my trips here have been filled with great experiences both personally and professionally. I plan to talk about a few of them.

WK03 20 min 5:55
HIGH PRECISION IN AN IMPRECISE WORLD: THE IMPORTANCE OF THE MOLECULAR SPECTROSCOPY SYMPOSIUM TO THE ARMY

DAVID SKATRUD, Army Research Office, Research Triangle Park, NC, 27709-2211.

The Army Research Office has been a consistent supporter of the OSU International Symposium on Molecular Spectroscopy for nearly 30 years. During this time, the Symposium has been of great value to the Army through a number of mechanisms. Not only have numerous specific research projects reported at the Symposium had major impacts on critical Army technologies; but in addition, an understanding of how to perform high-resolution spectroscopy research provides unique education and training on how to meaningfully model and explain many disparate complex phenomena. I will present historical examples, and also highlight related current Army research needs and thrusts.
In this talk we will consider some generalizations (based primarily on the author’s observations and experiences at 52 of the past 65 Columbus meetings) concerning the benefits and pleasures of OSU Symposium attendance to a molecular spectroscopist at each stage of his or her career, i.e., undergrad, grad student, post doc, new staff member, mature staff member, and retiree. In particular, we will examine the three topics of: (i) what type of people frequently attend this conference, (ii) what do they gain in terms of things received from the conference, and (iii) what do they gain by contributing to the conference.
RA01 15 min 8:30

**INTERSYSTEM CROSSING: A STEP BEYOND STATISTICS**


Traditional statistical models provide only a phenomenological description of intersystem crossing (ISC). They do not capture the dominant energy flow pathways and the state-specific mechanisms responsible for the mixing of zero-order bright state character into dark states. A time-dependent center of gravity metric is sensitive to patterns of bright dark state mixing that deviate from mechanism-free statistical pictures. Doorway-mediated ISC represents the first stage of pulling back the statistical curtain. The center of gravity metric is applied to incoherently excited, time-gated, high-resolution fluorescence excitation spectra of small molecules. It becomes possible to determine the energy of the doorway state relative to the bright state as well as the value of the bright doorway state spin-orbit matrix element. This sort of information was neither available nor dreamt of in the decades when ISC was subjected to intense spectroscopic and theoretical analysis.

RA02 15 min 8:47

**COLLISIONAL X- AND A-STATE KINETICS OF CN USING TRANSIENT SUB-DOPPLER HOLE BURNING**

M. L. HAUSE, TREVOR J. SEARS, and GREGORY E. HALL, *Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973-5000.*

We examine the collisional kinetics of the CN radical using transient hole-burning and saturation recovery. Narrow velocity groups of individual hyperfine levels in CN are depleted ($X^2\Sigma^+$) and excited ($A^2\Pi$) with a saturation laser, and probed by a counterpropagating, frequency modulated probe beam. Recovery of the unsaturated absorption is recorded following abrupt termination of an electro optically switched pulse of saturation light. Pressure-dependent recovery kinetics are measured for precursors, ethane dinitrile, NCCN, and pyruvonitrile, CH$_3$COCN, and buffer gases, helium, argon and nitrogen with rate coefficients ranging from $0.7-2.0 \times 10^{-9}$ cm$^3$ s$^{-1}$ molec$^{-1}$. In the case of NCCN, recovery kinetics are for two-level saturation resonances, where the signal observed is a combination of $X$- and $A$-state kinetics. Similar rates occur for three-level crossover resonances, which can be chosen to probe selectively the hole-filling in the $X$ state or the decay of velocity-selected $A$ state radicals. However in the case of CH$_3$COCN, which has a dipole moment of 3.45 D, the $X$-state kinetics are faster than the $A$-state due to an efficient dipole-dipole rotational energy transfer mechanism as the $X$-state dipole moment is 1.5 D and the $A$-state dipole moment is 0.06 D. The observed recovery rates are 2-3 times faster than the estimated rotationally inelastic contribution and are a combination of inelastic and velocity-changing elastic collisions.

Acknowledgement: This work was carried out under Contract No. DE-AC02-98CH10886 with the U.S. Department of Energy.
AMMONIA CLUSTER DISSOCIATION VIA NH STRETCH EXCITATION

AMANDA S. CASE, CORNELIA G. HEID and F. FLEMING CRIM, The University of Wisconsin-Madison, Department of Chemistry, 1101 University Avenue, Madison, WI 53706.

Ammonia clusters were formed in a supersonic expansion and interrogated with IR light in the NH stretching region. The ammonia molecules resulting from vibrational predissociation were detected using (2+1) resonance enhanced multiphoton ionization (REMPI) through the $\tilde{B}$ state. By monitoring various rotational levels of ammonia, we have also obtained an IR spectrum for the multiple clusters formed in our molecular beam.

PHOTODISSOCATION DYNAMICS OF THE $S_1$ AND $S_2$ STATES OF CH$_3$ONO: ENERGY DISTRIBUTION IN THE CH$_3$O PHOTOFRAGMENT

CHRISTOPHER J. ANNESLEY, ANDREW E. BERKE, F. FLEMING CRIM, Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706.

We studied the photodissociation dynamics of methyl nitrite excited to the $S_1$ and $S_2$ states by rediscovering the resonance enhanced multiphoton ionization of the CH$_3$O photofragment. While the NO photofragment’s state distributions are well known, the state distributions in the methoxy had not previously been determined.

DIFFUSION MONTE CARLO CALCULATIONS OF MINIMUM ENERGY PATHS FOR THE ISOTOPIC VARIANTS OF THE CH$_3$+ H$_2$ ↔ CH$_3$+ ↔ CH$_2$+ + H$_2$ REACTION

CHARLOTTE E. HINKLE, ANNE B. McCOY, Department of Chemistry, The Ohio State University, Columbus, OH 43210.

Protonated methane is of interest to astrochemists due to its presumed importance as a reaction intermediate in the reaction involving CH$_3^+$ + HD within the interstellar medium. However, within the interstellar medium there is a nonstatistical H/D isotopic abundance observed for the isotopologues of CH$_3^+$. Kinetic studies performed by Gerlich and co-workers determined that the reactions

$$CH_3-nD_n^+ + HD \rightarrow CH_4-nD_{n+1}^+ \rightarrow CH_2-nD_{n+1}^+ + H_2$$

have identical net rate constants regardless of the value of n.\textsuperscript{a} We have calculated zero-point corrected energies and wave functions of the CH$_3^+$ + H$_2$ system\textsuperscript{b} and its deuterated analogs as functions of the center of mass separation between CH$_3^+$ and H$_2$, $R$. We can divide these simulations into distinct ranges of $R$: long-range interactions, complexation, and intermediate distances. Analysis of the wave functions associated with these three ranges of $R$ allows us to study how zero-point energy influences the approach geometries that are sampled during low-energy collisions.


TIME-RESOLVED PHOTOELECTRON STUDIES OF IBr⁻: A CLASSICAL AND QUANTUM TUG-OF-WAR

Samantha Horvath and Anne B. McCoy, Department of Chemistry, The Ohio State University, Columbus, OH 43210.

To understand the dynamics of molecular species, especially those involved in photochemistry, we often turn to classical mechanics, which, despite the assumed quantum nature of small, light particles, has been extremely helpful in describing the underlying photophysics and can often explain the big picture of the dynamics. One such example is the recent duel experimental and theoretical study on the photodissociation of IBr⁻ performed by Sanov and co-workers.⁴ Of greater interest, though, is when does classical mechanics break down? More generally, when is a quantum approach needed to fully describe the system at the resolution of the experiment? In this work, we address these questions by investigating quantum interference effects on the time-resolved spectra of IBr⁻ where we look at how pulse width affects the overall signal. In the limit of an infinitely narrow pulse, we regain the Franck-Condon picture and the classical limit because all transitions are energetically allowed. In the limit of an infinitely wide pulse width, quantum interference effects become important and give rise to the bimodal character of the spectrum at short delay times (Δt < 350 fs). Results of the calculated IBr⁻ spectra are in good agreement with experiment and serve to illustrate how varying the pulse widths can shift the description of the dynamics from a classical picture to a quantum one.

RA07

HYDROGEN EXCHANGE BEFORE DISSOCIATION IN THE PHOTOLYSIS OF ACETALDEHYDE: A NON-TRANSITION STATE MECHANISM.


Non-transition state (TS) reaction mechanisms continue to attract a great deal of attention, experimentally and theoretically, because they challenge the paradigms of kinetic theories. The “roaming” mechanism was first described 5 years ago in the photolysis of H₂CO.⁴ It was originally described as a non-TS mechanism, although recent work has characterized a "roaming" TS, which is very flat, and without a well-defined structure. In addition, roaming reactions may re-cross this TS many times in an excursion from reactant to product and so conventional TS theories are still inadequate for predicting the rate of such reactions. Photolysis of the more complex acetaldehyde (CH₃CHO) has proven to be a benchmark molecule for studies of roaming because the higher molecular complexity, and the near energetic equivalence of the TS to CH₄ + CO and the C-C bond cleavage to CH₃ + HCO produces a much higher flux of roaming reactions.⁵ In this seminar, we shall present experimental results on the photolysis of isotopically-labeled acetaldehyde, CD₃CHO, and, hopefully, CH₃CDO. Photolysis of CD₃CHO is shown to produce almost 10% of the radical flux as DCO products. We have performed ab initio calculations of the critical points on the global C₂, D₃, H, O potential energy surface at energies below the experimental photolysis energy, revealing several pathways to DCO products. From these theoretical energies, vibrational frequencies and rotational constants we have calculated RRKM rates for each forward and reverse reaction on this surface. A master equation analysis of the product rates predicts that the yield of DCO, via these conventional TS pathways, should only be < 0.1%, which is about two orders of magnitude less than observed experimentally. We have not included the known roaming pathway to CH₄ + CO, but that would only reduce the DCO product. The mechanism for the observed DCO production is at the present time unknown, but we hypothesise that another roaming-type mechanism might efficiently exchange the H and D atoms, producing a transient CD₂HCDO intermediate which then dissociates in a conventional mechanism to produce CD₂H + DCO.

Intermission

Methyl nitrite, CH$_3$ONO, was photodissociated at 355 nm in a velocity-map ion imaging apparatus. The NO photoproduct was detected through state-resolved 1+1' resonance-enhanced multiphoton ionization. The NO products are highly oriented in the laboratory frame, indicating perpendicular transition and a prompt dissociation. The velocities of the NO products reveal that methyl nitrite undergoes rapid predissociation after 355 nm excitation.

Methyl nitrite, CH$_3$ONO, was photodissociated near 225 nm in a velocity-mapping time-of-flight mass spectrometer. The NO photoproduct was detected through state-resolved 1+1' resonance-enhanced multiphoton ionization. The NO products are highly oriented in the laboratory frame, indicating a parallel transition and a fast dissociation.

The link between energy-resolved spectra and time-resolved dynamics is explored quantitatively for acetylene ($^{12}$C$_2$H$_2$), $\tilde{X}^1\Sigma^+_g$ with up to 8,600 cm$^{-1}$ of vibrational energy. This comparison is based on the extensive knowledge of the vibration-rotation energy levels and on the model Hamiltonian used to fit them to high precision.$^a$ Simulated intensity borrowing features in high resolution absorption spectra and predicted survival probabilities for intramolecular vibrational redistribution (IVR) are first investigated for the $\nu_4 + \nu_5$ and $\nu_3$ bright states, for $J = 2, 30$ and 100. The dependence of the results on the rotational quantum number and on the choice of vibrational bright state reflects the interplay of three kinds of off-diagonal resonances: anharmonic, rotational $l$--type, and Coriolis. The dynamical quantities used to characterize the calculated time-dependent dynamics are the dilution factor $\phi_d$, the IVR lifetime $\tau_{IVR}$, and the recurrence time $\tau_{rec}$. For the two bright states $\nu_3 + 2\nu_4$ and $7\nu_4$, the collisionless dynamics for thermally averaged rotational distributions at $T=27, 270$ and 500 K were calculated from the available spectroscopic data. For the $7\nu_4$ bright state, an apparent irreversible decay of is found. In all cases, the model Hamiltonian allows a detailed calculation of the energy flow among all of the coupled zeroth-order vibration-rotation states.

RA11 15 min 11:26

ROTATIONAL AND VIBRATIONAL ENERGY TRANSFER FROM THE FIRST OVERTONE STRETCH OF ACETYLENE

M. C. HEAVEN, JIANDE HAN, and KEITH FREEL, Department of Chemistry, Emory University, Atlanta, GA 30322.

Gas lasers that are optically pumped by solid state devices are currently being considered for applications that require high powers and high beam quality. Optical pumping in the 1-2 μm region is of interest as there are efficient diode laser sources that operate in this spectral range. An optically pumped C2H2 laser was recently demonstrated by Wolfgang et al. at the University of New Mexico. Excitation of the CH overtone transition (νCH=2) at 1.52 μm yielded lasing on an asymmetric stretch combination band centered at 3.1 μm. Collisional energy transfer data for the νCH=2 level is needed for analysis and modeling of the laser performance. Although there have been numerous studies of energy transfer for vibrationally excited acetylene, the νCH=2 level has received very little attention. We are currently examining state-to-state ro-vibrational energy transfer processes for νCH=2 in self-collisions using a pulsed IR pump-UV probe technique. Pure rotational transfer has been characterized and rapid vibrational transfer has also been observed. Identification of the collisionally populated vibrational levels and measurements of the transfer rate constants are in progress.

RA12 15 min 11:43

PHOTODISSOCIATION DYNAMICS OF THE PHENYL RADICAL VIA PHOTOFRAGMENT TRANSLATIONAL SPECTROSCOPY

BOGDAN NEGRU, SCOTT J. GONCHER, AMY L. BRUNSVOLD, DANIEL M. NEUMARK, College of Chemistry, University of California, Berkeley, California 94720, and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA.

Photofragment translational spectroscopy was used to study the photodissociation dynamics of the phenyl radical at 193 and 248 nm. Time of flight data collected for the C6H4, C4H3, and C2H2 photofragments show the presence of two decomposition channels. The only C6H5 decomposition channel observed at 248 nm corresponds to CH bond fission from the cyclic radical producing ortho-benzylene. The translational energy distribution peaks at 0 kcal/mol and is consistent with no exit barrier for the H loss process. At 193 nm photodissociation, however, H loss was observed to be the minor channel, while the major decomposition pathway corresponds with decyclization of the C6H5 radical and subsequent fragmentation to n-C4H3 and C2H2. These two momentum matched photofragments have a translational energy distribution that peaks around 9 kcal/mol, indicative of a process that proceeds through a tighter transition state. Previous theoretical work on the unimolecular decomposition of the phenyl radical predicts a second H loss process that occurs after C6H5 decyclization resulting in the linear C6H4 photofragment. This channel cannot be unambiguously discerned from the C6H4⁺ time of flight data, but is believed to take place since decyclization is observed.

RB. MINI-SYMPOSIUM: BIOMOLECULES AND CLUSTER IONS

THURSDAY, JUNE 24, 2010 – 8:30 am

Room: 170 MATH ANNEX

Chair: THOMAS RIZZO, Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland

**RB01**

INVITED TALK - Abstract Rescheduled at Authors’ Request

30 min 8:30

COMBINING LASER SPECTROSCOPY AND MASS SPECTROMETRY FOR CONFORMATION-SPECIFIC STUDIES OF GAS-PHASE BIOMOLECULES

THOMAS R. RIZZO, OLEG V. BOYarkin, JAIME A. STEARNS, MONIA GUIDI, CAROLINE SEAIBY, NATALIA NAGORNOVA and ANNETTE SVENDSEN, Laboratoire de chimie physique moléculaire (LCPM), École polytechnique fédérale de Lausanne, CH-1015 Lausanne, Switzerland.

Developments over the last few years at the interface between laser spectroscopy and mass spectrometry have opened up new horizons for the spectroscopic study of biological molecules. The combination of electrospray ionization for producing large biological molecules in the gas phase with cooled ion traps and multiple-resonance laser schemes are allowing spectroscopic investigation of individual conformers of peptides of increasing size. Highly resolved infrared spectra of single conformations of such species provide important benchmarks for testing the accuracy of theoretical calculations.

This talk will give an overview of techniques employed in our laboratory for measuring conformer-selected vibrational spectroscopy of cold, gas-phase peptides of increasing size and complexity. I will show examples that demonstrate the power of these techniques and evaluate the challenges to extending them to still larger biological molecules.

**RB02**

15 min 9:05

EXAMINATION OF H$_2$CO–X$^+$ AND NH$_2$CH$_2$COOH–X$^+$ COMPLEXES [X$^+ = $ Li$^+$, Na$^+$, K$^+$] USING ELECTRONIC STRUCTURE THEORY

ANNIE L. LESIAK, SAMANTHA HORVATH, and ANNE B. McCOY, Department of Chemistry, The Ohio State University, Columbus, OH 43210.

Infrared spectroscopy is a powerful tool for studying molecular structure as changes in the frequency and intensity of infrared transitions provide a way to probe environment effects on molecular systems. In this study we investigate how the frequency and intensity of the C=O stretch vibration of formaldehyde and glycine change upon the introduction of alkali metal cations. Specifically we focus on the complexes of Li$^+$, Na$^+$, and K$^+$ with H$_2$CO and NH$_2$CH$_2$COOH. There is evidence of small changes in the harmonic C=O stretch frequency; however, the changes in intensity are much larger. For example the intensity of the C=O stretch in H$_2$CO–Li$^+$ is twice that in bare H$_2$CO. The ultimate goal of this work is to determine how the sensitivity of the C=O stretch vibration is affected by the particular alkali metal cation as well as the geometry of the complex. All calculations in this study were performed using Gaussian03 at the MP2/6-311G$^*$ level of theory/basis set.
ORIGINS OF IR INTENSITY IN OVERTONES AND COMBINATION BANDS IN HYDROGEN BONDED SYSTEMS

SAMANTHA HORVATH and ANNE B. McCOY, Department of Chemistry, The Ohio State University, Columbus, OH 43210.

As the infrared spectra of an increasing number of hydrogen bonded and ion/water complexes have been investigated experimentally, we find that they often contain bands with significant intensity that cannot be attributed to fundamental transitions. In this talk, we explore several sources of the intensity of these overtone and combination bands. A common source of intensity is mode-mode coupling, as is often seen between the proton transfer coordinate and the associated heavy atom vibration. A second important mechanism involves large changes in the dipole moment due to the loss of a hydrogen bond. This results in intense overtone transitions involving non-totally symmetric vibrations as well as the introduction of intense combination bands involving intramolecular bending coupled to hindered rotations. These effects will be discussed in the context of several systems, including the spectra of complexes of argon atoms with $\text{H}_3\text{O}^+$, $\text{F}^-\cdot\text{H}_2\text{O}$, $\text{Cl}^-\cdot\text{H}_2\text{O}$, protonated water clusters, and HOONO.

$^a$T. Guasco, S. Olesen and M. A. Johnson, private communication

VIBRATIONAL PREDISSOCIATION SPECTRA IN THE SHARED PROTON REGION OF PROTONATED FORMIC ACID WIRES

HELEN GERARDI, CHRIS LEAVITT, and MARK JOHNSON, Yale University, Department of Chemistry, New Haven, CT.

Protonated formic acid networks are thought to form long chains where the excess charge is distributed along the embedded H-bonds holding it together. This system therefore effectively captures anhydrous proton transport at an intermediate state, thereby allowing a detailed look at the underlying mechanism. We present vibrational predissociation spectra of the Ar-tagged $(\text{HCOOH})_n\text{H}^+$ cluster ions, formed via supersonic expansion of argon gas seeded with formic acid. The resulting data reveal the first well-defined spectral signatures associated with the collective vibrational motions of the H-bonding backbone, and we follow how these features evolve as the number of formic acid molecules is increased from 2 to 5. Bands in the 700-1500 cm$^{-1}$ range are found to strongly depend on cluster size, and the shifts displaying an even-odd alternation before stabilizing in the $n=4$ and 5 clusters. We interpret these trends in the context of charge delocalization and the resulting effect on the carbonyl stretches.
TRIGGERING INTRA-CLUSTER ELECTRON CAPTURE WITH VIBRATIONAL EXCITATION: AN IR STUDY OF THE CH$_3$NO$_2$(H$_2$O)$_6$ ANION

KRISTIN J. BREEN, TIMOTHY L. GUASCO and MARK A. JOHNSON, Sterling Chemistry Laboratory, Yale University, PO Box 208107, New Haven, CT 06520.

Nitromethane (NM), the simplest of the nitro-containing organic molecules, possesses a large dipole moment of 3.46 D. Nagata and co-workers$^b$ have demonstrated that Ar-mediated condensation of NM can trap a significant fraction of the collision complexes in a situation where the electron is retained in a diffuse hydrated electron configuration. This raises the possibility of triggering the electron capture onto NM to form the NM$^-$ radical anion, releasing the substantial exothermicity of the reaction by evaporation of water molecules and allows the barrier to evaporation to be probed. We report vibrational predissociation spectra of both the product NM$^-$(H$_2$O)$_n$ anions as well as the high energy species that features a diffuse electron cloud. Interestingly, the spectra indicate that the high energy isomer has a neutral NM moiety and occurs with the same spectral signature of the excess electron binding site as that in the isolated water hexamer anion, indicating that it is attached in a position remote from the charge. Detailed comparison of the C-H and N-O stretching regions suggests that the reactive isomer occurs with the NM molecule attached to the backside of the water network via accepting H-bonds rather than attachment of the methyl group to the electron cloud, where the NM and water network would share the electron cloud.


Intermission

FOLDAMERS, CROWNS, AND WATER: CONNECTIONS BETWEEN ISOLATED MOLECULES AND SOLUTION-PHASE BEHAVIOR

WILLIAM H. JAMES III, EVAN G. BUCHANAN, CHRISTIAN W. MÜLLER, and TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN 47907; LI GUO, and SAMUEL H. GELL-MAN, Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706.

This talk will provide an overview of recent results from our group that highlight the synergistic connections between single-conformation spectroscopy and laser-initiated isomerization data on isolated molecules and molecular clusters and issues of current interest to those studying solution-phase behavior. Single-conformation data in the C=O stretch region provide a foundation for those seeking to model 2D-IR data on polypeptides in solution. The infrared and ultraviolet spectra of size-selected crown-(H$_2$O)$_n$ and $\gamma$-peptide-(H$_2$O)$_n$ clusters reflect the ways in which first solvent shell water molecules interact with the binding pocket and H-bonding sites of these molecules. Infrared population transfer spectroscopy of the crown-water complexes will be used to probe energy flow between the water solvent and crown solute. Recent progress on methods that enable analogous studies on larger molecules will also be discussed.
HYDRATION OF A LARGE ANIONIC CHARGE DISTRIBUTION - NAPHTHALENE-WATER CLUSTER ANIONS

J. MATHIAS WEBER, CHRISTOPHER L. ADAMS, JILA, NIST, and Department of Chemistry and Biochemistry, University of Colorado at Boulder, 440 UCB, Boulder, CO 80309-0440, USA.

We report the infrared spectra of anionic clusters of naphthalene with up to three water molecules. Comparison of the experimental infrared spectra with theoretically predicted spectra from quantum chemistry calculations allow conclusions regarding the structures of the clusters under study. The first water molecule forms two hydrogen bonds with the $\pi$ electron system of the naphthalene moiety. Subsequent water ligands interact with both the naphthalene and the other water ligands to form hydrogen bonded networks, similar to other hydrated anion clusters. Naphthalene-water anion clusters illustrate how water interacts with negative charge delocalized over a large $\pi$ electron system. The clusters are interesting model systems that are discussed in the context of wetting of graphene surfaces and polyaromatic hydrocarbons.

LASER SPECTROSCOPIC STUDY ON ENCAPSULATION STRUCTURE OF FUNCTIONAL MOLECULES IN SUPERSONIC JETS

T. EBATA, Department of Chemistry, Graduate School of Science, Hiroshima University, Higashi-Hiroshima, 739-8526, Japan.

The structures of functional molecules (calixarene and crown ether) and their complexes have been investigated by laser spectroscopy and quantum chemical calculations. For calixarene we investigate calix[4]arene(C4A) and calix[5]arene(C5A), and for crown ether we investigate dibenzo-18-crown-6-ether(DB18C6) and dibenzo-24-crown-8-ether(DB24C8) as a host. We observe the electronic spectra and IR spectra for these molecules and complexes in supersonic beams. We discuss the size dependence of the electronic structure of the host molecules and their ability of the encapsulation for various guest species.

CONFORMATION-SPECIFIC INFRARED AND ULTRAVIOLET SPECTROSCOPY OF DIBENZO-15-CROWN-5-(H$_2$O)$_1$-CLUSTER: RESHAPING A BINDING POCKET

EVAN G. BUCHANAN, CHIRANTHA P. RODRIGO, ANNA K. GUTBERLET and TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN 47907.

Crown ethers are oxygen containing macrocycles noted for their ability to preferentially bind substrates such as ions and water. Despite the high symmetry inherent to the chemical structure, crown ethers are remarkably flexible, adapting their conformation to the substrate to which they are bound. Here, we present the conformational preferences of the singly hydrated dibenzo-15-crown-5 ether (DB15C) complex formed and cooled in a supersonic jet. The resonance enhanced two-photon ionization, UV-UV holeburning, and resonant ion-dip infrared spectra lead to the identification of a single DB15C-(H$_2$O)$_1$ conformer with the water doubly hydrogen bonded to the crown. Single vibronic level dispersed fluorescence identified both electronic origins and the coupling between the two chromophores. Finally, infrared population transfer spectroscopy is used to study the monomer conformer populations formed by infrared photodissociation of the complex via the water OH stretch transitions, providing unique insight to the energy flow between water and crown.
The prototypical $\gamma$-peptide, Ac-$\gamma^2$-hPhe-NHMe, has been previously studied in a supersonic jet expansion, with three different conformers observed. Two of the monomers form nine atom, intramolecular hydrogen bonded rings, which differ by the position of the aromatic chromophore relative to the backbone. The third monomer conformer has no intramolecular H-bonds, but forms instead an intramolecular, amide-amide stacked structure unique to the $\gamma$-peptide backbone. This talk focuses attention on the conformation-specific IR spectra of the Ac-$\gamma^2$-hPhe-NHMe-(H$_2$O)$_1$ complex, which is observed to form six unique conformational isomers, all of which preserve the two distinct monomer structural motifs. Three conformers are assigned to the nine atom intramolecular hydrogen bond family with the water hydrogen bonded to it as donor in different locations. The other three belong to the amide-amide stacking family with the water forming a bridge between the two amide planes. Infrared photodissocation of the water molecule from the complex to form $\gamma$-peptide monomer conformations will also be discussed.
RC01 10 min 8:30

MICROWAVE SPECTRUM OF $^{12}$C$^{16}$O

S.A. TASHKUN, S.N. MIKHAILENKO, Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, 634055, Tomsk, RUSSIA.

$^{12}$C$^{16}$O microwave spectrum of the 0-0, 1-1, 2-2, and 3-3 bands up to $J=50$ will be presented. The spectrum was calculated from an experimental dataset of energy levels. Calculated frequencies are given together with 99% confidence intervals. Comparison of the spectrum with microwave data containing in spectroscopic databanks will be discussed.

This work was supported by CRDF (USA) Grant RUG1-2954-TO-09 and by RFBR. Grant 09-05-92508.

RC02 15 min 8:42

CAN THE INVERSION-VIBRATION-ROTATION PROBLEM IN THE $\nu_4$ AND 2$\nu_2$ STATES OF NH$_3$ BE SOLVED TO EXPERIMENTAL ACCURACY?

J.C. PEARSON, S. YU and B.J. DROUIN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109, USA; O. PIRALI, M.-A. MARTIN, M. VERVLOET and D. BALCON, Ligne AILES–Synchrotron SOLEIL, L’Orme des Merisiers Saint-Aubin, 91192 Gif-sur-Yvette, France; C. P. ENDRES, I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany.

The problem of coupling between a large amplitude motion state and a small amplitude vibration state remains an area of considerable interest and few conclusions in molecular physics. The $\nu_4$ and 2$\nu_2$ states of NH$_3$ provide an excellent opportunity to study the coupling of large and small amplitude motions in an inversion system where the quantum mechanics have been worked out in detail. In spite of the well established Hamiltonian, a large body of high quality spectra remains to fit to experimental accuracy. Several recent studies have resulted in 2-10 times the infrared accuracy over restricted ranges of quantum numbers and have either been unable to fit or have completely ignored the 162 reported microwave transitions. Assessment of the perturbations details provides some insight into why previous analyses might have not completely succeeded; however, the ability of current Hamiltonian to completely model the large amplitude inversion coupled with small amplitude vibration remains to be adequately addressed. We report extensive new measurements of the rotation-inversion transitions in the $\nu_4$ and 2$\nu_2$ states, a global analysis of existing data and provide a complete assessment of the inversion-rotation-vibration Hamiltonian in NH$_3$.

---


THz SPECTROSCOPY OF THE $a^1\Delta_g$ STATE OF O$^{18}$O and $^{18}$O$_2$.

HARSHAL GUPTA, SHANSHAN YU, BRIAN J. DROUIN, AND CHARLES E. MILLER, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109; HOLGER S. P. MÜLLER, I. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, Köln, Germany.

Submillimeter-wave rotational spectra of O$^{18}$O and $^{18}$O$_2$ in the $a^1\Delta_g$ state have been detected in a new static discharge cell useful for studying rare isotopologues of transient molecules. Rotational transition frequencies of both species have been measured through 1.6 THz, to better than 1 part in 10$^7$, allowing precise determination of molecular constants. The first measurements with our static discharge cell provide a check on the isotopic predictions in the $a^1\Delta_g$ state.

FOURIER TRANSFORM MICROWAVE LABORATORY DETECTION OF HSiNH$_2$

VALEIRIO LATANZI, M.C. McCARTHY, P. THADDEUS, Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, and School of Engineering and Applied Science, Harvard University, Cambridge, MA 02138; and SVEN THORWIRTH, Max-Planck-Institut für Radioastronomie, Bonn, Germany, and I. Physikalisches Institut, Universität zu Köln, Germany.

HSiNH$_2$ has been detected by means of Fourier Transform Microwave spectroscopy through its fundamental rotational transition ($J=1_0, K_a=0_0, \rightarrow 0_0$). The molecule was produced in a discharge of a mixture of silane and ammonia heavily diluted in neon in the throat of a pulsed nozzle prior to supersonic expansion. High level $ab\ ini$tio calculations at the CCSD(T) level of theory have guided our laboratory search. The fundamental rotational transition has been detected within 0.1% of the predicted frequency and shows expected hyperfine structure from the presence of the nitrogen nucleus. Confirmation of the assignment is provided by the detection of the same transition for several isotopic species at precisely the expected predicted frequency, with the same hyperfine splitting. Microwave-microwave double-resonance techniques have been used to detect a second rotational transition.

SILICON-PHOSPHORUS BONDING: LABORATORY DETECTION OF HPSiH$_2$ EMPLOYING HIGH RESOLUTION MICROWAVE SPECTROSCOPY

VALEIRIO LATANZI, M.C. McCARTHY, P. THADDEUS, Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, and School of Engineering and Applied Science, Harvard University, Cambridge, MA 02138; and SVEN THORWIRTH, Max-Planck-Institut für Radioastronomie, Bonn, Germany, and I. Physikalisches Institut, Universität zu Köln, Germany.

HPSiH$_2$, the ground state isomer on the H$_3$SiP potential energy surface, has been detected by means of Fabry-Pérot FT microwave spectroscopy. The laboratory search has been guided by theoretical structure calculations performed at the CCSD(T)/cc-pwCVQZ level of theory corrected for zero-point vibrational effects at the CCSD(T)/cc-pV(T+d)Z level. A mixture of silane and phosphine in a discharge supersonic molecular beam has been used to produce the new species, allowing the detection of the three lowest $K_a=0$ rotational transitions. The discovery has been confirmed by successful identification of the same transitions of HP$^{28}$SiH$_2$, HP$^{30}$SiH$_2$, and DPSiD$_2$, at precisely the expected frequency shifts. The presence of other Si and some P bearing molecules in astronomical sources suggests, that this molecule is a plausible candidate for radio astronomical detection.
CHIRPED PULSE FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF SnCl

GARRY S. GRUBBS II AND STEPHEN A. COOKE, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH TEXAS, 1155 UNION CIRCLE #305070, DENTON, TX 76203-5017, U.S.A.

Tin metal has been laser ablated with the pulsed fundamental output of a Nd:YAG laser. Chlorine gas dissolved in argon was pulsed into the products of this ablation event. One outcome of this has been the formation of SnCl entrained in a supersonic expansion. The expansion occurred between the horn antenna of a chirped pulse, Fourier transform microwave spectrometer and accordingly the pure rotational spectra of SnCl, $X^2\Pi_r$, has been recorded for the first time between 8 and 18 GHz. Spectroscopic constants will be presented.

HYPERFINE STRUCTURE IN THE PURE ROTATIONAL SPECTRUM OF $^{208}$Pb$^{35}$Cl

CHRISTOPHER T. DEWBERRY, GARRY S. GRUBBS II, KERRY C. ETCHISON AND STEPHEN A. COOKE, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH TEXAS, 1155 UNION CIRCLE #305070, DENTON, TX 76203-5017, U.S.A.

Initially in our laboratory the pure rotational spectrum of the title molecule was studied using a Balle-Flygare Fourier transform microwave spectrometer. Analysis was troublesome and so the spectrum was remeasured using a chirped pulse Fourier transform microwave (CP-FTMW) spectrometer. The correct intensity aspect of the CP-FTMW experiment allowed successful quantum number assignments for the hyperfine structure for the correct isotopologue. Spectroscopic constants have been obtained from a fit to a data set consisting of our measurements combined with those of a prior study on the $X^2\Pi_\frac{3}{2} \rightarrow X^2\Pi_\frac{1}{2}$ fine structure transitions$^a$.


THE MILLIMETER/SUBMILLIMETER SPECTRUM OF CYANOPHOSPHINE, PH$_2$CN ($\tilde{X}^1A'$)

D. T. HALFEN, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721; D. J. CLOUTHIER, Department of Chemistry, University of Kentucky, Lexington, KY 40506; and L. M. ZIURYS, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.

Cyanophosphine, PH$_2$CN ($\tilde{X}^1A'$), is the third row analog of cyanamide, a known interstellar molecule, and could be a potential interstellar species. However, only the microwave spectrum has been measured to date, and predictions at millimeter/submillimeter wavelengths have high uncertainties. Therefore, the millimeter/submillimeter spectrum of cyanophosphine has been measured using direct absorption techniques. This molecule was created by the reaction of gas-phase phosphorus, (CN)$_2$, and H$_2$ in the presence of argon carrier gas and an AC glow discharge. Eleven transitions have been recorded in the range 305-422 GHz each with multiple asymmetry components from K$_a = 0$ to 8. No evidence of inversion splitting was visible in the spectrum. The data have been fit with an asymmetric top Hamiltonian, and the spectroscopic constants have been determined. The A rotational constant and several higher-order centrifugal distortion parameters have been determined for the first time, allowing accurate predictions in the millimeter/submillimeter region. Here we report our laboratory measurements and an astronomical search.
HIGH-RESOLUTION MICROWAVE SPECTROSCOPY OF IMINOSILICON, HNSi

M. C. MCCARTHY, P. THADDEUS, Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, U.S.A. and School of Engineering and Applied Sciences, Harvard University, 29 Oxford Street, Cambridge, MA 02138, U.S.A.; FILIPPO TAMASSIA, Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna, Vle Risorgimento 4, I-40136 Bologna, Italy; S. THORWIRTH, Max-Planck-Institut für Radioastronomie, 53121 Bonn, Germany, and I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany.

By means of Fourier transform microwave spectroscopy of a supersonic beam, the fundamental rotational transition of isotopic and vibrationally-excited iminosilicon HNSi has been detected. In addition to seven isotopic species, vibrational satellite transitions from more than 30 vibrationally-excited states, including the three fundamental modes, have been detected. Those from \( v_2 \) are particularly intense, enabling detection of transitions from as high as \((0, 22^0, 0)\) (i.e. \( \sim 10,000 \text{ cm}^{-1} \) above ground). At high spectral resolution, well-resolved nitrogen quadrupole structure has been observed in nearly every transition. Excitation of \( v_1 \) or \( v_3 \) changes \( eQq(N) \) little, but \( eQq(N) \) systematically decreases with increasing excitation of the \( v_2 \) bend, from a value of 0.376(5) MHz for \((0, 0^0, 0)\) to -2.249(5) MHz for \((0, 20^0, 0)\). With the large amount of new data in hand, it has been possible to determine more precise vibration-rotation constants and an improved semi-empirical structure for this triatomic molecule. An unsuccessful search for HSiN, a highly polar isomer calculated to lie nearly 3 eV above HNSi, is also reported.

MICROWAVE SPECTRUM AND AB INITIO CALCULATIONS FOR DIFLUOROSILYL ISOCYANATE, HF\(_2\)SiNCO

SEAN A. PEEBLES, DANIEL A. OBENCHAIN and REBECCA A. PEEBLES, Department of Chemistry, Eastern Illinois University, 600 Lincoln Avenue, Charleston, IL 61920; MICHAEL H. PALMER, School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK; GAMIL A. GUIRGIS, ZICHAO WANG and JONEL LIRJONI, Department of Chemistry and Biochemistry, College of Charleston, Charleston, SC 29424.

The rotational spectrum for the normal isotopologue of difluorosilyl isocyanate, HF\(_2\)SiNCO, has been measured in the 5–15 GHz range using a 480 MHz bandwidth chirped-pulse Fourier-transform (CP-FTMW) microwave spectrometer and a Balle-Flygare resonant cavity FT-microwave spectrometer. Clearly resolved nuclear quadrupole hyperfine splittings arising from the \(^{14}\text{N}\) nucleus are consistent with the predicted hyperfine patterns, and indicate near-cylindrical symmetry around the nitrogen atom \( \chi_{bb} - \chi_{cc} = -0.0214(58) \text{ MHz} \).

Ab initio optimizations at several levels of theory (up to CCSD(T)/6-311++G(3df,3pd)) yielded two energetically very similar structures which differ predominantly in the value of the H–Si–N=C dihedral angle ("cis" = 0° or "trans" = 180°). Both structures have rotational constants similar to the observed values \( A = 7111.2810(18) \text{ MHz}, B = 1565.7758(5) \text{ MHz} \) and \( C = 1347.5228(8) \text{ MHz} \), although the experimental constants, particularly \( A \), seem to point to the slightly higher energy "cis" structure as the observed species. However, at every level of theory the difference in energy between the two forms is small (less than 0.45 kJ mol\(^{-1}\)) and a variation of the \( A \) rotational constant with the chosen level is observed, since this constant is especially sensitive to the Si–N=C angle and Si–N=C=O dihedral. Details of the two possible structures and their stabilities will be presented based on the computational and experimental data, and the results for HF\(_2\)SiNCO will be compared to related molecules.
ANOMALOUS HYPERFINE STRUCTURE OF NSF\textsubscript{3} IN THE DEGENERATE VIBRATIONAL STATE $v_3=1$: LIFTING OF THE PARITY DEGENERACY BY THE FLUORINE SPIN-ROTATION INTERACTION

H. HARDER, S. MACHOLL, H. MAEDER, Institut für Physikalische Chemie, Universität Kiel, 24098 Kiel, Germany; L. FUSINA, Dipartimento di Chimica Fisica e Inorganica, Università di Bologna, 40136 Bologna, Italy; L. OZIER, Department of Physics and Astronomy, University of British Columbia, BC V6T 1Z1, Canada.

For the principal isotopomer $^{14}\text{N}^{32}\text{S}^{19}\text{F}_3$ of thiazyl trifluoride in the degenerate fundamental state ($v_3=1$), the hyperfine structure has been investigated in the $Q$-branch spectrum between 8 and 26.5 GHz using microwave Fourier transform waveguide spectrometers with a resolution limit of $\approx 30$ kHz. In addition to $l$-type doubling spectra and $l$-type resonance transitions with ($\Delta k = \Delta l = \pm 2$), perturbation-allowed spectra were measured with $\Delta (k-l) = \pm 3, \pm 6$. The range in $J$ was from 13 to 61; for the lower states, $k l = -3, -2, -1, 0, +1$. For all the transitions, the hyperfine patterns observed are predicted to be doublets when only the nitrogen quadrupole Hamiltonian $H_{Q}^{N}$ is taken into account. Doublets were indeed measured for transitions with $\Gamma_{RV} = A_1 \leftrightarrow A_2$, where $\Gamma_{RV}$ is the rovibrational symmetry. However, when $\Gamma_{RV} = E \leftrightarrow E$, triplets and quartets were observed in addition to doublets. These anomalous hyperfine patterns are shown to be due to the ($\Delta k = \pm 1$) and ($\Delta k = \pm 2$) matrix elements of the fluorine spin-rotation Hamiltonian $H_{F}^{N}$ characterized by the fluorine spin-rotation constants $c(1) = (c_{xx}+c_{zz})$ and $c(2) = (c_{xx}-c_{yy})$, respectively. These terms in $H_{F}^{N}$ lift the parity degeneracy for $\Gamma_{RV} = E$. The rovibrational Hamiltonian $H_{RV}$ was adopted from an earlier partner study.\(^1\) A good fit to the hyperfine data was obtained with a standard deviation of 3.1 kHz. In the fitting process, 12 rovibrational parameters were varied, while the remaining constants in $H_{RV}$ were left at the values of Ref. ($1$). In addition, 6 hyperfine parameters were determined: four in $H_{Q}^{N}$, and two in $H_{F}^{N}$. It was found that $|c(1)| = 7.48(24)$ kHz and $|c(2)| = 2.423(22)$ kHz. This determination of $|c(1)|$ is the first to be reported based on frequency measurements. The key to the observation of the parity doubling lies in the severe mixing into the eigenvalues of basis vectors with several different values of $k l$ as a result of the clustering\(^1\) of rovibrational levels at low $K$.


TOWARD A GLOBAL MODEL OF LOW-LYING VIBRATIONAL STATES OF CH\textsubscript{3}CN: THE $v_4 = 1$ STATE AT 920 cm\textsuperscript{-1} AND ITS INTERACTIONS WITH NEARBY STATES

HOLGER S. P. MÜLLER, I. Physikalisches Institut, Universität zu Köln, 50937 Köln; B. J. DROUIN, J. C. PEARSON, L. R. BROWN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA; I. KLEINER, LISA, Université Paris 12 & Paris 7 & CNRS, 94010 Créteil, France; R. L. SAMS, PNNL, Richland, WA 99352, USA.

Methyl cyanide, CH\textsubscript{3}CN, is an important interstellar molecule, in particular in hot and dense molecular cores, and it may play a role in the atmospheres of planets or of Titan. Therefore, we have recorded extensive rotational and rovibrational spectra up to $\sim 1.6$ THz and $\sim 1500$ cm\textsuperscript{-1}, respectively. The present investigation extends our analysis of states with $v_8 \leq 2$ at vibrational energies below 740 cm\textsuperscript{-1}\(^a\) and takes into consideration findings from an analysis of the $v_4$ band and the higher-lying $v_7$ (at $\sim 1042$ cm\textsuperscript{-1}) and $3v_4^2$ (at $\sim 1078$ cm\textsuperscript{-1}) bands.\(^b\) The rotational data extend to $J = 87$ and $K = 15$, infrared assignments currently extend to 55 and 12, respectively. Parameters affecting only $v_7 = 1$ or $v_8 = 3$ as well as some additional interaction parameters were kept fixed to values from ($b$). The largest perturbations of $v_4 = 1$ are caused by a $\Delta k = 0$, $\Delta l = 3$ interaction with $v_8 = 3$ at $K = 8$. Despite the inclusion of the interaction parameter and a centrifugal distortion correction, residuals amount to more than 200 MHz very close to the resonance. Removal of these residuals probably requires explicit inclusion of $v_8 = 3$ data. Several additional perturbations exist at lower as well as higher $K$ with $v_8 = 2$, $v_7 = 1$ and $v_8 = 3$. Higher values of $K$ are difficult to reproduce in spite of an extensive set of distortion parameters which, at highest orders, have rather large magnitudes, possibly indicating unaccounted interactions which would probably occur with states even higher than $v_8 = 3$.

\(^{a}\)H. S. P. Müller et al., contribution WG03, presented at the 62nd International Symposium on Molecular Spectroscopy, June 18–22, 2007, Columbus, Ohio, USA.

TOWARDS UNDERSTANDING QUANTUM MONODROMY IN QUASI-SYMMETRIC MOLECULES: FASSST ROTATIONAL SPECTRA OF CH$_3$NCO AND CH$_3$NCS

ZBIGNIEW KISIEL, Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland; SARAH FORTMAN, IVAN R. MEDVEDEV, MANFRED WINNEWISER, FRANK C. DE LUCIA, Department of Physics, The Ohio State University, Columbus, OH 43210; JACEK KOPUT, Department of Chemistry, Adam Mickiewicz University, 60-780 Poznań, Poland.

The recent studies of the rotational spectrum of the NCNCS molecule$^{a,b,c}$ demonstrated the success of quantum monodromy in describing the quasilinear behavior of this molecule, inclusive of the abrupt transition of spectroscopic behavior from the bent to the linear molecule regime. Similar, quasisymmetric behaviour, is known to be present in symmetric top molecules, and has been studied at lowest-$J$ transitions for two such molecules, CH$_3$NCO$^d$ and CH$_3$NCS.$^e$

Further progress requires more experimental data and presently we report FASSST rotational spectra of CH$_3$NCO and CH$_3$NCS. The spectra provide practically continuous 117-376 GHz coverage and are very rich, since the ladder of excited vibrational states associated with the quasilinear bending coordinate is multiplied by the nearly free internal rotation of the methyl group. Initial stages of the analysis leading up to an analysis in an extension of the framework used for NCNCS are described.

RD01

**INVITED TALK**

**BROADBAND SPECTROSCOPY WITH DUAL COMBS AND CAVITY ENHANCEMENT**

**RONALD HOLZWARTH, Max-Planck-Institute for Quantum Optics, 81748 Garching, Germany and Menlo Systems GmbH, 82152 Martinsried, Germany; BIRGITTA BERNHARDT, AKIRA OZAWA, THOMAS UDEM, THEODOR W. HÄNSCH, Max-Planck-Institute for Quantum Optics, 81748 Garching, Germany; PATRICK JACQUET, MARION JACQUEY, GUY GUELACHVILI, Laboratoire de Photophysique Moléculaire, CNRS, Batiment 350, Université Paris-Sud, 91405 Orsay, France; YOHEI KOBAYASHI, Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan; NATHALIE PICQUE, Max-Planck-Institute for Quantum Optics, 81748 Garching, Germany and Laboratoire de Photophysique Moléculaire, CNRS, Batiment 350, Université Paris-Sud, 91405 Orsay, France.**

Classical FTIRs handle the task of massively parallel spectroscopic probing by interferometric detection. In contrast a frequency comb Fourier transform spectrometer (FC-FTS) retains the principle of combining two interferometer beams but uses two inputs from two independent sources. Thus we can offset their frequencies to facilitate multifrequency heterodyne signal processing. The advantages of this spectrometer compared with the classical FTIR include ease of operation (no cumbersome moving delay lines), speed of acquisition (18 µs demonstrated), collimated long-distance propagation, possibly diffraction-limited microscopic probing, and mid infrared as well as THz operation if necessary.

In a recent proof of principle experiment we have dramatically improved the sensitivity by the implementation of an enhancement cavity around the probing volume\(^a\). We recorded, within 18 µs, spectra of the ammonia 1.0 µm overtone bands comprising 1500 spectral elements and spanning 20 nm with 4.5 GHz resolution and a noise-equivalent-absorption at one-second-averaging of \(1 \times 10^{-10} \text{cm}^{-1} \text{Hz}^{-1/2}\), thus opening a route to time-resolved spectroscopy of rapidly-evolving single-events. Since FC-FTS only needs one detector that is easily available in practically all spectral regions, it can be envisioned that cavity-enhanced FC-FTS will assume a position of dominance for the measurements of real-time ultra-sensitive spectra in the molecular fingerprint region.

\(^a\)B. Bernhardt et. al., *Nature Photonics* 4 (55), January 2010

RD02

**TUNABLE LASER SPECTROSCOPY REFERENCED WITH DUAL FREQUENCY COMBS**

**F. R. GIORGETTA, I. CODDINGTON, E. BAUMANN, W. C. SWANN, N. R. NEWBURY, NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY, BOULDER, CO 80305.**

Frequency combs provide broadband spectroscopic measurements with high frequency accuracy and precision. However, because the comb power is distributed over a broad spectrum, the sensitivity can be low unless some form of multiplexed detection or cavity enhancement is used. In contrast, tunable laser spectroscopy can achieve much higher sensitivities because the full laser power is within the measured frequency window, but the frequency accuracy and precision of a rapidly tuned laser is challenging to characterize and control. We propose to combine the advantages of these two forms of spectroscopy by performing tunable cw laser spectroscopy in conjunction with a dual frequency comb setup. The cw laser would provide broadband high SNR measurements of a samples transmission spectrum on a single detector, while dual frequency combs would provide absolute instantaneous frequency measurements of the cw laser. Preliminary measurements characterizing a tunable laser have demonstrated Kilohertz frequency accuracy and resolution with a measurement time of a few milliseconds over a 25 nm band around 1550 nm.
A mid-infrared frequency comb tunable from 2.7\( \mu \)m to 4.7\( \mu \)m (3700cm\(^{-1}\) to 2100cm\(^{-1}\)) has been produced using a fiber laser and difference frequency generation in a periodically poled LiNbO\(_3\) (PPLN) crystal. An amplified Yb-doped femtosecond fiber laser is centered at a wavelength of 1.04\( \mu \)m, with 100MHz repetition frequency and up to 2.5W average output power. Part of this laser power is focused into a photonic crystal fiber to produce a Raman-shifted soliton tunable over a range from 1.3\( \mu \)m to 1.7\( \mu \)m. The remaining 1.04\( \mu \)m light is combined with the wavelength-shifted spectrum and focused into the PPLN to produce a difference frequency comb spanning \( \sim 200\text{nm} \) (180cm\(^{-1}\)) in the mid-infrared. By adjusting the Raman-shifted soliton and PPLN, the center wavelength of the MIR comb is tuned over the output range, with a maximum power of up to 35mW near 3.3\( \mu \)m.

Sum frequency generation between the MIR comb and a CW 1064nm laser shifts the frequency comb spectrum back into the near-infrared around 800nm. This sum frequency step is taken in order to utilize detectors and techniques that are currently more accessible in the visible and near-infrared ranges. Preliminary results have shown MIR methane absorption lines observable in the upconverted 800nm spectrum on a commercial optical spectrum analyzer. We intend to measure this upconverted spectrum at high resolution using a two-dimensional dispersion and imaging technique\(^a\) to take advantage of the precisely known frequency characteristics of each individual MIR comb line.


---

Recent experiments have demonstrated that the precisely spaced spectral lines of a laser frequency comb can be harnessed for new techniques of multi-heterodyne Fourier transform spectroscopy (also called dual-comb spectroscopy) of molecules. In one such experiment\(^b\), an absorbing molecular gas was placed inside an optical cavity that is matched to the laser resonator so that it is resonant for each comb line. The sensitivity for weak absorption is much enhanced, as in cavity ring-down spectroscopy. The light transmitted by the cavity is superimposed on a second frequency comb with slightly different repetition frequency. A single fast photodetector then produces an output signal with a comb of radio frequencies due to interference between pairs of optical comb lines. The optical spectrum is thus effectively mapped into the radio frequency regime, where it becomes accessible to fast digital signal processing.

Experimental proof-of-principle is carried out in the near-infrared 1\( \mu \)m region. An Yb-doped fiber frequency comb is coherently coupled to a passive resonator with a finesse of 1200, resulting in an effective interaction length between the light and the gas enhanced to 880m. The weak 3\( \nu_1 \) band of ammonia is rotationally resolved for the first time to our knowledge. Recording times of 18\( \mu \)s are enough to span 220 cm\(^{-1}\) with a resolution of 0.15 cm\(^{-1}\). The signal to noise ratio of 380 leads to a minimum-detectable-absorption coefficient \( \alpha_{\text{min}} \) of \( 3 \times 10^{-9}\text{cm}^{-1} \).

Fourier transform spectroscopy based on time-domain interferences\textsuperscript{a} between two slightly detuned frequency comb sources holds much promise for the real-time diagnostic of gaseous, liquid or solid-state samples. In one very recent example\textsuperscript{b}, cavity-enhanced absorption spectroscopy with two infrared frequency combs has demonstrated a dramatically enhanced sensitivity, compared to conventional Fourier spectroscopy, with intriguing implications for instantaneous trace gas analysis. It however remains challenging to match continuously the comb and cavity modes across a broad spectral bandwidth during the time of a measurement.

An obvious alternative for reaching a long interaction path is a conventional multipass cell. Additionally, differential detection schemes may be devised to increase the dynamic range of the interferometric measurements, thus providing enhanced signal to noise ratio. Experimental demonstrations will be given in the 1.5 $\mu$m region with a dual comb set-up based on two Er-doped fiber femtosecond lasers. The versatility and performances of these solutions will be compared to the cavity-enhanced dual comb technique and other state-of-the-art alternatives.


By coupling a train of low-phase-noise, ultrashort pulses to a femtosecond enhancement cavity, it is possible to obtain a large enhancement of the pulse energy and subsequently drive the high harmonic generation process at $\geq 100 \text{ MHz}$ repetition rates. At these repetition frequencies, the generated VUV-XUV frequency combs could potentially be used for a multitude of experiments requiring short wavelength radiation with exceptional temporal coherence and/or high average photon flux. We will present recent progress, including power scaling of the driving field with a corresponding factor of 10 improvement in harmonic power over previous results, as well as initial coherence tests of the generated VUV frequency comb.

The ionization and dissociation energies of H$_2$, HD and D$_2$ are benchmark quantities in molecular quantum mechanics. Comparison between experimental and theoretical values for these quantities has a long history starting with the early measurement of Beutler$^a$ and the calculations of James and Coolidge.$^b$ Transition wave numbers from the $EF \ ^1\Sigma^+_g \ (v = 0, N = 0, 1)$ state to selected $np$ Rydberg states ($n \approx 60$) below the $X^+ \ ^2\Sigma^+_u \ (v^+ = 0, N^+ = 0, 1)$ ionization threshold have been measured in H$_2$,$^c$ HD and D$_2$ at a precision better than 10 MHz (0.0003 cm$^{-1}$). Combining the results with previous experimental and theoretical data for other energy level intervals, the ionization and dissociation energies of H$_2$, HD and D$_2$ could be determined at an absolute accuracy of better than 20 MHz. These new results represent an improvement over previous experimental results by more than one order of magnitude and the most precise values of dissociation and ionization energies measured to date in a molecular system. The results therefore offer the opportunity of a comparison with theoretical values. In particular they will be compared to the latest $ab\ initio$ calculations$^e$ which include nonadiabatic, relativistic and radiative effects. The comparison indicates that relativistic and radiative quantum electrodynamics corrections of order up to $\alpha^4$ are needed to account for the experimental results.

---

$^a$H. Beutler, Z. Phys. Chem. 29, 315 (1935)
The advent of laser frequency combs a decade ago has already revolutionized optical frequency metrology and precision spectroscopy. Extensions of laser combs from the THz region to the extreme ultraviolet and soft x-ray frequencies are now under exploration. Such laser combs have become enabling tools for a growing tree of applications, from optical atomic clocks to attosecond science.

Recently, the millions of precisely controlled laser comb lines that can be produced with a train of ultrashort laser pulses have been harnessed for highly multiplexed molecular spectroscopy. Fourier multi-heterodyne spectroscopy, dual comb spectroscopy, or asynchronous optical sampling spectroscopy with frequency combs are emerging as powerful new spectroscopic tools. Even the first proof-of-principle experiments have demonstrated a very exciting potential for ultra-rapid and ultra-sensitive recording of complex molecular spectra. Compared to conventional Fourier transform spectroscopy, recording times could be shortened from seconds to microseconds, with intriguing prospects for spectroscopy of short lived transient species. Longer recording times allow high resolution spectroscopy of molecules with extreme precision, since the absolute frequency of each laser comb line can be known with the accuracy of an atomic clock.

The spectral structure of sharp lines of a laser comb can be very useful even in the recording of broadband spectra without sharp features, as they are e.g. encountered for molecular gases or in the liquid phase. A second frequency comb of different line spacing permits the generation of a comb of radio frequency beat notes, which effectively map the optical spectrum into the radio frequency regime, so that it can be recorded with a single fast photodetector, followed by digital signal analysis. In the time domain, a pulse train of a mode-locked femtosecond laser excites some molecular medium at regular time intervals. A second pulse train of different repetition frequency interferometrically samples the transient response or free induction decay of the medium, akin to an optical sampling oscilloscope.

Laser combs in combination with other advancing tools of laser science, nonlinear optics, photonics, and electronic signal processing have the potential to vastly enhance the range and capabilities of molecular laser spectroscopy. The high versatility of frequency comb sources can indeed harness new techniques for ultra-rapid and ultra-sensitive recording of complex molecular spectra. The recent proof-of-principle demonstrations of dual comb Fourier transform spectroscopy have mostly been carried out in the near-infrared region, around 1.0 and 1.5 µm. The mode-locked ytterbium- or erbium-doped fiber femtosecond laser systems emitting in this range indeed require few adjustment thanks to their guided light and permit reliable unattended operation. With expanded wavelength coverage and continued improvements in speed and sensitivity, dual comb spectroscopy should find use as a novel, time-domain spectroscopic analytical tool. As far as molecular spectroscopy is concerned, the mid-infrared and visible-ultraviolet wavelength regions show both the potential for specificity and sensitivity for tracing molecules. In particular, the visible-ultraviolet region complements the mid-infrared molecular fingerprint range, as it provides access to many electronic transitions, in particular belonging to reactive species.

In this contribution, we report on our progress in the implementation of dual comb spectroscopy in the 520 nm green region. We present preliminary results on a powerful new sensitive ultra-rapid tool for linear rovibronic absorption spectroscopy, based on frequency-doubled ytterbium-doped fiber lasers and we discuss its intriguing prospects for spectroscopy of short lived transient species.
Immediately after their introduction in 1999, femtosecond laser frequency combs revolutionized the field of precision optical frequency metrology and are key elements in many experiments. Frequency combs based on femtosecond Er-fiber lasers were demonstrated in 2005, allowing additionally rugged, compact set-ups and reliable unattended long-term operation. The introduction of Yb-fiber technology led to a dramatic improvement in fiber-comb performance in various aspects. Low-noise Yb-fiber femtosecond oscillators enabled a reduction of relative comb tooth linewidth to the sub-Hz level as well as scaling of the fundamental comb spacings up to 1 GHz. This is beneficial for any frequency-domain comb application due to the higher power per comb-mode. Many spectroscopic applications require, however, frequency combs way beyond the wavelength range accessible with broad band laser materials, so nonlinear conversion and hence higher peak intensity is required. We demonstrated power scaling of Yb-fiber frequency combs up to 80 W average power in a strictly linear chirped-pulse amplification schemes compatible with low-noise phase control. These high-power Yb-fiber-frequency combs facilitated not only the extension to the mid-IR spectral region. When coupled to a passive enhancement cavity, the average power can be further scaled to the kW-level opening new capabilities for XUV frequency combs via high-harmonic generation. All these advances of fiber-based frequency combs will trigger many novel applications both in fundamental and applied sciences.

b Hartl et al., MF9 in Advanced Solid-State Photonics. 2009, Optical Society of America.
c Ruehl et al., AWC7 in Advanced Solid-State Photonics. 2010, Optical Society of America.
d Adler et al., Optics Letters 34 1330 (2009).
e Yost et al., Nature Physics 5 815 (2009).
RE01  15 min  8:30
THE PERFORMANCE OF A CONTINUOUS SUPERSONIC EXPANSION DISCHARGE SOURCE

CARRIE A. KAUFFMAN, KYLE N. CRABTREE, Department of Chemistry, University of Illinois, Urbana, IL 61801; BENJAMIN J. MCCALL, Departments of Chemistry and Astronomy, University of Illinois, Urbana, IL 61801.

Production of cold molecular ions is an integral component in performing high resolution spectroscopy of astronomically important ions at temperatures comparable to the interstellar medium. Frequently, pulsed supersonic expansion discharge sources have been used to produce ions at these temperatures. Yet, pulsed sources impose a limit on the duty cycle of the spectroscopic technique. To circumvent this limitation, a continuous supersonic expansion discharge source has been designed for use in the high resolution technique that is currently being developed in our lab, SCRIBES (Sensitive, Cooled, Resolved Ion BEam Spectroscopy). In order to characterize and optimize the source design, the R(1,0), R(1,1)$^u$, and R(2,2)$^i$ transitions within the $\nu_2 \leftrightarrow 0$ band of $\text{H}_3^+$ have been studied using continuous-wave cavity ringdown spectroscopy with a recently constructed difference frequency generation (DFG) laser. Temperature and ion column density were recorded as a function of discharge current. Observed temperatures were in the range of 50 to 110 K and the ion column densities between $8 \times 10^{10}$ and $2 \times 10^{12}$ cm$^{-2}$. The source was found to be robust; operation was sustained for a period of 200 hours. Future prospects to optimize this design using $\text{HN}_2^+$ will also be discussed.

RE02  15 min  8:47
FOURIER TRANSFORM INFRARED SPECTROSCOPY OF THE $\text{H}_2\text{F}^+ \nu_1, \nu_3$ AND $\nu_2$ BANDS

R. FUJIMORI, Y. HIRATA, K. KAWAGUCHI, Department of Chemistry, Faculty of Science, Okayama University, 3-1-1, Tsushima-Naka, Okayama 700-8530, JAPAN; I. MORINO, Satellite Remote Sensing Research Section, Center for Global Environmental Research, National Institute for Environmental Studies Ohogawa 16-2, Tsukuba, Ibaraki 305-8506, JAPAN.

Since HF is known as interstellar species, the protonated HF may exist with detectable abundance. Vibration-rotation spectra of $\text{H}_2\text{F}^+ \nu_1$ and $\nu_3$ bands were studied by infrared laser spectroscopy$^a$. The $\nu_2$ band and pure rotational spectra have not been reported. In this study, we report FTIR spectroscopy of $\text{H}_2\text{F}^+ \nu_1, \nu_3$ and $\nu_2$ bands. The ion was produced with hollow cathode discharge in $\text{F}_2$, He and $\text{H}_2$ mixture. A simultaneous analysis of FT data combined with laser spectroscopic data was carried out for $\nu_1$ and $\nu_3$ bands, to determine ground state molecular constants. Absorption lines in the $\nu_2$ region were assigned by using the ground state combination differences. Determined molecular constants can be used to predict pure rotational transition frequencies.

Metastable $^4\text{He}_2$ molecules $[\alpha 3\Sigma^+_u (v = 0, N = 1, 3, 5, 7)]$ were produced in a supersonic expansion of neat helium atoms by striking a discharge at the orifice of a pulsed valve. Transitions to np Rydberg states ($n$ up to 150) converging to the first rotational levels of the ground state of $\text{He}_2^+$ $[X^+ 2\Sigma^+_u (v^+ = 0, N^+ = 1, 3, 5)]$ were recorded at a precision better than $10^{-3}$ cm$^{-1}$ using the technique of Rydberg-state-resolved threshold ionization spectroscopy. The observed Rydberg series reveal strong perturbations caused by rotational channel interactions and the appearance of the spectra is strongly influenced by weak electric fields present in the excitation region. The extrapolation of the Rydberg series to their limits using multichannel quantum defect theory enabled the determination of the rotational structure of the helium dimer cation and of quantum defect parameters for the corresponding ionization channels. These results represent a benchmark for $ab$ initio calculations on three-electron systems.$^{\text{cd}}$


New, more detailed studies of the photoionization and Penning ionization of $\text{BF}_3$ trapped in solid neon have confirmed the earlier$^a$ infrared spectroscopic identification of $\text{BF}_2$ and $\text{BF}_2$ cation and have yielded a revised assignment for the infrared absorptions of $\text{BF}_3$ cation. The position of the absorption attributed to $\nu_3$ of that molecule is consistent with the distortion of the ground-state cation from $D_{3h}$ symmetry because of strong vibronic interaction between levels of the $B^2E'$ state and $E'$ levels of the $\tilde{X}^2A''_1$ ground state, as predicted by Haller and co-workers.$^b$ The facile reaction of $\text{BF}_3$ with traces of $\text{H}_2\text{O}$ desorbed from the walls of the vacuum system leads to the stabilization of sufficient $\text{BF}_2\text{OH}$ for the identification of two vibrational fundamentals of $\text{BF}_2\text{OH}$ cation.


Velocity modulation spectroscopy has traditionally been used with a unidirectional multipass White cell to obtain several passes through a plasma in order to obtain strong signals from the absorption of ions, but the total number of passes allowed by this type of setup is limited to $\sim 8$. By placing an optical cavity around a $N_2^+$ plasma and locking the cavity to a Ti:Sapphire laser, the effective number of passes has been increased to several hundred. Demodulating the signal from the transmitted light at twice the plasma frequency (due to the symmetric nature of the cavity) gives a $2^{nd}$ derivative lineshape for ions and a Gaussian lineshape for excited neutrals. $N_2^+$ and $N_2^-$ have been observed to be $78^\circ$ out of phase with one another. The different lineshapes and phases allow for discrimination and separation of the ion and neutral signals. The high intensity laser light within the cavity causes the transitions to saturate, which allows for the observation of lamb dips; this opens the door to sub-Doppler spectroscopy, as well as to studies of ion-neutral collisional rate coefficients.
TOWARDS HIGH RESOLUTION CAVITY ENHANCED SPECTROSCOPY WITH FAST ION BEAMS

ANDREW MILLS, BRIAN SILLER, MANORI PERERA, HOLGER KRECKEL, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801; BENJAMIN J. McCALL, Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

The spectroscopic study of gas phase molecular ions has been recognized as an important subject for many fields ranging from combustion to the chemistry of the interstellar medium. In order to perform high resolution spectroscopy with molecular ions, several challenges have to be overcome, including low sample densities and spectral congestion caused by neutral species. For many years, velocity-modulated AC plasmas have been used successfully to provide ion-neutral discrimination; however, they suffer from Doppler broadened line widths and high rotational temperatures. Furthermore, spectroscopy in an AC discharge is often burdened with an inherent uncertainty as to which species are actually present in the plasma.

To address these issues we are developing a new spectroscopic technique called SCRIBES (Sensitive, Cooled, Resolved Ion BEam Spectroscopy) that employs molecular ion beams to reduce Doppler line widths by kinematic compression. A time-of-flight mass spectrometer allows for exact identification of the ion beam composition during the measurements. The use of a supersonic ion source will reduce the rotational temperature and eliminate spectral congestion. In order to achieve the required spectroscopic sensitivity we utilize cavity-enhanced techniques, which require a high degree of mechanical stability. We will describe improvements made to our instrument to increase the mechanical stability of the cavity, and allow for simultaneous spectroscopy and mass analysis. We will also describe progress made towards integrating the cavity enhanced velocity modulation spectroscopy (CEVMS) method described in the previous talk with an uncooled fast ion beam.

CATION SPECTROSCOPY OF 3,4-DIFLUOROANILINE

WEN BIH TZENG, Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, 1 Section 4, Roosevelt Road, Taipei 10617, Taiwan.

Very few spectroscopic data of tri-substituted benzene are available in the literature. We applied the resonant two-photon ionization and mass analyzed threshold ionization spectroscopic techniques to record the vibronic and cation spectra of 3,4-difluoroaniline. The results give precise electronic excitation and adiabatic ionization energies. In addition, information about the active vibrations in the first electronically excited and cationic ground states are also obtained. The spectral assignment has been successfully done by comparing the present data with those of m-fluoroaniline and p-fluoroaniline. We have performed theoretical calculations to support our experimental findings. Keywords: 3,4-difluoroaniline, resonant multiphoton ionization, threshold ionization, cation spectra

Intermission
Acetaldehyde was photodissociated with near UV laser light, and the methyl (CH$_3$) and formyl (HCO) radical fragments were photoionized with vacuum ultraviolet (VUV) light. The fragments were detected by using both time of flight mass spectrometry and velocity ion map imaging. With the former technique, simultaneous detection of both fragments provided the intensity of HCO$^+$ relative to CH$_3^+$ with $I$(HCO$^+$/I(CH$_3^+$) $\approx$ 0.8. Because the absolute photoionization cross section of the CH$_3$ radical has been characterized ($\approx$ 5 Mb) at the VUV energies of interest, the absolute photoionization cross section of HCO could be determined from the intensity ratio, yielding an HCO cross section of $\approx$ 4 Mb at 10.3 eV. However, because some of the HCO fragments could be formed with enough internal energy to undergo secondary dissociation, velocity ion map imaging was employed to determine the extent of any secondary dissociation that occurred. The translational energy distributions obtained for both the CH$_3$ and HCO fragments are nearly identical, indicating that no HCO fragments underwent secondary dissociation. A surprising result was the smaller photoionization cross section of HCO relative to CH$_3$. Comparison to the isoelectronic species of NO will be discussed and a potential explanation will be offered for this observation.

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences under contract No. DE-AC02-06CH11357.
SUPEROXIDE PHOTOELECTRON ANGULAR DISTRIBUTIONS: VIBRATIONAL DEPENDENCE AS A CONSEQUENCE OF BORN-Oppenheimer Behavior

RICHARD MABBS, MATTHEW VAN DUZOR, FOSTER MBAIWA and JIE WIE, Department of Chemistry, Washington University, One Brookings Dr., Campus Box 1134 Saint Louis, Missouri 63130, USA; STEPHEN GIBSON, STEVEN CAVANAGH and B. R. LEWIS, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, Australian Capital Territory 0200, Australia.

For atomic anions the photoelectron angular distribution (PAD) is a signature of the bound excess electron wavefunction. However, even for relatively simple molecular anions the relationship between the detachment orbital and the PAD is more complicated. We demonstrate this with a series of near threshold photoelectron images for superoxide detachment, recorded over small photon energy increments. The highest occupied, π_g orbital has a strong resemblance to an atomic d-orbital. Detachment from the superoxide anion via the O_2(X^3Σ^−, v'' = 0) → O_2^−(X^2Π_g, v' = 0) transitions reveals that the electron kinetic energy dependence of the PAD resembles that of atomic anions. However, there is also a clear dependence on the vibrational energy deposited in the neutral O_2. Comparison with theoretical calculations reveals that this dependence is not due to non-adiabatic effects. Instead it arises in the change of the electronic transition moment across the X−X band, a direct consequence of the parametric dependence of the π_g orbital function on the internuclear separation.

THE PHOTOELECTRON ANGULAR DISTRIBUTION AS A PROBE OF ENERGETICALLY INDISTINGUISABLE CHANNELS IN PHOTODETACHMENT

MATTHEW VAN DUZOR, FOSTER MBAIWA, JIE WIE and RICHARD MABBS, Department of Chemistry, Washington University, One Brookings Dr., Campus Box 1134 Saint Louis, Missouri 63130, USA.

Photoelectron imaging measurements of I^-·CH_3CN are presented from the lowest energy I(2P_3/2)·CH_3CN channel threshold to 0.3 eV above the I(2P_1/2)·CH_3CN threshold. Excitation of the cluster just below the latter threshold leads to competition between direct detachment and the production of a dipole-bound state [I(2P_1/2)·CH_3CN]−. Subsequent relaxation of the I moiety (2P_1/2 → 2P_3/2) occurs via autodetachment of the dipole bound electron. However, the autodetached electrons are energetically equivalent to those directly detached via the 2P_3/2 channel. While the photoelectron spectrum is insensitive to this phenomenon, the kinetic energy dependence of the photoelectron angular distribution (PAD) of the 2P_3/2 channel reflects these dynamics. Dramatic changes are observed within a 100 meV window of the I(2P_1/2)·CH_3CN threshold. Although previously unreported, further results are presented that show sharp changes in the PAD are relatively common in I−·X cluster anions (X=polar molecule).

VIBRATIONAL AUTODETACHMENT IN NITROALKANE ANIONS

CHRISTOPHER L. ADAMS, J. MATTHIAS WEBER, JILA, NIST, and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309, USA.

Nitroalkanes have electron affinities ≥ 1370 cm⁻¹, well below the excitation energies for CH stretching modes, with the excess charge localized on the nitro group. Upon absorption of an IR photon in a CH stretching vibrational mode, the absorbed energy is redistributed in the molecule. If enough energy is transferred to the NO_2 stretching/wagging modes, the excess electron residing on the nitro group is emitted. Vibrational autodetachment (VAD) spectra encode information regarding intramolecular vibrational relaxation (IVR) processes leading up to electron emission. We present VAD photoelectron spectroscopy of polyatomic molecular anions and discuss how a VAD photoelectron spectrum can be modeled.
RF01 15 min 1:30

THE INTERSTELLAR DETECTION OF HSCN IN Sgr B2(N)

D. T. HALFEN, L. M. ZIURYS, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721; M. C. MCCARTHY, C. GOTTLEIB, and P. THADDEUS, Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138, and School of Engineering & Applied Sciences, Harvard University, 29 Oxford St., Cambridge, MA 02138.

HSCN (thiocyanic acid), an energetic isomer of the well-known species HNCS, has been detected toward Sgr B2(N) with the Arizona Radio Observatory 12m telescope. Eight rotational transitions in the $K_a = 0$ ladder were observed in the 2mm and 3mm bands. Five consecutive transitions in the 3 mm band are unblended, but three in the 2 mm band are partially masked by lines of other molecules. The line width and radial velocity of HSCN match closely with those of the ground state isomer HNCS, HNCO, and HOCN. Although HSCN is calculated to lie over 3000 K higher in energy than HNCS, its column density of $1.3 \times 10^{13}$ cm$^{-2}$ in Sgr B2(N) is only three times lower than that of HNCS. By analogy with the isomeric pair HCN and HNC, these two sulfur-bearing isomers are plausibly formed from a common cation precursor.

RF02 15 min 1:47

THE [HNCS]/[HSCN] RATIO IN SGRB2 AND TMC-1

G. ADANDE, D.T. HALFEN, L.M. ZIURYS, Department of Chemistry, Steward Observatory, University of Arizona, Tucson.

The formation of the metastable isomer pair, HNCS and HSCN, has been investigated in the warm molecular cloud SgrB2 and the dense cold core TMC-1. In Sagittarius B2, the $8_{0,8}$-$7_{0,7}$ and $9_{0,9}$-$8_{0,8}$ transitions of both isomers have been mapped over a $5 \times 3$ region around the central hot core SgrB2(M), using the Arizona Radio Observatory (ARO) 12m telescope. In TMC-1, the $8_{0,8}$-$7_{0,7}$ and $7_{0,7}$-$6_{0,6}$ lines of both isomers have been detected. Both molecules show extended emission across SgrB2 with a ratio [HNCS]/[HSCN] $1 - 10$. In TMC-1, the ratio is $1$. The high abundance of the metastable isomer HSCN relative to HNCS suggests that the main production route to both molecules is electron recombination from the ionic precursor HNCSH+, in analogy to HCN and HNC.
DETECTION OF INTERSTELLAR UREA WITH CARMA

H.-L. KUO, L. E. SNYDER, D. N. FRIEDEL, L. W. LOONEY, Department of Astronomy, University of Illinois at Urbana-Champaign; B. J. McCALL, Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana IL 61801; A. J. REMIJAN, NRAO, Charlottesville VA 22903; F. J. LOVAS, Optical Technology Division, NIST, Gaithersburg MD 20899-8441; J. M. HOLLIS, NASA/GSFC, Code 606, Greenbelt MD 20771.

Urea, a molecule discovered in human urine by H. M. Rouelle in 1773, has a significant role in prebiotic chemistry. Previous BIMA observations have suggested that interstellar urea [(NH$_2$)$_2$CO] is a compact hot core molecule such as other large molecules, e.g. methyl formate and acetic acid (2009, 64th OSU Symposium On Molecular Spectroscopy, WI05). We have conducted an extensive search for urea toward the high mass hot molecular core Sgr B2(N-LMH) using CARMA and the IRAM 30 m. Because the spectral lines of heavy molecules like urea tend to be weak and hot cores display lines from a wide range of molecules, a major problem in identifying urea lines is confusion with lines of other molecules. Therefore, it is necessary to detect a number of urea lines and apply sophisticated statistical tests before having confidence in an identification. The 1 mm resolution of CARMA enables favorable coupling of the source size and synthesized beam size, which was found to be essential for the detection of weak signals. The 2.5$''$×2$''$ synthesized beam of CARMA significantly resolves out the contamination by extended emission and reveals the eight weak urea lines that were previously blended with nearby transitions. Our analysis indicates that these lines are likely to be urea since the resulting observed line frequencies are coincident with a set of overlapping connecting urea lines, and the observed line intensities are consistent with the expected line strengths of urea. In addition, we have developed a new statistical approach to examine the spatial correlation between the observed lines by applying the Student T-test to the high resolution channel maps obtained from CARMA. The T-test shows similar spatial distributions from all eight candidate lines, suggesting a common molecular origin, urea. Our T-test method could have a broad impact on the next generation of arrays, such as ALMA, because the new arrays will require a method to systematically determine the credibility of detections of weaker signals from new and larger interstellar molecules.

METHANOL PHOTODISSOCIATION BRANCHING RATIOS AND THEIR INFLUENCE ON INTERSTELLAR ORGANIC CHEMISTRY

JACOB C. LAAS and SUSANNA L. WIDICUS WEAVER, Department of Chemistry, Emory University, Atlanta, GA 30322; ROBIN T. GARROD, Department of Astronomy, Cornell University, Ithaca, NY 14853.

Methanol is the most abundant organic molecule in interstellar ices, and its photodissociation is the dominant source of organic radicals in these ices. These organic radicals become mobile and react in warm (>30 K) environments. Such combination reactions lead to a variety of complex organic molecules with differing structural arrangements of organic functional groups. It is plausible, then, that methanol photodissociation branching ratios directly impact the relative abundances of structural isomers observed in interstellar environments. Previous laboratory investigations of the methanol photodissociation process yielded disparate results, and few of these experiments were conducted under conditions that can be directly applied to interstellar chemistry. We are therefore undertaking a combined laboratory spectroscopy and astrochemical modeling investigation of the methanol photodissociation reaction mechanism. In this talk, we will present our progress towards developing a submillimeter spectrometer designed to probe the gas-phase photodissociation branching ratios of methanol. We will also report on the results of an astrochemical modeling study that tests the influence of methanol photodissociation branching ratios on complex interstellar chemistry.
Active galactic nuclei (AGNs) are the centers of galaxies with supermassive blackholes whose accretion of mass causes very high luminosities of \( L \sim 10^{44}$ to $10^{46}$ erg s$^{-1}$. An accretion disk has a molecular component that extends to hundreds of pc from the central AGN core. The question of how much central illumination affects the disk and how much star formation is present near the core have been astrophysical interests. Rotational lines from these disks at a sub-kpc scale have been observed for molecules such as CO, HCO$^+$, HCN, and HNC. When ALMA becomes fully operational, it will be able to resolve these disks at much higher resolution than currently. Molecular observations at higher resolution may give some hints on the physics in the molecular disk. We modeled the chemical composition of a molecular disk in an AGN on a scale of tens of pc. To do this, we extended our standard gas-phase OSU network to include important processes at much higher temperatures, approaching 1000 K. We used the density model of Thompson et al.$^a$, and determined the temperature by the blackbody approximation from the luminosity of the AGN core. The ionization by X-rays from the AGN core, by cosmic-rays from the AGN core, supernovae and stellar winds, and by UV-photons from OB stars are considered. We will briefly mention the effects from other factors that may change the molecular abundances such as shock waves and inhomogeneity of the density of the disk.

$^a$T. Thompson, E. Quataert, and N. Murray, Astrophysical J. 630, 167 (2005)

---

Until last year the known stars in the Galactic center with sufficiently smooth spectra and of sufficient brightness to be suitable for high resolution infrared absorption spectroscopy of H$_3^+$ and CO were limited to a narrow range of longitudes, from the central cluster of hot stars to approximately 30 pc east of the center. In that region we have discovered a vast amount of warm \( (T \sim 250$ K) and diffuse \( (n \sim 100 \text{ cm}^{-3}) \) gas.$^{ab}$ In order to more fully characterize the gas within the r$\sim 180$ pc Central Molecular Zone (CMZ) it is necessary to find additional such stars that cover a much wider longitudinal range of sightlines. We are in the process of identifying luminous dust-embedded objects suitable for spectroscopy between 170 pc east and west and 14 pc north and south of Sgr A* using the Spitzer GLIMPSE and the 2MASS catalogues. Here we present spectra of H$_3^+$ and CO towards two such objects, one located 140 pc west of Sgr A* close to Sgr E, and the other located on a line of sight to the Sgr B molecular cloud complex 85 pc to the east of Sgr A*.$^c$ The sightline to the west passes through two dense clouds of unusually high negative velocities in Sgr E which show strong absorptions by both H$_3^+$ and CO. This sightline also samples a portion of the Expanding Molecular Ring (EMR) which shows strong H$_3^+$ absorption but undetectable CO clearly indicating that the gas is diffuse, similar to sightlines closer to Sgr A*.$^c$ The H$_3^+$ spectrum toward Sgr B reveals at least ten absorption components covering over 200 km s$^{-1}$ and by far the largest equivalent width ever observed in an interstellar H$_3^+$ line. The CO spectrum is similarly complex but covers a somewhat narrower velocity range indicating mixture of dense and diffuse environments is present along this line of sight. Together the CO and H$_3^+$ spectra appear to provide the first near-infrared view into that hotbed of star formation.

Although further characterization of gas in those two sightlines and many more new sightlines must await observations of H$_3^+$ and CO this July at the Gemini South Observatory, clearly we are opening up a new vista of the CMZ.

LINEAR ANALYSIS OF INFRARED CO SPECTRA

TAKESHI OKA, Department of Astronomy and Astrophysics, and Department of Chemistry, The Enrico Fermi Institute, the University of Chicago, IL 60637; Han Xiao, Department of Statistics, the University of Chicago, Chicago, IL 60637; T. R. GEBALLE, Gemini Observatory, Hilo, HI 96720.

The first overtone band $v = 2 \leftarrow 0$ of CO at $2.35 \mu m$ is a powerful probe for studying interstellar gas in a variety of environments in the long sightlines toward the Galactic center (GC), in particular the intervening spiral arms and the Central Molecular Zone (CMZ). We have been observing this band of CO together with the fundamental band of H$_3^+$ at $3.5 - 4.0 \mu m$ since the two bands give comparable absorption depths but are sensitive to different environments. The overtone CO band is essentially only a probe of dense clouds, while H$_3^+$, which is present in both diffuse and dense clouds, allows one to distinguish diffuse clouds from dense clouds, when both species are observed at high resolution. The foreground spiral arms show both spectra intensely, indicating dense clouds, while the CMZ contains significant amounts of both dense and diffuse gas.

Last year we started to develop a linear program for quantitative analysis of the overtone CO spectra similar to our program for the H$_3^+$ spectrum. The linearity is employed in two ways. First, since the transition dipole moment of the $v = 2 \leftarrow 0$ band is very small, $\mu_{2-0} = 0.00651$ Debye, the optical depth of the transition is orders of magnitude lower than radio and ultraviolet spectra and column densities can be obtained linearly from observed equivalent widths (integrated intensities) without the complications caused by radiation trapping in the radio and saturation in the ultraviolet. Second, we assume linearity in thermalization; that is, we ignore the effects of radiation trapping. This is a more serious neglect, but it is justified to some extent for the analysis of the gas in the CMZ because of the low CO column densities in the cloud clumps and the high velocity dispersion. Conditions for the applicability of the linear analysis and corrections to the approximation using the Sobolev escape probability method will be discussed. The calculation should also be applicable to the infrared CO fundamental band and even to the radio under some limited conditions.

---

INCLUSION OF REACTIONS WITH BARRIERS IN HOT CORE MODELS

GEORGE E. HASSEL, Department of Physics, The Ohio State University, Columbus, OH 43210; ERIC HERBST, Departments of Physics, Astronomy and Chemistry, The Ohio State University, Columbus, OH 43210; NANASE HARADA, Department of Physics, The Ohio State University, Columbus, OH 43210.

Previous models of the low-mass star-forming region L1527 investigated the observations of long-chain unsaturated hydrocarbon radicals in a gaseous envelope with slightly elevated temperature of $\approx 30$ K. These models gradually increased gas and grain temperatures from initially cold (10 K) conditions and demonstrated that the enhanced abundances could be explained by gas-phase ion-molecule chemistry following the evaporation of methane from warming grains. Further, the success of the fit was similar near $T \approx 30$ K if the warm-up was truncated at 30 K or allowed to continue upward toward larger temperatures representative of hot core conditions. A secondary conclusion indicated that the hydrocarbon radical species should remain in large abundance as the temperature grows to 200 K. The subsequent implication that these species might be detected in hot corinos and hot cores stands in contrast with the lack of detection toward such sources. As observational interest in low mass star formation grows, we have re-visited this issue. Primarily, we note that reactions between hydrocarbon radical chains and molecular hydrogen had been previously omitted from cold cloud models as irrelevant because of their non-zero activation barriers of $E_A \approx 1000$ K. These reactions have been included in a revised network, and as a result the abundances of hydrocarbon radical chain species are directly reduced in the revised, extended warm-up models as temperatures exceed $\approx 70$ K. This inclusion does not affect the quality of the previously reported agreement with observations of L1527 in “lukewarm” conditions.
The Stratospheric Observatory for Infrared Astronomy (SOFIA) is a joint U.S./German Project to develop and operate a 2.5-meter infrared airborne telescope in a Boeing 747-SP that flies in the stratosphere at altitudes as high as 45,000 feet and is capable of observations from 0.3 microns to 1.6 mm with an average transmission of greater than 80 percent. SOFIA will be staged out of the NASA Dryden Flight Research Center aircraft operations facility at Palmdale, CA and the SOFIA Science Mission Operations Center (SSMOC) will be located at NASA Ames Research Center, Moffett Field, CA. Open door test flights began in December of 2009. First science flights will begin in 2010, and the number of flights will ramp up annually with a flight rate of over 100 eight to ten hour flights per year expected by 2014. The observatory is expected to operate until the mid 2030’s. We review the status of the SOFIA facility and its initial complement of eight focal plane instruments that include broadband imagers, moderate resolution spectrographs that will resolve broad features due to dust and large molecules, and high resolution spectrometers capable of studying the kinematics of molecular and atomic gas lines at km/s resolution.

The joint U.S. and German Stratospheric Observatory for Infrared Astronomy (SOFIA) will be a premier facility for studying the physics and chemistry of the stellar evolution process for many decades. SOFIA’s first-generation instrument complement includes broadband imagers, moderate resolution spectrographs capable of resolving broad features due to dust and large molecules, and high resolution spectrometers suitable for kinematic studies of molecular and atomic gas lines at km/s resolution. SOFIA spectroscopic science applications will be discussed, with special emphasis on investigations related to infrared spectroscopy of astrophysical gas, grains, and ices. Examples will be given of imaging and spectroscopic studies of protostars, obscured sources in molecular cloud cores, circumstellar disks around young stellar objects, remnants of nova and supernova explosions, and winds of evolved stellar systems.

A makeover of the JPL Millimeter and Submillimeter Spectral Line Catalog has begun. This process is intended to provide ‘single-line-access’ to users and virtual astronomy facilities through a server/query interface. In order to provide these users with the maximum amount of reliability and trace-ability, the database format (traditionally ascii-text files on an http/ftp server) has been expanded to include data and data-sources in a format where the measurement data is listed independently of the model predicted line information. This information, although still accessible through the source text-files, is also compiled into a MySQL database. This methodology allows merging of measurement and prediction to be done at the meta-data level and gives the user quick access to the literature source. The creation of virtual observatories will give the astronomer a new interface tool, that, without this improved access, would otherwise be blind to much of the source information that has traditionally been kept in documentary files intended for human processing. As the users develop their model(s) to understand real astrophysical data, the virtual observatory, with open online database access, will fill the role of analysis tool, or perhaps provide input to it, and these format changes will allow the astrometric tools to track the catalog’s sources/updates.
ANALYSIS OF THE $\lambda = 1.3$ mm SPECTRUM OF ORION-KL

MARY L. RADHUBER, JAY A. KROLL, and SUSANNA L. WIDICUS WEAVER, Department of Chemistry, Emory University, Atlanta, GA 30322.

We previously reported on our observations of the Orion-KL star forming region from 223 – 251 GHz using the wideband $\lambda = 1.3$ mm receiver at the Caltech Submillimeter Observatory (CSO). A noise level of $\sim 30$ mK was obtained after the double sideband spectra were deconvolved. This noise level allows the identification of significantly more lines than were observed in previous surveys of this source. A total of 5378 spectral lines with peak intensities $>3\sigma$ have been identified. We have begun line assignment and spectral analysis of these results, first focusing our efforts on known interstellar molecules. From this initial analysis, many newly identified weak transitions of previously detected molecules have been assigned. Spectral lines from isotopologues and excited vibrational states of known molecules have also been identified. Yet comparison to the JPL and CDMS spectral line databases enables assignment of only $\sim 20\%$ of the observed spectral lines. Challenges in analysis also arise from the large amount of spectral data obtained in this broadband survey, which makes traditional by-eye line identification approaches inefficient. In this talk we will discuss the progress of the spectral line assignment for this survey, the software tools that we are developing to aid in the analysis, and the need for additional laboratory spectroscopic studies to aid in line identification.

BROADBAND, HIGH RESOLUTION SPECTROSCOPY WITH NRAO FACILITIES

ANTHONY J. REMIJAN, NRAO, 520 Edgemont Road, Charlottesville, VA 22903.

Over the next several years, NRAO facilities will provide the scientific community with unprecedented advances in high spatial resolution observations. What is not currently emphasized is at the same time, these observations will also provide broadband, high spectral resolution data in frequency ranges that are sparsely covered by any other astronomical facility. ALMA and the eVLA will be able to record over 2 GHz of instantaneous bandwidth at high spectral resolution and provide high fidelity, high spatial resolution images that are well suited for studies of Galactic sources. The GBT is currently being upgraded with a K band focal plane array that will provide information on the widespread distribution of species in addition to the 800MHz continuous spectral line coverage. Finally, the VLBA upgrade will provide higher sensitivity observations over much wider bandwidths to investigate phenomenon at the highest spatial and spectral resolution ever obtained. All these capabilities will be highlighted along with the current progress in the construction of ALMA, eVLA, GBT and VLBA.

ASTROCHEMISTRY WITH THE UPGRADED COMBINED ARRAY FOR RESEARCH IN MILLIMETER-WAVE ASTROMOMY

D. N. FRIEDEL, Department of Astronomy, University of Illinois, Urbana, IL 61801.

The Combined Array for Research in Millimeter-wave Astronomy (CARMA) has been actively observing at $\lambda = 1$ mm, 3mm, and 1cm frequencies (210-270 GHz, 85-115 GHz, and 30 GHz) for several years. This upcoming year will see many new improvements to the system, including a new correlator and dual polarization receivers. This talk will introduce the new, upgraded imaging capabilities of this state of the art instrument.
THE $^{14}$N/$^{15}$N ISOTOPE RATIO IN DENSE MOLECULAR CLOUDS

G. ADANDE, L.M. ZIURYS, Department of Chemistry, Steward Observatory, University of Arizona, Tucson.

Observations of the 3-2 and 1-0 transitions of HNC at 271.981 and 90.663 GHz, H$^{15}$NC at 266.567 and 88.865 GHz were conducted using the Arizona Radio Observatory (ARO) 12m at 2 and 3mm in wavelength and Submillimeter Telescopes (SMT) at 1mm. The $^{13}$C isotopomer was also observed to evaluate the high optical depth in the main isotope, hence the 3-2, 2-1, 1-0 transitions of HN$^{13}$C at 261.263, 174.179 and 87.090 GHz were recorded as well. Observations were made toward the molecular clouds SgrB2, W31, G34.3, W51M, M17-SW, DR-21, L134, Orion A, W3 (OH), NGC7538 and S156, located at various distances from the Galactic Center. The preliminary results indicate a ratio $^{14}$N/$^{15}$N of 120-200, similarly to the values found in comets.

QUANTUM CHEMICAL STUDIES OF LOW-ENERGY PATHWAYS TO ORGANIC SPECIES ON INTERSTELLAR ICY GRAIN MANTLES

D. E. WOON and L. CHEN, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

Quantum chemical density functional theory cluster calculations were used to investigate low-energy pathways on icy grain mantles that lead to the formation of organic molecules of relevance to astrobiology. After providing an update on a series of calculations on reactions between NH$_3$ and carbonyl species (formaldehyde, acetaldehyde, and acetone), we will present results about a new family of reactions, the low-energy deposition of various cations on ice clusters. It was found that a sequence of barrierless processes can occur that offer alternative pathways to well-known, abundant astromolecules. For example, the HCO$^+$ and CH$_3^+$ cations will react with H$_2$O in ice with no barrier to produce, respectively, protonated formic acid (HCOOH$^+$) and protonated methanol (CH$_3$OH$^+$). These intermediates then spontaneously lose their protons to the ice to yield formic acid and methanol. An incoming ion can also react with other species already adsorbed on ice. An example of this is the reaction of OH$^+$ with CO to yield HOCO$^+$, which subsequently loses its proton to yield CO$_2$. The calculations indicate that all of these ion-ice reactions can occur at ultracold temperatures with no energetic processing.
Infrared spectroscopy of metal containing molecules

Michael A. Duncan, Department of Chemistry, University of Georgia, Athens, GA 30602.

Transition metal cation-molecular complexes are produced in pulsed supersonic molecular beams by laser vaporization. These ions are mass-selected in a specially designed reflectron time-of-flight mass spectrometer and studied with infrared laser photodissociation spectroscopy. Infrared spectra are compared to the predictions of theory (DFT and/or MP2) to elucidate the structures of these ions and their electronic states. Transition metal (Co, V, Nb) carbonyls are studied in the C-O stretching region and transition metal-water complexes are studied in the O-H stretching region. In both cases, the spectra reveal coordination numbers and ligand or solvent molecular vibrational shifts as a function of cluster size.

Oscar Rodriguez Jr., and James M. Lisy, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

Experiments on M\(^{+}\)(CH\(_4\))\(_n\)(H\(_2\)O)\(_3\)\(_-\)\(_4\) clusters (M=Li, Na) have been carried out using tandem mass spectrometry and infrared spectroscopy in the O-H stretching region from 3400 cm\(^{-1}\) to 3800 cm\(^{-1}\). We have found, for example, that a single CH\(_4\) can induce hydrogen bonded conformers in the cases of Li\(^{+}\)(CH\(_4\))\(_1\)(H\(_2\)O)\(_2\)Ar\(_0\)\(_-\)\(_1\), which are absent in the Li\(^{+}\)(H\(_2\)O)\(_3\)Ar\(_0\)\(_-\)\(_1\) spectra\(^a,b\). Furthermore, upon addition of multiple CH\(_4\) ligands, hydrogen bonding is not only maintained, but features associated with H\(_2\)O···CH\(_4\) hydrogen bonds are more intense, indicating the affinity of CH\(_4\) to bind to available O-H sites. Spectra of Li\(^{+}\)(CH\(_4\))\(_1\)···H\(_2\)O and Na\(^{+}\)(CH\(_4\))\(_1\)···H\(_2\)O clusters will also be discussed, all of which exhibit the curious trait of H\(_2\)O···H\(_2\)O and H\(_2\)O···CH\(_4\) hydrogen bonding in the presence of hydrophobic, non-polar CH\(_4\). To better understand the nature and onset of H\(_2\)O···CH\(_4\) hydrogen bonding, the Li\(^{+}\)(CH\(_4\))\(_n\)(H\(_2\)O)\(_1\)\(_-\)\(_2\) spectra will be discussed.


Hossein Z. Jooya and Leah C. O’Brien, Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026-1652.

Platinum dimer has been studied using DFT and TDDFT methods, at B3LYP and BLYP levels, respectively. Segmented all-electron relativistically contracted in conjunction with the DouglasKrollHess (SARC-DKH) basis sets were used which include scalar relativistic effects. First, the potential energy curves are obtained and the properties of the ground state are discussed briefly. The fully optimized bond length and the calculated dissociation energy are compared with the results obtained from non-relativistic calculations and from experiment. The electronic structure of the ground and three low-lying excited states are also examined.
The 12937 cm\(^{-1}\) band of Pt dimer has been recorded with rotational resolution using intracavity laser absorption spectroscopy. Based on Pt isotope shifts, this band is identified as the (1,0) band of an \(\Omega = 1 \rightarrow X \Omega = 1\) transition. The results of the analysis will be presented and compared with previous work.

We report here single UV photon pulsed field ionization-zero electron kinetic energy (PFI-ZEKE) photoelectron spectra of jet-cooled Sc-[C\(_6\)H\(_6\)-\(n\)(CH\(_3\))\(_n\)] \((n = 2, 3, \text{ and } 6)\) complexes and two-photon IR-UV photoionization spectra of Sc-[C\(_6\)(CH\(_3\))\(_6\)]. Adiabatic ionization energies and low-frequency metal-ligand and ligand-based vibrational modes are measured from the single-photon PFI-ZEKE spectra, and C-H stretching frequencies are determined from the two-photon IR-UV spectra. The ionization energies of these Sc complexes decrease with increasing methyl substituions of hydrogen in the benzene ring. The C-H frequencies of hexamethylbenzene are significantly shifted due to Sc coordination. The ZEKE transitions of the di- and tri-methyl substituted complexes are sharp, while those of the hexa-methyl species are rather broad. The observed electronic transitions are \(1^1A \leftarrow 2^1A\) for Sc-[1,4-C\(_6\)H\(_4\)(CH\(_3\))\(_2\)] \((C\(_2\))\), \(1^1A' \leftarrow 2^1A'\) for Sc-[1,3,5-C\(_6\)H\(_3\)(CH\(_3\))\(_3\)] \((C\(_s\))\), and \(1^1A_1 \leftarrow 2^1A_1\) for Sc-[C\(_6\)(CH\(_3\))\(_6\)] \((C\(_{2v}\))\).

Lanthanum oxide, LaO\(_2\), is produced in a pulsed laser-vaporization metal-cluster source and studied by mass-analyzed threshold ionization (MATI) spectroscopy. From the MATI spectrum, the adiabatic ionization energy of LaO\(_2\) is determined to be 40134 (5) cm\(^{-1}\) or 4.976 (6) eV, and La\(^+\)-O stretching and O-La\(^+\)-O bending frequencies are measured as 656 and 120 cm\(^{-1}\). The measured ionization energy is about 3.0 eV lower than the value predicted by recent high-level ab initio calculations.\(^a\) In this talk, we will discuss the discrepancy between the experiment and theory and the electronic transition observed in our experiment.

Co\(^+\)Ne was generated via laser vaporization in a pulsed supersonic expansion source, mass selected, and analyzed by visible photodissociation spectroscopy. An electronic band system was observed with an origin beginning at 13503 cm\(^{-1}\). A progression of peaks beginning from the origin until the convergence limit can be seen, corresponding to the vibrational bands in the excited state of Co\(^+\)Ne. The excited state constants \((we=124 \text{ cm}^{-1})\) were determined and the electronic cycle leads to a ground state binding energy \((D_0=948 \text{ cm}^{-1})\). The ground state binding energy can be compared to other rare gas binding energies, which is correlated to the polarizability of the rare gas.

VECTOR CORRELATION IN THE PHOTODISSOCIATION OF METAL NITROSYLS

JEFFREY A. BARTZ, AMBER L. PEDEN, and RYAN D. KIEDA, Department of Chemistry, Kalamazoo College, 1200 Academy Street, Kalamazoo, MI 49006.

The vector correlation in the photodissociation of metal nitrosyls has been determined using linearly-polarized laser light and velocity-mapped ion imaging. The 225-nm dissociation beam excites a doubly-degenerate metal-to-ligand charge transfer in both $\eta^5$-C$_5$H$_5$NiNO and Co(CO)$_3$NO. State-resolved detection of the NO product through the A (v'=0) ← X (v''=0) transition reveals that both molecules dissociate promptly with a high degree of vector correlation.

Intermission

LASER EXCITATION SPECTROSCOPY OF $^{58}$NiH IN A MAGNETIC FIELD

CYRIL RICHARD, HEATHER HARKER, PATRICK CROZET and AMANDA J. ROSS, LASIM, Université Lyon 1 & CNRS, 43 Bd du 11 novembre 1918, F-69622 Villeurbanne, France; DENNIS TOKARYK, Department of Physics and Center for Laser, Atomic, and Molecular Sciences, University of New Brunswick, Fredericton, Canada E3B 5A3.

Recent laboratory measurements of isotopologue $^{58}$NiH by laser excitation around 17000–18000 cm$^{-1}$ in a magnetic field have allowed us to study several electronic systems of this molecule. Zeeman patterns were analysed using literature values for ground state Landé factors$^a$. Effective electronic Landé factors g$_{\text{eff}}$ have been determined. They show strong variation with parity in the rotational levels in some $\Omega'=3/2$ states, giving evidence for extensive mixing between excited electronic states.

Effective electronic Landé factors g$_{\text{eff}}$

<table>
<thead>
<tr>
<th>J</th>
<th>$E(\Omega = 3/2), v = 1$</th>
<th>$I(\Omega = 3/2), v = 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>e</td>
<td>f</td>
</tr>
<tr>
<td>1.5</td>
<td>1.058</td>
<td>1.142</td>
</tr>
<tr>
<td>2.5</td>
<td>0.992</td>
<td>1.365</td>
</tr>
<tr>
<td>3.5</td>
<td>0.844</td>
<td>1.737</td>
</tr>
<tr>
<td>4.5</td>
<td>0.587</td>
<td>2.238</td>
</tr>
<tr>
<td>5.5</td>
<td>0.415</td>
<td>2.933</td>
</tr>
<tr>
<td>6.5</td>
<td>0.233</td>
<td>3.671</td>
</tr>
</tbody>
</table>

$^a$McCarthy et al. JCP 107 (1997) 4179
ZEEMAN PATTERNS IN FOURIER TRANSFORM RESOLVED FLUORESCENCE SPECTRA OF NiH

AMANDA J. ROSS, PATRICK CROZET, HEATHER HARKER and CYRIL RICHARD, LASIM, Université Lyon 1 & CNRS, 43 Bd du 11 novembre 1918, F-69622 Villeurbanne, France; and STEPHEN H. ASHWORTH, School of Chemistry, University of East Anglia, Norwich NR4 7TJ, UK.

We have found that dispersed laser induced fluorescence spectra of NiH produced in a discharge source are characterized by remarkably strong emission bands from upper state levels populated by collisional energy transfer.\textsuperscript{a} When the molecules are formed in the presence of a static magnetic field, magnetic response can be measured simultaneously for many transitions, under identical experimental conditions. Working with magnetic fields of 5000 - 10000 Gauss, the Zeeman patterns of many lines are at least partially resolved, at Doppler limited resolution. If the initial excitation process is chosen to be isotopically selective, the entire spectrum features emission from a single isotopologue, which simplifies analysis considerably. \(M_J\) selectivity is also possible in some cases. Measurements have been made so far for \(^{58}\text{NiH}\) and \(^{60}\text{NiH}\). The magnetic response of NiH in the low-lying states \(W_1\,^2\Pi_{3/2}\), \(X_2\,^2\Delta_{3/2}\), and \(X_1\,^2\Delta_{5/2}\) states evidently changes with \(v''\). This illustrates the effects of mixing between states, described by the supermultiplet \(3d^9\) complex model given by Gray \textit{et al.}\textsuperscript{b}


HIGH RESOLUTION LASER EXCITATION SPECTROSCOPY OF BARIUM MONOSULFIDE

G. LI, J.-G. WANG, and P. F. BERNATH, Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK.

BaS molecules were synthesized using a Broida-type oven and detected by laser excitation spectroscopy using a single mode Ti:Sapphire laser. High resolution spectra of BaS were recorded in the 12200 – 12765 cm\(^{-1}\) region. The BaS spectra contain several bands, and preliminary assignments and least-squares fits were carried out using ground state microwave data. The main bands are provisionally assigned to the \(A^1\Pi - X^1\Sigma^+\) transition of BaS. Further analysis of the minor isotopologues will be performed in order to obtain a secure vibrational assignment of the upper state levels. More laser scans will also be carried out from 12200 cm\(^{-1}\) to the lower frequency limit of the Ti:Sapphire laser. Preliminary results on this ongoing project will be presented.
INVESTIGATING THE EXCITED ELECTRONIC STATES OF BaOH VIA LASER SPECTROSCOPY AND AB INITIO CALCULATION: FURTHER EVIDENCE OF PERTURBATION FROM THE $A^2\Delta$ STATE

J. D. TANDY, J.-G. WANG, P. F. BERNATH, Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK; J. LIÉVIN, Service de Chimie Quantique et Photophysique, Université Libre de Bruxelles, CP1 160/09, 50 av F.D. Roosevelt, B-1050 Bruxelles, Belgium.

Two bands for the $A^2\Delta - X^2\Sigma^+$ transitions of BaOH and BaOD have been rotationally analyzed using high-resolution V-type optical-optical double resonance spectroscopy. BaOH and BaOD molecules were synthesized in a Broida-type oven, using a single mode Ti:Sapphire laser and a single mode dye laser for molecular excitation. The observed spectra mimic a typical $2\Pi - \Sigma^+$ transition, believed to emanate from single or triple quanta of the bending vibration in the $A^2\Delta$ state. Measured rotational lines have been assigned and rotational and fine structure parameters determined through a combined least-squares fit with the millimeter-wave pure rotational data of the $X^2\Sigma^+$ state. Previous analyses of the $A^2\Pi - X^2\Sigma^+$ transitions of BaOH and BaOD yielded significantly different spin-orbit coupling constants, which were attributed to possible global and local perturbations arising from vibrationally excited bands of the $A^2\Delta$ state. Although the newly observed $A^2\Delta$ state bands could not be conclusively designated a specific spin state, the derived $\Lambda$-doubling constants also show significant $2\Pi$ character, further indicating a strong interaction between the $A^2\Pi$ and $A^2\Delta$ states of BaOH. To validate these conclusions, ab initio calculations have been carried out to further understand the nature of the BaOH excited states. The wavefunctions of the $D^2\Sigma^+, D^2\Sigma^+, C^2\Pi, B^2\Sigma^+, A^2\Pi, A^2\Delta$ and $X^2\Sigma^+$ states have been optimised with a state averaged multiconfigurational calculation using the MolPro software. Calculated vertical term energies show relatively good agreement with existing optical data.

SPECTROSCOPY IN SUPPORT OF PARITY NONCONSERVATION MEASUREMENTS: THE $A^2\Pi - X^2\Sigma^+$ (0,0) BAND OF BARIUM MONOFLUORIDE

ANH LE, SARAH FREY AND TIMOTHY C. STEIMLE, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287.

There is renewed interest in the spectroscopy of heavy metal containing polar radical diatomic molecules because they provide a sensitive venue for detection of parity nonconservation (PNC) either from the determination of the electric dipole moment (EDM) $\alpha$ of the electron, $d_e$, or detection of the interaction of the anapole moment of the nuclei with the unpaired electron $\beta$. The effects due to $d_e$ are nuclear spin independent and studies of both the even and odd nuclear spin isotopologues are relevant. Recently, DeMille et al proposed using an odd isotopologue of barium monofluoride, $^{137}$BaF, to measure the nuclear spin-dependent parity non-conservation (NSD-PNC) effect resulting from the interaction of the anapole moment of $^{137}$Ba with the unpaired electron of the $X^2\Sigma^+$ electronic state. Here we report on the analysis of the field-free spectrum of the $A^2\Pi - X^2\Sigma^+$ (0,0) band of $^{137}$BaF and an analysis of the $^{137}$Ba($I = 3/2$) and $^{139}$F($I = 1/2$) hyperfine interaction in the $A^2\Pi$ state. The hyperfine interaction in the $X^2\Sigma^+$ state has been previously characterized from the analysis of the pure rotation spectrum.$^c$ The optimal optical transitions for monitoring $^{137}$BaF in future PNC measurements will be discussed.


Copper hydroxide, CuOH, is one of the most thoroughly studied transition metal containing polyatomic molecules with the most recent investigation being the dispersed fluorescence and radiative lifetime study. The pure rotational spectrum was recorded and analyzed by Saito’s group some time ago. Recently a high level ab initio calculation predicted ground state permanent electric dipole moments, \( \mu_{el} \), ranging in value from 5.52D to 3.98D depending upon methodology used to treat electron correlation. Here we report on the first molecular beam study of the \( \text{B}^{1}A''-\text{X}^{1}A' \) band. The spectrum was recorded field-free and in the presence of a static electric field of up to 4000 V/cm. The hyperfine splitting is observed and analyzed for the first time. The determined \( \mu_{el} \) values are used to evaluate the computational methodologies and are compared with those of other copper containing molecules.


The rotational spectrum of CuCCH (\( \text{X}^{1}\Sigma^+ \)) has been measured using Fourier transform microwave (FTMW) spectroscopy. This work is the first gas-phase spectroscopic study of this molecule. The species was produced using Discharge Assisted Laser Ablation Spectroscopy (DALAS) in a supersonic jet expansion with HCCH as the precursor molecule. Four rotational transitions \( (J = 1 \rightarrow 0, 2 \rightarrow 1, 3 \rightarrow 2, \text{ and } 4 \rightarrow 3) \) have been measured for the \(^{63}\text{CuCCH}\) and \(^{65}\text{CuCCH}\) isotopologues in the range 8-33 GHz. Copper quadrupole splittings have been resolved in both species. The data have been analyzed, and rotational and hyperfine constants determined. Measurements of the carbon-13 and deuterium isotopologues are currently being conducted to establish a precise structure for CuCCH. Compounds of the form CuCCR play an important role in organic synthesis.
RH. MICROWAVE (ROTATIONAL)

THURSDAY, JUNE 24, 2010 – 1:30 pm

Room: 1000 McPHERSON LAB

Chair: THERESA HUET, University of Lille I, Villeneuve, France

RH01 10 min 1:30
TRANSIENT/PERMANENT CHIRALITY: ROTATIONAL SPECTRA OF THE DIMERS OF ISOPROPANOL

LUCA EVANGELISTI, FEDERICO PESCI and WALTHER CAMINATI. Dipartimento di Chimica “G. Ciamician” dell’Università, Via Selmi 2, I-40126 Bologna, Italy.

The two mirror images of gauche isopropanol are connected through the low energy barrier of the OH torsion potential energy surface. This produces large tunnelling splittings in the rotational spectrum, and we can talk of transient chirality. We assigned the rotational spectra of five conformers of the dimer of isopropanol, all of them involving at least one gauche monomer (see the Figure to the right). The inertial effects quench the tunneling and, in the time scale of MW spectroscopy, all these systems appear as made of a pair of “classical” enantiomers. From the relative intensities of the rotational transitions of the various conformers it has been possible to estimate their relative abundances. Some interesting features related to the molecular recognition, dynamic of formation of the dimers in the supersonic expansion and sizing of the Ubbelohde effect will be discussed.

RH02 15 min 1:42
TRIPLE RESONANCE FOR A THREE-LEVEL SYSTEM OF A CHIRAL MOLECULE

EIZI HIROTA, The Graduate University of Advanced Studies, Hayama, Kanagawa 240-0293, Japan.

A new spectroscopic method of triple resonance is proposed for studying chirality of a molecule of $C_1$ symmetry. Each enantiomer of such a molecule is of mixed parity and thus exhibits all three $a^-$, $b^-$, and $c^-$-types of rotational spectra. The present study concludes, by using time-dependent perturbation theory, that the transition probability between two of the three rotational levels under triple resonance differs for different enantiomer. This result can thus be of some significance for enantiomer differentiation.
Isopropyl methyl sulfide (CH$_3$)$_2$CHSCH$_3$ was investigated by Fourier transform microwave spectroscopy. Two rotational isomers gauche and trans were detected. The rotational spectra of gauche were found fit to an asymmetric rotor pattern, except for being split by the internal rotation of CH$_3$ attached to S with the potential barrier $V_3$ of 601.642 (65) cm$^{-1}$ and for exhibiting the effect of tunneling between the two equivalent gauche forms in a few high-$K$ transitions. The tunneling was discussed from a viewpoint of chirality. The trans spectra appeared generally similar to those of gauche, with $V_3$ to the S-CH$_3$ internal rotation of 559.00 (11) cm$^{-1}$, but satellite lines accompanied the ground torsional state lines in some high-$K$ transitions. These satellites were ascribed to the excited state of the C(isop)-S torsion. In fact, the potential function for this torsion was shown by an $ab$ initio calculation to be flat or even of double minima around the trans position, which was presumably caused by a gear coupling between the two methyl groups of the isopropyl group and the one in the S-CH$_3$.

Previous studies of 4-fluorobenzyl alcohol (4FBA) in the gas phase have revealed the existence of tunneling splittings in its high resolution electronic spectrum. These could be attributed either to the ground $S_0$ state, or the excited $S_1$ state, or both. Motivated by this finding, we report here a study of the CP-FTMW spectrum of 4FBA. Its pure rotational spectrum was collected using a series of 250 MHz chirped pulses, over the frequency range of 6.5-18 GHz. Analysis of this data shows that 4FBA has a gauche structure and yields the $V_2$ barrier for CH$_2$OH torsion, from which the predicted tunneling splittings in the ground state have been extracted.

The ground state rotational spectrum of 4,4-dimethylaminobenzonitrile (DMABN) was studied using chirped-pulsed Fourier transform microwave spectroscopy (CP-FTMW). The rotational spectrum from 6.5 to 18 GHz was collected using a compilation of 250 MHz chirped pulses and pieced together. DMABN is widely known as an important model for excited state twisted intramolecular charge transfer dynamics. It has been previously studied in our group using high resolution electronic spectroscopy, in which a strong coupling between methyl group internal rotation and overall rotation was discovered. We have recently determined that these couplings are not present in the ground state spectrum. The ground state structure and nuclear quadrupole coupling terms will also be discussed.
RH06 15 min 2:50

CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTRUM OF THE LOW GLOBAL WARMING POTENTIAL REFRIGERANT ALTERNATIVE, 2,3,3,3-TETRAFLUOROPROPENE

MARK D. MARSHALL, HELEN O. LEUNG, Department of Chemistry, Amherst College, P.O. Box 5000, Amherst, MA 01002-5000; JOHN S. MUENTER, Department of Chemistry, University of Rochester, Rochester, NY 14627.

A newly-constructed, chirped-pulse Fourier transform microwave spectrometer is used to obtain the microwave spectrum of 2,3,3,3-tetrafluoropropene, which has been proposed as an alternative to HFC-134a for use as a mobile air conditioning refrigerant. With a bandwidth of 6 GHz, this instrument has the potential to provide complete coverage of the microwave spectrum from 6 to 18 GHz in two steps, although smaller intervals may be utilized to increase the available power per unit bandwidth. Aided by ab initio calculations, the rotational spectrum of the normal isotopologue of 2,3,3,3-tetrafluoropropene is assigned and analyzed to give rotational and centrifugal distortion constants. With moderate signal averaging, the signal-to-noise ratio of the spectrum indicates that it should be possible to observe singly substituted $^{13}$C isotopologues in natural abundance.

RH07 15 min 3:07

A 480 MHz CHIRPED-PULSE FOURIER-TRANSFORM MICROWAVE SPECTROMETER: CONSTRUCTION AND MEASUREMENT OF THE ROTATIONAL SPECTRA OF DIVINYL SILANE AND 3,3-DIFLUOROPENTANE

DANIEL A. OBENCHAIN, AMANDA L. STEBER, ASHLEY A. ELLIOTT, REBECCA A. PEEBLES and SEAN A. PEEBLES, Department of Chemistry, Eastern Illinois University, 600 Lincoln Avenue, Charleston, IL 61920; CHARLES J. WURREY, Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110; GAMIL A. GUIRGIS, Department of Chemistry and Biochemistry, College of Charleston, Charleston, SC 29424.

A chirped-pulse Fourier-transform microwave (CP-FTMW) spectrometer based on the original Pate design has been constructed to allow analysis of any 480 MHz region in the 7 – 18 GHz range. A 1 µs chirped-pulse (0 – 240 MHz) from an arbitrary function generator is mixed with output from a microwave synthesizer and used to polarize a supersonic gas expansion; the resulting free induction decay is collected over 20 µs and Fourier-transformed on a 500 MHz oscilloscope to produce a rotational spectrum. A variety of molecules have now been studied with this instrument and results will be presented for numerous conformers of divinyl silane (predicted $\mu_{\text{total}} = 0.6 - 0.7$ D) and the more polar 3,3-difluoropentane (predicted $\mu_{\text{total}} = 2.5 - 2.8$ D).

Two of the three possible conformers of divinyl silane were assigned (both having a $C_1$=C$_2$–Si–C$_3$ dihedral angle of $-120^\circ$ and a C$_2$–Si–C$_3$=C$_4$ dihedral of either 0° ($C_3$ symmetry) or $-120^\circ$ ($C_2$ symmetry)). For 3,3-difluoropentane, three of the four possible conformers were identified: anti-gauche ($C_1$), gauche-gauche ($C_2$) and anti-anti ($C_{2v}$). While rotational spectra for only the silicon isotopologues were observed for divinyl silane, measurement of the $^{13}$C spectra of 3,3-difluoropentane allowed heavy atom structure determinations for the anti-gauche and gauche-gauche conformers. Initial assignments of all spectra were made on the CP-FTMW spectrometer, and a Balle-Flygare FTMW spectrometer was used to compare frequencies of measured transitions and also to provide Stark effect data. Substitution ($r_s$) and inertial fit ($r_0$) structures will be compared with computational data and instrumental details will be presented.

---

The pure rotational spectra of 1,1,1-trifluoro-2-butanone and of 3,3,3-trifluoropropionic acid have been investigated using the new chirped-pulse Fourier transform microwave (cp-FTMW) spectrometer at the University of Manitoba. Transitions due to the monosubstituted isotopologues with $^{13}$C in natural abundance were assigned using spectra from both the broadband instrument and the conventional Fourier transform microwave (FTMW) spectrometer. The observed spectra are consistent with planar structures of the species in the ground vibrational states. Quantum chemistry calculations, at the MP2/6-311++G(d,p) level, have been carried out in order to obtain information about the structure, relative stability and difference in populations of the conformers under study.

Intermission

The microwave spectrum of bis-(trifluoromethyl) peroxide, CF$_3$OOCF$_3$, was measured between 5 and 20 GHz frequency region. The spectrum of its $^{13}$C isotopologue was also recorded in natural abundance. All observed transitions were ambiguously assigned. The rotational and centrifugal distortion constants for the dominate CF$_3$OOCF$_3$ species are: $A = 2806.6567(2)$ MHz, $B = 795.3253(2)$ MHz, $C = 790.3212(2)$ MHz, $\Delta J = 68.0(3)$ Hz, $\Delta JK = 179(1)$ Hz, and $\delta J = -0.44(9)$ Hz. The ab initio and the density functional theory level of calculations were performed to optimize the molecular geometry and to predict the spectroscopic constants. The theoretical predictions are in moderate agreement with the experimental measurements.

The lowest energy conformer of perfluorohexane is helical and its microwave rotational spectrum has been observed and assigned. The molecular parameters were characterized by scaling computed models by the square root of the ratio of the observed second moments to those computed. The scaled structures exactly reproduce the observed second moments. From this scaling approach, the exterior C$_1$C$_2$C$_3$C$_4$ dihedral angle is $16.7^\circ$ and the interior C$_2$C$_3$C$_4$C$_5$ dihedral angle is $18.0^\circ$ away from trans. In addition, two conformers of 1H-heptfluoropropane have been observed and characterized by its microwave spectrum. The HCCC dihedral angle is analogous to the CCCC dihedral angle in butane and exhibits both trans and gauche conformations. The trans conformer shows no evidence of a helical twist. It appears that the steric and dipole interactions which cause a twist in longer perfluoroalkane oligomers are not sufficient in a three carbon chain. Computations at the PBE0/cc-pVTZ level are in excellent agreement with the experimental results for both compounds.
THE SHAPES OF CHLOROPENTAFLUOROACETONE AND 1,3-DICHLOROTETRAFLUOROACETONE IN THE GAS PHASE

GAUTAM KADIWAR, CHRISTOPHER T. DEWBERRY, GARRY S. GRUBBS II AND STEPHEN A. COOKE, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH TEXAS, 1155 UNION CIRCLE #305070, DENTON, TX 76203-5017, U.S.A.

The pure rotational spectra of the two title molecules have been recorded using a chirped pulse Fourier transform microwave (CP-FTMW) spectrometer and also using a Balle-Flygare FTMW spectrometer. In both cases sufficient resolution was available to determine the full chlorine nuclear electric quadrupole coupling tensor(s). Supporting quantum chemical calculations, coupled with the data available, show that for both molecules the CICCO dihedral angle is approximately 90°. The 1,3-dichlorotetrafluoroacetone species possesses a $C_2$ symmetry axis with the Cl centers on opposite sides of the CCC plane. Spectroscopic parameters and structural parameters will be presented.

ROTATIONAL ANALYSIS OF BANDS IN THE HIGH-RESOLUTION INFRARED SPECTRA OF trans, trans- AND cis, cis-1,4-DIFLUOROBUTADIENE-2-d$_1$

NORMAN C. CRAIG, DEACON J. NEMCHICK, CLAY C. EASTERDAY, ETHAN C. GLOR, and DREW F. K. WILLIAMSON, Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH 44074; THOMAS A. BLAKE and ROBERT L. SAMS, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352.

Ground state rotational constants for a series of isotopomers are being sought for use in determining the semi-experimental equilibrium structures of the isomers of 1,4-difluorobutadiene. Because fluorine substitution has a large influence on CC bond lengths in C$_3$ and C$_4$ rings, we asked how fluorine substitution affects butadiene. trans,trans- and cis,cis-1,4-Difluorobutadiene-2-d$_1$ have been synthesized, and high-resolution (0.0013 cm$^{-1}$) infrared spectra have been recorded for these nonpolar species. Analysis of the rotational structure in several bands is reported. For the trans,trans isomer, the C-type band at 709.0 cm$^{-1}$ for $\nu_{21}(a'')$ has been fully analyzed, and the C-type band at 914.3 cm$^{-1}$ for $\nu_{18}(a'')$ has been partially analyzed. Interfering with the analysis of the second band is overlap of its R branch with the P branch of the A/B-type band for $\nu_{13}(a')$ at 933 cm$^{-1}$. For the cis,cis isomer, as much as possible of the C-type band ($K_a' = 10$ to 34) for $\nu_{20}(a'')$ at 775.4 cm$^{-1}$ has been analyzed. An A-type band for $\nu_{13}(a')$ at 865.8 cm$^{-1}$ has also been analyzed into the band center. Small inertial defects confirm that these molecules are planar. Ground state rotational constants are reported for both isomers in comparison with those for the normal species.$^a$

FIRST MICROWAVE TRANSITIONS IN THE ROTATIONAL SPECTRUM OF $\nu_{17}$ OF ACETONE ASSIGNED BY MW-MW DOUBLE RESONANCE

P. Groner, Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110-2499; M. Unrath, D. Christen, Institute of Physical and Theoretical Chemistry, University of Tübingen, D-72076 Tübingen, Germany.

The first assignments of rotational transitions of acetone in the $\nu_{17}$ state, based on a study of the mm/sub-mm wave spectrum, were published two years ago. a Over 700 frequencies of transitions from all four torsional substates (AA, EE, AE, and EA) have been assigned; over 600 have been fit to an effective rotational Hamiltonian for molecules with two internal rotors. b However, the fit was not very good (standard deviation 0.48 MHz) and required a large number of ill-determined parameters, some of which were clearly outside the expected range. A search for transitions at lower frequencies by microwave-microwave double resonance has been moderately successful. So far, 12 double resonances involving 6 pump and 8 signal transitions have been found that connect 15 energy levels ($1 < J < 6$) in the EE torsional substate. These frequencies were found within a range of up to seven times the predicted standard errors. The newly assigned transitions were used in least-squares fits together with all previously assigned transitions (or subsets thereof) in an effort to determine more sensible parameters and to achieve more stable fits. We are hoping to assign more transitions, specifically transitions in the AA torsional substate.

---

THE MILLIMETER-WAVE ROTATIONAL SPECTRUM OF PHENYLACETYLENE

Zbigniew Kisiel, Adam Kraśnicki, Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland.

The rotational spectrum of phenylacetylene, C$_6$H$_5$−C≡C−H, has hitherto only been studied in the centimeter-wave region, at room-temperature, a and in supersonic expansion. b There appears to be continuing astrophysical interest in polar species closely related to benzene and we decided to extend the knowledge of the laboratory spectrum of phenylacetylene up to the submillimeter-wave region. We report extensive measurements of the room-temperature spectrum at frequencies from 90 to 340 GHz. Precise spectroscopic constants are determined for the ground state, and the two lowest excited vibrational states: $v_{24} = 1$ and $v_{36} = 1$.

The two excited states belong to the out-of-plane and the in-plane C−C≡C bending modes, and are very strongly coupled by an a-axis Coriolis interaction. It was, nevertheless, possible to successfully fit the measured transitions with a minimal number of interaction constants. The present results from rotational spectroscopy are compared with previous normal mode analyses for phenylacetylene and with additional anharmonic force field calculations carried out in this work.

---

We present the ground state spectrum for m-methylbenzaldehyde taken with a chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer. The presence of a methyl rotor on the molecule introduces a threefold internal rotation barrier. Tunneling through this barrier leads to splitting of the torsional energy level degeneracy into A and E states. Theory predicts a low torsional barrier for both the cis and trans conformers, which leads to large splitting in the frequency spectrum. The A states are simulated using the rigid rotor approximation and subsequent distortion terms. In order to predict the E states, a $V_3$ parameter must be determined that correlates to the torsional barrier. All four possible species have been fit and parameters will be presented, including rotational constants, distortion terms and $V_3$ values.
RI. INFRARED/RAMAN (VIBRATIONAL)

THURSDAY, JUNE 24, 2010 – 1:30 pm

Room: 1015 McPHERSON LAB

Chair: OLIVIER PIRALI, Laboratoire de Photophysique Moleculaire, CNRS, Orsay, France

RI01 15 min 1:30

FEMTO-FANTASIO: A VERSATILE EXPERIMENTAL SET-UP TO INVESTIGATE MOLECULAR COMPLEXES


Several improvements have been made on the apparatus developed in Brussels for the study of jet-cooled molecules, named FANTASIO, for "Fourier trAnsform, Tunable, diode and quadrupole mAss spectrometers interfaced to a Supersonic expansion". The upgraded setup, called Femto-FANTASIO, is presented.

These improvements include: a doubling of the pumping efficiency, by adding another turbomolecular pump Leybold MAG-W3200 CT; an increase in sensitivity in the 1.5 $\mu$m range thanks to a new CRDS system, consisting in new cavity mirrors, leading to a ring down time of 125 $\mu$s and a new detector, decreasing the noise level; a new injection system to probe samples liquid at STP conditions; a temperature controlled nozzle/slit; and as an alternative probe technique, an absorption source, tunable from 3000 to 9000 cm$^{-1}$, coupling an optical parametric oscillator (OPO), pumped by a Ti:Sa femtosecond laser, to a high resolution continuous scan Fourier transform interferometer.

Femto FANTASIO will be used to investigate molecular complexes. First results and achievements of this new setup are presented.

---

RI02 10 min 1:47

INVESTIGATION OF VAN DER WAALS COMPLEXES IN A FREE EXPANSION OF $\text{C}_2\text{H}_2$/X (X=NOBLE GAS) USING CW CAVITY RING-DOWN SPECTROSCOPY IN THE OVERTONE RANGE


CW cavity ring down spectroscopy around 1.5 $\mu$m was used to probe a free supersonic expansion of mixed acetylene and noble gas (He, Ne, Ar and Kr). Pure $\text{C}_2\text{H}_2$ and mixed complexes are observed at sub-Doppler resolution around the 2CH acetylenic band. The effects of the different noble gases on the complexation are discussed. The updated or new spectral analysis of the spectra will be presented.

---


We will present ab initio calculations performed at the MP2 and CCSD(T) levels of theory on acetylene containing complexes. We used large basis sets including or not midbond functions and corrected all results for the basis set superposition error. The influence of the monomer geometries on the properties of the complexes has been investigated. The topology of the intermolecular potential energy surfaces of the various complexes will be compared and the methodological approach adapted to the considered systems will be discussed.

Infrared spectroscopy of Li(methylamine)$_n$(NH$_3$)$_m$ clusters

Recent work in our laboratory has led to the first size-selective infrared spectra of neutral Li(NH$_3$)$_n$ clusters. Here we report on new work extending these studies to mixed cluster species, where ammonia derivatives such as methylamine (MA) replace some of the ammonia molecules. Spectra recorded using mass-selective IR depletion spectroscopy will be reported for Li(MA)$_m$(NH$_3$)$_n$, with the emphasis on $n + m = 4$ clusters. The impact of replacing NH$_3$ with bulkier ligands on the solvent structure will be described. In addition the IR spectrum of the smaller cluster Li(MA)(NH$_3$)$_2$ will be reported for the first time.

High resolution spectra of carbon dioxide clusters in the $\nu_3$ band region

There is widespread interest in carbon dioxide clusters from a variety of experimental and theoretical perspectives. But in terms of high resolution spectroscopy, the only definitive information concerns (CO$_2$)$_2$ and (CO$_2$)$_3$. The dimer has a planar slipped parallel geometry with $C_{2h}$ symmetry. Two isomers are known for the trimer: a planar cyclic form with $C_{3h}$ symmetry and a sort of "barrel-shaped" form with $C_2$ symmetry. Here we analyze two new bands in the CO$_2$ $\nu_3$ region. The first is a dimer combination band near 2382 cm$^{-1}$ whose assignment raises interesting questions about the intermolecular vibrations of (CO$_2$)$_2$. The second band is a trimer band near 2370 cm$^{-1}$ which is very similar to one we observed previously near 2364 cm$^{-1}$. We assign it to a combination involving another out-of-plane vibration of the cyclic trimer. In addition to these newly assigned bands, we also discuss a number of clear and (mostly) well-resolved bands which apparently must belong to (CO$_2$)$_N$ clusters with $N$ in the range 6 $\sim$ 15. Although they cannot be precisely assigned at this time, these bands offer intriguing future prospects for learning more about the structures and vibrational dynamics of CO$_2$ clusters in a challenging and important size range.

---

In an effort to observe the spectra of acetylene clusters ($\text{C}_2\text{H}_2$)$_n$ with $n \geq 4$ and the very weakly bound He-$\text{C}_2\text{H}_2$ complex, spectra of acetylene-$\text{D}_2$ clusters in the region of the $\text{C}_2\text{D}_2$ $\nu_3$ fundamental ($\sim 2439 \text{ cm}^{-1}$) were recorded using a tunable diode laser to probe a pulsed supersonic slit jet expansion. So far, several bands below $2439 \text{ cm}^{-1}$ have been recorded. Two can be attributed to a parallel $\nu_3^\parallel$ and perpendicular $\nu_3^\perp$ band for the T-shaped $\text{C}_2\text{D}_2$ dimer. The interconversion splittings are clearly seen in these bands. There are other mystery bands whose origins are being investigated both experimentally and theoretically. In this talk I will discuss possible assignments of these bands to $\text{C}_2\text{D}_2$ clusters.

---

A NEW POTENTIAL ENERGY SURFACE FOR $\text{N}_2\text{O}$–He, AND PIMC SIMULATIONS PROBING INFRARED SPECTRA AND SUPERFLUIDITY

LECHENG WANG, DAIQIAN XIE, School of Chemistry and Chemical Engineering, Nanjing University, No.22 Hankou Road, Nanjing, Jiangsu, China, 210093; HUI LI, ROBERT J. LE ROY, and PIERRE-NICHOLAS ROY, Guelph-Waterloo Centre for Graduate Work in Chemistry and Biochemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

High resolution infrared spectra of an $\text{N}_2\text{O}$ molecule seeded in ultra-cold helium clusters have been reported by two groups.$^a, b$ Early simulations of $\text{N}_2\text{O}$–(He)$_n$ clusters$^c, d$ were performed using potential energy surfaces (PESs) for which the dopant $\text{N}_2\text{O}$ molecule was frozen at its equilibrium geometry. Since the evolution of the shift of the $\nu_3$ band-origin of $\text{N}_2\text{O}$ provides a key link to bridge the gap between micro and macro world, a new 3D PES was generated which incorporated the asymmetric-stretch $Q_3$ vibrational motion of the $\text{N}_2\text{O}$.$^e$ Bosonic PIMC simulations$^f$ based on this surface were then used to study rotational dynamics, and energetic and superfluid properties of $\text{N}_2\text{O}$–(He)$_n$ clusters. The evolution of the calculated shifts agree reasonably with the experimental results, but some quantitative discrepancies remain. To address this problem, a new four-dimensional $\text{N}_2\text{O}$–He PES has now been obtained which also takes account of the change in the average value of the $Q_1$ symmetric-stretch coordinate on excitation of $\nu_3$. It has been fitted to a generalized MLR functional form$^g$ which imposes better long-range behaviour. Results obtained using this new surface will be presented.

---


INFRARED SPECTRA OF (CO$_2$)$_2$-OCS COMPLEX: INFRARED OBSERVATION OF TWO DISTINCT BARREL-SHAPED ISOMERS

J. NOROOZ OLIAEE, M. DEHGHANY, F. MIVEHVAR, N. MOAZZEN-AHMADI, Department of Physics and Astronomy, University of Calgary, Calgary, AB T2N 1N4, Canada; A.R.W. MCKELLAR, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, ON K1A 0R6, Canada.

Spectra of (CO$_2$)$_2$-OCS complex in the region of the OCS $\nu_1$ fundamental ( $\sim$2062 cm$^{-1}$) are observed using a tunable diode laser to probe a pulsed supersonic slit jet expansion. A previous microwave study of the complex by Peebles and Kuczkowski$^a$ gave a distorted triangular cylinder. The geometrical disposition of the three dimer faces of this trimer are quite similar to the slipped CO$_2$ dimer, the lowest energy form of OCS-CO$_2$ (isomer a), also observed and analyzed in the microwave region,$^b$ and the higher energy form of OCS-CO$_2$ (isomer b), first observed by our group in the infrared region.$^c$

Here we report the observation and analysis of two infrared bands, corresponding to two distinct isomers of the (CO$_2$)$_2$-OCS complex. A band around 2058.8 cm$^{-1}$ was assigned to isomer I, which is the same as that studied previously by microwave spectroscopy. A second band around 2051.7 cm$^{-1}$ was assigned to a higher energy isomer of the complex, isomer II, which has not been observed previously, but expected on the basis of $ab initio$ calculations.$^d$ Approximate structural parameters for this new isomer were obtained by means of isotopic substitution. In contrast to isomer I, the geometrical disposition of the faces containing OCS and CO$_2$ in isomer II are similar to isomer b of the OCS-CO$_2$ complex.

---

FUNDAMENTALS AND TORSIONAL COMBINATION BANDS OF TWO ISOMERS OF THE OCS-CO$_2$ COMPLEX

J. NOROOZ OLIAEE, M. DEHGHANY, F. MIVEHVAR, MAHIN AFSHARI, N. MOAZZEN-AHMADI, Department of Physics and Astronomy, University of Calgary, 2500 University Dr., N.W., Calgary, Alberta T2N 1N4, Canada; A.R.W. MCKELLAR, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, K1A 0R6, Canada.

Infrared spectra of two isomers of the weakly bound OCS-CO$_2$ complex were observed using a tunable diode laser to probe a pulsed supersonic slit-jet. Spectra were recorded in the regions of OCS $\nu_1$ ( $\sim$2060 cm$^{-1}$) and CO$_2$ $\nu_3$ ( $\sim$2349 cm$^{-1}$) fundamental stretching vibrations. The lowest energy isomer (isomer a) was previously studied by microwave spectroscopy.$^a$ Here we report the first infrared observation of isomer a and also detection of a new higher energy form (isomer b). Structures were determined with the help of isotopic substitution. Both isomers are planar, with slipped near-parallel geometries. In isomer a, the intermolecular (centre of mass) separation is 3.55 Å and the C atom of the CO$_2$ is closer to the S atom of the OCS. In isomer b, the C atom of CO$_2$ slides closer to the O atom of OCS and the center of mass separation increases to 3.99 Å.$^b$ Three combination bands involving the intermolecular torsional (out-of-plane bend) vibrations were also analyzed. The out-of-plane torsional frequencies were measured to be 18.8 cm$^{-1}$ and 15.9 cm$^{-1}$ for isomers a and b, respectively, indicating that isomer a is indeed more bound than isomer b.

---


RI10 10 min 4:14
INFRAED SPECTROSCOPY OF LARGE-SIZED PHENOL-WATER CLUSTERS PhOH-(H2O)n (10 ≤ n ≤ 50)

TORU HAMASHIMA, KENTA MIZUSE and ASUKA FUJII, Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan.

We report infrared spectra of moderately size-selected phenol-(H2O)n−1 (10 ≤ n ≤ 50), which have essentially the same network structures as (H2O)n. The spectra in the OH stretching region are observed. Detailed analyses of these spectra aided by density functional theory calculations reveal the development process of the hydrogen bond network.

RI11 15 min 4:26
INFRAED SPECTRA OF OCS-C6H6, OCS-C6H6-HE AND OCS-C6H6-NE VAN DER WAALS COMPLEXES

M. DEHGHANY, J. NOROOZ OLLAE, MAHIN AFSHARI, N. MOAZZEN-AHMADI, Department of Physics and Astronomy, University of Calgary, 2500 University Dr., N.W., Calgary, Alberta T2N 1N4, Canada; A.R.W. McKELLAR, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, K1A 0R6, Canada.

The infrared spectrum of weakly-bound OCS-C6H6 is studied in the region of the ν1 fundamental band of OCS (∼2060 cm−1) using a tunable diode laser spectrometer to probe a pulsed supersonic jet expansion. A very simple band is observed, corresponding to a parallel transition of a symmetric top. It is shifted by -11.1 cm−1 with respect to the free OCS monomer. The resulting structure has OCS located along the benzene C6 symmetry axis in an S-bonded configuration with a center of mass separation of 4.42 Å, in good agreement with previous microwave spectra. The isotopomers OCS-13C12C5H6 and OC34S-C6H6 are also observed. Similar bands are observed for the OCS-C6H6-He and OCS-C6H6-Ne trimers, whose structure is obtained by adding an on-axis rare gas atom to the other side of the benzene. However, the analogous band for OCS-C6H6-Ar was not detected, raising the possibility that the stable form of this trimer may not have the same symmetrical structure.

RI12 15 min 4:43
INFRAED SPECTRA OF SIZE-SELECTED METHANOL CLUSTERS USING IR-VUV PHOTOTIONIZATION

HUI-LING HAN, Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan; YUAN-PERN LEE, Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan and Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan.

We investigated the CH and OH stretching modes of size-selected methanol clusters, (CH3OH)n, with n ≤ 5, in a pulsed supersonic jet with the IR-VUV ionization technique. Emission at 118 nm, frequency tripled in a mixture of Xe and Ar from the 355 nm nm output of a Nd:YAG laser, serves as the ionization source of a time-of-flight mass spectrometer. The tunable IR laser emission from an OPA/OPO system pumped with a second Nd:YAG laser serves as a source of predissociation or excitation before ionization. The variation of intensity of each ion signal was monitored as the IR laser light was tuned across the range 2700 – 3750 cm−1. Careful processing of raw data based on photoionization efficiencies and the production and loss of each cluster due to predissociation yields identical IR spectra for the size-selected cluster even under diverse experimental conditions. The OH region of methanol clusters has been investigated a, but the spectra in the CH region are new. In the region 2800 – 3050 cm−1, each absorption band of the methanol monomer splits into two components for the methanol dimer that correspond to proton donor and proton acceptor, indicating that methanol dimer has a preferred open-chain structure. In contrast, for the methanol trimer, the splitting diminishes and the band widths become narrower, indicating a preferred cyclic structure. For tetramer and pentamer, spectral patterns similar to those of the trimer but with greater widths are observed, supporting theoretical computations that predict the most stable structure to be cyclic.

RI13  15 min  5:00
INFRARED PREDISSOCIATION SPECTRA OF Cl\(^-\) (CH\(_3\)OH)\(_n\) Ar CLUSTER IONS, n=1-3

JORDAN P. BECK, JAMES M. LISY, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

Infrared predissociation spectra of Cl\(^-\) (CH\(_3\)OH)\(_n\) Ar and Cl\(^-\) (CH\(_3\)OD)\(_n\) Ar, n=1-3, will be presented and discussed in terms of isomer trapping and cooperative enhancement of hydrogen bonds. Due to the strong ionic hydrogen bonds between the chloride ion and methanol, spectra with d\(_1\)-methanol were obtained to distinguish between CH stretches and hydrogen-bonded OH features. For Cl\(^-\) (CH\(_3\)OH)\(_1\) Ar, the ionic hydrogen bond shifts the OH stretch -584 cm\(^{-1}\) from the gas-phase value of neutral methanol, which is slightly larger than the shift reported for the non-argonated, Cl\(^-\) (CH\(_3\)OH)\(_1\) cluster\(^a\). A methanol···methanol hydrogen bond was observed as the dominant feature in the n=2 spectrum. For n=3, we observe three isomers, including a methanol trimer chain which is calculated to be approximately 9 kJ/mol above the minimum-energy isomer. The cooperative effects of hydrogen bonding are pronounced in the n=2-3 spectra. The largest effect comes in the methanol trimer chain where the ionic hydrogen bond results in a shift of the OH stretch of -364 cm\(^{-1}\) compared to the n=1 structure, or in comparison to neutral methanol, a remarkable -948 cm\(^{-1}\) shift. These results indicate that high-energy isomers which exhibit very strong hydrogen bonds can be readily formed by introducing Cl\(^-\) into cold, argonated methanol clusters.


RI14  10 min  5:17
LONG RANGE PROTON-MIGRATION IN VUV PHOTOIONIZATION OF ACETONE CLUSTERS

KEN-ICHI HANAUE, YOSHIYUKI MATSUDA, KEISUKE OHTA, NAOHIKO MIKAMI and ASUKA FU-JII, Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan.

Infrared spectroscopic investigations of neutral and cationic clusters of acetone reveals proton-migration for keto-enol tautomerization in their ionization processes. In the reaction, the methyl proton of acetone is transferred to its carbonyl oxygen through the intracluster long range proton-migration.

RI15  15 min  5:29
OVERTONE SPECTROSCOPY OF PEROXYACETIC ACID AND PEROXYFORMIC ACID: INFLUENCE OF INTRAMOLECULAR HYDROGEN BONDING

MONTU K. HAZRA, MICHELLE KUANG, and AMITABHA SINHA, Department of Chemistry and Biochemistry, University of California-San Diego 9500 Gilman Drive, La Jolla, California 92093-0314.

The absorption of solar radiation by hydrogen-bonded (H-bonded) complex, particularly those containing water, is important in atmospheric chemistry. However, because of their low concentration, intermolecular hydrogen bonded complexes of atmospheric interest are difficult to study in the gas phase. Consequently, our initial efforts have been directed towards investigating the spectroscopy of molecules with internal hydrogen bonds. In this talk, we present the vapor phase vibrational overtone spectra of peroxyacetic acid (PAA) and peroxyformic acid (PFA), two molecules of atmospheric importance, and discuss the effect of intramolecular hydrogen-bonding on their OH stretching overtone transition strength and band positions. A comparison of the results of PAA and PFA with those of other intramolecular H-bonded and non-H-bonded molecules provides a useful gauge of the extent of hydrogen bonding in these peroxyacids.
STUDY OF SURFACE ENHANCED RAMAN SCATTERING OF ALIZARIN AND CRYSTAL VIOLET DYES

RAM GOPAL and RAJ KUMAR SWARNKAR, Laser Spectroscopy and Nanomaterials Lab, Department of Physics (UGC-CAS), University of Allahabad, Allahabad-211002, India.

Surface enhanced Raman scattering (SERS) plays a vital role in analytical chemistry to characterize ultra trace quantity of organic compounds and biological samples. Two mechanisms have been considered to explain the SERS effect. The main contribution arises from a huge enhancement of the local electromagnetic field close to surface roughness of the metal structures, due to the excitation of a localized surface plasmon, while a further enhancement can be observed for molecules adsorbed onto specific sites when resonant charge transfer occurs. SERS signals have been observed from adsorbates on many metallic surfaces like Ag, Au, Ni, Cu etc. Additionally, metal oxide nanoparticles also show SERS signals. It has now been established that SERS of analyte material is highly dependent on the type of substrate involved. Many types of nanostructures like nanofilms, nanorods, nanospheres etc. show highly efficient SERS signals. In particular, there are two routes available for the synthesis of these nanomaterials: the chemical route and the physical route. Chemical route involves many types of reducing agents and capping agents which can interfere in origin and measurement of these signals. The physical route avoids these anomalies and therefore it is suitable for the study of SERS phenomenon. Pulsed laser ablation in liquid medium is an excellent top down technique to produce colloidal solution of nanoparticles with desired shape and size having surface free from chemical contamination, which is essential requirement for surface application of nanoparticles. The present work deals with the study of SERS of Crystal violet dye and Alizarin group dye on Cu@Cu2O and Ag colloidal nanoparticles synthesized by pulsed laser ablation.

ANAMIKA MUKHOPADHYAY, Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India; AMIT K. SAMANTA, ; BIMAN BANDYOPADHYAY, ; PRASENJIT PANDEY, ; and TAPAS CHAKRABORTY.

Non-bonded interactions between a weakly acidic CH group and an oxygen atom of a functional group belonging to the same or of a different molecule are categorized as weak hydrogen bonds. Recently, our group has studied a number of dimeric molecular complexes by infrared spectroscopy, where CH–O hydrogen bonding has been invoked to be the dominant binding force for stability of those complexes in ground electronic state. An intriguing spectroscopic attribute of such hydrogen bonding, identified though in a handful of favourable cases, is spectral blue shifting of the donor CH stretching fundamental. Citing examples of the complexes between various cyclic ketones and haloforms studied by our group, the correlation that has been understood partly between the spectral blue shifts and geometries of the complexes will be discussed. An important issue here is whether such hydrogen bonds are stabilized by cooperative interaction, an underlying feature for excess stability of interconnected classical hydrogen bonds, and the spectral manifestation of this effect for the complexes we have studied will be presented. IR spectroscopy measurements have been performed in the gas phase, in carbontetrachloride solution at different temperatures and by isolating the complexes in cold inert gas matrices.
RJ01  
INVITED TALK  
30 min  1:30

CALCULATING RO-VIBRATIONAL SPECTRA OF VAN DER WAALS MOLECULES

XIAOGANG WANG and TUCKER CARRINGTON, Jr., Chemistry Department, Queen’s University, Kingston, Canada.

Van der Waals molecules are loosely bound and strongly coupled and their spectroscopy can therefore not be understood with a rigid rotor + harmonic oscillator model. Useful insight can be obtained by numerically solving the ro-vibrational Schroedinger equation using a basis set. The most obvious impediment is the size of the basis required to obtain converged results. Nonetheless, by using an iterative eigensolver and exploiting the structure of quadrature approximations for potential matrix elements, it is possible to do calculations for many molecules of interest. I shall discuss how the choice of the vibrational coordinates and the molecule-fixed axis system influence the calculation of ro-vibrational spectra of Van der Waals molecules and present new results for (NNO)₂, H₂-O, and SF₆-He₂.

RJ02  
15 min  2:05

PREDICTION OF VIBRATIONAL ENERGY LEVELS USING A MIXED APPROACH OF NUMERICAL AND ANALYTICAL INTEGRATION

J. VÁZQUEZ, M. E. HARDING, J. F. STANTON, Institute for Theoretical Chemistry, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712; J. GAUSS, Institut für Physikalische, Universität Mainz, Jakob Welder Weg 11, D-55128 Mainz, Germany.

A method for the computation of vibrational energy levels based on Watson’s simplified form of the complete rotation-vibration nuclear Hamiltonian⁶ is presented. The Hamiltonian matrix is constructed within a harmonic oscillator product basis using a discrete variable representation of the potential energy and a quasi-analytic treatment of the remaining terms. The latter are obtained by an expansion of the modified reciprocal moment of inertia with respect to the normal coordinates and the integration is carried out using a string-based formalism. Results for linear and nonlinear molecules demonstrate the excellent performance of the present implementation.


RJ03  
15 min  2:22

COMPUTATION OF INFRARED SPECTROSCOPIC FEATURES USING SYMMETRY

J. VÁZQUEZ, J. F. STANTON, Institute for Theoretical Chemistry, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712.

An efficient algorithm for the prediction of anharmonic infrared features of symmetric top molecules in the framework of second-order vibrational perturbation theory is presented. Higher-order derivatives of the energies are obtained by numerical differentiation of analytic second derivatives in conjunction with symmetry projection which leads to a major reduction of the computational demand. The performance of the implementation is illustrated by several examples.
NINE DIMENSIONAL THEORETICAL STUDIES ON METHOXY FREE RADICAL

JAYASHREE NAGESH and E. L. SIBERT III, Department of Chemistry and Theoretical Chemistry Institute, University of Wisconsin-Madison, WI 53706.

The Jahn-Teller type of degeneracy in electronic states in polyatomic molecules greatly affects its vibrational dynamics. The methoxy free radical possesses $C_{3v}$ symmetry at the Jahn-Teller conical intersection ($\tilde{X}^2E$) and provides an ideal system for understanding how the Jahn-Teller phenomenon affects the dynamics. Despite many efforts to clearly elucidate the dynamics, calculation of the potential hypersurface and vibronic states in the molecule remains a theoretical challenge. We adopt a diabatic framework to describe the 9-dimensional hypersurface, which allows us to treat the dynamics in a more straightforward manner. A 9-dimensional force field is calculated for both the $\tilde{A}^2A_1$ and $\tilde{X}^2E$ surfaces using various levels of theory and basis sets. Quartic and quadratic force fields, expressed in internal coordinates, are obtained for the ground and excited states, respectively. The least squares fit was obtained solely using points with $C_s$ symmetry, yet is shown to agree well with $ab initio$ points obtained at lower symmetry. The Hamiltonian is shown to take on a particularly simple form when expressed in terms of circular raising and lowering operators for both the electronic and vibrational degrees of freedom. The variational calculation in the diabatic representation is carried out in a series of prediagonalization steps, adding vibrational degrees of freedom in a systematic manner. Theoretical and experimental fundamental frequencies are shown to be in good agreement.

VIBRATIONAL DYNAMICS AROUND THE CONICAL INTERSECTION OF METHOXY

J. NAGESH and E. L. SIBERT III, Department of Chemistry and Theoretical Chemistry Institute, University of Wisconsin-Madison, WI 53706.

The stimulated emission pumping (SEP) spectrum of the methoxy molecule resulting from the transition from the $\tilde{A}^2A_1$ to the $\tilde{X}^2E$ state is calculated and compared to experiment. This work builds on the results of the talk by Nagesh and Sibert in which force fields for these surfaces are calculated and the vibrational states are calculated variationally using a curvilinear normal mode zero order representation. The role of the Jahn-Teller distortion on the increased spectral complexity is examined for this system as well as simple model systems. Specifically, a model Hamiltonian consisting of two vibrational degrees of freedom and the coupling between them is presented in a diabatic representation of the doubly degenerate electronic degrees of freedom. The observed complex dynamics are understood in terms of the multiple timescales that arise as the initial wave packet passes through the conical intersection. This time-dependent approach is extended to interpret the SEP spectrum of methoxy.

CALCULATING ANHARMONIC VIBRATIONAL STATES WITHOUT A PRE-EXISTING POTENTIAL ENERGY SURFACE

ANDREW S. PETIT and ANNE B. McCoy, Department of Chemistry, The Ohio State University, Columbus, OH 43210.

The calculation of anharmonic vibrational states, especially of highly fluxional systems, is complicated by the need to first obtain the full-dimensional potential energy surface (PES). Reduced dimensional approaches, where appropriate, can greatly help to ease the computational cost of these calculations but their application is highly system dependent, preventing the development of a general methodology. We report here our recent efforts to develop an algorithm capable of accurately calculating anharmonic vibrational energies, even for very floppy systems, without first obtaining a PES. More specifically, the potential energy and G-matrix elements are calculated on a grid of points obtained from a Monte Carlo sampling of the most important regions of configuration space. The Hamiltonian matrix is then constructed using an evolving basis which, with each iteration, captures the effect of building $H$ from an ever-increasing harmonic oscillator basis despite the fact that the actual dimensionality of $H$ is fixed throughout the calculation. This latter property of the algorithm also greatly reduces the size of basis needed for the calculation relative to more traditional variational approaches. The results obtained from the application of our method to several test systems will also be reported along with its observed convergence properties.
The dimethyl ether is a non-rigid molecule with three internal motions: the two methyl rotations and the COC bending. This motion is studied using MP2 and CCSD(T) calculations using an aug-cc-pVTZ basis set and applying the ZPVE corrections. With these results the 3D spectra is calculated.

The spectra of AlCl molecule are of astrophysical interest since AlCl has been detected in the envelope of the carbon star IRC + 10216 by microwave spectroscopy. Ab initio and Density Functional Theory calculations on the spectra and structure of AlCl molecule and their cation are carried out. The Einstein A spontaneous emission coefficients for the ro-vibrational transitions in the $A^1\Pi - X^1\Sigma^+$ electronic band systems of AlCl molecule for $v = 0 - 4$ and $J = 0-100$ in each electronic state have been computed using LEVEL program. The values of radiative lifetimes of $A^1\Pi$ state for $v' \leq 9$ levels are determined. We have obtained the high transition probabilities for the diagonal bands in this electronic system. The results obtained in the present work are found in agreement with the experimental value.

\textsuperscript{a}Present address: Department of Physics, Agrasen Kanya PG College, Varanasi


Intermission
REACTION PATH HAMILTONIAN CALCULATION OF TUNNELING SPLITTING IN PROTONATED METHANOL AND METHYLAMINE.

A. R SHARMA, J. M BOWMAN, Cherry L. Emerson Center for Scientific Computation, Department of Chemistry, Emory University, Atlanta GA 30322, USA; S. C CARTER, Department of Chemistry, University of Reading, RG6 2AD, England.

Both protonated methanol(CH$_3$OH$^+$) and methylamine(CH$_3$NH$_2$) show two interesting large amplitude motion, namely, internal rotation and inversion. The internal rotation spectrum results from the rotation of the CH$_3$ moiety against the OH$_2$ group in case of protonated methanol and of NH$_2$ group in the case of methylamine. The other interesting phenomenon is inversion involving the OH$_2$ group and NH$_2$ group in the case of protonated methanol and methylamine, respectively.

The influence of inversion in methylamine, on bands in the near and middle infrared has been investigated. Microwave and far-IR spectrum of methylamine has been measured and spectral frequency calculations derived from rotation-internal rotation-inversion analysis has been reported. However, in the past, detection of protonated methanol (CH$_3$OH$_2^+$), in interstellar clouds has been impossible due to the lack of both laboratory spectra and calculation.

In this contribution ab initio based potential energy surface (PES) and dipole moment surface (DMS) is presented for both protonated methanol and methylamine. The PES and DMS are developed by least squares fitting of ab initio energy values computed at CCSD(T)/AVTZ level of theory and dipole moments at MP2/AVTZ level of theory. Internal rotation and inversion transition states and normal-mode frequencies will be reported. One-dimensional tunneling splitting calculations will be reported. Tunneling splittings at higher dimensionality, ro-vibrational states and transition intensities are calculated using reaction path Hamiltonian(RPH) as implemented in MULTIMODE(MM) code. MM treats polyatomic molecules with large-amplitude motion as and one special coordinate which is the large-amplitude vibrational coordinate. Complete integration is performed over reaction path coordinate, and the N-mode MULTIMODE coupling approximation for the evaluation of the matrix elements applies only to the 3N - 7 normal coordinates.

ELECTRONIC STRUCTURE AND SINGLET-TRIPLET ENERGY SPLITTINGS IN ETHYNYL CYCLOBUTADIENES

STEPHANIE J. THOMPSON, FRANK LEE EMMERT III, and LYUDMILA V. SLIPCHENKO, Department of Chemistry, Purdue University, West Lafayette, IN 47907.

We investigated the effects of ethynyl substituents on singlet-triplet gaps in cyclobutadiene. These species are involved in Bergman Cyclization reactions$^a$ and are possible intermediates in the formation of fullerenes and graphite sheets.$^b$

Prediction of the singlet-triplet splitting in cyclobutadienes is challenging for single-reference ab initio methods such as HF, MP2 or DFT because of Jahn-Teller distortions and the diradical character of the singlet state. Ethynyl substituents in cyclobutadienes are thought to stabilize the triplet states and invert the order of the singlet and triplet in some of them.

We determined the singlet-triplet energy splittings in substituted cyclobutadienes using the equations of motion spin flip coupled cluster with single and double excitations (EOM-SF-CCSD) method that accurately describes diradical states and singlet-triplet gaps in diradicals.$^c$

Fundamental studies of electronic coupling between flexible bichromophores are needed to validate and refine models used for solar energy conversion in conjugated organic semiconductors and models found in many other areas which involve energy transfer or exciton propagation. Diphenylmethane (DPM) is a prototypical flexible bichromophore for which highly accurate spectroscopic data is available.\(^a\) We investigated the splitting between the $S_1$ and $S_2$ exciton states of DPM along the $C_2$ axis with respect to the ring torsional coordinate. We showed that the state crossing occurs at $\tau_1 = \tau_2 = 70^\circ$ torsional angles and explained it qualitatively with orbital analysis. We constructed the relaxed ground state potential energy surface and the $S_1$ and $S_2$ excited energy potential energy surfaces of DPM with regards to ring torsional angles using EOM-CCSD/cc-pVDZ and TD-DFT(\(\omega\)B97X-D)/cc-pVTZ levels of theory. We found that TD-DFT and EOM-CCSD surfaces are qualitatively similar, however, both methods overestimate the experimentally observed $S_1 - S_2$ splitting of $123\ \text{cm}^{-1}$ by four to five times.\(^b\) We also obtained the transition dipole moment surface and investigated the accuracy of the dipole-dipole model in the prediction of the coupling of the exciton states in DPM.

In molecular spectroscopy, it is often considered that sophisticated group theoretical and tensorial formalism methods are only really useful for spherical top (i.e., highly symmetrical) molecules, for which they have proven their high efficiency. Consequently, it is usually admitted that symmetric and asymmetric tops (i.e., only really useful for spherical top) are parameters that define a complete set of allowed paths for any using more “conventional” methods. However, some key elements of the formalism developed in our group for tetrahedral or octahedral molecules can be used with great profit even for less symmetrical systems: the ability of performing systematic developments of all rovibrational interactions in case of complex polyads and the so-called “vibrational extrapolation” which makes global analyses much easier. Firstly, we present the development of a tensorial formalism adapted to the study of XY₃Z type molecules which possess integer angular momenta (i.e., in a singlet electronic state) by using the O(3) ⊆ C₃ᵥ ⊆ C₃ₑ point group. We present also the C₃ₑ ⊆ S(C₃ᵥ) Top Data System software for spectrum simulation dedicated to the study of symmetric-top molecules belonging to the C₃ₑ point group. Secondly, we present the development of a tensorial formalism adapted to the study of XY₃Z type open-shell species which possess half-integer angular momenta by using the SU(2) ⊆ C₉ ⊆ C₃ₑ group chain.

Recently, Hougen showed an ad hoc symmetry-based parameterization scheme for analyzing tunneling dynamics and high resolution spectra of fluxional molecular structure similar to by using the S(3) ⊆ C₃ᵥ ⊆ C₃ₑ chain. We present also the C₃ₑ ⊆ S(C₃ᵥ) Top Data System software for spectrum simulation dedicated to the study of symmetric-top molecules belonging to the C₃ₑ point group. Then we apply local symmetry conditions to each irrep D(e) = (g₃) that has already been reduced with respect to local symmetry L. This amounts to setting each off-diagonal component D(f) = (g₄) to zero.

Local symmetry conditions may tell which parameters are redundant or zero and directly determine d(ℓ)G tunneling matrix eigenvalues that give E(ℓ) levels as well as eigenvectors. Otherwise one may need to choose a particular localizing subgroup chain L ⊆ L₁ ⊆ L₂ ...G and further reduce the number of path parameters to facilitate spectral fitting.

**References**

2. W.G. Harter and J. C. Mitchell, 2009 MSS RJ05 (See also following talk.)
High-resolution spectra of spherical-top molecules are known to demonstrate rotational level clustering. This clustering is well described as a rotational phase-space effect\(^a\). Multiple equivalent phase-space regions allow tunneling and thus splitting of the rotational clusters\(^b\). So far this has been done with an ad hoc tunneling Hamiltonian. Similar splittings have been shown for low-dimensional systems\(^c\), also with an ad hoc parameterization. While ad hoc tunneling parameterization is simple to understand, it becomes extremely difficult to apply for higher symmetries and for locally low-symmetry clustering when many tunneling paths are possible. Symmetry-based parameterization mitigates this complication.

This presentation will discuss how symmetry-based tunneling is applied for octahedral molecules and demonstrate how local-$C_1$, $C_2$, $C_3$ or $C_4$ clusters may be evaluated perturbatively. Connections to non-rotational systems, such as large amplitude motion, will be discussed as well.

---

\(^a\)W.G. Harter and C.W. Patterson, Phys Rev Lett 38, 224 (1977)
\(^b\)W.G. Harter and C.W. Patterson, J Chem Phys 66, 4872 (1977)
\(^c\)J.T. Hougen J Mol Spect 123, 197 (1987)
FA. INFRARED/RAMAN (VIBRATIONAL)
FRIDAY, JUNE 25, 2010 – 8:30 am
Room: 160 MATH ANNEX

Chair: JOSEPH R. ROSCIOLI, University of Colorado, Boulder, Colorado

FA01  15 min  8:30
HIGHEST RESOLUTION FOURIER TRANSFORM INFRARED SPECTROSCOPY WITH AN ELEVEN CHAMBER BRUKER INTERFEROMETER AT THE SWISS SYNCHROTRON

S. ALBERT, K.K. ALBERT, M. QUACK, PHYSICAL CHEMISTRY, ETH ZÜRICH, CH-8093 ZÜRICH, SWITZERLAND; PH. LERCH, L. QUARONI, SWISS LIGHT SOURCE, PAUL-SCHERRER-INSTITUTE, CH-5232 VILLIGEN, SWITZERLAND; A. KEENS, BRUKER OPTICS, D-76275 ETTLINGEN, GERMANY.

We have interfaced a newly constructed eleven chamber interferometer, the ETH-SLS Bruker IFS 125 HR prototype 2009, to the infrared port available at the Swiss Light Source (SLS), located at the Paul-Scherrer-Institute. The Maximum Optical Path Difference (MOPD) of this spectrometer is 11.70 m allowing for a best theoretical unapodized resolution of 0.00053 cm\(^{-1}\) (18 MHz). The ETH-SLS Bruker spectrometer is a further development of our nine chamber interferometer Bruker IFS 120/125 Zurich prototype 2001 which has an MOPD of 9.4 m and unapodized resolution of 0.00068 cm\(^{-1}\) (23 MHz). We present spectra of CO and pyrimidine (C\(_4\)H\(_4\)N\(_2\)) as examples to illustrate the improved resolution. Due to the high brightness of the synchrotron source the signal-to-noise ratio is effectively 5 to 20 times better than that of conventional thermal sources in the spectral region between 180 and 900 cm\(^{-1}\) (6-28 THz). We present examples of pyrimidine (C\(_4\)H\(_4\)N\(_2\)) and CDBrClF spectra in the region 600 to 900 cm\(^{-1}\) and of phenol (C\(_6\)H\(_5\)OH) and aniline (C\(_6\)H\(_5\)NH\(_2\)) spectra in the region 180 to 350 cm\(^{-1}\). Due to the excellent resolution and the bright synchrotron source we were able to detect the spin statistical weights in the pyrimidine spectra and found new combination bands in the CDBrClF spectra. We were able to rotationally resolve the torsional c-type band of phenol with \(\nu_{0a} = 309.1141\) cm\(^{-1}\) and \(\nu_{0b} = 309.5517\) cm\(^{-1}\) and detect a torsional splitting of 0.4376 cm\(^{-1}\) in the \(v = 1\) torsional level. In addition, we were able to rotationally resolve and assign the very weak two torsional b-type subbands of aniline with \(\nu_{0a} = 234.8\) cm\(^{-1}\) and \(\nu_{0b} = 304.3\) cm\(^{-1}\) showing the mode selective inversion splitting.

\(^a\)S. Albert, K.K. Albert and M. Quack, Trends in Optics and Photonics, 2003, 84, 177.

FA02  15 min  8:47
HIGH-RESOLUTION SPECTROSCOPY OF THE \(\nu_8\) BAND OF METHYLENE BROMIDE USING A QUANTUM CASCADE LASER-BASED CAVITY RINGDOWN SPECTROMETER

JACOB T. STEWART, BRIAN E. BRUMFIELD, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801; MATTHEW D. ESCARRA, CLAIRE F. GMACHL, Department of Electrical Engineering, Princeton University, Princeton Institute for the Science and Technology of Materials, Princeton, NJ 08544; BENJAMIN J. McCALL, Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

Our group has constructed a cavity ringdown spectrometer based on a quantum cascade laser (QCL) in an effort to obtain a high-resolution gas phase spectrum of buckminsterfullerene (C\(_{60}\)). To test the performance of our spectrometer we have observed the \(\nu_8\) band of methylene bromide (CH\(_2\)Br\(_2\)) from 1196 to 1197.5 cm\(^{-1}\). This band had previously only been recorded at low resolution. Cold methylene bromide molecules were produced in a continuous supersonic expansion from a 700 \(\mu\)m pinhole and probed using continuous wave cavity ringdown spectroscopy (cw-CRDS). To our knowledge, this is the first experiment to measure a supersonic jet-cooled sample using a QCL-based cw-CRDS spectrometer. We have assigned the observed ro-vibrational lines from the three isotopomers of CH\(_2\)Br\(_2\) to effective Hamiltonians, and find that the molecules have been cooled to a rotational temperature of \(\sim3\)–10 K.
FTIR SPECTROMETERS UTILIZING MID-INFRARED QUANTUM CASCADE LASERS.

CHRISTIAN PFLUGL, LORAN DIEHL, FEDERICO CAPASSO, School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, 02138; MARK F. WITINSKI, Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts, 02138; SERGEY SHILOV, PANG WANG, THOMAS TAGUE, Bruker Optics, 19 Fortune Drive, Billerica, Massachusetts, 01821.

A Fabry-Perot Quantum Cascade Laser source can be used in conjunction with a Fourier Transform Infrared Spectrometer to perform spectroscopic experiments that require orders of magnitude more photons than are emitted by a thermally radiant blackbody source. Three proof-of-concept experiments including laser transmission through liquids, transmission through gases over long distances, and reflection from powders and tablets demonstrated how the increased brightness of a Quantum Cascade Laser enables many important avenues in gas and condensed phase analysis.

MID- AND LONGWAVE INFRARED TOTAL AND DIFFUSE REFLECTANCE MEASUREMENTS USING AN INTEGRATING SPHERE WITH A TWO-SAMPLE-PORT DESIGN

THOMAS A. BLAKE and TIMOTHY J. JOHNSON, Pacific Northwest National Laboratory, P.O. Box 999, Mail Stop K8-88, Richland, WA 99352 (PNNL is operated for the US Department of Energy by the Battelle Memorial Institute under contract DE-AC05-76RL01830); MICHAEL JUETTE and ARNO SIMON, Bruker Optik GmbH Rudolf-Plank-Straße 27, D-76275 Ettlingen Germany.

We report here improved methodologies for the use of the Bruker A 562-G integrating sphere for quantitative total and diffuse reflectance measurements. The sphere has an internal diameter of 75 mm and the interior surface is coated with matte gold. It has an input port (20 mm diameter), top (32 mm) and bottom (19 mm) sample ports, all on a sphere circumference defined by a vertical plane that includes the sphere center, and a baffled port (10 mm) for an MCT detector (2 mm x 2 mm), that is on a sphere circumference defined by a horizontal plane that includes the sphere center. An interior flip mirror is used to direct light from the input port to either the top or bottom sample ports. The sphere sits in the sample compartment of a benchtop Fourier transform spectrometer. Total reflectance measurements are made by placing the sample in one of the sample ports and blocking the other sample port with a matte gold reference material, recording spectra with the flip mirror pointed towards the sample and then towards the reference material, and then ratio-ing the two spectra. Using this method excellent agreement (< 2% difference) was observed between measurements made using the Bruker sphere and FTIR and reported values for five NIST-calibrated total reflectance standards. Diffuse reflectance measurements are made by placing the sample in one of the sample ports and blocking the other sample port with a matte gold reference material, recording spectra with the flip mirror pointed towards the sample and then towards the reference material, and then ratio-ing the two spectra. Using this method excellent agreement (< 2% difference) was observed between measurements made using the Bruker sphere and FTIR and reported values for five NIST-calibrated total reflectance standards. Diffuse reflectance measurements are made by placing the sample in one of the sample ports and leaving the other port open to allow the specular reflectance component of the sample to exit the sphere, recording spectra with the flip mirror pointing towards the sample and then towards a point on the sphere wall. The two spectra are again ratioed. The diffuse spectrum is thus the total spectrum less the specular component. In the shortwave infrared, where there is sufficient overlap, total and diffuse measurements using the Bruker sphere and FTIR compare favorably with results from a Varian Spectralon-coated integrating sphere and Cary 5000i spectrometer for a number of different materials.
VIBRATIONAL SPECTRA OF CHLOROFORM, FREON-11 AND SELECTED ISOTOPOMERS IN THE TERAHERTZ REGION

CHRISTA HAASE, JINJUN LIU and FRÉDÉRIC MERKT, Laboratorium für Physikalische Chemie, ETH-Zürich, 8093 Zürich, Switzerland.

The fundamental bands of the CCl$_3$ asymmetric deformation modes of selected isotopomers of chloroform (CHCl$_3$) and freon-11 (CFCl$_3$) have been measured between 7 and 8 THz in a static cell at ambient temperature using a laser-based source of tunable radiation in the terahertz region (0.1-10 THz) of the electromagnetic spectrum. Simulation of the rotational contour of the $\nu_6$ fundamental transition of $^{12}$CH$^{35}$Cl$_3$ confirmed previously suggested values for $C_6$ and $C_6\zeta_6$. The fundamental frequencies were derived with a precision of 2 GHz for all compounds except CF$^{35}$Cl$_3$, where the precision amounted to 3 GHz. The frequencies are in agreement with values calculated ab initio. Extension of the experimental setup to enable measurement of THz spectra of molecules in supersonic jet expansions and partially resolve their rotational structure is in progress.

$^a$current address: Department of Chemistry, Laser Spectroscopy Facility, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210, USA.


EXPERIMENTAL ENERGY LEVELS OF HD$^{18}$O AND D$_2$$^{18}$O

S.N. MIKHAILENKO, O.V. NAUMENKO, S.A. TASHKUN, Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, 634055, Tomsk, RUSSIA; A.-W. LIU, S.-M. HU, Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, CHINA.

Extended sets of experimental energy levels of HD$^{18}$O and D$_2$$^{18}$O have been obtained as the result of the analysis of recent high-resolution spectra $^a$, $^b$ and previously reported data $^c$, $^d$, $^e$, $^f$, $^g$, $^h$, $^i$, $^j$. Spectra of the enriched by deuterium and oxygen-18 water samples were recorded with a Bruker IFS 120HR spectrometer at room temperature in the 1000 - 9200 cm$^{-1}$ range $^a$, $^b$ for this purpose. The RITZ code $^h$ was used for analysis of the rotation-vibration transitions and the energy levels determination.

New energy levels as well as comparison with previous experimental and theoretical studies will be presented. This work was supported by Grant nos. 06-03-39014 and 10-05-91176 of RFBR (Russia) and by Grant nos. 20903085 and 10574124 of NSFC (China). Work of SNM and SAT was also partly supported by CRDF (USA) Grant RUG1-2954-TO-09 and by RFBR. Grant 09-05-92508.


$^j$O.V. Naumenko et al., JQSRT, 111, 36-44 (2010).
SPECTRA OF ETHANE IN He DROPLETS IN THE 3 μm RANGE

LUIS GOMEZ, EVGENIY LOGINOV, DMITRY SKVORTSOV, HIROMICHI HOSHINA, and ANDREY F. VILESOV, Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482.

The infrared spectra of ethane molecules embedded in He droplets have been studied via depletion spectroscopy in the ν = 2880-3000 cm⁻¹ spectral range. Four features observed in the spectra are assigned as the ν₅, ν₈+₁₁ (perpendicular and parallel components), and ν₇ vibrational bands. Band origins and rotational constants for ethane in He are obtained and compared with corresponding gas phase values. Spectra of large ethane clusters (C₂H₆)ₙ (with n = 1300-13000) in He are also reported.

Intermission

PURE ROTATIONAL CARS THERMOMETRY IN NANOSECOND PULSE BURST AIR AND HYDROGEN-AIR PLASMAS

YVETTE ZUZEK, INCHUL CHOI, SHERRIE BOWMAN, IGOR V. ADAMOVICH AND WALTER R. LEMPERT, Department of Mechanical Engineering, The Ohio State University, 201 W. 19th Ave., Columbus OH, 43210.

Pure rotational Coherent Anti-Stokes Raman Scattering (CARS) is used to study low temperature plasma kinetics and ignition in a repetitively pulsed nanosecond discharge in air and hydrogen-air at stoichiometric and fuel lean conditions at 40 Torr pressure. Air and hydrogen-air mixtures are excited by a burst of high-voltage nanosecond pulses at a 40 kHz pulse repetition rate and 10 Hz burst repetition rate. The number of pulses within the burst has been varied from a few pulses to 1,000 pulses. These temperature measurements are then compared to a hydrogen-air plasma chemistry model which includes nonequilibrium plasma processes and low temperature hydrogen-air chemistry. Sensitivity analysis shows that generation of radicals by the nanosecond discharge is critical to low temperature plasma chemical fuel oxidation and associated heat release. With phi = 1.0 and phi = 0.5, a distinct maximum in temperature with respect to discharge burst duration is observed, as predicted by the code, indicative of ignition occurring.

INVESTIGATION OF A SPARK IGNITION INTERNAL COMBUSTION ENGINE VIA IR SPECTROSCOPY

STEPHEN SAKAI, ALLEN R. WHITE, Department of Mechanical Engineering, Rose-Hulman Institute of Technology, Terre Haute, IN; KEVIN GROSS, Department of Engineering Physics, Air Force Institute of Technology, Dayton, OH; REBECCA B. DEVASHER, Department of Chemistry, Rose-Hulman Institute of Technology, Terre Haute, IN.

Previous work has shown that the automotive fuel components of isopropanol and ethanol can be excited by a 10.2 um and 9.3 um CO2 lasers, respectively. Through the use of a monochromator and an indium antimonide detector, the decay time of the excited molecules was measured and found to be significantly long enough to allow for the possibility of experimentation in an internal combustion (IC) engine. In order to pursue In Situ measurements in an internal combustion engine, a MegaTech Mark III transparent engine was modified with a sapphire combustion chamber. This modification will allow the transmission of infrared radiation for time-resolved spectroscopic measurements by an infrared spectrometer. By using a Telops FIRST-MVE imaging Fourier transform spectrometer, temporally and spatially resolved infrared spectral data can be acquired and compared for combustion in the engine both with and without laser excitation. Measurements performed with system provide insight into the energy transfer vectors that precede combustion as well as provide an in situ measurement of the progress of combustion.
DIRECT AND COLLISIONAL EXCITATION OF AUTOMOTIVE FUEL COMPONENTS)

ALLEN R. WHITE, KYLE WILSON, STEPHEN SAKAI, Department of Mechanical Engineering, Rose-Hulman Institute of Technology, 5500 Wabash Ave., Terre Haute, IN 47803; REBECCA B. DEVASHER, Department of Chemistry, Rose-Hulman Institute of Technology, 5500 Wabash Ave., Terre Haute, IN 47803.

Adding energy directly into the vibrational modes of automotive fuel may reduce the threshold energy required for combustion, without raising the combustion charge temperature. This energy can be supplied either directly via incident laser radiation or indirectly through collision with directly excited molecules. The most common chemical in commercial gasoline, isooctane, does not absorb infrared radiation sufficiently at any wavelength for which an infrared laser is readily available. However, CO2 lasers are relatively cheap, and are available at wavelengths which are absorbed by isopropanol as well as ethanol, which is also a component of commercial gasoline. In this study, the infrared absorption of isopropanol and ethanol in balance isooctane were measured at three wavelengths (10.6 m, 10.2 m, and 9.3 m) of incident CO2 laser radiation. Additional time-resolved emission measurements were performed for these mixtures. The data support the existence of the proposed collisional pathway for energy transfer from ethanol and isopropanol to isooctane.

STRUCTURES OF TWO ISOMERS OF NITROUS OXIDE TETRAMER FROM THEIR INFRARED SPECTRA

J. NOROOZ OLLIAE, F. MIVEHVAR, M. DEHGHANY, N. MOAZZEN-AHMADI, Department of Physics and Astronomy, University of Calgary, Calgary, AB T2N 1N4, Canada; A.R.W. MCKELLAR, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, ON K1A 0R6, Canada.

Weakly bound complexes provide a convenient starting point for a detailed understanding of different pathways that can be taken between the gas and condensed phases of matter. In this regard, it is of considerable interest to determine the number of isomers for a cluster size and if and how geometrical choices made in the early stages of condensation influence the growth of larger clusters. Although it is expected that the number of isomers grows rapidly with cluster size, in many cases only a single isomer is observed experimentally.

High resolution spectroscopy has provided information on structural and vibrational dynamics of a large number of binary and ternary complexes formed from related linear triatomic molecules such as CO2, N2O, OCS and CS2. But, there are much fewer detailed experimental studies which provide structures for the important cluster sizes in the range of 4 ∼ 10 monomers.

Here we report the structural determination of two isomers of nitrous oxide tetramer from their infrared spectra in the ν1 fundamental region (∼ 2230 cm⁻¹). Two bands are observed and analyzed, corresponding to two distinct isomers of the complex. A perpendicular band centered at 2232.209 cm⁻¹ has been assigned to an isomer with S4 symmetry (a subgroup of D2d group). This is a rare symmetry group, but provides all the necessary ingredients. It allows for a tilt of the monomers from the symmetry axis of the complex as well as a twist. The experimentally determined structure has the monomers more or less perpendicular to the symmetry axis. A second band centered at 2237.424 cm⁻¹ was assigned to a structure close to a perfect barrel-shaped tetramer with D2d symmetry. This is a prolate symmetric top which gives parallel bands for the pure isotopomers and a c-type band for the mixed isotopomer containing three 15N2O monomers. This isomer is the same species as that observed by R.E. Miller and L. Pederson. a

Vibrational predissociation spectra of the Ar-tagged [H₃O⁺·X], X = CH₄, CD₄, N₂, and Ar complexes are analyzed to explore the hydrogen bonding acceptor properties of an alkane. The observed redshift in the OH stretching transition of the donor is found to be significantly smaller than anticipated by the previously reported trend in this value with the proton affinity of the acceptor. Specifically, the alkane-induced redshift of the OH stretching frequency is less than that caused by the conventional proton acceptor, N₂, even though the latter is a weaker base than methane. The origin of this effect is discussed in the context of the structures of the complexes and the molecular rearrangements required for complete proton transfer to hydrocarbons as opposed to the situation in conventional H-bond acceptors.

Coherence-converted population transfer microwave-infrared double resonance spectroscopy is employed to record the rotationally state-selected infrared spectra of jet-cooled CH₃OD in the C-H stretch region (2750−3020 cm⁻¹). The observed infrared spectra result from the E-species microwave transitions (1₀ ← 1₋₁ at 18.957 GHz, 2₀ ← 2₋₁ at 18.991 GHz, and 3₀ ← 3₋₁ at 19.005 GHz). The present spectra of CH₃OD contain 17 interacting vibrational bands (J′ = 0). In addition to the three C-H stretch fundamentals (ν₃:2841.7 cm⁻¹, ν₉: 2954.4 cm⁻¹ and ν₂: 2998.9 cm⁻¹), 14 additional band origins are found in the region of the binary combinations of the CH bends (2890−2950 cm⁻¹). Although the A-species was inaccessible in the present work, the pattern of E-species reduced energies suggests that the torsional tunneling splittings of ν₃ and ν₉ are normal, whereas ν₂ is inverted. The number and distribution of the observed vibrational bands support a stepwise coupling scheme in which the CH stretch bright state couples first to the binary C-H bend combinations, and then to all of the higher order vibrational combinations. A time-dependent interpretation in the asymmetric region indicates a fast (170 fs) initial decay of the bright state.

The critical features of a burst mode diagnostic imaging system is described, along with representative NO PLIF measurements at 1MHz, in a Mach 10 hypersonic flow, and Rayleigh imaging and CH PLIF at 10kHz in turbulent flames.
FA15  Post-deadline Abstract  15 min  12:29
FAR INFRARED HIGH RESOLUTION SYNCHROTRON FTIR SPECTROSCOPY OF THE LOW FREQUENCY BENDING MODES OF DMSO

ARNAUD CUISSET, IRINA SMIRNOVA, ROBIN BOCQUET, FRANCIS HINDLE, GAELE MOURET, DMITRI A. SADOVSKII, Laboratoire de Physico-Chimie de l’Atmosphère, CNRS UMR-8101, Université du Littoral Côte d’Opale, 189A Ave. Maurice Schumann, 59140 Dunkerque, France; OLIVIER PIRALI, PASCALE ROY, Ligne AILES (Advance InfraRed Line Exploited for Spectroscopy), synchrotron SOLEIL, L’Orme des Merisiers, Saint Aubin, BP 48, 91192 Gif-sur-Yvette, France.

In addition to its importance for industrial and environmental studies, the monitoring of DimethylSulfOxyde (DMSO, (CH₃)₂SO) concentrations is of considerable interest for civil protection. The existing high resolution gas phase spectroscopic data of DMSO only concerned the pure rotational transitions in the ground state. In the Far-IR domain, the low-frequency rovibrational transitions have never previously resolved. The high brightness of the AILES beamline of the synchrotron SOLEIL and the instrumental sensitivity provided by the multipass cell allowed to measure for the first time these transitions. 1581 A-type and C-type transitions in the ν₁₁ band have been assigned and 25 molecular constants of Watson’s s-form hamiltonian developed to degree 8 have been fitted within the experimental accuracy. The use of then synchrotron radiation has opened many possibilities for new spectroscopic studies. Together with several other recent studies, our successful measurement and analysis of DMSO convincingly demonstrates the potential of the AILES beamline for high resolution FIR spectroscopy. Thus our present work is just at the beginning of unraveling the rovibrational structure of low frequency bending and torsional vibrational states of DMSO and yielding important comprehensive structural and spectroscopic information on this molecule.

bV. Typke, M. Dakkouri, J. Molec. Struct., 599,(177),2001

FA16  Post-deadline Abstract  10 min  12:46
ANHARMONIC RESONANCES AMONG LOW-LYING VIBRATIONAL LEVELS OF METHYL ISO-CYANIDE (H₃CNC)

P PRACNA, J. URBAN, J. Heyrovský Institute of Physical Chemistry, v.v.i., Academy of Sciences of the Czech Republic, 18223 Prague 8, Czech Republic; Š. URBAN, J. VARGA, Department of Analytical Chemistry, Institute of Chemical Technology, 16628 Prague 6, Czech Republic; V.-M. HORNEMAN, Department of Physical Sciences, University of Oulu, Linnanmaa, FIN-90570 Oulu, Finland.

Vibrational levels up to 1000 cm⁻¹ of H₃C-N≡C are currently studied in FTIR spectra together with rotational transitions within these levels. This investigation comprises the low-lying excited vibrational levels of the CNC doubly degenerate bending vibration ν₈ = 1±1 (267.3 cm⁻¹), ν₈ = 2⁰,±2 (524.6 cm⁻¹(A), 545.3 cm⁻¹(E)), and ν₈ = 3±1,±3 (792.5 cm⁻¹(A1+A2), 833.9 cm⁻¹(E)), respectively, and the next higher fundamental level of the C-N valence vibration ν₄ = 1 (945 cm⁻¹). All these vibrational levels exhibit cubic and quartic anharmonic resonances localized to moderate values of the rotational quantum number K ≤ 10. Therefore the system of rovibrational levels has to be treated as a global polyad in order to describe all the available data quantitatively. The ground state constants have been improved considerably by extending the assignments to higher J/K rotational states both in the purely rotational spectra recorded in the ground vibrational level and in the ground state combination differences generated from the wavenumbers assigned in the fundamental ν₄ band. Similarities and differences with respect to isoelectronic molecules CH₃CN and CH₃CCH are discussed.
MOLECULAR HYDROGEN ADSORPTION IN METAL-ORGANIC FRAMEWORKS

S. FITZGERALD, M. FRIEDMAN, J. GOTDANK, B. THOMPSON, Department of Physics and Astronomy, Oberlin College, Oberlin, OH 44074; J. ROWSELL, Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH 44074.

There is presently much interest in studying hydrogen storage materials for fuel cell applications. A promising class of physisorbents for this purpose is metal-organic frameworks, which consist of metal ions bridged by rigid organic molecules that assemble as highly porous molecular "scaffolds". We will report on a novel application of diffuse reflectance IR spectroscopy to probe the ro-vibrational modes of molecular hydrogen adsorbed within these materials. Experiments with H$_2$, HD, and D$_2$ illustrate the importance of quantum mechanical considerations and the necessity for rotational translational coupling models. Data reveal the propensity of exposed metals sites to produce some of the largest recorded interaction energies with adsorbed hydrogen. This leads to large frequency redshifts in the H$_2$ vibrational mode (65 - 130 cm$^{-1}$) along with a dramatic increase in the overtone intensity. The magnitude of the effect is shown to follow the Irving-Williams sequence in which the frequency shift for H$_2$ bound to Ni$^{2+}$ > Co$^{2+}$ > Zn$^{2+}$.

STRUCTURE OF COLD, MIXED PARAHYDROGEN-DEUTERIUM CLUSTERS

RUSSELL SLITER and ANDREY F. VILESOV, Department of Chemistry, University of Southern California, Los Angeles, CA 90089.

Vibrational spectra of para-H$_2$ molecules in clusters consisting of para-H$_2$ or para-H$_2$/D$_2$ seeded in He have been obtained using coherent anti-Stokes Raman spectroscopy. The Q$_1$(0) line of para-H$_2$, obtained upon expansion of neat para-H$_2$/D$_2$, exhibits a high frequency vibrational shift of about 2.6 cm$^{-1}$ with change of D$_2$ concentration from 0 to 98%. This shift is assigned to a decrease of the para-H$_2$ vibron band width in mixed clusters, similar to that previously observed in bulk H$_2$/D$_2$ solid. 1% para-H$_2$/D$_2$ clusters in He are liquid and show a much smaller shift of about 0.5 cm$^{-1}$ and indicate phase separation into a predominantly D$_2$ core and H$_2$ shell. The onset of phase separation in para-H$_2$/D$_2$ mixtures is predicted at approximately 3 K providing further evidence of super-cooled liquid hydrogen clusters previously studied.
The in situ photochemistry of dopant molecules isolated in solid parahydrogen (pH$_2$) typically differs from analogous studies in rare gas crystals for two main reasons: (1) solid pH$_2$ has a negligible cage effect so that photodissociation of a precursor molecule can lead efficiently to well-separated fragments, and (2) radical fragments can potentially react with the pH$_2$ matrix. Our group is currently studying the 193 nm photochemistry of a number of precursor molecules isolated in solid pH$_2$ via high-resolution FTIR spectroscopy in hopes of identifying trapped atomic species. Currently we are revisiting the photochemistry of NO in solid pH$_2$ that has previously been investigated by Momose and co-workers. The 193 nm photodynamics of NO in rare gas matrices has also been extensively studied. The studies by Momose showed that NO is photolabile at 193 nm and that the product N and O atoms react to form NH$_3$ and H$_2$O, respectively. Preliminary experiments in this laboratory show evidence for the production of the imidogen (NH) radical as well, and the most recent results and analysis will be presented.

---

Earlier studies have shown that pure quantum mechanical effects of the “light” methyl radical at low temperature minimize the anisotropy of CW EPR spectra to a high resolution character while new experiments under different conditions display greater EPR anisotropy. In this work the effects of the solid H$_2$ quantum matrix and three other typical inert-gas solid matrices on the $hf_i$ (hyperfine interaction) constant of trapped methyl radicals, usually called matrix shifts, are studied in some detail. Experimental EPR data at liquid-He temperatures were used to explore the dependence of the broadening and the spectral anisotropy of the hosted methyl radicals. An attempt was made to correlate the experimental spectral anisotropy data to matrix-radical interaction. Models relating the anisotropy and the matrix shift of the hyperfine ($hf$) coupling constant to the van der-Waals ($vdW$) attraction and / or to the Pauli repulsion between the host-matrix molecules and the methyl radical showed that both must be involved to explain the matrix shift while the Pauli repulsion is the major source for the extra anisotropy. The present work defines a quantitative measure of the methyl spectrum anisotropy and assigns a significantly greater value to the Ne matrix than to the quantum p-H$_2$ matrix due to the enhanced motional freedom in the latter. On the contrary, depending on the closer radical-matrix approach the magnitude of the hf interaction of the methyl radical in the Ne matrix was greater compared to that of p-H$_2$. Here, we also report new experimental results for EPR of CH$_3$ radicals in Ne, Ar and Kr matrices at temperatures above 4.2 K. Higher sample temperatures make possible EPR observation of higher CH$_3$ rotational states. Based on the experimental results, the hindrance of the radical rotation in $J = 1$ state is discussed.

---

*Support by Russian Foundation for Basic Research under grant 08-02-90409-Ukr a is gratefully acknowledged*
FB05

HIGH RESOLUTION STUDIES OF THE $\nu_3$ BAND OF METHYL FLUORIDE IN SOLID PARAHYDROGEN USING A QUANTUM CASCADE LASER

A.R.W. MCKELLAR, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, ON K1A 0R6, Canada; ASAO MIZOGUCHI and HIDETO KANAMORI, Department of Physics, Tokyo Institute of Technology, Ohokayama 2-12-1, Meguro-ku, Tokyo, 152-8551 Japan.

The $\nu_3$ band of CH$_3$F isolated in solid para-H$_2$ exhibits a clearly resolved series of lines due to clusters of CH$_3$F with residual ortho-H$_2$ molecules, CH$_3$F-(ortho-H$_2$)$_N$, with $N = 0 \sim 12$. We have examined this spectrum in detail using a quantum cascade laser source. Solid hydrogen crystals were formed by direct vapor phase deposition on a BaF$_2$ window at 2 K followed by annealing (4.6 K for 10 minutes) or “super-annealing” (7 K for 10 seconds). The cw laser (Hamamatsu Corp.) was a room temperature DFB device with output powers up to 30 mW and a tuning range of about 1042 - 1036 cm$^{-1}$ for device temperatures of 0 - 37$^\circ$ C. This power level was easily strong enough to modify the sample by means of spectral hole-burning effects. It was therefore necessary to strongly attenuate the laser in order to record normal “static” spectra. But we also took advantage of the power to make interesting “dynamic” measurements in which a transition could be bleached away and forced to reappear in a new position. Line widths as narrow as 0.0065 cm$^{-1}$ were observed and line profiles were Lorentzian. The $N = 0$ line at 1040.19 cm$^{-1}$ was resolved into two closely-spaced ($\sim$0.008 cm$^{-1}$) components which we believe correspond to the $K = 0$ (A) and 1 (E) levels of CH$_3$F, arising from partially free a-axis rotation in the crystal. Numerous extra satellite lines were observed around each main feature ($N = 0, 1, 2, 3, 4$) as well as some weak but sharp transitions almost mid-way between $N = 0$ and 1.


FB06

ALKALI-METAL ATOMS AS SPIN LABELS ON HELIUM NANODROPLETS

MARKUS KOCH, MARTIN RATSCHEK, CARLO CALLEGARI$^a$, and WOLFGANG E. ERNST, Institute of Experimental Physics, TU Graz, Petersgasse 16, 8010 Graz, Austria.

We have recently achieved electron spin resonance (ESR) of single alkali-metal atoms isolated on helium (He) nanodroplets$^{abc}$. A two-laser pump/probe setup for optically detected magnetic resonance is applied, which is based on magnetic circular dichroism to selectively address spin states. The influence of the helium droplet on the alkali-metal valence-electron wave function is directly noticeable as a shift of the ESR transitions with respect to that of free atoms. This perturbation depends on the size of the droplets and can be modeled with an increase of the hyperfine constant, that is an increase of the Fermi contact interaction.

After careful characterization of the Rb–He-droplet system the method is being developed into a more universal diagnostic tool to study spin dynamics. ESR silent species located inside the droplet can be investigated by utilizing the surface Rb atom as spin label, and the droplet size is a convenient handle to control the distance between the two. In case of species with a nuclear spin (e.g., $^{129}$Xe) spin exchange between the optically pumped Rb atom and the nuclear spin can be studied. We are also extending our method to study magnetically active materials of technological importance, such as Cr, Cu, and small clusters thereof, and we strive to present the first results at the meeting.

$^a$present address: Sincrotrone Trieste, Strada Statale 14 - km 163.5, 34149 Basovizza, Trieste, Italy

Intermission
Infrared spectra in the 2800-3150 cm$^{-1}$ region are presented for CH$_3$F embedded in helium nanodroplets. We observe both the $\nu_1({a_1})$ symmetric C-H stretch and the $\nu_4(e)$ asymmetric C-H stretch. Transitions from $K=0(A)$ and $K=1(E)$ are observed due to nuclear spin statistics. The symmetric stretch is split due to a Fermi resonance between $\nu_1$ and $2\nu_5$ (overtone of the asymmetric bend). The ($\nu_4,2\nu_5$) Fermi resonance is an $A_1-A_1$ type parallel band and $\nu_4$ is an $E-A_1$ type perpendicular transition. The upper diad of the ($\nu_1,2\nu_5$) Fermi resonance, found around 2960 cm$^{-1}$ is homogeneously broadened due to efficient vibrational relaxation to the lower diad. Furthermore, the $J=2, K=2 \leftarrow J=1, K=1$ transition ($^1R_1(1)$) is significantly broadened due to rotational resonances with the phonon and roton modes of the helium droplet. Further attempts to observe broadening effects are studied by measuring the Stark Spectra of all three bands at many electric field strengths.

Small hydrogen chloride-water clusters are of great theoretical and experimental interest, with much recent attention focusing on HCl charge dissociation in small water clusters. We have employed Helium Nanodroplet Isolation techniques to definitively assign bands in the 2570-2900 cm$^{-1}$ range to specific (HCl)$_m$(H$_2$O)$_n$ clusters. Vibrational Transition Moment Angle (VTMA) analysis, dipole moment measurements, optically selected mass spectrometry (OSMS), pick up cell pressure dependence studies and ab initio calculations are all used together to arrive at the assignments. We will discuss these new assignments in the context of the vibrational dynamics of the H$_3$O$^+$(H$_2$O)$_n>^3$Cl$^-$ charge separated species.

Infrared laser spectroscopy has been used to characterize the solvation of HCl with small number of water molecules in helium nanodroplets. Complexes of (HCl)$_m$(H$_2$O)$_n$ with $m = 1 – 3$ and $n = 1 – 3$ have been identified, and the assignment was confirmed via measurement of the pickup pressure dependence of the bands intensity. Bands of larger complexes have not been identified, indicating they contribute to a broad unresolved band in the range of 2500–2800 cm$^{-1}$. Structure of the (HCl)$_m$(H$_2$O)$_n$ complexes is discussed.
FOURIER TRANSFORM INFRARED SPECTRAL INVESTIGATION OF THE $\nu_6$ BAND OF CYCLIC-C$_3$H$_2$

PRADEEP RISIKRISHNA VARADWAJ, RYUJI FUJIMORI, KENTAROU KAWAGUCHI, Department of Chemistry, Faculty of Science, Okayama University, 3-1-1, Tsushima-Naka, Okayama 700-8530, JAPAN.

The gas phase absorption spectrum of the $\nu_6$ band (out of plane in phase CH bend) of cyclopropenylidene (c-C$_3$H$_2$) has been observed using a high-resolution Fourier transform infrared spectrometer for the first time. The molecule was produced by microwave discharge through a flow of allene (25 mTorr) and Ar (30 mTorr) mixture inside a glass cell. The observed spectrum shows c-type ro-vibrational transitions in which the Q-branch lines (J values up to 34 and K$_a$ values up to 8) are strongly and distinctly stand out in the spectrum. A least squares fitting of a total of 357 transitions (332 ro-vibrational transitions from this work and 25 transitions from the millimeter-wave spectrum with $10^6$ times larger statistical weight) results in the determination of the rotational and centrifugal distortion constants in the upper state. The rotational constants agree with those determined by millimeter-wave spectrum$^a$ and thereby confirming the $\nu_6$ band ($\nu_0 = 776.11729(17)$ cm$^{-1}$) of c-C$_3$H$_2$.


MICROWAVE SPECTRA OF FLUOROFORMYLOXYL AND FLUOROSULFATE RADICALS

ˇS. URBAN, J. VARGA, L. KOLESNIKOVÁ, Z. MELTZEROVÁ, T. UHLÍKOVÁ, J. KOUCKÝ, P. KANIA, Department of Analytical Chemistry, Institute of Chemical Technology, 16628 Prague 6, Czech Republic; H. BECKERS, H. WILLNER, Bergische Universität Wuppertal, FB 9, Anorganische Chemie, Gaußstr. 20, 42097 Wuppertal, Germany.

Rotational spectra of fluoroformyloxyl (FCO$_2$) and fluorosulfate radicals (FSO$_3$) were studied in their ground states. The spectra measured involve fine structures due to a unpaired electron as well as hyperfine interaction features due to $^{19}$F nucleus that can give rise to an additional hyperfine doubling of levels. These radicals are of the atmospheric interest, for example the FCO$_2$ radical may be produced by stratospheric degradations of HCFCs and HFCs. Their atmospheric presence can be now supported by Eyjafjallajokull volcano massive eruptions of gasses and dust particles containing Fluor and Sulfur. Both the radicals were prepared by a pyrolysis of a suitable precursor$^a$ directly in a sample cell. Besides the radical spectra, the majority of spectral lines in observed spectra belongs to other molecular species. Therefore the identification of the radical lines was simplified by using an external magnetic field affecting only the radical species by the molecular Zeeman effect.

The radicals FCO$_2$ and FSO$_3$ were measured in the frequency regions 125 - 242 GHz and 93 - 430 GHz, respectively. From obtained transition frequencies the set of rotational, centrifugal distortion, fine and hyperfine constants were calculated. The study of the fluorosulfate radical was performed in the Prague laboratory for the first time.


Dimethyl ether (DME) is highly abundant in hot cores and numerous transitions within the vibrational ground state have been detected in various interstellar line surveys of sources such as Orion KL\textsuperscript{a,b}. As a nearly prolate asymmetric top with two internal rotors, it shows a complex spectrum with low lying torsional modes. The energy levels of the two lowest torsional states ($v_{11}$, and $v_{15}$) lie only 200 and 240 cm$^{-1}$ above the ground state (barrier height $\approx 915$ cm$^{-1}$), and are thus sufficiently populated in these interstellar sources to exhibit transitions in line surveys due to high excitation temperatures in hot cores. So far, the lack of sufficiently accurate predictions for the two lowest excited torsional states prevented their identification in astronomical spectra. Therefore, we analyzed spectra, which have been recorded within the context of the investigations of the ground state\textsuperscript{c,d}. In total, more than 9500 transitions have been assigned covering the frequency range from 38 up to 1670 GHz. The enlarged splitting of each rotational level into four substates ($AA$, $EE$, $AE$, $EA$) compared to its size in the ground state and a large number of perturbed transitions hampered not only the line assignment but also the astrophysical modelling. However, the inclusion of interaction terms between both excited states in the model of an effective Hamiltonian for a symmetric two-top rotor, allowed us to model both excited states within a global fit, and also to accurately determine the energy difference between both states. Frequency predictions have been calculated based on this analysis and have been used to unambiguously assign numerous rotational transitions within these excited states in the astronomical line survey of the hot core region G327.3-0.6.

\textsuperscript{d}C.P. Endres, B.J. Drouin \textit{et al.}, \textit{Astronom.Astrophys.}, \textbf{504}, (2009) 635–640
The rotational spectrum of singly and doubly $^{13}$C-substituted dimethylether

Monika Koerber, Christian P. Endres, Frank Lewen, Thomas F. Giesen, Stephan Schlemmer, I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany; Roland Pohl, Axel Klein, Institut für Anorganische Chemie, Universität zu Köln, 50939 Köln, Germany.

Dimethylether (DME) is a nearly prolate asymmetric top with two internal rotors (methyl groups) which undergo periodic large amplitude motions and show a complicated torsional splitting of each rotational energy level. Due to its complex spectrum and its high abundance in hot cores such as Orion KL or Sagittarius B2 at temperatures exceeding 100 K, DME is very prominent in astronomical line surveys and contributes to spectral line confusion of such sources. The interpretation of astronomical observations therefore depends on the knowledge of accurate rest frequencies and reliable intensities. Precise predictions for the ground state of DME’s main isotopologue are now available up to 2.1 THz. In contrast, very little is known about $^{13}$C-substituted DME. Only a few data are available on singly $^{13}$C-substituted DME, $^{12}$CH$_3$O$^{13}$CH$_3$. However, no data are available on doubly $^{13}$C-substituted DME, ($^{13}$CH$_3$)$_2$O, yet. While in ($^{13}$CH$_3$)$_2$O the two internal rotating methyl groups are equivalent and the splitting of rotational energy levels into four substates is comparable to the main isotopologue, singly $^{13}$C-substituted DME has two non-equivalent internal rotors resulting in torsional splitting of rotational energy levels into five substates. The purpose of our new laboratory measurements is to extend the knowledge on the astrophysically relevant species $^{12}$CH$_3$O$^{13}$CH$_3$. To analyze the complicated spectrum resulting from a $^{13}$C-enriched sample of DME, containing all different $^{13}$C-substituted species as well as the main isotopologue, also precise data on doubly $^{13}$C-substituted DME are inevitable. We performed measurements in the frequency region 35-120 GHz using an all solid state spectrometer. Rotational as well as torsional parameters have been obtained for ($^{13}$CH$_3$)$_2$O as well as $^{12}$CH$_3$O$^{13}$CH$_3$ by fitting the assigned transitions to an effective rotational Hamiltonian introduced by Peter Groner.

---

$^{b}$C. P. Endres et al., Astronomy & Astrophysics 504, 635-640 (2009)
ACETYLENE $^{12}$C$_2$H$_2$ LABORATORY MEASUREMENTS FOR ASTROPHYSICAL APPLICATIONS

D. JACQUEMART, L. GOMEZ, N. LACOME, Université Pierre et Marie Curie-Paris 6; CNRS; Laboratoire de Dynamique, Interactions et Réactivité (LADIR), UMR 7075, Case Courrier 49, 4 Place Jussieu, 75252 Paris Cedex 05, France; J.-Y. MANDIN, Université Pierre et Marie Curie-Paris 6; CNRS; Laboratoire de Physique Moléculaire pour l’atmosphère et l’astrophysique (LPMAA), UMR 7092, Case courrier 76, 75252 Paris Cedex 05, France; O. PIRALI, and P. ROY, Synchrotron SOLEIL, L Orme des Merisiers Saint-Aubin, 91192 Gif-sur-Yvette cedex, France.

The acetylene molecule is important for atmospheric, planetary, and astrophysical applications. This organic molecule, known as a precursor of amino acids, shows numerous vibration-rotation bands in the IR. Two recent works on line intensities measurements will be presented.

A study around 7.7 $\mu$m was motivated by SPITZER observations of C$_2$H$_2$ in this spectral region that cannot be modeled using the current line list of HITRAN/GEISA due to the lack of data. High resolution spectra have been recorded with the Bruker HR IFS 120 of the LADIR and analyzed to deduce absolute line intensities of several bands included the one present in HITRAN, the $(\nu_4+\nu_5)^0_+$ strong band. On the whole, line intensities of 2 cold bands and 15 hot bands have been studied, and a complete line list has been generated.

Another study using SOLEIL synchrotron will be presented in the spectral region around 100 cm$^{-1}$ of interest for astrophysical applications (SPITZER, ALMA, HERSCHEL,...). High resolution spectra have been recorded with the Bruker HR IFS 125 of SOLEIL. For accurate line intensities measurement based on the FIR beam of the synchrotron, the strong wavenumber dependence of the beam radius had to be modeled in the apparatus function calculation. Absolute line intensities of the intense $\nu_5-\nu_4$ band have been measured, and those of the 4 weaker hot bands are in progress.

---

FC04 15 min 9:16

TERAHERTZ AND FAR-INFRARED SPECTROSCOPY OF HIGH-J TRANSITIONS OF THE GROUND AND $v_2 = 1$ STATES OF NH$_3$

O. PIRALI, M.-A. MARTIN, M. VERVLOET and D. BALCON, Ligne AILES–Synchrotron SOLEIL, L’Orme des Merisiers Saint-Aubin, 91192 Gif-sur-Yvette, France; S. YU, J. PEARSON and B. DROUIN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109, USA; C. P. ENDRES, I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany; T. SHIRAISHI, K. KOBAYASHI, and F. MATSUSHIMA, Department of Physics, University of Toyama, Gofuku, Toyama 930-8555, Japan.

Since its first detection in 1968, ammonia was discovered as a major constituent of several planetary atmospheres. More recently, ammonia has been suggested in the atmosphere of cool brown dwarf$^a$ and is expected to be present in quantity in the atmospheres of many newly discovered exoplanets and brown dwarf stars where temperatures are in the order of 1000 K$^b$. For such temperatures, spectroscopic knowledge of ammonia’s IR spectrum needs to be improved both in term of line positions and intensities. Even for the two lowest vibrational levels (ground state and $v_2 = 1$) its large amplitude inversion motion complicates the spectral modelling and the experimental dataset have been (up to now) limited to low quantum numbers (J of about 20). We associated experimental results obtained from far infrared techniques$^cd$ and terahertz spectroscopy$^e$ to obtain accurate energies for highly excited J levels (as high as J=35) in the ground state and $v_2 = 1$. This work significantly increases the experimental dataset available to support astronomical observations; we will present the techniques developed in this work as well as the spectral analysis and fit of the new dataset.

---


FC05 15 min 9:33
ISOMER-SPECIFIC SPECTROSCOPY OF GAS-PHASE $\alpha$-HYDRONAPHTHYL, $\beta$-HYDRONAPHTHYL, AND 1,2,3-TRIHYDRONAPHTHYL RADICALS

JOSHUA A. SEBREE, TIMOTHY S. ZWIER. Department of Chemistry, Purdue University, West Lafayette, IN 47907; VADIM V. KISLOV, ALEXANDER M. MEBEL, Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199.

The jet-cooled two-color, resonant two-photon ionization (2C-R2PI) spectra for $\alpha$-hydrionaphthyl, $\beta$-hydrionaphthyl, and 1,2,3-trihydronaphthyl radicals have been collected in the region from 18900-23400 cm$^{-1}$. Radicals were produced with an electric discharge of a select precursor in argon prior to supersonic expansion. 1,4-dihydronaphthalene and tetralin (1,2,3,4-tetrahydronaphthalene) were used to obtain spectra of the $\alpha$-hydrionaphthyl and 1,2,3-trihydronaphthyl radicals respectively. Discharge of 1,2-dihydronaphthalene yielded the $\alpha$-hydrionaphthyl radical spectrum with additional peaks that were tentatively assigned to the $\beta$-hydrionaphthyl radical. Visible-visible holeburning was used to confirm this assignment. The $S_0$-$S_n$ origins of the $\alpha$-hydrionaphthyl (18949 cm$^{-1}$), $\beta$-hydrionaphthyl (19363 cm$^{-1}$), and 1,2,3-trihydronaphthyl radicals (21372 cm$^{-1}$) are in the visible region of the spectrum. Two-color photoionization efficiency scans were used to measure the adiabatic ionization potentials for the three free radicals to high accuracy. All three radicals have low ionization energies ($<6.65$ eV) compared to that of their precursors ($>8$ eV). A thermochemical cycle using these ionization potentials produces the C-H bond dissociation energy for the three free radicals, with values of 121.2, 103.6, and 168 kJ/mol for $\alpha$-hydrionaphthyl, $\beta$-hydrionaphthyl, and 1,2,3-trihydronaphthyl radical respectively. It is proposed that these resonantly stabilized radicals may play an important role in photochemical processes in Titans atmosphere and the interstellar medium because of the extra stability gained from delocalizing the radical across the neighboring conjugated $\pi$ system.

FC06 15 min 9:50
SYNCHROTRON-BASED HIGHEST RESOLUTION FOURIER TRANSFORM INFRARED SPECTROSCOPY OF NAPHTHALENE (C$_{10}$H$_8$): ROVIBRATIONAL ANALYSIS OF THE $\nu_{46}$ BAND

S. ALBERT, K.K. ALBERT, M. QUACK, PHYSICAL CHEMISTRY, ETH ZÜRICH, CH-8093 ZÜRICH, SWITZERLAND; PH. LERCH, SWISS LIGHT SOURCE, PAUL-SCHERRER-INSTITUTE, CH-5232 VILL-GEN, SWITZERLAND.

One of the great challenges of astronomical infrared spectroscopy is the identification of the Unidentified Infrared Bands (UIBs) found in several interstellar objects. Polycyclic Aromatic Hydrocarbons (PAHs) have been proposed to be the carrier of the UIBs$^a$. For that reason we have started to investigate the rotationally resolved FTIR spectrum of the bicyclic naphthalene$^b$ as a simple prototypical spectrum for a PAH infrared spectrum. These investigations at very high resolution, $\Delta \nu < 0.0008$ cm$^{-1}$, are only possible thanks to a new FTIR setup. We have interfaced an eleven chamber interferometer, the ETH-SLS Bruker prototype 2009, to the infrared port available at the Swiss synchrotron, the Swiss Light Source (SLS), located at the Paul-Scherrer-Institute. Due to the high brightness of the synchrotron radiation, which is effectively 5 to 10 times brighter than conventional thermal sources in the spectral region between 500 and 900 cm$^{-1}$ (17-30 THz), and the high resolution of the new interferometer (unapodized resolution of 0.00053 cm$^{-1}$, 18 MHz), it was possible to analyze the newly rotationally resolved infrared spectrum of naphthalene (C$_{10}$H$_8$) previously recorded only at modest resolution in the IR$^c$ and at high resolution in the UV$^d$. Here, we present a rovibrational analysis of the strongest band, consisting of $c$-type transitions of naphthalene in this region, the out-of-plane mode $\nu_{46}$. We can simulate this band at different resolutions based on our analysis. Due to the unique band shape of a $c$-type band we propose a simple check for the UIBs to determine whether planar PAHs can be the carriers of these bands.

Recently, we recorded the THz centrifugal distortion-induced spectrum of methane using synchrotron radiation at the SOLEIL facility. Intensities of pure rotation lines of \( \text{CH}_4 \) were precisely measured, from which the induced dipole moment of this weak spectrum, of great interest for planetology, was accurately inferred.\(^a\) This study should in particular help to measure methane concentrations in Titan’s atmosphere.\(^b\)

Here, we continue the work by presenting spectra of \( \text{CH}_4/\text{N}_2 \) mixtures, again recorded with a 150 m optical path in a White cell and a Bruker IFS 125 HR FTIR spectrometer at the AILES beamline of SOLEIL. More precisely, the spectra were recorded with 5 % of \( \text{CH}_4 \) in \( \text{N}_2 \) at various total pressures (ca. 100, 200, 400, 600 and 800 mbar). These spectra will allow to measure collisional broadening and shift coefficients, as well as line-mixing parameters, with \( \text{N}_2 \) as a perturber (like in Titan’s atmosphere).


Titan has an extremely thick atmosphere dominated by nitrogen, but includes a range of trace species such as hydrocarbons and nitriles. One such hydrocarbon is propane (\( \text{C}_3\text{H}_8 \)). Propane has 21 active IR bands covering broad regions of the mid-infrared. Therefore, its ubiquitous signature may potentially mask weaker signatures of other undetected species with important roles in Titan’s chemistry. Cassini’s Composite Infrared Spectrometer (CIRS) observations of Titan’s atmosphere hint at the presence of such molecules. Unfortunately, \( \text{C}_3\text{H}_8 \) line atlases for the vibration bands \( \nu_8, \nu_{21}, \nu_{20}, \) and \( \nu_7 \) (869, 922, 1054, and 1157 cm\(^{-1}\), respectively) are not currently available for subtracting the \( \text{C}_3\text{H}_8 \) signal to reveal, or constrain, the signature of underlying chemical species. Using spectra previously obtained by Jennings et al.\(^a\) at the McMath-Pierce FTIR at Kitt Peak, AZ, as the source and automated analysis utilities developed for this application, we are compiling an atlas of spectroscopic parameters for propane that characterize the ro-vibrational transitions in the above bands. In this paper, we will discuss our efforts for the spectral region near the \( \nu_{21} \) band, present initial results for spectroscopic parameters including absolute line intensities and transition frequencies, and show how these optical constants will be used in searching for other trace chemical species in Titan’s atmosphere.

\(^a\)This work was supported by the NASA Cassini Data Analysis Program, grant number NNX09AK55G.

\(^b\)Nadler and Jennings, 1989, JQSRT, 42, 399.
OBSERVING A COLUMN-DEPENDENT $\zeta$ IN THE HORSEHEAD PDR

**P.B. Rimmer**, Department of Physics, Ohio State University, Columbus, OH 43210; **O. Moreta**, Institute of Astronomy and Astrophysics, Academia Sinica, Taipei 11677, Taiwan; **E. Roueff**, Observatoire de Paris, LUTH and Université Denis Diderot, Place J. Janssen 92190 Meudon, France; **E. Herbst**, Departments of Astronomy, Physics, and Chemistry, Ohio State University, Columbus, OH 43210.

The molecules CCH, C$_4$H, HCO$_+^+$, and HC$_3$N have been observed at the edge of the Horsehead Nebula in abundances far higher than those predicted by Photodissociation Region (PDR) models$^a$. Using a column-dependent cosmic ray ionization rate ($\zeta$)$^b$, we model the edge of the Horsehead Nebula as a one-dimensional nearly-"edge-on" heterogeneous PDR with temperature ranging from 15-250 K, number density from $10^3 - 5 \times 10^5$ cm$^{-3}$, and $\zeta = 10^{-16} - 10^{-14}$ s$^{-1}$. The resulting abundances for the molecules listed above are much closer to the observed abundances. In this talk, we will discuss this method, its results, and the usefulness of incorporating a column-dependent $\zeta$ in astrochemical PDR models, especially in the advent of ALMA.

---


CONSTRAINING THE FLUX OF LOW-ENERGY COSMIC RAYS ACCELERATED BY THE SUPERNOVA REMNANT IC 443

**Nick Indriolo**, Department of Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801; **Geoffrey A. Blake**, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125; **Miwa Goto**, Max Planck Institute for Astronomy, Königstuhl 17, Heidelberg D-69117, Germany; **Tomonori Usuda**, Subaru Telescope, Hilo, HI 96720; **Thomas R. Geballe**, Gemini Observatory, Hilo, HI 96720; **Takeshi Oka**, Department of Astronomy & Astrophysics and Department of Chemistry, University of Chicago, Chicago, IL 60637; **Benjamin J. McCall**, Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

It has long been theorized that supernova remnants (SNR) accelerate the majority of Galactic cosmic rays. Observations in the $\gamma$-ray, X-ray, and radio regimes support this theory, at least for cosmic rays with energies above a few GeV. However, there is no direct evidence that SNRs accelerate cosmic rays in the MeV–GeV range. These low-energy cosmic rays are of great importance, as they are the primary means by which H$_2$ is ionized in the interstellar medium. Collisions between H$_2^+$ and H$_2$ will rapidly form H$_3^+$, a molecule which can then be observed to infer the ionization rate of H$_2$. Using the Subaru and Keck telescopes, we have searched for H$_3^+$ absorption in sight lines which probe molecular material known to be interacting with the SNR IC 443. By computing the ionization rate of H$_2$ in these sight lines, we constrain the flux of low-energy cosmic rays generated by this particular supernova remnant.

DARK WATER - IMPLICATIONS OF RECENT COLLISIONAL COOLING MEASUREMENTS

**Brian J. Drovin**, Michael J. Dick, John C. Pearson, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099; **Edwin Bergin**, Department of Astronomy, University of Michigan, Ann Arbor, MI 48109-1090.

We have continued efforts to elucidate the water-hydrogen collisional pair under interstellar conditions. The classical pressure-broadening picture, wherein the broadening parameter increases exponentially with decreasing temperature, fails for all measured transitions below approximately 80 K. Instead, dramatic decreases in the pressure broadening are observed. This situation is at odds with calculated collisional cross-sections, which indicate a strong collisional interaction at these temperatures. We will discuss the implications of these measurements in the interstellar environment in relation to SWAS, Odin and Herschel HIFI data, including its effects on the radiative rate of water, the cooling capacity of water in collapsing clouds and the effect on the elemental oxygen abundance.
PROGRESS IN COMPUTING ACCURATE INFRARED LINELISTS FOR CO$_2$

XINCHUAN HUANG, SETI Institute, 515 N. Whisman Road, Mountain View, CA, 94043; DAVID W. SCHWENKE, MS T27B-1, NASA Ames Research Center, Moffett Field, CA, 94035; and TIMOTHY J. LEE, MS 245-1, NASA Ames Research Center, Moffett Field, CA, 94035.

Following the "Best Theory + High-resolution Experimental Data" strategy, we have made progress on computing a reliable CO$_2$ infrared (IR) line list. A procedure that is similar to the one used for ammonia is adopted to generate a global potential energy surface (PES), including various small corrections such as relativistic correction, basis-set extrapolation and a higher-order correlation correction, which will be followed by refinements using accurate high-resolution laboratory data. The purely ab initio PES includes a long-range Morse-potential part and a short-range local interaction part. Finite-Field approximations were adopted in dipole moment calculations using the CCSD(T)/aug-cc-pVQZ level of theory. Quadruple-moment terms were computed and included. Exact variational rovibrational calculations on the purely ab initio PES and dipole surface have led to our first set of an IR line list. A comparison with HITRAN data will be discussed.

A GAS GRAIN MODEL OF INTERSTELLAR CLOUD CORES WITH MOMENT EQUATIONS TO TREAT SURFACE CHEMISTRY

YEZHE PEI, Department of Physics, The Ohio State University, Columbus, OH 43210; ERIC HERBST, Department of Physics, Astronomy and Chemistry, The Ohio State University, Columbus, OH 43210.

We have built a gas-grain model of homogeneous cold cloud cores with time-independent physical conditions. In this model, we use the full OSU gas phase network, which involves 458 gas phase species and more than 4000 reactions, and treat it by rate equations which is totally deterministic. A small surface reaction network accounts for the productions of stable molecules such as H$_2$O, CO, CO$_2$, H$_2$CO, CH$_3$OH, NH$_3$ and CH$_4$. The surface reactions are treated by a hybrid method of moment equations (Barzel & Biham 2007) and rate equations: when the abundance of a surface species is lower than a specific threshold, say one per grain, we use the stochastic moment equations to simulate the evolution; when its abundance goes above this threshold, we use the rate equations. A continuity technique is utilized to secure a smooth transition between these two methods.

We have run chemical simulations for a time up to $10^8$ yr at three temperatures: 10 K, 15 K, and 20 K. The results will be compared with those generated from (1) a completely deterministic model that uses rate equations for both gas phase and grain surface chemistry, and (2) modified rate equations (Garrod 2008) that partially take into account the stochastic effect for surface reactions. At 10 K, our model results agree with the above two methods, while discrepancies appear at higher temperatures and smaller grain sizes.

STRUCTURE OF THE LARGE MOLECULE DISTRIBUTION IN THE TAUROS MOLECULAR CLOUD

GLEN R. LANGSTON and KYLE WOOLARD, National Radio Astronomy Observatory, Green Bank, WV 24915.

We present observations of the distribution of long carbon chain molecules in TMC-1. The molecular line intensities for three cyanopolyne molecules HCC$_5$N, HCC$_7$N and HCC$_9$N were observed in a 25’ diameter region. The four molecular line transitions were observed towards TMC-1 using the Robert C. Byrd Green Bank Telescope (GBT). These observations were made simultaneously in the frequency range 12780 to 13540 MHz. The images show the emission is primarily along a narrow ridge. We present images of the molecular line intensity as a function of position, and compare the locations of peak molecular emission. Near the location of peak line intensity, the emission is well fit by a Gaussian profile. We present the ratio of molecular line intensities for the three species. The angular distribution of the molecules is very similar. We interpret the similarity of structure in terms of the chemical age of regions of the cloud.

In addition, if all goes well, we will also present first results form the GBT 18 to 26 GHz Focal Plane Array receiver.
ROTATIONAL SPECTRA OF THE MOLECULAR IONS H$_2$NCO$^+$ AND NCO$^-$

**VALERIO LATTANZI, CARL A. GOTTLIEB, PATRICK THADDEUS, and MICHAEL C. McCARTHY,**

*Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, and School of Engineering and Applied Science, Harvard University, Cambridge, MA 02138; and SVEN THORWIRTH, Max-Planck-Institut für Radioastronomie, Bonn, Germany, and I. Physikalisches Institut, Universität zu Köln, Germany.*

We report the first high resolution spectroscopic detection of H$_2$NCO$^+$, the protonated cation of isocyanic acid, in a discharge through HNCO heavily diluted in hydrogen in the throat of a supersonic nozzle. Spectroscopic constants derived from the two lowest rotational transitions agree very well with theoretical structure calculations of the ground state isomer, in which protonation occurs at the nitrogen atom, yielding an isomer of C$_2$v symmetry\(^a\). In the same molecular beam, the fundamental rotational transition of NCO$^-$ was observed with well-resolved nitrogen quadrupole hyperfine structure. Detection of NCO$^-$ in our beam was subsequently confirmed by observation of several millimeter-wave transitions in a low pressure discharge through cyanogen and water. The spectroscopic constants of NCO$^-$ obtained earlier by infrared laser spectroscopy\(^b\) are in good agreement with the highly accurate constants derived here. Owing to the high abundance of HNCO in many galactic molecular sources, both ions are excellent candidates for astronomical detection in the radio band.

\(^{a}\)Structure calculated at the CCSD(T)/cc-pCV5Z level of theory and zero-point vibrational effects at CCSD(T)/cc-pVQZ.


CHEMICAL CHARACTERIZATION OF THE FIRST STAGES OF PROTOPLANETARY DISK FORMATION

**U. HINCELIN, V. WAKELAM, S. GUILLOTEAU and F. HERSANT,**

*Université de Bordeaux, Observatoire Aquitain des Sciences de l’Univers, 2 rue de l’Observatoire, BP 89, F-33271 Floirac Cedex, France, and, CNRS, UMR 5804, Laboratoire d’Astrophysique de Bordeaux, 2 rue de l’Observatoire, BP 89, F-33271 Floirac Cedex, France.*

Low mass stars, like our Sun, are born from the collapse of a molecular cloud, which is composed of interstellar matter. This matter (gas and grain) falls in the center of the cloud, creating a protostar and a protoplanetary disk. Planets and other solar system bodies will be formed in the disk, so the chemical composition of the interstellar matter and its evolution during the formation of the disk are important to better understand the formation process of these objects.

We study the disk chemistry using the gas-grain code Nautilus (Hersant et al. 2009) developed at the Laboratoire d’Astrophysique de Bordeaux, based on the models from the Ohio State University (Eric Herbst’s team). The change in physical conditions during the formation of disk is not well constrained (by observations or theory) up to now. We thus assume several scenarios for the possible thermal and density history of the gas and dust during the formation of the disk, partly based on Visser et al. (2009). One goal is to understand the importance of initial conditions for disk chemistry and to quantify the fraction of the parent cloud material that survives the disk formation.

Our first results show that the disk chemical evolution will depend on the initial conditions (parent cloud composition). Changing for instance the age (10$^4$ to 10$^9$ yr) of the initial molecular cloud can modify by several orders of magnitude the chemical composition of ice mantles (CH$_3$OH, CH$_3$OCH$_3$, H$_2$CO, H$_2$O$_2$, H$_2$S...) in a 10$^5$ yr old protoplanetary disk.
FD01  
INVITED TALK  
LASER FREQUENCY COMBS FOR PRECISION RADIAL VELOCITY MEASUREMENTS IN ASTROPHYSICS

RONALD WALSWORTH, Harvard-Smithsonian, Cambridge, MA.

Laser frequency combs adapted to serve as wavelength calibrators for astrophysical spectrographs (astro-combs) may greatly advance precision astrophysical spectroscopy, and thus provide a crucial tool for cosmology and the search for Earth-like exoplanets. I will discuss recent progress in developing astro-comb calibrators and bringing them into practice at observatories, with an emphasis on their utility for improving radial velocity precision in exoplanet studies.

FD02  
15 min 9:05

PRECISION CAVITY ENHANCED VELOCITY MODULATION SPECTROSCOPY

ANDREW MILLS, BRIAN SILLER, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801; BENJAMIN J. McCALL, Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

The study of gas phase ions has been recognized as an important field for many applications in combustion and physical chemistry, as well as astrochemistry. There are several challenges to overcome to study such molecular ions with high resolution spectroscopy, including ion/neutral discrimination, a dilute analyte, and Doppler line broadening. Recently our group has demonstrated the coupling of cavity enhanced absorption spectroscopy with velocity modulation (CEVMS) to help overcome these challenges. Cavity enhanced absorption spectroscopy can be more sensitive than non-cavity enhanced techniques, making it easier to study dilute analytes. Velocity modulation is used to distinguish between ions and neutrals.

The final challenge arises as the line frequency accuracy is often limited by the Doppler broadening of molecules due to the ensemble average of many molecules with different velocities. In CEVMS, because an optical cavity is used, the electric field intensity increases such that a Lamb dip is observed. Owing to the co-linear back-reflection, only molecules with zero velocity along the axis of laser propagation contribute to the Lamb dip. Thus, spectroscopy which records the transition frequencies of the Lamb dip have an inherently higher precision to the measurement. However, traditional wavemeters usually have accuracy specifications on the order of hundreds of MHz. Therefore, by using an optical frequency comb to measure the transition frequencies of the sub-Doppler Lamb dip, we can increase the accuracy and precision of infrared transitions that have (or have not yet) been measured.

In addition to demonstrating the use of Precision Cavity Enhanced Velocity Modulation Spectroscopy (P-CEVMS), we will discuss the power and pressure broadening of the Lamb dip. By studying the power dependence of the Lamb dip in N$_2^+$, we hope to be able to obtain a measure of the transition strength for a single ro-vibrational line.
CAVITY-ENHANCED DIRECT FREQUENCY COMB VELOCITY MODULATIONS SPECTROSCOPY

LAURA SINCLAIR, KEVIN COSSEL, WILLIAM AMES, JUN YE AND ERIC CORNELL, JILA, University of Colorado Boulder, and the National Institute for Standards and Technology, Boulder, Colorado 80309.

We have developed a novel technique for broad bandwidth and high resolution survey spectroscopy of molecular ions. Cavity-enhanced direct frequency comb spectroscopy (CE-DFCS) provides broad bandwidth and high resolution by using individual comb lines as parallel detection channels. Here we combine CE-DFCS with velocity modulation spectroscopy to provide ion-specific detection with further enhanced sensitivity. The first application of this technique will map the electronic states of Hf$^+$ and Th$^+$, which are integral to the JILA electron electric dipole moment experiment.

APPLICATIONS OF CAVITY-ENHANCED DIRECT FREQUENCY COMB SPECTROSCOPY

KEVIN C. COSSEL, FLORIAN ADLER, JILA, National Institute of Standards and Technology and University of Colorado Department of Physics, University of Colorado, Boulder, Colorado 80309-0440, USA; PIOTR MASLOWSKI, JILA, National Institute of Standards and Technology and University of Colorado Department of Physics, University of Colorado, Boulder, Colorado 80309-0440, USA and Instytut Fizyki, Uniwersytet Mikolaja Kopernika, ul. Grudziadzka 5/7, 87-100 Toruń, Poland; and JUN YE, JILA, National Institute of Standards and Technology and University of Colorado Department of Physics, University of Colorado, Boulder, Colorado 80309-0440, USA.

Cavity-enhanced direct frequency comb spectroscopy (CE-DFCS) is a unique technique that provides broad bandwidth, high resolution, and ultra-high detection sensitivities. This is accomplished by combining a femtosecond laser based optical frequency comb with an enhancement cavity and a broadband, multichannel imaging system. These systems are capable of simultaneously recording many terahertz of spectral bandwidth with sub-gigahertz resolution and absorption sensitivities of $1 \times 10^{-7}$ cm$^{-1}$ Hz$^{-1/2}$. In addition, the ultrashort pulses enable efficient nonlinear processes, which makes it possible to reach spectral regions that are difficult to access with conventional laser sources. We will present an application of CE-DFCS for trace impurity detection in the semiconductor processing gas arsine near 1.8 $\mu$m and the development of a high-power, mid-infrared frequency comb for breath analysis in the 2.8-4.8 $\mu$m region.

FREQUENCY STABILIZATION OF HIGH-POWER 3.3 $\mu$m CW LASER WITH A FREQUENCY COMB SYSTEM

SUSUMU KUMA and TAKAMASA MOMOSE, Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, British Columbia V6T1Z1, Canada.

The development of optical frequency combs has enabled a broad range of lasers to be stabilized. In this study, we have developed a system to stabilize high-power CW mid-infrared (MIR) radiation at 3.3 $\mu$m using a NIR-VIS frequency comb. The mid-infrared radiation at 3.3 $\mu$m were generated as an idler of a CW OPO laser pumped by a 1.064 $\mu$m fibre laser. To stabilize the MIR radiation with a frequency comb system in 450 nm to 1.25 $\mu$m range, the pump frequency at 1.064 $\mu$m and the sum frequency of the MIR radiation and the pump radiation were locked simultaneously to the comb laser. The sum frequency of the MIR and pump radiations was generated in a PPLN crystal. With this technique, we have successfully obtained a width of better than 50 kHz at 3.3 $\mu$m with a power of more than 1 W. The stability is currently limited by the response of the PZT in an OPO cavity. Further improvement is underway. The stabilized MIR radiation at 3.3 $\mu$m can be used as a source for ultra-high-resolution spectroscopy of vibration-rotation transitions of molecules. Especially, it may be used to decrease the frequency uncertainty of the $\nu_3 F_2^{(2)}$ component of the P(7) transition of CH$_4$, which is one of the optical frequency standards recommended by CIPM. Another application of frequency stabilized MIR radiation is to build-up MIR radiation in a cavity for optical manipulation and trapping of cold molecules we have proposed in New. J. Phys. 11, 055023 (2009).
Intermission

FD06 15 min 10:30
TWO-PHOTON TRANSITIONS VIA OPTICAL FREQUENCY COMB TO FORM ULTRACOLD MOLECULES

SVETLANA MALINOVSKAIA, WUFU SHI, Department of Physics and Engineering Physics, Stevens Institute of Technology, Hoboken, NJ 07030.

We show that a single femtosecond optical frequency comb may be used to induce two-photon transitions between molecular vibrational levels to form ultracold molecules, e.g., KRb. The phase across an individual pulse in the pulse train is sinusoidally modulated with a carefully chosen amplitude and modulation frequency. Piecewise adiabatic population transfer is fulfilled to the final state by each pulse in the applied pulse train providing a controlled population accumulation in the final state. Similar results are obtained using a standard optical frequency comb with zero carrier-envelop-offset frequency.

FD07 15 min 10:47
PROGRESS REPORT ON A PORTABLE Ti:SAPPHIRE COMB LASER WITH FREQUENCIES REFERRING TO CESIUM ATOM TWO-PHOTON TRANSITIONS

WANG-YAU CHENG, CHIEN-MING WU, TZ-WEI LIU, YO-HUAN CHEN, IAMS, Academia Sinica, No. 1, Roosevelt Rd., Sec. 4, Taipei, Taiwan.

A portable Ti:sapphire comb laser would contribute significantly to generalize comb-laser applications, such as the astrocomb missions or other interdisciplinary collaborations. To develop a portable comb laser, three barriers lie ahead: one is to miniaturize and robotize the frequency reference system of the comb laser; the second is to ensure the long-term frequency accuracy without satellite connection, and the third is to miniaturize the pumping laser system. We developed two hand-size cesium-stabilized diode lasers at 822 nm and 884 nm to serve as frequency references for a comb laser and we carried out a comb-laser-based CPT experiment with one single cesium cell that might offer a locking procedure for long-term comb laser accuracy. We will also report our plans and progress on a fiber laser pumped Ti:sapphire comb laser.
The mid-infrared part of the electromagnetic spectrum is the so-called molecular fingerprint region because gases have tell-tale absorption features associated with molecular rovibrations. It also contains windows (in particular 2.0-2.4 µm, 3-5 µm and 8-13 µm) where the atmosphere is relatively transparent. These regions can be for instance exploited to detect small traces of environmental and toxic vapours down to sensitivities of parts-per-billion in atmospheric and industrial applications. Novel Fourier transform spectroscopy without moving parts, based on time-domain interferences between two comb sources, can in particular benefit optical diagnostics and precision spectroscopy. To date, high-resolution and -sensitivity proof-of-principle experiments have only been reported in the near-infrared region where frequency comb oscillators are conveniently available. However, as most of molecular transitions in this region are due to weak overtone bands, such techniques can hardly be harnessed for sensitive trace gas detection. Developing mid-infrared dual comb Fourier transform spectroscopy is therefore a demanding but highly desirable task.

Here we present a proof-of-principle experiment of frequency comb Fourier transform spectroscopy with two Cr²⁺:ZnSe femtosecond oscillators directly emitting in the 2.4 µm mid-infrared region. Spectra of acetylene in the region of the ν₁ + ν₁₅ band extend from 3970 cm⁻¹ to 4200 cm⁻¹. With 0.4 cm⁻¹ resolution, the acquisition time of the corresponding interferograms is 10 µs, without averaging. This demonstrates the feasibility of our approach.
FD10 15 min 11:38
HIGH PRECISION MID-IR SPECTROSCOPY OF $^{12}$C$^{16}$O$_2$ NEAR 2.7 $\mu$m

WEI-JO TING, JOW-TSONG SHY, Department of Physics, National Tsing Hua University, Hsinchuo, Taiwan 30013, R.O.C.

We have observed the sub-Doppler saturation spectrum of the $^{12}$C$^{16}$O$_2$ [10$^{01}$, 02$^{01}1$]$_t$ $\rightarrow$ 00$^{00}$0 band transitions near 2.7 $\mu$m using a mW-level DFG (Difference Frequency Generation) source. The DFG radiation is generated by a Ti:sapphire laser and a Nd:YAG laser amplified by a 10-W fiber amplifier in a 44-mm long PPLN (Periodically-Poled Lithium Niobate) crystal. We are able to generate 5 mW DFG power at 2.7 $\mu$m. The saturation spectrum is observed by monitoring the saturated 4.3 $\mu$m fluorescence using a conventional saturation spectroscopy arrangement. To increase the signal a 20-cm longitudinal cell having gold coating inside is used to collect the 4.3 $\mu$m fluorescence. This method provides zero background and better signal-to-noise ratio. It also eliminates the interference fringes completely. To measure the center frequency of a 2.7 $\mu$m transition, the Nd:YAG laser is frequency-doubled and frequency stabilized on one $^{127}$I$_2$ hyperfine transition. The Ti:sapphire laser is locked onto the center of the spectrum of the transition and its frequency is measured by an OFC (Optical Frequency Comb). In this talk, we will report our new measurements about this band and also the molecular constants obtained.

FD11 10 min 11:55
Post-deadline Abstract
SPECTROSCOPY WITH COMB-REFERENCED DIODE LASERS

MATTHEW CICH, GARY V. LOPEZ, PHILIP M. JOHNSON AND TREVOR J. SEARS, Department of Chemistry, Stony Brook University, Stony Brook, New York 11794; CHRISTOPHER P. MCRAVEN, Homer L. Dodge Department of Physics and Astronomy, The University of Oklahoma, Norman, OK 72019-2061.

Extended cavity diode lasers have been stabilized by locking to components of an erbium-doped fiber laser-based frequency comb with a 250 MHz comb spacing centered at 1.5$\mu$m. We find the Allan variance of the diode laser frequency relative to the single comb component to which it is locked is of the order of a few Hz. For the system as a whole, the absolute frequency accuracy is approximately 1.5 parts in 10$^{12}$. In order to characterize the system more completely, we have recorded saturation dip absorption spectra of several transitions in the $\nu_1 + \nu_3$ combination band of acetylene near 6530 cm$^{-1}$. We find good agreement with published absolute frequency measurements for these transitions, which have been used as secondary frequency standards in the past. Aside from extremely precise saturation dip measurements such as these, comb-stabilized lasers should permit excellent measurements of Doppler-broadened lineshapes, both to compare with theory and for analytical applications. Progress along these lines will be reported at the meeting.

Acknowledgments: T. J. Sears gratefully acknowledges support from a Brookhaven National Laboratory program development grant that enabled this work and also support for research at Brookhaven National Laboratory which was carried out under Contract No. DE-AC02-98CH10886 with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences.
To date the principal application for photomixing sources has been for high resolution spectroscopy of gases due to the large tuning range and spectral purity. New Developments of the Opto-Electronic THz Spectrometer have been performed in order to obtain a powerful tool for High-Resolution Spectroscopy. The combination of two extended cavity laser diodes and fast charge carrier lifetime semiconductor materials has allowed a continuous-wave THz spectrometer to be constructed based on optical heterodyning. Unlike many THz sources, this instrument gives access to all frequencies in the range 0.3 to 3.5 THz with a resolution of 1 MHz. The main spectroscopic applications of this spectrometer were dedicated to line profile analysis of rotational transitions referenced in the spectroscopic databases.\textsuperscript{a,b} One limitation of the THz spectrometer was accuracy with which the generated frequency is known. Recently, this obstacle has been circled with the construction of a photomixing spectrometer where the two pump lasers are phase locked to two modes of a repetition rate stabilized frequency doubled fiber laser frequency comb.\textsuperscript{c} In order to achieve a tuning range in excess to 100 MHz a third cw laser was required in the new configuration of the THz spectrometer. To assess the performances of this instrument, the frequencies of the pure rotational transitions of OCS molecules have been measured between 0.8 to 1.2 THz. A rms inferior to 100 kHz, deduced from the frequencies measured, demonstrates that the THz photomixing synthesizer is now able to be competitive with microwave and submillimeter techniques.


FE01 15 min 8:30
PHOTOCHEMISTRY OF MONOCHLORO COMPLEX OF COPPER (II) IN SOLUTION BY MEANS OF TRANSIENT ABSORPTION TIME-RESOLVED ULTRAFAST SPECTROSCOPY

A. S. MERESHCHENKO, P. EL-KHOURY, S. PAL, A. N. TARNOVSKY, Bowling Green University, Department of Chemistry and Center for Photochemical Sciences, Bowling Green, Ohio 43403.

The photodissociation mechanism of copper (II) chloro complexes in methanol is studied by means of ultrafast broadband time-resolved deep-UV/UV/vis spectroscopy using $[Cu^{II}(MeOH)_5Cl]^+$ as a model molecule. Upon 255 nm excitation, the majority of $[Cu^{II}(MeOH)_5Cl]^+$ dissociate to form chlorine atoms $Cl^-$ and pentacoordinate copper(I) solvated complexes $[Cu^I(MeOH)_5]^+$, which is followed by recombination back to the parent molecules. A three body-dissociaiton in which the nascent $[Cu^I(MeOH)_5]^+$ fragment undergoes a methanol-ligand loss is observed to be of minor importance. The solvent influence on the photoreaction will be discussed.

FE02 10 min 8:47
ULTRAFAST EXCITED-STATE DYNAMICS IN MODEL HEXABROMOPLATINATE (IV) AND HEXABROMOOSMiate (IV) DIANIONS IN THE CONDENSED PHASE

I. L. ZHELDAKOV, A. S. MERESHCHENKO, A. N. TARNOVSKY, Bowling Green University, Department of Chemistry of Photochemical Sciences, Bowling Green, Ohio 43403.

Photoexcitation of hexabromoplatinate and hexabromoosmate dianions in CT and ligand field states results in remarkably fast formation (sub 100 fs) of coherently excited photoproducts assigned to $^3PtBr_5^-$ and $^3OsBr_5^-$. This is explained by the fact that one of the lowest triplet excited states in both $PtBr_6^{2-}$ and $OsBr_6^{2-}$ is repulsive. Surprisingly, the damping time and amplitude of the observed coherent oscillations in the pentabromoosmate (209 cm$^{-1}$) and pentabromoplatinate (112 cm$^{-1}$) species is quite different. The shorter damping time (0.4 ps) of $^3PtBr_5^-$ in comparison with the damping time (1 ps) of $^3OsBr_5^-$ in aqueous solution is related to faster dephasing in $^3PtBr_5^-$. The large-amplitude bending oscillations in pentabromoplatinate are tentatively assigned to the passage of the wavepacket through the Jahn-Teller conical intersection(s), whereas in pentabromoosmate, the umbrella type of oscillations appears to be due to the coupling to the Os-Br symmetric stretching mode in the parent dianion. The coherent oscillations in both photoproducts show no dependence on solvent. The results are supported by DFT, TD-DFT and CASSCF/CASPT2 calculations of electronic structures, vertical electronic transitions and harmonic frequencies of initial dianions and photoproducts.
DYNAMICS AND MECHANISM OF (6-4) PHOTOPRODUCT REPAIR IN DAMAGED DNA BY PHOTOLYASE

J. LI, Z. LIU, C. TAN, X. GUO, L. WANG and D. ZHONG, Departments of Physics, Chemistry, and Biochemistry, Programs of Biophysics, Chemical Physics, and Biochemistry, 191 West Woodruff Avenue, The Ohio State University, Columbus, Ohio 43210; A. SANCAR, Department of Biochemistry and Biophysics, University of North Carolina School of Medicine, Chapel Hill, North Carolina 27599.

(6-4) photoproduct, the second major DNA lesion induced by UV irradiation, is repaired by (6-4) photolyase using light energy. The molecular mechanism of enzymatic repair is poorly understood. Here we report the direct observation of catalytic processes by synchronizing the enzymatic dynamics with the repair function through femtosecond spectroscopy. We observed forward electron transfer from the excited flavin cofactor to damaged DNA at 225 ps, backward electron transfer from unrepaired DNA to flavin at 50 ps, and electron returns from repaired DNA to flavin at tens of nanoseconds. Strikingly, a 425-ps electron-induced proton transfer was observed for the first time, which is crucial for repair efficiency by competing with the non-repair backward electron transfer channel.

MAPPING THYMINE DIMER SPLITTING IN DAMAGED DNA BY PHOTOLYASE

ZHEYUN LIU, CHUANG TAN, JIANG LI, XUNMIN GUO, LIJUAN WANG, and DONGPING ZHONG, Department of Physics, Chemistry, and Biochemistry, The Ohio State University, Columbus, OH 43210.

Photolyases uses light energy to convert UV-damaged cyclobutane pyrimidine dimer (CPD) to normal bases. We observed the formation and decay of semiquinone flavin and CPD anion intermediate, the recovery of hydroquinone flavin in ground state, and the formation of normal thymine bases in real time with femtosecond time resolution. By monitoring the decay and formation of all reactants, intermediates and products, the functional dynamics of the elementary steps during CPD repair have been mapped out. All elementary reaction steps, namely forward electron transfer, back electron transfer, bond breakage and electron return occur in sub-nanosecond scale. These dynamics are synergistically correlated for maximum of repair efficiency through a redox photocycle with no net change of electrons.

2D IR LINE SHAPES FOR DETERMINING THE STRUCTURE OF A PEPTIDE IN A BILAYER

ANN MARIE WOYS, Y. S. LIN, J. S. SKINNER, M. T. ZANNI, Department of Chemistry, University of Wisconsin, Madison, WI 53706; A. S. REDDY, J. J. DE PABLO, Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706.

Structure of the antimicrobial peptide, ovispirin, on a lipid bilayer was determined using 2D IR spectroscopy and spectra calculated from molecular dynamics simulations. Ovispirin is an 18 residue amphipathic peptide that binds parallel to the membrane in a mostly alpha helical conformation. 15 of the 18 residues were $^{13}C^{18}O$ isotopically labeled on the backbone to isolate the amide I vibration at each position. 2D IR spectra were collected for each labeled peptide in 3:1 POPC/POPG vesicles, and peak width along the diagonal was measured. The diagonal line width is sensitive to the vibrators electrostatic environment, which varies through the bilayer. We observe an oscillatory line width spanning 10 to 24 cm$^{-1}$ and with a period of nearly 3.6 residues. To further investigate the position of ovispirin in a bilayer, molecular dynamics simulations determined the peptide depth to be just below the lipid headgroups. The trajectory of ovispirin at this depth was used to calculate 2D IR spectra, from which the diagonal line width is measured. Both experimental and simulated line widths are similar in periodicity and suggest a kink in the peptide backbone and the tilt in the bilayer.

Aluminum nanoparticles are widely considered attractive as fuels due to the high heat of reaction associated with their oxidation, and the potential for fast reaction due to their small size. However, the reaction dynamics can also be strongly influenced by the passivation layer that coats the reactive metal surface. Typically, this takes the form of a naturally-occurring oxide shell on the nanoparticle, but other passivation schemes are now available. We have recently developed a sonochemical synthesis procedure to produce aluminum nanoparticles capped with oleic acid. These nanoparticles have an aluminum metal core, some organic-provided oxide, and an organic shell. To investigate the effect of the passivation method on the chemical dynamics in energetic materials, we have studied samples consisting of a mixture of a metal nanoparticle fuel and an ammonium nitrate or ammonium perchlorate oxidizer. The metal fuel is either commercially available oxide-coated aluminum nanoparticles, or the oleic acid-capped nanoparticles. The energetic samples are ignited with an IR laser pulse. Following ignition, the chemical dynamics are studied using visible emission spectroscopy and mass spectrometry. Preliminary results suggest that our Al-oleic acid nanoparticles are able to react more rapidly than those that are conventionally passivated with a naturally-occurring oxide shell.

---

In this work, we investigate the time-resolved photoelectron spectra of IBr\(^-\)(CO\(_2\)).\(^a\) In the photodetachment studies performed by Lineberger and co-workers,\(^b\) IBr\(^-\)(CO\(_2\)) is prepared in its electronic ground state (2\(\Sigma^-\)) which upon it is excited to its \(\tilde{A}'\) (2\(\Pi_{3/2}\)) excited state, before electron photodetachment/photoionization and dissociation on the \(\tilde{C} (1\Pi_1)\) excited state of IBr. Previous experimental work showed that dissociation of bare IBr\(^-\) yields only I\(^-\) + Br products.\(^b\) However in IBr\(^-\)(CO\(_2\)), a small fraction (\(\sim 3\%\)) of the dissociating molecules undergo an electron transfer from I to Br at 350 fs after the initial excitation. Thus a single solvent molecule can initiate a non-adiabatic transition from the \(\tilde{A}'\) state to either the lower \(\tilde{A}\) or \(\tilde{X}\) state, thereby producing I + Br\(^-\) (+ CO\(_2\)) prior to photoionization. To study the dynamics, we perform high level \textit{ab initio} calculations (MR-SO-CISD/\textit{aug}-cc-pVTZ(-PP)) as well as classical molecular dynamics (MD) simulations. The MD simulations capture much of the dynamics of the photodissociation but underestimate the charge-transfer channel. Results of the \textit{ab initio} calculations show how CO\(_2\) bend vibrational excitation could increase the percentage of non-adiabatic transitions and how the CO\(_2\) modifies the charge distribution of IBr\(^-\) to make the charge transfer accessible. The proposed mechanism and timescales are consistent with the observed Br\(^-\) products.

---


---


Recent advances in the study of open-shell systems have generated significant interest in both experimental and theoretical research. What is particularly intriguing about these systems is the presence of van der Waals wells in the potential energy surfaces, which allow for the exploration of pre-reactive species. In this study, we focus on the asymmetric hydrogen-transfer reaction of F(2P) + HCl. The reaction is initiated by vibrationally exciting the HCl stretching motion of the pre-reactive F···HCl complex in the van der Waals well. The wave packet is propagated on a three-dimensional, fully coupled potential energy surface constructed based on electronic energies calculated at the multi-reference configuration interaction+Davidson correction (MRCI+Q) level of theory with an aug-cc-pVnZ (n=2,3,4) basis. Product state distributions were calculated for reactions initiated in the first three vibrationally excited states of HCl, v=1, 2, and 3. Specifically, we analyzed the final electronic, vibrational, and rotational distributions.

Previous studies on the hydrogen-transfer reaction of the Cl(2P) + HCl system focused on whether vibrational excitation of the HCl stretch would promote the reaction and, if so, how the reaction dynamics reflect the coupling among the diabatic potential surfaces that describe this system. We also compare our F(2P) + HCl results to those of a related system.

---

**FE09**

ULTRAFAST SOLVATION DYNAMICS OF FLAVODOXIN IN THREE OXIDATION STATES

TING-FANG HE, CHIH-WEI CHANG, and DONGPING ZHONG, Programs of Ohio State Biochemistry, Biophysics, and Chemical Physics, and Departments of Physics, Chemistry, and Biochemistry, The Ohio State University, Columbus, OH 43210.

We report here the complete characterization of the dynamic solvation processes at the FMN binding site of flavodoxin in three oxidation states. The local solvation dynamics of flavodoxin are investigated by examining the fluorescence transients and time-resolved emission spectra of the prosthetic FMN chromophore. Our results show a great difference between these three oxidation states. In oxidized state, the solvation processes are featured by a multi-exponential decay in 1 ps, 28 ps, and 670 ps. The solvation rate significantly slows down in semiquinone state due to the presence of the hydrogen bond between the N(5)H of FMN and the backbone carbonyl oxygen of G61. In hydroquinone state, the solvation rate is similar to that in the oxidized state, but with much larger stabilization energy. This result was supported by our MD simulations in which we observed more polar environment of FMN binding site in hydroquinone state due to the more water entry into the pocket through the repulsion between the negative charged flavin cofactor and nearby residues.
FE10 15 min 11:18

DYNAMICS AND MECHANISM OF EFFICIENT DNA REPAIR REVIEWED BY ACTIVE-SITE MUTANTS

CHUANG TAN, ZHEYUN LIU, JIANG LI, XUNMIN GUO, LIJUAN WANG and DONGPING ZHONG,
Departments of Physics, Chemistry, and Biochemistry, Programs of Biophysics, Chemical Physics, and Bio-
chemistry, The Ohio State University, Columbus, Ohio, 43210.

Photolases repair the UV-induced pyrimidine dimers in damage DNA via a photoreaction which includes a series of light-driven electron transfers between the two-electron-reduced flavin cofactor FADH$^-$ and the dimer. We report here our systematic studies of the repair dynamics in E.coli photolyase with mutation of several active-site residues. With femtosecond resolution, we observed the significant change in the forward electron transfer from the excited FADH$^-$ to the dimer and the back electron transfer from the repaired thymines by mutation of E274A, R226A, R342A, N378S and N378C. We also found that the mutation of E274A accelerates the bond-breaking of the thymine dimer. The dynamics changes are consistent with the quantum yield study of these mutants. These results suggest that the active-site residues play a significant role, structurally and chemically, in the DNA repair photocycle.

FE11 15 min 11:35

REACTION DYNAMICS OF THE BROMINE-BROMOFORM COMPLEX IN SOLUTION

THOMAS J. PRESTON, MAITREYA DUTTA and F. FLEMING CRIM, The University of Wisconsin-
Madison, Department of Chemistry, 1101 University Avenue, Madison, WI 53706.

We have followed the evolution of the bromine species that arise from the photolysis of bromoform in the condensed phase. Solvent caging promotes the formation of iso-bromoform (CHBr$_2$-Br), which can then release a Br atom by breaking the newly formed Br-Br bond. This ejected Br can form a van der Waals complex (Br-CHBr$_3$) with a nearby un-photolyzed bromoform molecule, which is stable during our 1 ns time-window. Using the van der Waals complex as a reservoir for Br atoms, we now proceed to drive hydrogen abstraction from CHBr$_3$ by Br. Estimates indicate that the barrier to this reaction is a few thousand wavenumbers. Our goal is to introduce excitation into the C-H stretching motion of a nearby solvent CHBr$_3$ to access the activated complex region of the bimolecular potential energy surface.

FE12 15 min 11:52

VIBRATIONAL SPECTROSCOPY AND DYNAMICS OF THE HYDRAZOIC AND ISOTHIOCYANIC ACIDS IN PROTIC AND APROTIC SOLVENTS

C. HOUCHINS, D. WEIDINGER*, Code 6111, U.S. Naval Research Laboratory, Washington, DC 20375-
5342; D. BROWN, U.S. Naval Academy, Chemistry Department, Annapolis, MD 21402; J. OWRUTSKY,
Code 6111, U.S. Naval Research Laboratory, Washington, DC 20375-5342.

In order to investigate the effects of solute charge as well as solvent-isotope effects on solute vibrational spectra and dynamics, infrared pump-probe studies have been carried out to determine vibrational energy relaxation (VER) times for the CN and antisymmetric NNN stretching bands for the pseudohalide acids, XNCS and XN$_3$ (X=H, D), in protic and aprotic solvents to compare with the well studied azide and thiocyanate anions. The studies indicate that the deuterium effects on the frequency shifts for HN$_3$ and relaxation times for both HNCS and HN$_3$ resemble the solvent isotope effects for azide and thiocyanate in water. While it is expected that VER times will be shorter for charged than neutral solutes, this is not observed in all cases.

*CH and DW acknowledge the Naval Research Laboratory - National Research Council Research Associateship.
## AUTHOR INDEX

<table>
<thead>
<tr>
<th>Author</th>
<th>Indexes</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADAM, A. G.</td>
<td>MH08</td>
</tr>
<tr>
<td>ADAMOVICH, I. V.</td>
<td>TG16, FA08</td>
</tr>
<tr>
<td>ADAMS, C. L.</td>
<td>RB07, RE12</td>
</tr>
<tr>
<td>ADANDE, G.</td>
<td>RF02, RF15</td>
</tr>
<tr>
<td>ADLER, F.</td>
<td>MA01, FD04</td>
</tr>
<tr>
<td>AFSHARI, M.</td>
<td>RI05, RI09, RI11</td>
</tr>
<tr>
<td>AGNEW, A.</td>
<td>MJ12</td>
</tr>
<tr>
<td>AL-SAMRA, E. H.</td>
<td>TG13</td>
</tr>
<tr>
<td>ALBERDING, B. G.</td>
<td>MH13</td>
</tr>
<tr>
<td>ALBERT, K. K.</td>
<td>FA01, FC06</td>
</tr>
<tr>
<td>ALBERT, S.</td>
<td>MF04, FA01, FC06</td>
</tr>
<tr>
<td>ALEKSEEV, E. A.</td>
<td>WH08</td>
</tr>
<tr>
<td>ALONSO, J. L.</td>
<td>TH10, WH06</td>
</tr>
<tr>
<td>ALSTADT, V. J.</td>
<td>RH05</td>
</tr>
<tr>
<td>ALTUNATA, S. N.</td>
<td>TG06</td>
</tr>
<tr>
<td>AMANO, T.</td>
<td>TJ07, TJ08</td>
</tr>
<tr>
<td>AMES, W.</td>
<td>FD03</td>
</tr>
<tr>
<td>AMYAY, B.</td>
<td>MF07, RA10</td>
</tr>
<tr>
<td>ANCILOTTO, F.</td>
<td>TG03</td>
</tr>
<tr>
<td>ANDERSON, D. T.</td>
<td>FB03</td>
</tr>
<tr>
<td>ANDREWS, D.</td>
<td>RA07</td>
</tr>
<tr>
<td>ANNESLEY, C. J.</td>
<td>RA04</td>
</tr>
<tr>
<td>ANTONOV, I. O.</td>
<td>WI03</td>
</tr>
<tr>
<td>ARUNAN, E.</td>
<td>TF06, WI01, WI02</td>
</tr>
<tr>
<td>ASAMI, H.</td>
<td>TB05</td>
</tr>
<tr>
<td>ASHIZAWA, N.</td>
<td>MG05, MG06</td>
</tr>
<tr>
<td>ASHWORTH, S. H.</td>
<td>RG10</td>
</tr>
<tr>
<td>ASMIS, K. R.</td>
<td>WI03</td>
</tr>
<tr>
<td>AUBÖCK, G.</td>
<td>WI05</td>
</tr>
<tr>
<td>AUSTEN-MILLER, G.</td>
<td>TF13</td>
</tr>
<tr>
<td>AUWEREA, J. V.</td>
<td>MJ03, FC07</td>
</tr>
<tr>
<td>AVOIRD, A. V. D.</td>
<td>RA04</td>
</tr>
<tr>
<td>BABA, M.</td>
<td>MG01, MG05, MG06, WI05</td>
</tr>
<tr>
<td>BACH, A.</td>
<td>MI05</td>
</tr>
<tr>
<td>BAHOU, M.</td>
<td>TD09</td>
</tr>
<tr>
<td>BALABIN, R. M.</td>
<td>MF13, MF14</td>
</tr>
<tr>
<td>BALCON, D.</td>
<td>MF11, TE04, RC02, FC04</td>
</tr>
<tr>
<td>BALL, C. D.</td>
<td>TE11</td>
</tr>
<tr>
<td>BALLANDRAS, A.</td>
<td>MF10</td>
</tr>
<tr>
<td>BANDYOPADHYAY, B.</td>
<td>TB04, TF03, WI10, RI17</td>
</tr>
<tr>
<td>BAQUERO, E. E.</td>
<td>TB08</td>
</tr>
<tr>
<td>BARBE, A.</td>
<td>MF05, MF06</td>
</tr>
<tr>
<td>BARKER, B. J.</td>
<td>WI01</td>
</tr>
<tr>
<td>BARTZ, J. A.</td>
<td>RA08, RA09, RG08</td>
</tr>
<tr>
<td>BASTIAAN, B. J.</td>
<td>WJ10</td>
</tr>
<tr>
<td>BATHEL, B.</td>
<td>FA14</td>
</tr>
<tr>
<td>BAUM, O.</td>
<td>TJ13</td>
</tr>
<tr>
<td>BAUMANN, C. A.</td>
<td>TD10</td>
</tr>
<tr>
<td>BAUMANN, E.</td>
<td>RD02</td>
</tr>
<tr>
<td>BECK, J. P.</td>
<td>RI13</td>
</tr>
<tr>
<td>BECKLIN, E. E.</td>
<td>RF09, RF10</td>
</tr>
<tr>
<td>BEJIANI, M.</td>
<td>TD07</td>
</tr>
<tr>
<td>BELLINCHI, A.</td>
<td>TJ12</td>
</tr>
<tr>
<td>BENETIS, N.</td>
<td>FB04</td>
</tr>
<tr>
<td>BENNER, D. C.</td>
<td>MJ01, MJ02, MJ04, MJ07</td>
</tr>
<tr>
<td>BERNATH, P. F.</td>
<td>WG08, WI09, RG11, RG12</td>
</tr>
<tr>
<td>BERNHARD, B.</td>
<td>RD04</td>
</tr>
<tr>
<td>BERNHARDT, B.</td>
<td>RD01</td>
</tr>
<tr>
<td>BHALLA, N.</td>
<td>TG08, WI04, RI04</td>
</tr>
<tr>
<td>BENSADON, N. S.</td>
<td>TA07</td>
</tr>
<tr>
<td>BHATTACHARYY, S.</td>
<td>WH03</td>
</tr>
<tr>
<td>BIRD, R. G.</td>
<td>RH04, RH05</td>
</tr>
<tr>
<td>BIRER, O.</td>
<td>TD12</td>
</tr>
<tr>
<td>BISHOF, M.</td>
<td>WG07</td>
</tr>
<tr>
<td>BISSCHOF, S.</td>
<td>FC01</td>
</tr>
<tr>
<td>BISWAL, H.</td>
<td>TB06</td>
</tr>
<tr>
<td>BITTINGER, K. L.</td>
<td>RA01</td>
</tr>
<tr>
<td>BLAKE, G. A.</td>
<td>WG05, FC10</td>
</tr>
<tr>
<td>BLAKE, T. A.</td>
<td>MF09, MF16, MJ04, RH12, FA04</td>
</tr>
<tr>
<td>BLANCO, S.</td>
<td>WH06</td>
</tr>
<tr>
<td>BOQUET, R.</td>
<td>FA15, FD12</td>
</tr>
<tr>
<td>BOHN, J. L.</td>
<td>MA01</td>
</tr>
<tr>
<td>BOHN, R. K.</td>
<td>RH10</td>
</tr>
<tr>
<td>BONDYBEY, V. E.</td>
<td>WI01</td>
</tr>
<tr>
<td>BORHO, N.</td>
<td>TH14</td>
</tr>
<tr>
<td>BORN, B.</td>
<td>TD12</td>
</tr>
<tr>
<td>BOUCHER, D. S.</td>
<td>TA06</td>
</tr>
<tr>
<td>BOUDON, V.</td>
<td>MF10, MF11, RJ13, FC07</td>
</tr>
<tr>
<td>BOWMAN, J. M.</td>
<td>WJ10, RJ09</td>
</tr>
<tr>
<td>BOWMAN, S.</td>
<td>FA08</td>
</tr>
<tr>
<td>BOYARKIN, O. V.</td>
<td>TB11, RB01</td>
</tr>
<tr>
<td>BOYLE, E.</td>
<td>MJ09</td>
</tr>
<tr>
<td>BOZZI, A. T.</td>
<td>TH11, TH13</td>
</tr>
<tr>
<td>BRAY, C.</td>
<td>MJ11</td>
</tr>
<tr>
<td>BREEN, K. J.</td>
<td>RB05</td>
</tr>
<tr>
<td>BRINEY, K. A.</td>
<td>TA05, TA06</td>
</tr>
<tr>
<td>BRITES, V.</td>
<td>TI02</td>
</tr>
<tr>
<td>BROWN, D.</td>
<td>FE12</td>
</tr>
<tr>
<td>BROWN, D. J.</td>
<td>MH15</td>
</tr>
<tr>
<td>BROWN, L. R.</td>
<td>MJ01, MJ02, MJ03, MJ04, TE07, RC12</td>
</tr>
<tr>
<td>BRUBACH, J. B.</td>
<td>FC07</td>
</tr>
<tr>
<td>BRUHNS, H.</td>
<td>WG10</td>
</tr>
<tr>
<td>BRUMFIELD, B. E.</td>
<td>FA02</td>
</tr>
<tr>
<td>BRUNSVOLD, A. L.</td>
<td>RA12</td>
</tr>
<tr>
<td>BRÜKEN, S.</td>
<td>TJ10</td>
</tr>
<tr>
<td>BUCCHINO, M. P.</td>
<td>MH02</td>
</tr>
<tr>
<td>BUCHANAN, E. G.</td>
<td>TB07, TB08, RB06, RB09, RB10</td>
</tr>
<tr>
<td>BUNKER, C. E.</td>
<td>FE06</td>
</tr>
<tr>
<td>BUNKER, P. R.</td>
<td>RJ12</td>
</tr>
<tr>
<td>BUNTING, P. C.</td>
<td>MH12, TF15</td>
</tr>
<tr>
<td>BURROWS, J. P.</td>
<td>TE03</td>
</tr>
<tr>
<td>BURSTEN, B. E.</td>
<td>TI10</td>
</tr>
<tr>
<td>CABELAS, C.</td>
<td>WH06</td>
</tr>
<tr>
<td>CALLEGLARI, C.</td>
<td>TG03, WI05, FB06</td>
</tr>
<tr>
<td>CAMINATI, W.</td>
<td>MG11, WH05, WH07, RH01</td>
</tr>
<tr>
<td>CAMPARQUE, A.</td>
<td>TE01, TE07, WF03</td>
</tr>
<tr>
<td>CAPASSO, F.</td>
<td>FA03</td>
</tr>
<tr>
<td>CARRAVETTA, V.</td>
<td>TD11</td>
</tr>
<tr>
<td>CARRINGTON JR., T.</td>
<td>RJ01</td>
</tr>
<tr>
<td>CARROLL, B.</td>
<td>TC11, TJ14</td>
</tr>
<tr>
<td>CARTER, S.</td>
<td>WI10</td>
</tr>
<tr>
<td>CARTER, S. C.</td>
<td>RJ09</td>
</tr>
<tr>
<td>CARVAJAL, M.</td>
<td>TJ11</td>
</tr>
<tr>
<td>CASE, A. S.</td>
<td>RA03</td>
</tr>
<tr>
<td>CASTANO, F.</td>
<td>TA09, TA10, TA11, WH04</td>
</tr>
<tr>
<td>CASTO, C.</td>
<td>TE02</td>
</tr>
<tr>
<td>CAUET, E.</td>
<td>RI03</td>
</tr>
<tr>
<td>CAVANAGH, S.</td>
<td>RE10</td>
</tr>
<tr>
<td>CEBRAN, A.</td>
<td>MG04</td>
</tr>
<tr>
<td>CHAB, V.</td>
<td>TD11</td>
</tr>
<tr>
<td>CHAKRABORTY, T.</td>
<td>MG17, RI17</td>
</tr>
<tr>
<td>CHALYAVI, N.</td>
<td>WG09</td>
</tr>
<tr>
<td>CHANG, B.</td>
<td>MI10, MI12</td>
</tr>
<tr>
<td>CHANG, C.</td>
<td>MG16, MI11, FE09</td>
</tr>
<tr>
<td>CHANG, J.</td>
<td>MG09</td>
</tr>
<tr>
<td>CHAO, J.</td>
<td>MI09</td>
</tr>
<tr>
<td>CHELIN, P.</td>
<td>MJ12, MJ15</td>
</tr>
<tr>
<td>CHENG, C.</td>
<td>MI09</td>
</tr>
</tbody>
</table>
CHEN, G. – WF02
CHEN, I. – TG02
CHEN, K. J. – TI01
CHEN, L. – RE09, RF16
CHEN, M. – MI08, WJ04
CHEN, Y. – FD07
CHENG, T. C. – TB04, WJ10, RG07
CHENG, W. – FD07
CHEUNG, A. S. – WF02
CHHANTY AL-PUN, R. – MI07
CHIOU, L. – MJ10
CHISHOLM, M. H. – TF14
CHISHOLM, M. H. – MH12, MH13, TF15
CHOI, I. – TG16, FA08
CHOI, M. Y. – MG09, FB09, FB10
CHOI, S. H. – TB08
CHOU, Y. – WH01
CHOWDHURY, E. – WF06
CHRISTEN, D. – RH13
CICH, M. – FD11
CINGOZ, A. – RD07
COAKLEY, J. A. – MJ07
COCINERO, E. J. – WH04, WH05
CODY, T. – MI08, WJ04
CODD, T. – MI08, WJ04
CODDINGTON, I. – RD02, FD09
COHEN, E. A. – TE10
COHEN, P. M. – TH11
COLIN, R. – WG08
COLONDO, A. P. – TG01
CONDE, A. P. – TA09, TA10, TA11
CONRAD, A. R. – WH02
CONTINENZI, R. E. – TA08
CQTERAS, E. S. – TH01
COOKE, S. – MI12
COOKE, S. A. – TC04, RC06, RC07, RH11
CORENO, M. – MG11
CORNELL, E. – FD03
CORNELL, E. A. – MA01
COSSEL, K. – FD03
COSSEL, K. C. – FD04
COSSELL, K. – MA01
COTO, P. B. – TA12
COUDE, L. H. – TE04, TJ04, TJ05, TJ06, TJ11
COY, L. S. – TG06
CRAIG, N. C. – TC05, RH12
CRAWFORD, T. J. – MJ01, MJ02
CRESPO-HERNÁNDEZ, C. E. – MG12, MG14
CRIM, F. F. – TA04, TA05, TA06, RA03, RA04, FE11
CROZET, P. – RG09, RG10
CUISSET, A. – FA15, FD12
CURL, R. – WK02
DAILY, J. W. – TD08
DALY, A. – WH03
DALY, A. M. – TH08, TH09
DANEY, P. – FA14
DAUMONT, L. – TE06
DE BACKER-BARILLY, M. R. – MF05, MF06
DE GHELLINCK, X. – RI01
DE LUCIA, F. C. – MF12, MJ13, MJ14, TE02, TE11, TJ02, TJ03, RC13
DE PABLO, J. J. – FE05
DEAN, J. C. – TB08
DECATOIRE, D. – TE06
DEGHANY, M. – RI05, RI06, RI08, RI09, RI11, FA11
DEMAISON, J. – RI03
DEMOULIN, P. – MJ10
DEVASHER, R. B. – FA09, FA10
DEVI, V. M. – MJ01, MJ02, MJ04, MJ07
DEWBERRY, C. T. – MJ12, TC04, RC07, RH11
DIAN, B. C. – TC08, TC09, TC12, RH15
DICK, M. J. – FC11
DIDDAMS, S. A. – RD03
DIDRICH, K. – RI01, RI02
DIEHL, Y. – FA03
DINGI, J. – MJ09
DMITRIEV, V. A. – FB04
DDO, D. – WG04
DOMENECH, J. L. – MF15
DON, F. – WA01
DOUBERLY, G. E. – MI06, FB07, FB08
DOUGLASS, K. O. – WH09
DRABBELS, M. – MG10
DROSBACK, M. M. – WG06
DROUN, B. – FC04
DROUN, B. J. – TC03, TE10, TJ10, TJ14, RC02, RC03, RC12, RF11, FC01, FC11

D

E

EASTERDAY, C. C. – RH12
EBATA, T. – TB09, RB08
ECIJA, P. – WH04
EDDINGSAAS, N. – WJ06
EIDELSBERG, M. – WG01
EL-KHOURY, P. – WF05, FE01
EL-KHOURY, P. Z. – TD02, TD03
ELIET, S. – FD12
ELLIOIT, A. A. – TH04, RH07
ELLIS, A. M. – TG08, WJ04, RI04
ELLISON, G. B. – TD08
EMMERT III, F. L. – RJ10, RJ11
ENDO, Y. – MI01, MI02, TG11, TG12
ENDRES, C. P. – TJ13, RC02, FC01, FC02, FC04
ERNST, W. E. – TG03, WJ05, WJ06, FB06
ESCARRA, M. D. – FA02
ETCHISON, K. C. – RC07
EVANGELOSTI, L. – MG11, WH05, RH01, RH08
EVERITT, H. O. – MJ13, MJ14

F

FAWZY, W. M. – MI15
FAY, A. – MF07, RA10
FECHNER, L. – WJ06
FEDERMAN, S. R. – WG01
FELINTO, D. – RD06
FERMANN, M. E. – RD07, RD11
FERNANDO, K. A. – FE06
FERNÁNDEZ, J. A. – WH04
FEYER, V. – MG11, TD11
FIELD, R. W. – TG01, TG06, RA01
FIKIC, A. – TF01
FILLION, J. H. – WG01
FIRESTONE, R. S. – TH01
FITZGERALD, S. – FB01
FLAUD, J. – MJ05
FLAUD, J. - M. – MJ04, MJ15
FLEISHER, A. J. – MG03, MG04, 
MG08, TA02, TA03, WF08, 
WF09
FLYNN, S. D. – MI06, FB07, FB08
FOLDES, T. – RI01, RI02
FORTHOMME, D. – MH08
FORTMAN, S. – RC13
FORTMAN, S. M. – TJ02, TJ03
FOURNIER, J. A. – MG03, MG04,
MG08, TA02, TA03, WF08,
WF09
FLEISHER, A. J. – MG03, MG04,
MG08, TA02, TA03, WF08,
WF09
FLYNN, S. D. – MI06, FB07, FB08
FOLDES, T. – RI01, RI02
FORTHOMME, D. – MH08
FORTMAN, S. – RC13
FORTMAN, S. M. – TJ02, TJ03
FOURNIER, J. A. – RH10
FRANK, A. J. – TE11
FREEL, K. – RA11
FREY, J. A. – MI05
FREY, S. – RG13
FRIEDEL, D. N. – RF03, RF14
FRIEDMAN, M. – FB01
FRIEDMAN, S. D. – WG06, WG07
FROHMAN, D. J. – TH01, TH05
FUJIHARA, A. – RB11
FUJIMORI, R. – WJ07, RE02, FB11
FUJIWARA, T. – TA12
FUKE, K. – TB03
FUKUSHIMA, M. – TG11, TG12
FUNAHARA, I. – MI01
FUNATO, W. – MI02
FUNKNER, S. – TD12
G
GABARD, T. – FC07
GABET, K. – FA14
GAMACHE, R. R. – MJ08
GAO, J. – MG04
GARROD, R. T. – RF04
GASSER, M. – MI05
GAUSCO, T. L. – FA12
GAUSS, J. – RJ02
GEBALLE, T. R. – WG05, RF06, 
RF07, FC10
Gehr, R. D. – RF09, RF10
GELLMAN, S. H. – TB07, TB08, 
RB06, RB10
GEORGES, L. – TD01, TD02, TD03
GERAKINES, P. A. – TD06
GERARDI, H. – RB04
GERECHT, E. – WH09
GHARABEH, M. A. – TG07
GIBSON, S. – RE10
GIESE, C. – WI06
GIESEN, T. F. – FC01, FC02
GIOGETTA, F. R. – RD02
GISLER, A. W. – WA01
GIULIANO, B. M. – MG11
GLOAGUEN, E. – TB06
GLO, E. C. – RH12
GLOVER, S. C. O. – WG10
GMACHL, C. F. – FA02
GNANASEKARAN, R. – TD12
GOMEZ, L. – WI07, WI08, FA07, 
FC03
GONCHER, S. J. – RA12
Gopal, R. – WF10, RI16
GORDON, I. E. – TE01, WF03
GORSHELEV, V. – TD12
GROSS, K. – FA09
GRUBBS II, G. S. – RC06, RC07, 
RH11
GRUNER, B. – WI06
GUASCO, T. L. – RB05
GUELACHVILI, G. – RD01, RD05
GUIDI, M. – RB01
GUILLAUMET, J. – MJ12
GUILLAUMET, J.- C. – TJ11, TJ12
GUILLOTEAU, S. – FC16
GUIRGIS, G. A. – RC10, RH07
GULLANTS, E. A. – FE06
GUO, L. – TB07, TB08, RB06, RB10
GUO, X. – FE03, FE04, FE10
GUPTA, H. – RC03
GUPTA, M. – MI03
H
HAASE, C. – FA05
HALFEN, D. T. – MH05, RC08, 
RF01, RF02, RG15
HALL, G. E. – MI11, MI12, RA02
HALONEN, L. – MJ06
HAMASHIMA, T. – RI10
HAMMER, S. – TA12
HAN, H. – RI12
HAN, J. – TG04, RA11
HANTAUE, K. – RI14
HANDLER, K. – TF08, TF09
HARADA, K. – MI03, TH02
HARADA, N. – RF05, RF08
HARDER, H. – RC11
HARDING, M. E. – TI05, TI06, RJ02
HARGREAVES, R. J. – WJ09
HARKER, H. – RG09, RG10
HARR, R. – TFV, TF08
HARRIS, S. J. – MH04
HARRIS, A. J. – FG06
HARRIS, A. J. – MG03, MG04,
MG08, TA02, TA03, WF08,
WF09
HARRIS, R. A. – TG01
HARRIS, S. J. – MI05
HARRIS, S. J. – MH04
HARRUFF, B. A. – FE06
HARTER, W. – RH14, RH15
HART, L. – RC07, RD11
HARTMANN, J. M. – MJ10
HASBROUCK, S. – RG07
HASEL, G. – RF08
HAUGEN, C. – WF01
HAUPERT, L. M. – TD04
HAUSE, M. L. – RA02
HAUSER, A. W. – WI05, WI06
HAVENITH, M. – MF08, TD12
HAY, K. G. – TA01, TE08, TE09
HAYASHI, H. – MG15
HAYASHI, M. – MI03
HAYRA, M. – RI15
HE, T. – FE09
HEAVEN, M. C. – TF06, TG04, 
WI01, WI02, RA11
HEAZLEWOOD, B. R. – RA07
HEID, C. G. – RA03
HELDEN, G. V. – RJ12
HENDR, S. – MJ09
HERBERT, J. M. – TI09, TI15, TI16
HERBST, E. – TJ09, RF05, RF08, 
FC09, FC13
HERMAN, L. – TA05
HERMAN, L. V. – TA06
HERMAN, M. – MF07, RA10, RI01, 
RI02
HERSANT, F. – RC16
HEWAGAMA, T. – FC08
HEYDEN, P. V. D. – MF05, MF06, 
TE06
HIGHET-WALKER, A. R. – WH07
HILALI, A. E. – TJ05, TJ06, RJ13
HINCELIN, U. – FC16
HINDLE, F. – FA15, FD12
HINDS, E. A. – WA03
HINKLE, C. E. – RA05
HINKLE, K. H. – MG05
YABUGUCHI, H. – TB03
YAMADA, T. – WH10
YANG, C. – FD12
YANG, D. – MH10, MH11, RG05, RG06
YANG, G. – TB10
YANG, S. – MI10
YE, J. – MA01, RD07, FD03, FD04

YOOON, Y. W. – MI14
YORK, D. G. – WG06, WG07
YOST, D. – RD07
YOUNG, J. W. – MG02, MG03, MG08, TA03, WF09
YOUNGBLOOD, W. J. – MJ12
YU, S. – TC03, TJ10, RC02, RC03, RF11, FC04

ZACK, L. N. – MH02
ZALESKI, D. P. – TC11, TJ15
ZANDER, R. – MJ10
ZANNI, M. T. – FE05
ZAYTSEVA, I. L. – MG11

ZHANG, C. – RG06
ZHELDAKOV, I. L. – FE02
ZHONG, D. – FE03, FE04, FE09, FE10
ZHOU, Y. – TG01
ZHUANH, X. – TF04, TF05
ZIEMKIEWICZ, M. – WA01
ZIURYS, L. M. – MH01, MH02, MH05, MH06, WG02, WG03, WG04, RC08, RF01, RF02, RF15, RG15
ZUZEEK, Y. – FA08
ZVEREVA-LOÈTE, N. – MF10
ZWIER, T. S. – TB07, TB08, WF07, RB06, RB09, RB10, FC05
The Symposium expresses its appreciation to **Elsevier**
for its support of the
Journal of Molecular Spectroscopy Special Lecture
The Symposium expresses its appreciation to COHERENT for Subsidizing the Cost of the Coffee

Lasers for Spectroscopy.

Coherent is the expert in more types of CW, pulsed and quasi-CW laser technology than any other company. This includes our unique and scalable OPSL (Optically Pumped Semiconductor Laser) technology that can be designed to produce any target wavelength or power level in the IR, visible, and near-UV. And because we are vertically integrated, with the complete control over quality at every level, our lasers also deliver the industry’s highest reliability and longest lifetimes.

To learn more about the most comprehensive and capable lasers for spectroscopy available, visit our website at www.Coherent.com.
The Symposium thanks

**Quantel**

for its support in the memory of Ralph Swaine

for the Women’s Lunch

Providing a pulsed laser solution is much more than just meeting specifications.

Since 1970, the Quantel Group has delivered thousands of flashlamp and diode-pumped pulsed lasers for applications in labs, instruments, and tough industrial environments.

Partnerships with scientists and industrial customers all over the world have given us the specialised knowledge to give you the best solution for a wide range of applications.

After sale, our service and support network ensures you get productivity on top of the best-in-class pulsed laser solution.

www.quantel-laser.com

877 - QUANTEL
The Symposium thanks **BW Tek** for Subsidizing the Cost of the Doughnuts
The Symposium thanks
The Journal of Physical Chemistry A
for Subsidizing the Cost of the Picnic for the Students