Welcome to the 66th
OSU International
Symposium on Molecular Spectroscopy

On behalf of the Executive Committee, Frank DeLucia, Eric Herbst, Anne B. McCoy, and myself, I welcome all the attendees to the 66th Spectroscopy Symposium and to The Ohio State University and Columbus.

The Symposium presents recent work in fundamental molecular spectroscopy, and in a variety of closely related areas and applications. The number of talks, their variety, and the fact that many are given by students, all indicate the continued vitality and significance of the field. This Abstract Book documents the presentations which are the heart of the meeting. Additional information flows from informal exchanges and discussions as well as the talks. As organizers, we strive to provide an environment that facilitates both kinds of interactions.

The essence of the meeting lies in the scientific discussions and your personal experiences this week independent of the number of times that you have attended this meeting. Whether you are a 50+ times veteran or a first-timer, 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

SCHEDULE OF TALKS
Monday (M)...............1
Tuesday (T).............15
Wednesday (W)..........41
Thursday (R)...........58
Friday (F)...............80

ABSTRACTS
Monday (M)...............90
Tuesday (T)............123
Wednesday (W)........185
Thursday (R)..........220
Friday (F)...............274

AUTHOR INDEX..........301
ACKNOWLEDGMENTS.....309
Special Sessions

For the 66th Symposium, Robert W. Field, MIT, is organizing a mini-symposium entitled, “Spectroscopic Perturbations: Molecules Behaving Badly?” Spectroscopic perturbations are windows onto unknown or unexpected classes of states and can reveal intramolecular dynamics. This mini-symposium will cover both experimental observation and theoretical interpretation of perturbations. Invited speakers include Mark Child, University of Oxford, Robert Field, MIT, and Anthony Merer, Academia Sinica. A second mini-symposium is being organized by Eric Herbst, The Ohio State University, on the subject of “The THz Cosmos.” This mini-symposium features new spectroscopic studies of the interstellar medium in the far-infrared obtained with the Herschel Space Observatory and the Stratospheric Observatory for Infrared Astronomy (SOFIA). Invited talks for this mini-symposium will be given by Edwin Bergin, University of Michigan, and Maryvonne Gerin, Ecole Normale Superieure. A third mini-symposium is being organized by Trevor Sears, Brookhaven National Lab, and Neil Shafer-Ray, University of Oklahoma, entitled “Molecular Spectroscopy in Support of Fundamental Physics.” This mini-symposium focuses on molecular spectroscopy that probes the fundamental underpinnings of physics, including parity and time-reversal violations and the universality of fundamental constants. Invited speakers include David DeMille, Yale University, and Jens-Uwe Grabow, Leibniz-Universitat Hannover. A session on theory is being organized by Anne McCoy, John Herbert, and Russell Pitzer, Ohio State University, featuring an invited talk by Kirk Peterson, Washington State University.

Picnic

The Symposium picnic will be held on Wednesday evening, June 22, 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 Coblenzt Society is the host for refreshments at 6:30pm before the picnic which is scheduled to commence at 7:30pm at the Fawcett Center.
**Sponsorship**

We are pleased to announce the sponsorship for the 66th Symposium. Principal funding comes from the **Army Office of Research** (ARO). We are most grateful to ARO for their continued support. We also acknowledge the many efforts and contributions of **The Ohio State University** in hosting the meeting. Our Corporate sponsors are **Elsevier**, **BW Tek, Inc.**, **Coherent**, **Journal of Physical Chemistry A**, **Quantel**, and **Virginia Diodes**. **Elsevier** is supporting the Journal of Molecular Spectroscopy Special Lecture. We are pleased to acknowledge **Andor Technology**, **Bristol Instruments**, **Bruker Optics**, **Continuum**, **CVI Melles Griot**, **Daylight Solutions**, **Horiba Scientific**, **Lighthouse Photonics**, **Lockheed Martin/Aculight**, **Newport/Spectra-Physics**, **Princeton Instruments**, **Qioptiq**, and **Virginia Diodes** as Contributing sponsors. **IOS Press** has a special insert in your conferee packet. **Bruker Optics** will have a special Tuesday lunch technical presentation. 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 2010 meeting will be presented. The winners are **Hui-Ling Han**, National Chiao Tung University; **Samantha Horvath**, The Ohio State University; and **Solveig Gaarn Olesen**, University of Copenhagen. 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 is administered by a Prize Committee chaired by Yunjie Xu, University of Alberta and comprised of Kevin Lehmann, University of Virginia; John Muenter, University of Rochester; Brooks Pate, University of Virginia; Douglas Petkie, Wright State 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).

**Information**

**ACCOMMODATIONS:** The check-in for dormitory accommodations is located in the Lane Avenue Residence Hall (LARH), 328 W. Lane Avenue, open at 3p.m. Saturday, June 18, and remain open 24 hours a day through the Symposium.

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 mention that you are with the Molspec 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 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 the 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 LARH upon 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 10, please call the Symposium Office to find out your options.

**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: Equipment for computer presentations, i.e. Powerpoint, will be available for each session. For computer presentations, you must go to the Digital Presentation link on our web site and follow the instructions. Your PowerPoint file and all supporting documents can be uploaded. 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 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
Caroline C. Whitacre, Vice President for Research
The Ohio State University

MA01 40 min 9:00
SPECTROSCOPY AND DYNAMICS OF THE HOCO RADICAL

ROBERT E. CONTINETTI\(^a\), BERWYCK L. J. POAD, Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, CA 92093; CHRISTOPHER J. JOHNSON, Department of Physics, University of California San Diego, La Jolla, CA 92093; MICHAEL E. HARDING, JOHN F. STANTON, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712.

\(^a\)This work supported by the US Department of Energy under grant number DE-FG03-98ER14879

MA02 40 min 9:45
SPECTROSCOPIC AND THEORETICAL STUDY ON THE STRUCTURES AND DYNAMICS OF FUNCTIONAL MOLECULES - TOWARDS AN UNDERSTANDING OF THE MOLECULAR RECOGNITION FOR ENCAPSULATION COMPLEXES

TAKAYUKI EBATA, RYOJI KUSAKA, YOSHIYA INOKUCHI, Department of Chemistry, Graduate School of Science, Hiroshima University, Higashi-Hiroshima, 739-8526, Japan; SOTIRIS S. XANTHEAS, Pacific Northwest National Laboratory, 902 Battelle Boulevard, PO Box 999, MS K1-83, Richland, WA 99352.

Intermission

RAO AWARDS
Presentation of Awards by Yunjie Xu, University of Alberta

2010 Rao Award Winners
Hui-Ling Han, National Chiao Tung University
Samantha Horvath, The Ohio State University
Solveig Gaarn Olesen, University of Copenhagen

MA03 40 min 11:05
ELECTRONIC SPECTROSCOPY OF CARBON CHAINS OF ASTROPHYSICAL RELEVANCE

JOHN P. MAIER, Department of Chemistry, University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland.
MF01 15 min 1:30
THEORETICAL STUDIES OF OBSERVABLE TRANSITIONS TO RECOUPLED PAIR BONDED STATES OF SULFUR HALIDE COMPOUNDS: SF/SCl (X^2Π→A^2Σ−), SF2/SCl2 (X^1A1→1^1B1, X^1A1→1^1A2), AND SFCI (X^1A′→A^1A′′)

JEFF LEIDING, DAVID E. WOON and THOM H. DUNNING, JR., Department of Chemistry, University of Illinois at Urbana-Champaign, Box 86-6, CLSL, 600 South Mathews, Urbana IL, 61801.

MF02 10 min 1:47
BLUE-DETUNED PHOTOASSOCIATION SPECTRUM IN Rb2


MF03 15 min 1:59
AN ACCURATE NEW POTENTIAL FUNCTION FOR GROUND-STATE XeO2 FROM UV AND VIRIAL COEFFICIENT DATA

ROBERT J. LE ROY, J. CAMERON MACKIE, PRAGNA CHANDRASEKHAR, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

MF04 15 min 2:16
LASER-INDUCED FLUORESCENCE STUDIES OF THE JET-COOLED ALUMINUM ACETYLIDE RADICAL (Al-CCH/AICCD)

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

MF05 15 min 2:33
THE ELECTRONIC SPECTRUM OF H2PO, THE PROTOTYPICAL PHOSPHORYL FREE RADICAL

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

MF06 15 min 2:50
DETECTION OF THE H2PS FREE RADICAL BY LASER SPECTROSCOPY

ROBERT A. GRIMMINGER, DENNIS J. CLOUTHIER, Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055, USA; RICCARDO TARRONI, Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna, 40136 Bologna, Italy.
MF07 15 min 3:07
A SPECTROSCOPIC STUDY OF THE LINEAR-BENT ELECTRONIC TRANSITIONS OF JET-COOLED BCl₂ AND HBCl

RAMYA NAGARAJAN, JIE YANG and DENNIS J. CLOUTHIER, Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.

Intermission

MF08 15 min 3:40
TWO-DIMENSIONAL (2+n) REMPI SPECTROSCOPY: STATE INTERACTIONS, PHOTOFRAGMENTATIONS AND ENERGETICS OF THE HYDROGEN HALIDES

JINGMING LONG, HUASHENG WANG, AGUST KVARAN, Science Institute, University of Iceland, Dunhagi 3, 107 Reykjavik, Iceland.

MF09 15 min 3:57
OPTICAL STARK SPECTROSCOPY OF THE \( \tilde{A}^2\Pi - \tilde{X}^2\Sigma^+ \) BAND OF BaOH

SARAH E. FREY AND TIMOTHY C. STEIMLE, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287, USA.

MF10 15 min 4:14
LASER INDUCED FLUORESCENCE SPECTROSCOPY OF BORON CARBIDE

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

MF11 15 min 4:31
IMPROVEMENT OF SPECTROSCOPIC CONSTANTS FOR THE \( \tilde{A}^3\Pi_1 \leftarrow \tilde{X}^1\Sigma^+_g \) SYSTEM OF Br₂

NOBUO NISHIMIYA, TOKIO YUKIYA, and MASAO SUZUKI, Department of Electronics and Information Technology, Tokyo Polytechnic University, Iiyama 1583, Atsugi-City, 243-0297 Kanagawa, Japan; ROBERT J. LE ROY, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

MF12 15 min 4:48
ACCURATE ANALYTIC POTENTIALS FOR THE \( \tilde{A}^3\Pi_1 \) and \( \tilde{X}^1\Sigma^+ \) STATES OF IBr FROM A COMBINED-ISOTOPOLOGUE DIRECT-POTENTIAL-FIT DATA ANALYSIS

TOKIO YUKIYA, NOBUO NISHIMIYA, Department of Electronics and Information Technology, Tokyo Polytechnic University, Iiyama 1583, Atsugi City, Kanagawa 243-0297, Japan; ROBERT J. LE ROY, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

MF13 15 min 5:05
TRANSITION STRENGTHS IN THE VISIBLE ABSORPTION SPECTRUM OF I₂: ONE MORE PASS

J. TELLINGHUISEN, Department of Chemistry, Vanderbilt University, Nashville, TN 37235.
PHOTOELECTRON SPECTROSCOPY OF ICN⁻: CHARACTERIZATION OF A CONICAL INTERSECTION IN ICN

ELISA M. MILLER, LEONID SHEPS,a YU-JU LU, JILA, Department of Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, CO 80309; ANNE B. McCLOY, Department of Chemistry, The Ohio State University, Columbus, OH, 43210; and W. CARL LINEBERGER, JILA, Department of Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, CO 80309.

aPresent address: Sandia National Laboratories, Livermore, CA 94551
**MG. INFRARED/RAMAN**

**MONDAY, JUNE 20, 2011 – 1:30 pm**

**Room: 170 MATH ANNEX**

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

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**MG01 15 min 1:30**

NEAR-INFRARED OVERTONE SPECTROSCOPY OF TRITIATED WATER

*KAORI KOBAYASHI, TOMOYA ENOKIDA, DAISUKE IIO, YUTA YAMADA, Department of Physics, University of Toyama, 3190 Gofuku, Toyama, 930-8555 Japan; MASANORI HARA, YUJI HATANO, Hydrogen Isotope Research Center, University of Toyama, 3190 Gofuku, Toyama, 930-8555 Japan.*

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**MG02 10 min 1:47**

ASSIGNMENT OF INFRARED AMMONIA SPECTRA

*J. TENNYSON, M. J. DOWN, C. HILL and R. J. BARBER, Department of Physics and Astronomy, University College London, London, WC1E 6BT, UK; S. N. YURCHENKO, Technische Universität Dresden, Physikalische Chemie, D–01062 Dresden, Germany.*

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**MG03 15 min 1:59**

MODELING VIBRATIONAL STRUCTURE USING HARMONICALLY-COUPLED MORSE OSCILLATORS: A GLOBAL DESCRIPTION OF THE C-H STRETCHES IN METHYL RADICAL AND ITS DEUTERATED ISOTOPOMERS

*MELANIE A. ROBERTS, DAVID J. NESBITT, JILA, National Institute of Standards and Technology and University of Colorado, and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309; ANNE B. McCOY, Department of Chemistry, The Ohio State University, Columbus, OH 43210.*

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**MG04 15 min 2:16**

HIGH-RESOLUTION FOURIER TRANSFORM INFRARED SPECTROSCOPY OF SMALL BORON–CONTAINING MOLECULES

*G. LI and P. F. BERNATH, Department of Chemistry, University of York, Heslington, York YO10 5DD.*

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**MG05 15 min 2:33**

INFRARED LINE INTENSITIES FOR FORMALDEHYDE FROM SIMULTANEOUS MEASUREMENTS IN THE INFRARED AND FAR INFRARED SPECTRAL RANGES

*L. FISSIAUX, Laboratoire Lasers et Spectroscopies, Facultés Universitaires Notre Dame de la Paix, 61 rue de Bruxelles, B-5000 Namur, Belgium; T. FÖLDES, Service de Chimie Quantique et Photophysique, Université Libre de Bruxelles, CP 160/09, 50 avenue F.D. Rooseveilt, B-1050 Brussels, Belgium; F. KWABIA TCHANA, Laboratoire Interuniversitaire des Systèmes Atmosphériques, CNRS, Universités de Paris Est Créteil et Paris 7, 61 avenue du Général De Gaulle, F-94010 Créteil cedex, France; L. DAUMONT, Groupe de Spectrométrie Moléculaire et Applications, UMR CNRS 6089, Université de Reims Champagne Ardenne, Campus du Moulin de la Housse, BP 1039, 51067 Reims Cedex 2, France; M. LEPÈRE, Laboratoire Lasers et Spectroscopies, Facultés Universitaires Notre Dame de la Paix, 61 rue de Bruxelles, B-5000 Namur, Belgium; J. VANDER AUWERA, Service de Chimie Quantique et Photophysique, Université Libre de Bruxelles, CP 160/09, 50 avenue F.D. Rooseveilt, B-1050 Brussels, Belgium.*
INFRARED SPECTROSCOPY OF CARBON- AND CARBON-SILICON CLUSTERS

J. KRIEG, V. LUTTER, I. GOTTBEHÜT, T. F. GIESEN, S. SCHLEMMER, and S. THORWIRTH, I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany.

Intermission

HYDROGEN BOND RING OPENING AND CLOSING IN PROTONATED METHANOL CLUSTERS PROBED BY INFRARED SPECTROSCOPY WITH AND WITHOUT AR TAGGING

TORU HAMASHIMA, KENTA MIZUSE, ASUKA FUJI, Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan; and JER-LAI KUO, Institute of Atomic and Molecular Sciences, Taipei10617, Taiwan.

C...H...N HYDROGEN BOND FORMATION IN TRIMETHYLAMINE DIMER UPON ONE-PHOTON IONIZATION

YUICHIRO NAKAYAMA, YOSHIYUKI MATSUDA, ASUKA FUJI, Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan.

NON-CYCLIC ISOMERS OF (H₂O)₄ IN HELIUM NANODROPLETS: INFRARED SPECTROSCOPY AND AB INITIO CALCULATIONS


MATRIX ISOLATION FTIR AND AB INITIO STUDIES ON THE CONFORMATIONS OF DIMETHYL AND DIETHYL CARBONATE AND THEIR COMPLEXES WITH WATER

BISHNU PRASAD KAR, N. RAMANATHAN, K. SUNDARARAJAN and K. S. VISWANATHAN, Chemistry Group, Indira Gandhi Centre for Atomic Research, Kalpakkam, 603 102, India.

CONFORMATIONS OF TRIMETHYL PHOSPHITE: A MATRIX ISOLATION INFRARED AND AB INITIO STUDY

N. RAMANATHAN, K. SUNDARARAJAN, BISHNU PRASAD KAR and K. S. VISWANATHAN, Chemistry Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India.

INTERMOLECULAR ASSOCIATION COMPLEXES OF 1,3-CYCLOHEXANEDIONE: PROBING OF KETO-ENOL TAUTOMERIC EQUILIBRIA IN COLD INERT GAS MATRIX, SOLUTION AND VAPOR PHASE BY INFRARED SPECTROSCOPY AND QUANTUM CHEMISTRY STUDY

BIMAN BANDYOPADHYAY, PRASENJIT PANDEY, Physical Chemistry Department, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India; AMIT K. SAMANTA, Department of Chemistry, University of Southern California, Los Angeles, CA 90089, U.S.A.; ANAMIKA MUKHOPADHYAY and TAPAS CHAKRABORTY, Physical Chemistry Department, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India.
VIBRON AND PHONON HYBRIDIZATION IN DIELECTRIC NANOSTRUCTURES

T. C. PRESTON and R. SIGNORELLI, Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada.
MH. MICROWAVE  
MONDAY, JUNE 20, 2011 – 1:30 pm  
Room: 1000 McPHERSON LAB

Chair: STEVEN SHIPMAN, New College of Florida, Sarasota, Florida

MH01  15 min  1:30
MICROWAVE SPECTRA AND STRUCTURES OF H₄C₂···AgCl AND H₄C₂···CuCl

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

MH02  15 min  1:47
MICROWAVE SPECTRA AND STRUCTURE OF CF₃I···CO

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

MH03  15 min  2:04
INTERMOLECULAR INTERACTION BETWEEN CO OR CO₂ AND ETHER OR THIOETHER OR PROPYLENE OXIDE IN A COMPLEX, INVESTIGATED BY FOURIER TRANSFORM MICROWAVE SPECTROSCOPY AND ABINITIO CALCULATIONS

YOSHIYUKI KAWASHIMA, YUKARI ORITA, and AKINORI SATO, Department of Applied Chemistry, Faculty of Engineering, Kanagawa Institute of Technology, Atsugi, Kanagawa 243-0292, JAPAN; EIZI HIROTA, The Graduate University for Advanced Studies, Hayama, Kanagawa 240-0193, JAPAN.

MH04  10 min  2:21
DOES WATER PREFER TO DONATE A PROTON TO AN F OR TO a Cl ATOM? - A ROTATIONAL STUDY OF CH₃CHClF...H₂O

GANG FENG, LUCA EVANGELISTI and W. CAMINATI, Dipartimento di Chimica “G. Ciamicain” dell’Università, Via Selmi 2, I-40126 Bologna, Italy; LAURA B. FAVERO, Istituto per lo Studio dei Materiali Nanostrutturati (ISMN, Sezione di Bologna), CNR, Via Gobetti 101, I-40129 Bologna, Italy; JENS-UWE GRABOW, Lehrgebiet Physikalische Chemie A, Institut für Physikalische Chemie und Elektrochemie, Universität Hannover, Callinstr. 3A, D-30167 Hannover, Germany; ZHINING XIA, Chemistry and Chemistry Engineering College, Chongqing University, Chongqing, 400030, P. R. China.

MH05  15 min  2:33
DETERMINATION OF THE STRUCTURE OF THE ARGON CYCLOPENTANONE AND NEON VAN DER WAALS COMPLEXES

WEI LIN, Department of Chemistry and Environmental Sciences, University of Texas at Brownsville, 80 Fort Brown - MO1.114, Brownsville, TX 78520; DANIEL J. FROHMAN, ANDREW H. BROOKS, Department of Chemistry, Wesleyan University, Hall-Atwater Laboratories, 52 Lawn Avenue, Middletown, CT 06459-0180; ANDREA J. MINEI, Division of Natural Sciences, Chemistry Department, College of Mount Saint Vincent, 6301 Riverdale Avenue, Riverdale, NY 10471; CHINH H. DUONG, STEWART E. NOVICK, and WALLACE C. PRINGLE, Department of Chemistry, Wesleyan University, Hall-Atwater Laboratories, 52 Lawn Avenue, Middletown, CT 06459-0180.
IMPROVED DIPOLE MOMENTS FOR ACRYLONITRILE AND PROPIONITRILE

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

NOTATION CONFUSION OF SYMMETRY SPECIES FOR MOLECULES WITH SEVERAL LARGE-AMPLITUDE INTERNAL MOTIONS

P. GRONER, Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110-2499.

SEMI-EXPERIMENTAL \( \frac{r_s}{r_e} \) STRUCTURES FOR THE HEAVY ATOM BACKBONES OF TWO MODERATELY LARGE MOLECULES OBTAINED FROM MICROWAVE SPECTROSCOPY AND QUANTUM CHEMICAL CALCULATIONS

NORMAN C. CRAIG, Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH 44074; ALBERTO LESARRI, Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47011 Valladolid, Spain; EMILIO J. COCINERO, Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Ap. 644, E-48080 Bilbao, Spain; JENS-UWE GRABOW, Institut für Physikalische Chemie und Elektrochemie, Gottfried-Wilhelm-Leibniz-Universität Hannover, Callinstrasse 3A, D30167 Hannover, Germany.

VIBRATIONAL ENERGIES FOR ACRYLONITRILE FROM MM-WAVE TO THZ ROTATIONAL SPECTRA

ZBIGNIEW KISIEL, LECH PSZCZÓŁKOWSKI, Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland; BRIAN J. DROUIN, CAROLYN S. BRAUER, SHANSHAN YU, JOHN C. PEARSON, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109-8099, USA; IVAN R. MEDVEDEV, Department of Physics, Wright State University, Dayton, OH 45435, USA; SARAH FORTMAN, CHRISTOPHER NEESE, Department of Physics, The Ohio State University, Columbus, OH 43210, USA.

ROOM-TEMPERATURE CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE (RT-CP-FTMW) SPECTRUM OF PYRIDINE

AUSTIN L. MCIJUNKINS, K. MICHELLE THOMAS, APRIL RUTHVEN, AND GORDON G. BROWN, Department of Science and Mathematics, Coker College, 300 E College Ave., Hartsville, SC 29550.

THE ROTATIONAL SPECTRUM OF BIOMOLECULAR RELATED COMPOUNDS.a

VANESA VAQUERO, and DAVID W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

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*aWork supported by NSF(CHE-0911117)*
MH12 15 min 4:51
FLUORINE SUBSTITUTION IN NEUROTRANSMITTERS: MICROWAVE SPECTROSCOPY AND MODELLING OF THE CONFORMATIONAL SPACE AND NON BONDING INTERACTIONS

S. MELANDRI, A. MARIS and A. MERLONI, Dipartimento di Chimica Ciamician, Università di Bologna, via Selmi 2, 40126 Bologna, Italy.

MH13 15 min 5:08
LA-MB-FTMW STUDIES OF SUGARS


MH14 15 min 5:25
NEUROTRANSMITTERS IN THE GAS PHASE: LA-MB-FTMW STUDIES

MI. RADICALS AND IONS
MONDAY, JUNE 20, 2011 – 1:30 pm
Room: 1015 McPHERSON LAB

Chair: DMITRY MELNIK, The Ohio State University, Columbus, OH

M101 10 min 1:30
ISOTOPIC EFFECTS IN CHEMICAL REACTIONS OF SINGLE IONS

JAMES E. GOEDERS, CRAIG R. CLARK, and KENNETH R. BROWN, Georgia Institute of Technology.

M102 15 min 1:42
MODELING THE INFLUENCE OF NUCLEAR SPIN IN THE REACTION OF H$_3^+$ WITH H$_2$

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

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

M103 15 min 1:59
SPECTROSCOPIC MEASUREMENTS OF THE REACTION H$_3^+$ + H$_2$ → H$_2$ + H$_3^+$

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

*Present Address: Department of Chemistry, United States Air Force Academy, Air Force Academy, CO 80840, USA
*Present Address: Department of Chemistry, Emory University, Atlanta, GA 30322, USA

M104 15 min 2:16
INFRARED PHOTODISSOCIATION SPECTROSCOPY OF FIRST ROW TRANSITION METAL-CARBONYL CATIONS

ANTONIO D. BRATHWAITE, ALLEN M. RICKS, ZACH D. REED, MICHAEL A. DUNCAN, Department of Chemistry, University of Georgia, Athens, GA 30602-2256.

M105 15 min 2:33
INFRARED PHOTODISSOCIATION SPECTROSCOPY OF METAL ION WATER COMPLEXES

B. BANDYOPADHYAY, P. D. CARNEGIE and M. A. DUNCAN, University of Georgia, Athens, Georgia-30605, USA.

M106 15 min 2:50
VIBRATIONALLY DRIVEN ELECTRON TRANSFER IN CH$_3$NO$_2$·CH$_3$I CLUSTERS

BENJAMIN J. KNURR, CHRISTOPHER L. ADAMS and J. MATHIAS WEBER, JILA, NIST and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309.

M107 15 min 3:07
PHOTOELECTRON IMAGING OF NITROETHANE, NITROPROPANE AND NITROBUTANE

CHRISTOPHER L. ADAMS, BENJAMIN J. KNURR and J. MATHIAS WEBER, JILA, NIST and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309.
Intermission

MI08 15 min 3:40

ROTATIONAL SPECTRA OF $\text{N}_2\text{OH}^+$ AND $\text{CH}_2\text{CCHNH}^+$ MOLECULAR IONS

OSCAR MARTINEZ, JR., VALERIO LATTANZI, 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; SVEN THORWITH, Max-Planck-Institut für Radioastronomie, Bonn, Germany, and I. Physikalisches Institut, Universität zu Köln, Germany.

MI09 15 min 3:57

NOISE IMMUNE CAVITY ENHANCED OPTICAL HETERODYNE VELOCITY MODULATION SPECTROSCOPY

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

MI10 15 min 4:14

LINESHAPE AND SENSITIVITY OF SPECTROSCOPIC SIGNALS OF $\text{N}_2^+$ IN A POSITIVE COLUMN COLLECTED USING NOISE IMMUNE CAVITY ENHANCED OPTICAL HETERODYNE VELOCITY MODULATION SPECTROSCOPY

ANDREW MILLS, BRIAN SILLER, MICHAEL PORAMBO, 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.

MI11 15 min 4:31

PROGRESS AND RECENT DEVELOPMENTS IN SENSITIVE, COOLED, RESOLVED ION BEAM SPECTROSCOPY (SCRIBES)

MICHAEL PORAMBO, ANDREW MILLS, BRIAN SILLER, HOLGER KRECKEL, MANORI PERERA, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801; BENJAMIN McCALL, Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

MI12 15 min 4:48

PHOTODISSOCIATION SPECTROSCOPY OF $\text{Ca}^+\cdot\text{H}_2\text{O}$ IN THE TEMPERATURE-VARIABLE ION TRAP

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

*Present address: Osaka Prefecture University, Japan

MI13 15 min 5:05

HIGH-RESOLUTION IR ACTION SPECTRUM OF $\text{C}_2\text{H}_2^+$

SABRINA GÄRTNER, JÜRGEN KRIEG, OSKAR ASVANY and STEPHAN SCHLEMMER, I. Physikalisches Institut, Universität zu Köln.
MJ. MATRIX/CONDENSED PHASE

MONDAY, JUNE 20, 2011 – 1:30 pm

Room: 2015 McPHERSON LAB

Chair: DAVID ANDERSON, University of Wyoming, Laramie, Wyoming

MJ01 15 min 1:30

FLUORESCENCE OF MATRIX-ISOLATED BIACETYL

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

MJ02 15 min 1:47

EXPERIMENTAL THERMOCHEMISTRY OF GAS PHASE CYTOSINE TAUTOMERS


MJ03 10 min 2:04

TAUTOMERS OF CYTOSINE AND THEIR EXCITED ELECTRONIC STATES: A MATRIX ISOLATION SPECTROSCOPIC AND QUANTUM CHEMICAL STUDY

GÁBOR BAZSÓ, GYÖRGY TARCZAY, Laboratory of Molecular Spectroscopy, Institute of Chemistry, Eötvös Loránd University, Pf. 32, Budapest, H-1518, Hungary; GÉZA FOGARASI, PÉTER G. SZALAY, Laboratory of Theoretical Chemistry, Institute of Chemistry, Eötvös Loránd University, Pf. 32, Budapest, H-1518, Hungary.

MJ04 15 min 2:16

PULSED JET DISCHARGE MATRIX ISOLATION AND COMPUTATIONAL STUDY OF HALOGEN ATOM COMPLEXES: Br–BrCH₂X (X=H,Cl,Br)

AIMABLE KALUME, LISA GEORGE AND SCOTT A. REID, Department of Chemistry, Marquette University, Milwaukee, WI 53233.

MJ05 15 min 2:33

PHOTOINDUCED ELECTRON TRANSFER IN THE C₂H₄–Br₂ COMPLEX

AIMABLE KALUME, LISA GEORGE AND SCOTT A. REID, Department of Chemistry, Marquette University, Milwaukee, WI 53233.

MJ06 15 min 2:50

INFRARED SPECTRA OF THE 2-CHLOROETHYL RADICAL IN SOLID PARA-HYDROGEN

JAY C. AMICANGELO, School of Science, Penn State Erie, Erie, PA 16563; MOHAMMED BAHOU, BARBARA GOLEC, AND 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.

Intermission
MJ07  
FTIR ISOTOPIC AND DFT STUDIES OF SiC\textsubscript{5} TRAPPED IN SOLID Ar

T. H. LE, and W. R. M. GRAHAM, Molecular Physics Laboratory, Department of Physics and Astronomy, Texas Christian University, Fort Worth, TX 76129.

MJ08  
FTIR AND DFT STUDIES OF THE MgC\textsuperscript{3-} ANION IN SOLID Ar

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

MJ09  
DIMINISHED CAGE EFFECT IN \textit{p}-H\textsubscript{2}: IR IDENTIFICATION OF INTERMEDIATES IN ADDITION REACTIONS OF CL ATOM WITH UNSATURATED HYDROCARBONS

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, BARBARA GOLEC, Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan.

MJ10  
MOLECULAR HYDROGEN INTERACTIONS WITHIN METAL-ORGANIC FRAMEWORKS

S. FITZGERALD, C. PIERCE, J. SCHLOSS, B. THOMPSON, Department of Physics and Astronomy, Oberlin College, Oberlin, OH 44074; J. ROWSELL, Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH 44074.

MJ11  
ELECTRON SPIN RESONANCE INVESTIGATION OF FORMATION MECHANISMS OF MATRIX ISOLATED H\textsuperscript{+}\textsubscript{4}

M. CORRENTI, J. BANISAUKAS, L. B. KNIGHT, JR., Department of Chemistry, Furman University, Greenville, SC.
<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Title</th>
<th>Authors</th>
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<tbody>
<tr>
<td>8:30</td>
<td>TA01</td>
<td>TIME RESOLVED FTIR ANALYSIS OF COMBUSTION OF ETHANOL AND GASOLINE COMBUSTION IN AN INTERNAL COMBUSTION ENGINE</td>
<td>ALLEN R. WHITE, 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.</td>
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<tr>
<td>8:42</td>
<td>TA02</td>
<td>TIME RESOLVED FTIR ANALYSIS OF TAILPIPE EXHAUST FOR SEVERAL AUTOMOBILES</td>
<td>ALLEN R. WHITE, JAMES ALLEN, 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.</td>
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<tr>
<td>8:54</td>
<td>TA03</td>
<td>HIGH-RESOLUTION MID-INFRARED SPECTROSCOPY OF DEUTERATED WATER CLUSTERS USING A QUANTUM CASCADE LASER-BASED CAVITY RINGDOWN SPECTROMETER</td>
<td>JACOB T. STEWART, BRIAN E. BRUMFIELD, 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.</td>
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<tr>
<td>9:11</td>
<td>TA04</td>
<td>MID-IR CAVITY RING-DOWN SPECTROMETER FOR BIOLOGICAL TRACE NITRIC OXIDE DETECTION</td>
<td>VINCENT KAN, AHEMID RAGAB, VITALI STSIAPURA, KEVIN K. LEHMANN, Department of Chemistry and School of Medicine, University of Virginia, Charlottesville VA, 22904-4319; BENJAMIN M. GASTON, School of Medicine, University of Virginia, Charlottesville VA, 22904-4319.</td>
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<tr>
<td>9:28</td>
<td>TA05</td>
<td>OFF-AXIS CAVITY RING DOWN SPECTROSCOPY BASED ON A CONTINUOUS-WAVE OPTICAL PARAMETRIC OSCILLATOR</td>
<td>JARI PELTOLA, MIKAEL SILTANEN and LAURI HALONEN, Laboratory of Physical Chemistry, Department of Chemistry, P.O. BOX 55 (A.I. Virtasen aukio 1), FI-00014 University of Helsinki, Finland; MARKKU VAINIO, Laboratory of Physical Chemistry, Department of Chemistry, P.O. BOX 55 (A.I. Virtasen aukio 1), FI-00014 University of Helsinki, Finland and Centre for Metrology and Accreditation, P.O. Box 9, FIN-02151 Espoo, Finland.</td>
</tr>
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</table>
OH DETECTION USING OFF-AXIS INTEGRATED CAVITY OUTPUT SPECTROSCOPY (OA-ICOS)

CHRISTOPHE LENGIGNON, WEIXIONG ZHAO, WEIDONG CHEN, ERIC FERTEIN, CECILE COEUR, DENIS PETITPREZ, Laboratoire de Physico-Chimie de l'Atmosphere, Universite du littoral Cote d’Opale, Dunkerque - France; Laboratoire de Physicochimie des Processus de Combustion et de l’Atmosphere, Universite des Sciences et Technologies de Lille, 59655 Villeneuve d’Ascq Cedex - France.

This work is supported by the IRENI program of the Region Nord-Pas de Calais. The support of the Groupement de Recherche International SAMIA between CNRS (France), RFBR (Russia) and CAS (China) is acknowledged.

Intermission

CAVITY RINGDOWN LASER ABSORPTION SPECTROSCOPY (CRLAS) of ISOTOPICALLY LABELED ACETYLENE BETWEEN 12,500 - 13,600 cm$^{-1}$

CHRISTOPHER J. LUE, MICHAEL N. SULLIVAN, MARK E. DRAGANJAC, and SCOTT W. REEVE, Arkansas Center for Laser Applications and Science and Department of Chemistry and Physics, Arkansas State University, P.O. Box 419, State University, AR 72467.

AUTOMATIC TUNING OF AN ACULIGHT OPTICAL PARAMETRIC OSCILLATOR


PRECISION MEASUREMENT OF CARBON DIOXIDE HOTBAND TRANSITION AT 4.3 MICRON USING A HOT CELL

PEI-LING LUO, JYUN-YU TIAN, HSHAN-CHEN CHEN, Institute of Photonics Technologies, National Tsing Hua University, Hsinchu, Taiwan 30013; YU-HUNG LIEN, JOW-TSONG SHY, Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 30013.

HIGH PRECISION MID-IR SPECTROSCOPY OF $^{14}$N$_2$,$^{16}$O NEAR 4.5 μm

WEI-JO TING, JOW-TSONG SHY, Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 30013, R.O.C.

MID-IR SATURATION SPECTROSCOPY OF HeH$^+$ MOLECULAR ION

HSUAN-CHEN CHEN, CHUNG-YUN HSIAO, Institute of Photonics Technologies, National Tsing Hua University, Hsinchu, Taiwan, R.O.C.; JIN-LONG PENG, Center of Measurement Standards, Industrial Technology Research Institute, Hsinchu, Taiwan, R.O.C.; TAKAYOSHI AMANO, Department of Chemistry and Department of Physics and Astronomy, University of Waterloo, Canada, and JOW-TSONG SHY, Department of Physics and Institute of Photonics Technologies, National Tsing Hua University, Hsinchu, Taiwan, R.O.C.
STATE OF WATER MOLECULES AND SILANOL GROUPS IN OPAL MINERALS: A NEAR INFRARED SPECTROSCOPIC STUDY OF OPALS FROM SLOVAKIA

MIROSLAV BOBON, Department of Physics, Faculty of Natural Sciences, Constantine the Philosopher University in Nitra, Slovakia; ALFRED A. CHRISTY, Department of Science, Faculty of Engineering and Science, University of Agder, Serviceboks 422, 4604 Kristiansand, Norway; DANIEL KLUVANEČ and L’UDMILA ILLASOVA, Gemological Institute, Faculty of Natural Sciences, Constantine The Philosopher University in Nitra, Slovakia.

C-H STRETCH OVERTONE SPECTRA OF FLUORINATED ETHERS

SHIZUKA HSIEH, Chemistry Department, Smith College, Northampton, MA 01063.
TB01  10 min  8:30
FREE-INDUCTION DECAY SIGNALS USING A VOLTAGE MODULATED QUANTUM CASCADE LASER

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

TB02  15 min  8:42
OBSERVATION OF INFRARED FREE INDUCTION DECAY AND OPTICAL NUTATION SIGNALS FROM NITROUS OXIDE USING A VOLTAGE MODULATED QUANTUM CASCADE LASER

G. DUXBURY and N. LANGFORD, Department of Physics, SUPA, John Anderson Building, University of Strathclyde, 107 Rottenrow, Glasgow G4 0NG, Scotland, UK; J. F. KELLY and T. F. BLAKE, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, PO Box 999, MS K-88, Richland, Washington 99352.

TB03  15 min  8:59
SUB-DOPPLER SPECTRA OF INFRARED HYPERFINE TRANSITIONS OF NITRIC OXIDE USING A PULSE MODULATED QUANTUM CASCADE LASER

G. DUXBURY and N. LANGFORD, Department of Physics, SUPA, John Anderson Building, University of Strathclyde, 107 Rottenrow, Glasgow G4 0NG, Scotland, UK; J. F. KELLY and T. F. BLAKE, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, PO Box 999, MS K-88, Richland, Washington 99352.

TB04  15 min  9:16
KINETIC INVESTIGATION OF COLLISION INDUCED EXCITATION TRANSFER IN Kr*(4p55p1) + Kr (4p6) AND Kr*(4p55p1) + He (1s2) MIXTURES

MD. HUMAYUN KABIR and MICHAEL C. HEAVEN, Department of Chemistry, Emory University, Atlanta, GA 30322.

TB05  15 min  9:33
IR/THZ DOUBLE RESONANCE SPECTROSCOPY ENERGY DYNAMICS AT ATMOSPHERIC PRESSURES

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, Weapon Sciences Directorate, Redstone Arsenal, AL 35898; IVAN R. MEDVEDEV, Department of Physics, 3640 Colonel Glenn Hwy, Wright State University, Dayton, OH 45435; JENNIFER HOLT, CHRISTOPHER F. NEESE, and FRANK C. DE LUCIA, Department of Physics, 191 Woodruff Ave, Ohio State University, Columbus, OH 43210.
ULTRAFAST STRUCTURAL DYNAMICS OF TERTIARY AMINES UPON ELECTRONIC EXCITATION

XINXIN CHENG, MICHAEL P. MINITTI, SANGHAMITRA DEB, YAO ZHANG, JAMES BUDARZ, PETER M. WEBER, Department of Chemistry, Brown University, Providence, Rhode Island 02912.

ULTRAFAST STRUCTURAL DYNAMICS OF 1,3-CYCLOHEXADIENE: ELECTRONIC STATE DEPENDENCE

CHRISTINE C. BÜHLER, MICHAEL P. MINITTI, SANGHAMITRA DEB, PETER M. WEBER, Department of Chemistry, Brown University, Providence, Rhode Island 02912; JIE BAO, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

Intermission

PHOTOCHEMISTRY OF BENZYLALLENE: PHOTOCHEMICAL PATHWAYS TO NAPHTHALENE

JOSHUA A. SEBREE, NATHAN KIDWELL, TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN 47907; ALEX NOLAN, ROBERT MCMAHON, Department of Chemistry, University of Wisconsin, Madison WI 53706; TALITHA SELBY, Department of Chemistry, University of Wisconsin Washington County, West Bend, WI 53095; MAREK ZGIERSKI, National Research Council Canada, Ottawa, ON.

BIMOLECULAR REACTIONS OF A DIFFERENT COLOR: CH₃D + CHLORINE WITH VARIED PHOTOLYSIS WAVELENGTHS

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

COMPARATIVE TORSION-INVERSION DYNAMICS FOR CH₃CH₂⁺, CH₃OH⁺ AND CH₃NH₂

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

STATE-TO-STATE ROTATIONAL AND VIBRATIONAL ENERGY TRANSFERS FOLLOWING VIBRATIONAL EXCITATION OF (101000) AND (011200) IN THE GROUND ELECTRONIC STATE OF ACETYLENE

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

VIBRATIONAL PREDISSOCIATION DYNAMICS OF THE (H₂O)₂ DIMER

L. C. CH'NG, B. E. ROCHER, A. K. MOLLNER, and H. REISLER, Department of Chemistry, University of Southern California, Los Angeles, CA, 90089.

DETERMINATION OF THE DISSOCIATION ENERGY OF AMMONIA DIMER: A VIBRATIONAL PREDISSOCIATION STUDY

AMANDA S. CASE, CORNELIA G. HEID, SCOTT H. KABLE, and F. FLEMING CRIM, Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706.
TC. MICROWAVE
TUESDAY, JUNE 21, 2011 – 8:30 am
Room: 1000 McPHERSON LAB

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

TC01 10 min 8:30
EASY-GOING ON-SPECTROMETER OPTIMISATION OF PHASE MODULATED HOMONUCLEAR DECOUPLING SEQUENCES IN SOLID-STATE NMR

TC02 15 min 8:42
QUANTUM-CHEMICAL CALCULATIONS OF SPECTROSCOPIC PARAMETERS FOR ROTATIONAL SPECTROSCOPY: THE NEED OF THE INTERPLAY BETWEEN EXPERIMENT AND THEORY
CRISTINA PUZZARINI, Dipartimento di Chimica "G. Ciamician", Università di Bologna, I-40126 Bologna, Italy.

TC03 15 min 8:59
ROTATIONAL SPECTRUM OF CH₂FI FROM 5 GHZ UP TO 1 THZ: ACCURATE SPECTROSCOPIC AND HYPERFINE PARAMETERS
CRISTINA PUZZARINI, GABRIELE CAZZOLI, Dipartimento di Chimica "G. Ciamician", Università di Bologna, I-40126 Bologna, Italy; JUAN CARLOS LÓPEZ, JOSÉ LUIS ALONSO, Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47005, Valladolid, Spain; AGOSTINO BALDACCI, ALESSANDRO BALDAN, Dipartimento di Chimica Fisica, Università “Ca’ Foscari” Venezia, D.D. 2137, I-30123 Venezia, Italy; STELLA STOPKOWICZ, LAN CHENG, JÜRGEN GAUSS, Institut für Physikalische Chemie, Universität Mainz, D-55099 Mainz, Germany.

TC04 15 min 9:16
ANALYSIS OF THE ROTATIONAL SPECTRUM OF HDO IN ITS \( v_2 = 0 \) AND 1 VIBRATIONAL STATES UP TO 2.8 THz
HOLGER S. P. MÜLLER, S. BRÜNKEN, C. P. ENDRES, F. LEWEN, I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany; J. C. PEARSON, S. YU, B. J. DROUIN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA; H. MÄDER, Institut für Physikalische Chemie, Christian-Albrechts-Universität, 24098 Kiel, Germany.

TC05 15 min 9:33
ROTATIONAL SPECTROSCOPY OF HD\(^{18}\)O
JOHN C. PEARSON\(^a\), SHANSHAN YU, HARSHAL GUPTA and BRIAN J. DROUIN, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109.

\(^a\)A part of this work was performed at the Jet Propulsion Laboratory, California Institute of Technology under contract with the National Aeronautics and Space Administration. Copyright 2010 © California Institute of Technology. All rights reserved.
CHIRPED-PULSE TERAHERTZ SPECTROSCOPY FOR BROADBAND TRACE GAS SENSING

EYAL GERECHT, KEVIN O. DOUGLASS, DAVID F. PLUSQUELLIC, NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY, OPTICAL TECHNOLOGY DIVISION, GAITHERSBURG, MD 20899.

Intermission

VIBRATIONAL POPULATION DISTRIBUTION IN FORMALDEHYDE EXPANDING FROM CHEN PYROLYSIS NOZZLE MEASURED BY CHIRPED PULSE MILLIMETER WAVE SPECTROSCOPY

KIRILL KUYANOV-PROZUMENT, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139; ANGAYLE VASILIOU, Department of Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, CO 80309; G. BARRATT PARK, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139; JOHN S. MUENTER, Department of Chemistry, University of Rochester, Rochester, NY 14627; JOHN F. STANTON, Department of Chemistry, University of Texas, Austin, TX 78712; G. BARNEY ELLISON, Department of Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, CO 80309; ROBERT W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

THE MILLIMETER/SUBMILLIMETER SPECTRUM OF METHYLPHOSPHINE, CH$_3$PH$_2$ ($\tilde{X}^1A$)

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.

FOURIER TRANSFORM MICROWAVE SPECTRUM OF THE FeCN RADICAL ($\tilde{X}^4\Delta_i$) AND CONFIRMATION OF THE GROUND ELECTRONIC STATE

D. T. HALFEN, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721; M. A. FLORY, CNA, Frankfort, KY; B. J. HARRIS, and L. M. ZIURYS, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.

THE PURE ROTATIONAL SPECTRUM OF THE ZnSH RADICAL ($\tilde{X}^2A'$)

MATTHEW P. BUCCHINO, GILLES R. ADANDE and LUCY M. ZIURYS, Department of Chemistry and Biochemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, Arizona 85721.

HYPERFINE SPLITTING AND ROTATIONAL ANALYSIS OF THE DIATOMIC MOLECULE ZINC MONOSULFIDE, ZnS.$^a$

DANIEL J. FROHMAN, G. S. GRUBBS II, and STEWART E. NOVICK, Department of Chemistry, Wesleyan University, Hall-Atwater Laboratories, 52 Lawn Avenue, Middletown, CT 06459-0180.

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$^a$Support from CHE-1011214
CAVITY AND CHIRPED PULSE ROTATIONAL SPECTRUM OF THE LASER ABLATION SYNTHESIZED, OPEN-SHELL MOLECULE TIN MONOCHLORIDE, SnCl \(^a\)

G. S. GRUBBS II, DANIEL J. FROHMAN, STEWART E. NOVICK. Department of Chemistry, Wesleyan University, Hall-Atwater Laboratories, 52 Lawn Avenue, Middletown, CT 06459-0180; and S. A. COOKE, Department of Chemistry, University of North Texas, 1155 Union Circle # 305070, Denton, TX 76203-5017.

\(^a\)Support from CHE-1011214
TD. ELECTRONIC
TUESDAY, JUNE 21, 2011 – 8:30 am
Room: 1015 McPherson Lab

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

TD01 15 min 8:30
SPECTROSCOPIC CHARACTERIZATION OF $\text{Be}_2^+ \ X^2\Sigma_u^+$ AND THE IONIZATION ENERGY OF $\text{Be}_2$

I. O. ANTONOV, B. J. BARKER, V. E. BONDYBEY, M. C. HEAVEN, Department of Chemistry, Emory University, Atlanta, GA 30322.

TD02 15 min 8:47
FOURIER TRANSFORM EMISSION SPECTROSCOPY OF THE $B^2\Sigma^+ - X^2\Sigma^+$ (VIOLET) SYSTEM OF $^{13}\text{C}^{14}\text{N}$

R. S. RAM and P. F. BERNATH, Department of Chemistry, University of York, Heslington, York YO10 5DD.

TD03 15 min 9:04
FOURIER TRANSFORM EMISSION SPECTROSCOPY OF THE $E^2\Pi - X^2\Sigma^+$ TRANSITION OF CaH AND CaD

R. S. RAM, K. TERESZCHUK and P. F. BERNATH, Department of Chemistry, University of York, Heslington, York YO10 5DD, UK; I. E. GORDON, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138, USA; K. A. WALKER, Department of Physics, University of Toronto, Toronto, Ont., M5S 1A7, Canada.

TD04 15 min 9:21
JET-COOLED LASER-INDUCED FLUORESCENCE SPECTROSCOPY OF LARGE SECONDARY ALKOXY RADICALS

JINJUN LIU, MING-WEI CHEN, TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, the Ohio State University, 120 W. 18th Ave., Columbus, Ohio 43210; W. L. MEERTS, Radboud University, Institute for Molecules and Materials, Heyendaalseweg 135, NL-6525 AJ Nijmegen, The Netherlands.

TD05 15 min 9:38
HIGH RESOLUTION LASER SPECTROSCOPY OF SrOCH$_3$

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, L. E. DOWNIE, W. S. HOPKINS, 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.

**Intermission**

TD06 15 min 10:15
DEVELOPMENT OF BROAD RANGE SCAN CAPABILITIES WITH JET COOLED CAVITY RINGDOWN SPECTROSCOPY

TERRANCE J. CODD, MING-WEI CHEN and TERRY A. MILLER, Laser Spectroscopy Facility, The Ohio State University, Columbus, Ohio 43210.
THE JET-COOLED HIGH RESOLUTION $\tilde{A}^2E' - \tilde{X}^2A'_2$ VIBRONIC BANDS OF NO$_3$

MING-WEI CHEN, TERRANCE J. CODD, GABRIEL M. P. JUST, 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, Berkeley, CA 94720

CAVITY RINGDOWN SPECTROSCOPY AND KINETICS OF HO$_2$+HCHO: DETECTION OF THE $\nu_1$ AND $\tilde{A} - \tilde{X}$ BANDS OF HOCH$_2$OO

MATTHEW K. SPRAGUE, MITCHIO OKUMURA, California Institute of Technology, Division of Chemistry, MC 127-72, Pasadena, CA 91125; and STANLEY P. SANDER, Jet Propulsion Laboratory, California Institute of Technology, MS 183-901, Pasadena, CA 91109.

*Support from the NDSEG Fellowship, California Air Resources Board Contracts 03-333 and 07-730, and NASA Upper Atmosphere Research Program Grants NAG5-11657, NNG06GD88G and NNX09AE21G are gratefully acknowledged

CAVITY RINGDOWN SPECTROSCOPY AND KINETICS OF BUTOXY ISOMERIZATION: DETECTION OF THE $\tilde{A} - \tilde{X}$ BAND OF HOC$_4$H$_8$OO

MATTHEW K. SPRAGUE, MITCHIO OKUMURA, California Institute of Technology, Division of Chemistry, MC 127-72, Pasadena, CA 91125; and STANLEY P. SANDER, Jet Propulsion Laboratory, California Institute of Technology, MS 183-901, Pasadena, CA 91109.

*Support from the NDSEG Fellowship, California Air Resources Board Contracts 03-333 and 07-730, and NASA Upper Atmosphere Research Program Grants NAG5-11657, NNG06GD88G and NNX09AE21G are gratefully acknowledged

STUDY OF PHENYLACETYLENE BY CA VITY RING-DOWN SPECTROSCOPY

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

*also: Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973

SPECTROSCOPY AND IONIZATION THRESHOLDS OF ISOELECTRONIC 1-PHENYLALLYL AND BENZYLALLYL-LENYL RESONANCE STABILIZED RADICALS

JOSHUA A. SEBREE, NATHAN KIDWELL, EVAN BUCHANAN, TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN 47907; MAREK ZGIERSKI, National Research Council Canada, Ottawa, ON.
TE. ATMOSPHERIC SPECIES
TUESDAY, JUNE 21, 2011 – 8:30 am
Room: 2015 McPHERSON LAB

Chair: VINCENT BOUDON, CNRS - Universite de Bourgogne, Dijon, France

TE01 15 min 8:30
LINE PARAMETERS OF CARBON DIOXIDE IN THE 4850 CM$^{-1}$ REGION

D. CHRIS BENNER, V. MALATHY DEVI, EMILY NUGENT, Department of Physics, College of William and Mary, Williamsburg, VA 23187-8795; KEEYON SUNG, LINDA R. BROWN, CHARLES E. MILLER, ROBERT A. TOTH, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109, U.S.A.

TE02 15 min 8:47
TOWARDS AN ACCURATE INFRARED LINELIST FOR CO$_2$ AND ISOTOPOLOGUES

TIMOTHY J. LEE, MS 245-1, NASA Ames Research Center, Moffett Field, CA, 94035; XINCHUAN HUANG, SETI Institute, 189 Bernardo Ave, Suite 100, Mountain View, CA, 94043; DAVID W. SCHWENKE, MS T27B-1, NASA Ames Research Center, Moffett Field, CA, 94035; and SERGEY TASHKUN, Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, SB, Russian Academy of Science, 634055, Tomsk, Russia.

TE03 15 min 9:04
SELF- AND AIR-BROADENING OF $^{12}$C$^{16}$O, $^{13}$C$^{16}$O AND $^{12}$C$^{18}$O AT 2.3 $\mu$m


TE04 15 min 9:21
MEASUREMENTS OF LINE POSITIONS AND INTENSITIES OF $^{14}$NH$_3$ IN THE 1.5 $\mu$m REGION

KEEYON SUNG, LINDA R. BROWN, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109, U.S.A.; XINCHUAN HUANG, SETI Institute, Mountain View, CA 94043, U.S.A.; DAVID W. SCHWENKE, TIMOTHY J. LEE, NASA Ames Research Center, Moffett Field, CA, 94035, U.S.A.

TE05 15 min 9:38
THE 5-0 OVERTONE BAND OF HCl BY INTRACA VITY LASER ABSORPTION SPECTROSCOPY

JAMES J. O’BRIEN, STEVEN A. RYAN, Department of Chemistry and Biochemistry, University of Missouri, St Louis, MO 63121-4499; LEAH C. O’BRIEN, Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026-1632.

Intermission
FREQUENCY COMB-REFERENCED MEASUREMENTS OF SELF- AND NITROGEN-PERTURBED LINE SHAPES IN THE $\nu_1 + \nu_3$ BAND OF ACETYLENE

MATTHEW J. CICH, GARY V. LOPEZ, TREvor J. SEARS*, Department of Chemistry, Stony Brook University, Stony Brook, New York 11794; C. P. MCRAVEN, Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973; A. W. MANTZ, Department of Physics, Astronomy, and Astrophysics, Connecticut College, New London, CT 06320; and DANIEL HURTMANS, Service de Chimie Quantique et de Photophysique(Atoms, Molecules et Atmospheres), Universite Libre de Bruxelles, Bruxelles, Belgium B-10050.

*also: Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973

TEMPERATURE DEPENDENCE OF SELF- and NITROGEN-GAS LINE SHAPE PERTURBATIONS IN THE $\nu_1 + \nu_3$ BAND OF ACETYLENE

MATTHEW J. CICH, GARY V. LOPEZ, TREvor J. SEARS*, Department of Chemistry, Stony Brook University, Stony Brook, New York 11794; C. P. MCRAVEN, Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973; A. W. MANTZ, Department of Physics, Astronomy, and Astrophysics, Connecticut College, New London, CT 06320; and DANIEL HURTMANS, Service de Chimie Quantique et de Photophysique(Atoms, Molecules et Atmospheres), Universite Libre de Bruxelles, Bruxelles, Belgium B-10050.

*also: Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973

REVISION OF SPECTRAL PARAMETERS FOR THE B- AND $\gamma$-BANDS OF OXYGEN AND THEIR VALIDATION USING ATMOSPHERIC SPECTRA WITH THE SUN AS SOURCE

I. E. GORDON, L. S. ROTHMAN, Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge MA 02138, USA; G. C. TOON, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA.

ROTATIONAL AND HYPERFINE ANALYSIS OF THE $a_1 \Delta_g \leftarrow X_3^{3\Sigma_g}$ BAND OF $^{17}$O-CONTAINING ISOTOPOLOGUES OF OXYGEN MEASURED BY CRDS AT ROOM AND LIQUID NITROGEN TEMPERATURES

O. M. LESHCHEHISHINA, S. KASSI, Université de Grenoble, CNRS UMR 5588, LIPHY, 38041 Grenoble, France; I. E. GORDON, Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge MA 02138-1516, USA; S. YU, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA; A. CAMPARGUE, Université de Grenoble, CNRS UMR 5588, LIPHY, 38041 Grenoble, France.

A GLOBAL FIT OF THE $X^{3\Sigma_g}, a_1 \Delta_g, b_1^{1\Sigma_g}+$ AND $B^{3\Sigma_u}$ STATES OF THE SIX ISOTOPOLOGUES OF OXYGEN

SHANSAN YU, CHARLES E. MILLER AND BRIAN J. DROUIN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109; HOLGER S.P. MÜLLER, I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany.

NEW HIGH RESOLUTION OZONE ABSORPTION CROSS SECTIONS

ANNA SERDYUCHENKO, VICTOR GORSHCHEV, MARK WEBER, and JOHN P. BURROWS, Institute for Environmental Physics, University of Bremen, Otto-Hahn Allee 1, D-28359 Bremen, Germany.
LINE MIXING IN ATMOSPHERIC OZONE

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

TUESDAY, JUNE 21, 2011 – 1:30 pm
Room: 160 MATH ANNEX

Chair: NATHAN CROCKETT, University of Michigan, Ann Arbor, Michigan

TF01 15 min 1:30
GISBERT WINNEWISER: AN APPRECIATION
ERIC HERBST, Departments of Physics, Chemistry, and Astronomy, The Ohio State University, Columbus OH.

TF02 15 min 1:47
SCRUTINY OF THE CORE OF THE GALACTIC CENTER BY H$_3^+$ AND CO: GCIRS 3 AND GCIRS 1W
M. GOTO, Max-Planck-Institute for Astronomy, Heidelberg, D-69117, Germany; T. USUDA, Subaru Telescope, Hilo, HI 96720; T. R. GEBALLE, Gemini Observatory, Hilo, HI 96720; N. INDRIOLO, B. J. McCALL, Department of Astronomy and Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801; T. OKA, Department of Astronomy and Astrophysics and Department of Chemistry, University of Chicago, Chicago, IL 60637.

TF03 15 min 2:04
INVESTIGATING THE COSMIC-RAY IONIZATION RATE IN THE GALACTIC ISM WITH H$_3^+$ OBSERVATIONS
NICK INDRIOLO, Department of Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801; 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 Astronomy and Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

TF04 10 min 2:21
CAVITY RING DOWN SPECTROSCOPY OF MOLECULAR IONS IN THE 3 $\mu$m REGION
JOSEPH S. GUSS, HARALD VERBRAAK and HAROLD LINNARTZ, Leiden Observatory, University of Leiden, 2300 RA Leiden, The Netherlands.

TF05 15 min 2:33
SUBMILLIMETER-WAVE ROTATIONAL SPECTROSCOPY OF H$_2$F$^+$
R. FUJIMORI, K. KAWAGUCHI, Department of Chemistry, Faculty of Science, Okayama University, 3-1-1, Tsushima-Naka, Okayama 700-8530, Japan; T. AMANO, Department of Chemistry and Department of Physics and Astronomy, University of Waterloo, 200 University Avenue West, Waterloo, ON N2L 3G1, Canada.

TF06 15 min 2:50
DETECTION OF FeCN (X$^4\Delta_i$) IN THE CIRCUMSTELLAR ENVELOPE OF IRC+10216
L. N. ZACK, D. T. HALFEN, and L. M. ZIURYS, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ, 85721.
Intermission

TF07 15 min 3:07
THE QUEST FOR COMPLEX MOLECULES IN SPACE. SEARCHES FOR CYANIDES RELATED TO n-PROPYL CYANIDE IN SGR B2(N)

HOLGER S. P. MÜLLER, S. SCHLEMMER, I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany; A. BELLOCHE, K. M. MENTEN, MPIfR, 53121 Bonn, Germany; A. COUTENS, A. WALTERS, Université de Toulouse and CNRS, 31028 Toulouse, France; J.-U. GRABOW, Institut für Physikalische Chemie und Elektrochemie, Lehrgebiet A, Universität Hannover, 30167 Hannover, Germany.

TF08 10 min 3:40
WHAT MOLECULAR LINES CAN TELL ABOUT EARLY STAGES OF MASSIVE STARS

TATIANA VASYUNINA, ERIC HERBST, Ohio State University, 191 W. Woodruff Ave., 43210, Columbus, OH, USA; HENDRIK LINZ, THOMAS HENNING, HENRIK BEUTHER, Max Planck Institute for Astronomy (MPIA), Königstuhl 17, D-69117 Heidelberg, Germany; IGOR ZINCHENKO, Institute of Applied Physics of the Russian Academy of Sciences, Ulyanova 46, 603950 Nizhnii Novgorod, Russia; MAXIM VORONKOV, Australia Telescope National Facility, CSIRO Astronomy and Space Science, PO Box 76, Epping, NSW 1710, Australia.

TF09 15 min 3:52
NUCLEAR SPIN OF H3+ IN DIFFUSE MOLECULAR CLOUDS

KYLE N. CRABTREE, NICK INDRIOLO, HOLGER KRECKEL, BRIAN A. TOM,a BENJAMIN J. McCALL, Department of Chemistry, University of Illinois, Urbana, IL 61801, USA.

TF10 15 min 4:09
MOLECULAR ABUNDANCES IN THE DISK OF AN ACTIVE GALACTIC NUCLEUS

N. HARADA, Department of Physics, The Ohio State University, Columbus, OH, U.S.A., 43210; T. A. THOMPSON, Department of Astronomy and Center for Cosmology and Astro-Particle Physics (CCAPP), The Ohio State University, Columbus, OH, U.S.A., 43210; and E. HERBST, Departments of Physics, Astronomy, and Chemistry, The Ohio State University, Columbus, OH, U.S.A., 43210.

TF11 15 min 4:26
A STUDY OF HCO+ AND CS IN PLANETARY NEBULAE

JESSICA L. EDWARDS, L. M. ZIURYS, N. J. WOOLF, Department of Chemistry and Biochemistry, Department of Astronomy, Steward Observatory, The University of Arizona, Tucson, AZ 85721.

TF12 15 min 4:43
THE ARO 1 mm SURVEY OF THE OXYGEN-RICH ENVELOPE OF SUPERGIANT STAR NML CYGNUS

JESSICA L. EDWARDS, L. M. ZIURYS, N. J. WOOLF, Department of Chemistry and Biochemistry, Department of Astronomy, Steward Observatory, The University of Arizona, Tucson, AZ 85721.

TF13 15 min 5:00
WATER COLLISIONS WITH NORMAL AND PARAHYDROGEN

BRIAN J. DROUIN, JOHN C. PEARSON, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099; LAURENT WIESENFELD, ALEXANDRE FAURE, UJF-Grenoble I/CNRS, Institut de Planéétologie et d’Astrophysique de Grenoble (IPAG) UMR 5274, Grenoble, F-38041, France.
TF14 15 min 5:17

LOW TEMPERATURE LINESHAPE OF HYDROGEN DEUTERIDE

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

TF15 15 min 5:34

A QUANTUM CHEMICAL INVESTIGATION OF THE STABILITY AND CHEMISTRY OF THE ANIONS OF CO AND H$_2$CO IN ASTROPHYSICAL ICES

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

TF16 15 min 5:51

WARM AND DIFFUSE GAS AND HIGH IONIZATION RATE NEAR THE GALACTIC CENTER

T. OKA, C. P. MORONG, Department of Astronomy and Astrophysics and Department of Chemistry, University of Chicago, Chicago, IL 60637; T. R. GEBALLE, Gemini Observatory, Hilo, HI 96720; N. INDRILO, B. J. MCCALL, Department of Astronomy and Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801; M. GOTO, Max-Planck-Institute for Astronomy, Heidelberg, D-69117, Germany; T. USUDA, Subaru Telescope, Hilo, HI 96720.
TG01 15 min 1:30
FREQUENCY AND TIME DOMAIN STUDIES OF TOLUENE

ADRIAN M. GARDNER, ALISTAIR M. GREEN, JULIA A. DAVIS, KATHARINE L. REID and TIMOTHY G. WRIGHT, School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom.

TG02 15 min 1:47
HYDROGEN-BOUND COMPLEXES OF TROPOLONE: GATEWAYS FOR THE INTERROGATION OF MULTIPLE PROTON-TRANSFER EVENTS

DEACON J. NEMCHICK, KATHRYN CHEW, JOHN E. WOLFF, and PATRICK H. VACCARO, Department of Chemistry, Yale University, P.O. Box 208017, New Haven, CT 06520-8107 USA.

TG03 15 min 2:04
ROTATION-TUNNELING ANALYSIS OF EXCITED-STATE PROTON TRANSFER IN DEUTERATED TROPOLONE

KATHRYN CHEW, DEACON J. NEMCHICK, JOHN E. WOLFF, and PATRICK H. VACCARO, Department of Chemistry, Yale University, P.O. Box 208107, New Haven, CT 06520-8107 USA.

TG04 15 min 2:21
LASER SPECTROSCOPIC STUDY ON STRUCTURES OF 3n-CROWN-n (n = 4, 5, 6) COMPLEXES WITH PHENOL

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

TG05 15 min 2:38
HIGH RESOLUTION STARK SPECTROSCOPY OF MODEL DONOR-ACCEPTOR AMINOBENZONITRILES IN THE GAS PHASE. a

ADAM J. FLEISHER, CASEY L. CLEMENTS, RYAN G. BIRD, DAVID W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260; LEONARDO ALVAREZ-VALTIERRA, División de Ciencias e Ingenierías, Universidad de Guanajuato, Campus León, León, Gto. 37150, Mexico.

aWork supported by the NSF (CHE-0911117).

TG06 15 min 2:55
ROTATIONALLY RESOLVED ELECTRONIC SPECTROSCOPY OF BIOMOLECULES IN THE GAS PHASE. MELATONIN.

JOHN T. YI, and DAVID W. PRATT, University of Pittsburgh, Department of Chemistry, Pittsburgh, PA 15260, USA; CHRISTIAN BRAND, MIRIAM WOLLENHAUPT, and MICHAEL SCHMITT, Heinrich-Heine-Universität, Institut für Physikalische Chemie I, 40225 Düsseldorf, Germany; W. LEO MEERTS, Radboud University Nijmegen, Institute for Molecules and Materials, Heyendaalseweg 135, NL-6525 AJ Nijmegen, The Netherlands.
VIBRONIC SPECTROSCOPY OF JET-COOLED 1,4-PHENYLENE DIISOCYANIDE

DEEPALE N. MEHTA, ANNA K. GUTBERLET, and TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN 47907.

Intermission

EXCITED STATE DYNAMICS OF 7-AZAINDOLE HOMODIMER IN FROZEN NITROGEN MATRIX

MOITRAYEE MUKHERJEE, BIMAN BANDYOPADHYAY, SHREETAMA KARMAKAR and TAPAS CHAKRABORTY, Physical Chemistry Department, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India.

EXCITED STATE PERTURBATIONS OF 7-AZAINDOLE MEDIATED THROUGH MICRO-SOLVATION.

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

Work supported by NSF (CHE-0911117)

CHIROPTICAL SPECTROSCOPY IN THE VAPOR PHASE

PRIYANKA LAHIRI, BENJAMIN D. LONG, KENNETH B. WIBERG, and PATRICK H. VACCARO, Department of Chemistry, Yale University, P.O. Box 208107, New Haven, CT 06520-8107 USA.

THE ROLE OF $\pi\sigma^*$ STATE IN INTRAMOLECULAR CHARGE TRANSFER OF 4-(DIMETHYLAMINO)-BENZONITRILE AND RELATED MOLECULES

TAKASHIGE FUJIWARA, Department of Physics, The Ohio State University, Columbus OH 43210; MAREK Z. ZGIESKI, Steacie Institute for Molecular Science, National Research Council of Canada, Ottawa, K1A 0R6 CANADA; EDWARD C. LIM, Department of Chemistry and The Center for Laser and Optical Spectroscopy, The University of Akron, Akron OH 44325-3601.

ULTRAFAST DYNAMICS IN NITRO- AND (ORGANOPHOSPHINE)GOLD(I)-POLYCYCLIC AROMATIC HYDROCARBONS

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

EXCITED STATE DYNAMICS IN 2-AMINOPURINE RIBONUCLEOSIDE: FROM FEMTOSECOND TO MICROSECOND TIME SCALE

CHENGWEI WEN, CHRISTIAN REICHARDT, CARLOS E. CRESPO-HERNÁNDEZ, Department of Chemistry and Center for Chemical Dynamics, Case Western Reserve University, 10900 Euclid Ave., Cleveland, Ohio 44106.
TH. MINI-SYMPOSIUM: SPECTROSCOPIC PERTURBATIONS

TUESDAY, JUNE 21, 2011 – 1:30 pm
Room: 1000 McPHERSON LAB

Chair: CAROLINE CHICK JARROLD, Indiana University, Bloomington, Indiana

TH01
Journal of Molecular Spectroscopy Review Lecture
PERTURBATIONS I HAVE KNOWN AND LOVED

ROBERT W. FIELD, Department of Chemistry, MIT, Cambridge, MA.

TH02
VIBRONIC PERTURBATIONS IN THE ELECTRONIC SPECTRUM OF BeC

BEAU J. BARKER, IVAN O. ANTONOV, MICHAEL C. HEAVEN, Department of Chemistry, Emory University, Atlanta, GA 30322; RICHARD DAWES, Department of Chemistry, Missouri University of Science and Technology, Rolla, MO 65409.

TH03
PERTURBATIONS IN THE SPECTRA OF HIGH RYDBERG STATES: CHANNEL INTERACTIONS, STARK AND ZEEMAN EFFECTS

CHRISTA HAASE, MARTIN SCHÄFER, STEPHEN D. HOGAN and FRÉDÉRIC MERKT, Laboratorium für Physikalische Chemie, ETH-Zürich, 8093 Zürich, Switzerland.

TH04
DATA AND ANALYSIS OF SPIN-ORBIT COUPLED $A^1\Sigma_u^+$ AND $b^3\Pi_u$ STATES OF Cs$_2$

ANDREY V. STOLYAROV*, Department of Chemistry, Moscow State University, GSP-2 Leninskie gory 1/3, Moscow 119992, Russia; THOMAS H. BERGEMAN, Department of Physics and Astronomy, State University of New York, Stony Brook, New York 11794-3800.

*Support by RFBR is gratefully acknowledged

TH05
SPECTROSCOPIC SIGNATURES OF ISOMERIZATION IN THE $S_1$ STATE OF C$_2$H$_2$

J. H. BARABAN, A. H. STEEVES, R. W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA; J. F. STANTON, Institute for Theoretical Chemistry, Departments of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712; A. J. MERER, Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan.

TH06
EVIDENCE OF PERTURBATIONS ON THE $S_1$ SURFACE OF ACETYLENE FROM PATTERNS IN STIMULATED EMISSION PUMPING SPECTRA

G. BARRATT PARK, JOSHUA H. BARABAN, ADAM H. STEEVES, and ROBERT W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.
Intermission

TH07 15 min 3:45
THE GERADE RYDBERG STATES OF MOLECULAR HYDROGEN

DANIEL SPRECHER 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.

TH08 15 min 4:02
ROTATIONALLY RESOLVED SPECTROSCOPY OF THE ELECTRONICALLY EXCITED C AND D STATES OF ArXe AND KrXe

LORENA PITICCO, MARTIN SCHÄFER, and FRÉDÉRIC MERKT, ETH Zürich, Laboratorium für Physikalische Chemie, Wolfgang-Pauli-Strasse 10, 8093 Zürich, Switzerland.

TH09 15 min 4:19
ANALYSIS OF STRONGLY PERTURBED \(1^1\Pi - 2^3\Sigma^+ \rightarrow b^3\Pi\) STATES OF THE KRb MOLECULE

J. T. KIM, Department of Photonic Engineering, Chosun University, Gwangju, 501-759, Korea; Y. LEE, Department of Chemistry, Mokpo National University, Jeonnam 534-729, Korea; B. KIM, Department of Chemistry, KAIST, Daejeon, 305-701, Korea; D. WANG, Department of Physics, The Chinese University of Hong Kong, Shatin, Hong Kong; W. C. STWALLEY, P. L. GOULD, and E. E. EYLER, Department of Physics, University of Connecticut, Storrs, CT 06269, USA.

TH10 15 min 4:36
OBSERVATION OF THE SYSTEM \((1)^{1}\Sigma^+ - (1)^{3}\Pi_u\) of SR\(_2\) BY FOURIER TRANSFORM SPECTROSCOPY AND ITS ANALYSIS

A. STEIN, H. KNÖCKEL, and E. TIEMANN, Institut für Quantenoptik, Leibniz Universität Hannover, Welfengarten 1, 30167 Hannover, Germany.

TH11 15 min 4:53
A NEW ANALYSIS OF A VERY OLD SPECTRUM: THE HIGHLY PERTURBED \(^A2\Pi_i - ^X2\Pi_i\) BAND SYSTEM OF THE CHLORINE CATION (Cl\(_2^+\))

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

TH12 15 min 5:10
PROBING THE ELECTRONIC STRUCTURE OF THE NICKEL MONOHALIDES: SPECTROSCOPY OF THE LOW-LYING ELECTRONIC STATES OF NiX (X=Cl, Br, I)

LLOYD MUZANGWA, VICTORIA AYLES, SILVER NYAMBO AND SCOTT A. REID, Department of Chemistry, Marquette University, Milwaukee, WI 53233.

TH13 15 min 5:27
LASER-INDUCED FLUORESCENCE SPECTROSCOPY ON ROTATIONAL DISTRIBUTION OF HfF PHOTOIONS

MATT GRAU, HUANQIAN LOH, TYLER YAHN, RUSSELL STUTZ, JILA, NIST and University of Colorado, and Department of Physics, University of Colorado, Boulder, Colorado 80309-0440; ROBERT W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139; and ERIC A. CORNELL, JILA, NIST and University of Colorado, and Department of Physics, University of Colorado, Boulder, Colorado 80309-0440.
PERTURBATIONS IN THE GROUND ELECTRONIC STATE ROTATIONAL SPECTRUM OF TRANSITION-METAL CONTAINING MOLECULES

D. T. HALFEN, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721; R. W. FIELD, Department of Chemistry, MIT, Cambridge, MA 02139; and L. M. ZIURYS, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.
TI01 15 min 1:30
INFRARED SPECTRA OF COMPLEXES CONTAINING ACETYLENE-d2

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

TI02 15 min 1:47
HIGH RESOLUTION OVERTONE SPECTROSCOPY OF ACETYLENE VAN DER WAALS COMPLEXES


TI03 10 min 2:04
HIGH RESOLUTION OVERTONE SPECTROSCOPY OF THE ACETYLENE VAN DER WAALS DIMER, \( ^{12}(C_2H_2)_2 \)

K. DIDRICHE, C. LAUZIN, T. FOLDES, D. GOLEBIOWSKI, 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; C. LEFORESTIER, ACTMM-CC 15.01, Institut Charles Gerhardt, 34095 Montpellier, France.

TI04 15 min 2:16
THE WEAKLY–BOUND CO\(_2\)–ACETYLENE COMPLEX: FUNDAMENTAL AND TORSIONAL COMBINATION BAND IN THE CO\(_2\) \( \nu_3 \) REGION

C. LAUZIN, Laboratoire de Chimie quantique et Photophysique, CP160/09 Faculté des Sciences, Université Libre de Bruxelles (U.L.B.), Ave. Roosevelt, 50 B-1050 Brussels, Belgium; J. NOROOZ OLIAEE, M. REZAEI, N. MOAZZEN-AHMADI, Department of Physics and Astronomy, University of Calgary, Calgary, AB T2N 1N4, Canada.

TI05 15 min 2:33
HIGH RESOLUTION INFRARED AND MICROWAVE SPECTRA OF NH\(_3\)-HCCH AND NH\(_3\)-OCS COMPLEXES: STUDIES OF WEAK C-H \( \cdots \) N HYDROGEN BOND AND ELECTRIC MULT POLE INTERACTIONS

XUNCHEN LIU, YUNJIE XU, Department of Chemistry, University of Alberta, Edmonton, Canada, T6G 2G2.

TI06 15 min 2:50
INFRARED SPECTRA OF WATER BENDING BANDS OF PROPYLENE OXIDE–W A T ER COMPLEXES: SEQUENTIAL SOLVATION OF A CHIRAL MOLECULE IN WATER

XUNCHEN LIU, YUNJIE XU, Department of Chemistry, University of Alberta, Edmonton, Canada, T6G 2G2.
Intermission

**TI07**  
FIRST INFRARED SPECTRA OF CN-RARE GAS AND CN-H\textsubscript{2}/D\textsubscript{2} COMPLEXES VIA IR-UV FLUORESCENCE DEPLETION SPECTROSCOPY\textsuperscript{*}

BRIDGET A. O’DONNELL, MELODIE TING, JOSEPH M. BEAMES, and MARSHA I. LESTER, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323.

\textsuperscript{*}Research is supported by the Chemistry Division of the National Science Foundation

**TI08**  
CARBON DIOXIDE CLUSTERS: (CO\textsubscript{2})\textsubscript{6} TO (CO\textsubscript{2})\textsubscript{13}

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

**TI09**  
THEORETICAL AND EXPERIMENTAL STUDY OF THE ROVIBRATIONAL SPECTRA OF CO\textsubscript{2}-(para-H\textsubscript{2})-He TRIMERS

HUI LI, Institute of Theoretical Chemistry, State Key Lab. of Theoretical & Computational Chemistry, Jilin Univ., 2519 Jiefang Rd, Changchun 130023, P.R.China; Chemistry Dept., Univ. of Waterloo, Waterloo, Ontario N2L 3G1, Canada; ROBERT J. LE ROY, PIERRE-NICHOLAS ROY, Chemistry Dept., Univ. of Waterloo, Waterloo, Ontario N2L 3G1, Canada; A. R. W. McKELLAR, Steacie Institute for Molecular Sciences, NRCC, Ottawa, Ontario K1A 0R6, Canada.

**TI10**  
SPECTROSCOPIC OBSERVATION OF CS\textsubscript{2} DIMER

M. REZAEI, J. NOROOZ OLIAEE, 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.

**TI11**  
INFRARED SPECTRA OF CS\textsubscript{2} TRIMER: OBSERVATION OF AN ISOMER WITH D\textsubscript{3} SYMMETRY

M. REZAEI, J. NOROOZ OLIAEE, 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.

**TI12**  
INFRARED SPECTRA OF He–CS\textsubscript{2}, Ne–CS\textsubscript{2}, AND Ar–CS\textsubscript{2}

F. MIVEHVAR, J. NOROOZ OLIAEE, N. MOAZZEN-AHMADI, Department of Physics and Astronomy, University of Calgary, Calgary, AB T2N 1N4, Canada.
TJ01
A SEMICLASSICAL DIRECT POTENTIAL FITTING SCHEME FOR DIATOMICS
J. TELLINGHUISEN, Department of Chemistry, Vanderbilt University, Nashville, TN 37235.

TJ02
UNEXPECTED PROPERTIES OF THE MORSE OSCILLATOR
ANNE B. McCOY, Department of Chemistry, The Ohio State University, Columbus, OH 43210.

TJ03
IMPROVED DIABATIC MODEL FOR VIBRONIC COUPLING IN THE GROUND ELECTRONIC STATE OF NO₃
J.F. STANTON, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712.

TJ04
EFFECT OF JAHN-TELLER AND SPIN-ORBIT COUPLING ON $\tilde{X}^2E$ INFRARED SPECTRUM OF $CH_3O$
JAYASHREE NAGESH and EDWIN L. SIBERT III, Department of Chemistry and Theoretical Chemistry Institute, University of Wisconsin-Madison, WI 53706.

TJ05
VIBRATIONAL DYNAMICS AROUND THE CONICAL INTERSECTION RESULTING FROM THE $\tilde{A} \rightarrow \tilde{X}$ LASER INDUCED FLUORESCENCE OF THE METHOXY (CH₃O) RADICAL
JAYASHREE NAGESH and EDWIN L. SIBERT III, Department of Chemistry and Theoretical Chemistry Institute, University of Wisconsin-Madison, WI 53706.

TJ06
BREAKING THE SYMMETRY IN JAHN-TELLER ACTIVE MOLECULES BY ASYMMETRIC ISOTOPIC SUBSTITUTION: SPLITTING THE ZERO-POINT VIBRONIC LEVEL.
DMITRY G. MELNIK, JINJUN LIU, TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210; ROBERT F. CURL, Department of Chemistry and Rice Quantum Institute, Rice University, Houston, Texas 77005.

TJ07
AN ALGEBRAIC METHOD FOR EXPLORING QUANTUM MONODROMY AND QUANTUM PHASE TRANSITIONS IN NON-RIGID MOLECULES
D. LARESE, Department of Chemistry, Yale University, New Haven CT 06520-8107, USA; F. IACHELLO, Center for Theoretical Physics, Yale University, New Haven CT 06520-8120, USA.
VIBRATIONALLY AVERAGED LONG-RANGE MOLECULE-MOLECULE DISPERSION COEFFICIENTS FROM COUPLED-CLUSTER CALCULATIONS

MATTHEW SCHMIDT and MARCEL NOOIJEN, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

Intermission

EXOMOL: MOLECULAR LINE LISTS FOR EXOPLANET AND OTHER ATMOSPHERES

J. TENNYSON, R. J. BARBER, A. AZZAM, M. DOWN, and C. HILL, Department of Physics and Astronomy, University College London, London, WC1E 6BT, UK; S. N. YURCHENKO, Technische Universität Dresden, Physikalische Chemie, D-01062 Dresden, Germany.

USING DIFFUSION MONTE CARLO TO PROBE THE ROTATIONALLY EXCITED STATES OF H$_3^+$ AND ITS ISOTOPOLOGUES

BETHANY A. WELLEN, ANDREW S. PETIT, and ANNE B. McCOY, Department of Chemistry, The Ohio State University, Columbus, OH 43210.

COMPUTATIONAL HIGH-FREQUENCY OVERTONE SPECTRA OF THE WATER AMMONIA COMPLEX

ELINA SÄLLI and LAURI HALONEN, Laboratory of Physical Chemistry, University of Helsinki, Finland (email to elina.salli@helsinki.fi).


TEEMU SALMI, LAURI HALONEN, Laboratory of Physical Chemistry, P.O. Box 55 (A.I. Virtasen aukio 1), FIN-00014 University of Helsinki, Finland.

COLLISION INDUCED VELOCITY CHANGES FROM MOLECULAR DYNAMIC SIMULATIONS. APPLICATION TO THE SPECTRAL SHAPE OF THE Q(1) RAMAN LINES OF H$_2$/H$_2$ TRAN and J.M. HARTMANN, Laboratoire Interuniversitaire des Systemes Atmospheriques, Universite paris Est Creteil et Universite paris Diderot, 94010 Creteil Cedex, France.

EFFECTIVE POTENTIAL APPROACH TO THE SIMULATION OF LARGE PARA-HYDROGEN CLUSTERS AND DROPLETS

JING YANG and PIERRE-NICHOLAS ROY, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.
TJ15 15 min 5:32
SIMULATION STUDIES OF THE VIBRATIONAL DYNAMICS OF \textit{para}-HYDROGEN CLUSTERS

\textsc{Nabil F. Faruk, Jing Yang, Robert J. Le Roy, Pierre-Nicholas Roy, Department of Chemistry,}
\textit{University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.}

TJ16 15 min 5:49
MIXED CLUSTERS OF H$_2$ AND H$_2$O: INSIGHTS FROM THEORY AND SIMULATIONS

\textsc{Tao Zeng, Hui Li, Robert J. Le Roy, Pierre-Nicholas Roy, Department of Chemistry, University of}
\textit{Waterloo, Waterloo, Ontario N2L 3G1, Canada.}
WA. PLENARY

WEDNESDAY, JUNE 22, 2011 – 8:30 am

Room: AUDITORIUM, INDEPENDENCE HALL

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

WA01 40 min 8:30
THE ATMOSPHERIC CHEMISTRY EXPERIMENT, ACE: LATEST RESULTS

P. F. BERNATH, Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK.

WA02 40 min 9:15
CHASING NONEXISTENT COMPOUNDS WITH LASERS: ELECTRONIC SPECTROSCOPY OF MAIN GROUP TRANSIENT MOLECULES, FREE RADICALS, AND IONS

DENNIS J. CLOUTHIER, Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.

Intermission

WA03 40 min 10:20
WATCHING CONFORMATIONS OF BIOMOLECULES: A MICROWAVE SPECTROSCOPY APPROACH


WA04 40 min 11:05
POLAR MOLECULES IN THE QUANTUM REGIME

DEBORAH S. JIN, JUN YE, JILA, NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY AND UNIVERSITY OF COLORADO, BOULDER, CO 80309-0440, USA.
WF01 15 min 1:30
INTERSTELLAR NITRILE CHEMISTRY AS REVEALED BY CHIRPED-PULSE FTMW SPECTROSCOPY

DANIEL P. ZALESKI, JUSTIN L. NEILL, MATT T. MUCKLE, AMANDA L. STEBER, and BROOKS H. PATE, Department of Chemistry, University of Virginia, McCormick Rd., P.O. Box 400319, Charlottesville, VA 22904.; JOANNA F. CORBY, Department of Astronomy, University of Virginia, McCormick Rd., P.O. Box 400325, Charlottesville, VA 22904.; VALERIO LATTANZI and MICHAEL C. MCCARTHY, Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138, and School of Engineering and Applied Sciences, Harvard University, 29 Oxford St., Cambridge MA 02138.; ANTHONY J. REMIJAN, National Radio Astronomy Observatory, 520 Edgemont Rd., Charlottesville, VA 22904-2475.

WF02 15 min 1:47
3-D SUBMILLIMETER SPECTROSCOPY OF ASTROPHYSICAL 'WEEDS' – CONTINUED ANALYSIS

SARAH M. FORTMAN, IVAN R. MEDVEDEV, CHRISTOPHER F. NEESE, and FRANK C. DE LUCIA, Department of Physics, 191 W. Woodruff Ave., The Ohio State University, Columbus, OH 43210-1106 USA.

WF03 10 min 2:04
PERFORMANCE OF THE NEW 0.4 mm RECEIVER (602-720 GHz) AT THE SUB-MILLIMETER TELESCOPE OF THE ARIZONA RADIO OBSERVATORY


WF04 15 min 2:16
HIGHLY ACCURATE QUARTIC FORCE FIELDS, VIBRATIONAL FREQUENCIES, AND SPECTROSCOPIC CONSTANTS FOR CYCLIC AND LINEAR C$_3$H$_3^+$ INCLUDING $^{13}$C AND DEUTERIUM ISOTOPOLOGUES

TIMOTHY J. LEE, MS 245-1, NASA Ames Research Center, Moffett Field, CA, 94035; XINCHUAN HUANG, SETI Institute, 189 Bernardo Ave, Suite 100, Mountain View, CA, 94043; and PETER R. TAYLOR, Victorian Life Sciences Computation Initiative and Department of Chemistry, University of Melbourne, Vic 3010, Australia.

WF05 15 min 2:33
A SEARCH FOR HYDROXYLAMINE (NH$_2$OH) TOWARDS IRC+10216, ORION-S, ORION(KL), SGRB2(N), SGRB2(OH), W51M AND W3(IRS5)

ROBIN L. PULLIAM, ANTHONY J. REMIJAN, National Radio Astronomy Observatory, Charlottesville, VA 22903; JOANNA CORBY, Dept. of Astronomy, Dept. of Chemistry, University of Virginia and National Radio Astronomy Observatory, Charlottesville, VA 22903.
A SEARCH FOR INTERSTELLAR CARBON-CHAIN ALCOHOL HC₄OH IN THE STAR FORMING REGION L1527

MITSUNORI ARAKI, Department of Chemistry, Faculty of Science Division I, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo, 162-8601, Japan; SHURO TAKANO, Nobeyama Radio Observatory, 462-2 Nobeyama, Minamimaki, Minamisaku, Nagano, 384-1305, Japan; HIROMICHI YAMABE NAHOIRO KOSHIKAWA, KOICHI TSUKIYAMA, Department of Chemistry, Faculty of Science Division I, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo, 162-8601, Japan; AYA NAKANE, TOSHIKAZU OKABATA YASHI, Department of Chemistry, Faculty of Science, Shizuoka University, 836 Oya, Suruga-ku, Shizuoka 422-8529, Japan; ARISA KUNIMATSU and NOBUHIKO KUZE, Department of Materials and Life Sciences, Faculty of Science and Technology, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo, 102-8554, Japan.

LABORATORY SUBMILLIMETER SPECTROSCOPY AS A PROBE OF METHANOL PHOTODISSOCIATION

JACOB C. LAAS and SUSANNA L. WIDICUS WEAVER, Department of Chemistry, Emory University, Atlanta, GA 30322.

NEW ACETYLENE ¹²C₂H₂ MEASUREMENTS USING SOLEIL SYNCHROTRON

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; O. PIRALI, Synchrotron SOLEIL, L Orme des Merisiers Saint-Aubin, 91192 Gif-sur-Yvette cedex, France.

THE MILLIMETERWAVE SPECTRUM OF n-BUTYL CYANIDE

MATTHIAS H. ORDU, HOLGER S. P. MÜLLER, FRANK LEWEN, STEPHAN SCHLEMMER, I. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, 50937 Köln, Germany; MARC NUÑEZ, and ADAM WALTERS, IRAP: Université de Toulouse, UPS-OMP, CNRS; 9 Av. colonel Roche, BP 44346, 31028 Toulouse cedex 4, France.

ROTATIONALLY RESOLVED SPECTRA OF THE B²Π - X²Π 0₀,₀ AND μ²Σ - μ²Σ 1₁,₁ TRANSITIONS OF C₄H AND C₄D

D. ZHAO, M.A. HADDAD, Institute for Lasers, Life and Biophotonics Amsterdam, De Boelelaan-1081, NL 1081 HV Amsterdam, Netherlands; H. LINNARTZ, Raymond and Beverly Sackler Laboratory for Astrophysics, Leiden Observatory, Leiden University, P.O. Box 9513, NL-2300 RA Leiden, and Institute for Lasers, Life and Biophotonics Amsterdam, De Boelelaan 1081, NL-1081 HV Amsterdam, Netherlands; W. UBACHS, Institute for Lasers, Life and Biophotonics Amsterdam, De Boelelaan-1081, NL 1081 HV Amsterdam, Netherlands.

Intermission
WF11 10 min 4:15

PROSPECTIVE WORK FOR ALMA: THE MILLIMETERWAVE AND SUBMILLIMETERWAVE SPECTRUM OF DEUTERATED GLYCOLALDEHYDE

A. BOUCHEZ, L. MARGULÈS, R. A. MOTIYENKO, Laboratoire PhLAM, CNRS UMR 8523, Université de Lille 1, 59655 Villeneuve d’Ascq Cedex, France; A. WALTERS, S. BOTTELLINI, IRAP, Université de Toulouse, UPS-OMP, CNRS; 9 Av. colonel Roche, BP 44346, 31028 Toulouse Cedex 4, France; C. ECCECARELLI, C. KAHANE, IPAG: Université Joseph Fourier, CNRS, BP 53 F-38041, GRENOBLE Cedex 9; and J.-C. GUILLEMIN, Sciences Chimiques de Rennes, UMR 6226 CNRS-ENSCR, Avenue du Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France.

*Permanent address: IRAP, Université de Toulouse, UPS-OMP, CNRS; 9 Av. colonel Roche, BP 44346, 31028 Toulouse cedex 4, France.

WF12 15 min 4:27

THE MICROWAVE SPECTRUM OF PARTIALLY DEUTERATED SPECIES OF DIMETHYL ETHER*

D. LAUVERGNAT, Laboratoire de Chimie Physique, Bât. 349, CNRS, UMR8000, Université Paris-Sud, Orsay, F-91405, France; L. MARGULÈS, R. A. MOTIYENKO, Laboratoire PhLAM, CNRS/Université des Sciences et Technologies de Lille 1, Bât. P5, 59655 Villeneuve d’Ascq, France; J.-C. GUILLEMIN, Sciences Chimiques de Rennes, UMR6226 CNRS-ENSCR, Avenue du Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France; AND L. H. COUDERT, LISA, CNRS/Universités Paris Est et Paris Diderot, 61 Avenue du Général de Gaulle, 94010 Créteil, France.

*This work is supported by ANR-08-BLAN-0054, ANR-08-BLAN-0225, and by the PCMI French program.

WF13 15 min 4:44

PROSPECTIVE WORK FOR ALMA: THE MILLIMETERWAVE AND SUBMILLIMETERWAVE SPECTRUM OF $^{13}$C-GLYCOLALDEHYDE

IMANE HAYKAL, LAURENT MARGULÈS, THERESE R. HUET, ROMAN MOTIYENKO, Laboratoire PhLAM, UMR8523 CNRS-Université Lille 1, F-59655 Villeneuve d’Ascq Cedex, France; AND J.-C. GUILLEMIN, UMR6226 CNRS-Ecole Nationale Supérieure de Chimie de Rennes, F-35700 Rennes, France.

WF14 15 min 5:01

EXPERIMENTAL ELECTRONIC SPECTROSCOPY OF TWO PAHs: NAPHTHALENE AND 2-METHYL NAPHTHALENE

H. FRIHA, ISMO, CNRS, Université Paris- Sud, Orsay, 91400, France; G. FERAUD, ISMO, CNRS, Université Paris- Sud, Orsay, 91400, France; T. PINO, ISMO, CNRS, Université Paris- Sud, Orsay, 91400, France; PH. BRECHIGNAC, ISMO, CNRS, Université Paris- Sud, Orsay, 91400, France; P. PARNEIX, ISMO, CNRS, Université Paris- Sud, Orsay, 91400, France; Z. DHAOUDI, LSAMA, Faculté des Sciences de Tunis, Campus Universitaire 2092, Manar II, Tunisie; N. JAIDANE, LSAMA, Faculté des Sciences de Tunis, Campus Universitaire 2092, Manar II, Tunisie; H. GALILA, LSAMA, Faculté des Sciences de Tunis, Campus Universitaire 2092, Manar II, Tunisie; T. TROY, School of Chemistry, The University of Sydney, NSW 2006, Australia; T. SCHMIDT, School of Chemistry, The University of Sydney, NSW 2006, Australia.
HIGH RESOLUTION SPECTROSCOPY AND GLOBAL ANALYSIS OF THE TETRADECAD REGION OF METHANE $^{12}$CH$_4$

A. NIKITIN, Institute of Atmospheric Optics, 634055 Tomsk, Russia and Laboratoire GSMA, UMR 6089 CNRS-Université de Reims Champagne Ardenne, Moulin de la Housse BP 1039, Cases 16-17, F-51687 Reims Cedex 2, France; V. BOUDON, C. WENGER, Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 5209 CNRS-Université de Bourgogne, 9, Av. A. Savary, BP 47870, F-21078 Dijon Cedex, France; L. R. BROWN, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California 91109, USA; S. BAUERECKER, Physical Chemistry, ETH Zürich, CH-8093 Zürich, Switzerland and Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, D-38106, Germany; S. ALBERT, M. QUACK, Physical Chemistry, ETH Zürich, CH-8093 Zürich, Switzerland.

LONG PATH- HIGH RESOLUTION SPECTRUM OF METHANE. TOWARDS TITAN’S ATMOSPHERE

LUDOVIC DAUMONT, VLADIMIR TYUTEREV, LAURENCE REGALIA, XAVIER THOMAS, PIERRE VON DER HEYDEN, Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 6089, Université de Reims Champagne-Ardenne, U.F.R. Sciences, B.P. 1039, 51687 Reims Cedex 2, France; ANDREI NIKITIN, Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics, Russian Academy of Sciences, 1, Akademicheskaya Avenue, 634055 Tomsk, Russian Federation; LINDA BROWN, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA.

THE $4\nu_3$ SPECTRAL REGION OF METHANE

D. CHRIS BENNER, V. MALATHY DEVI, JENNIFER HAYS, 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. SPICKLER, C. P. HOUCK, J. A. COAKLEY, KASIE J. HAGA, JUSTIN D. DOLPH, Department of Physics, Bridgewater College, Bridgewater, VA 22812.
WG01 15 min 1:30
APPROXIMATE THEORETICAL MODEL FOR THE FIVE ELECTRONIC STATES ($\Omega = 5/2, 3/2, 3/2, 1/2, 1/2$) ARISING FROM THE GROUND $3d^9$ CONFIGURATION IN NICKEL HALIDE MOLECULES AND FOR ROTATIONAL LEVELS OF THE TWO $\Omega = 1/2$ STATES IN THAT MANIFOLD

JON T. HOUGEN, Optical Technology Division, NIST, Gaithersburg, MD 20899-8441, USA.

WG02 15 min 1:47
OBSERVATION OF $\Omega = 1/2$ STATES IN NiH THROUGH COLLISIONALLY INDUCED FLUORESCENCE

C. RICHARD*, P. CROZET, A. J. ROSS, Université Lyon 1; CNRS; LASIM UMR 5579, 43 Bd du 11 novembre 1918, F-69622 Villeurbanne, France; D. W. TOKARYK, Department of Physics and Center for Laser, Atomic, and Molecular Sciences, University of New Brunswick, Fredericton, Canada E3B 5A3.

*Current address: Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge MA 02138, USA

WG03 15 min 2:04
NEW BANDS OF NICKEL FLUORIDE IN THE NEAR INFRARED BY INTRACAVITY LASER ABSORPTION SPECTROSCOPY

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

WG04 10 min 2:21
INTRACAVITY LASER ABSORPTION SPECTROSCOPY OF PLATINUM FLUORIDE IN THE NEAR INFRARED

LEAH C. O’BRIEN, KAITLIN WOMACK, Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026-1652; JAMES J. O’BRIEN, MEREDITH REDDICK, REBECCA STEINBERG, Department of Chemistry and Biochemistry, University of Missouri, St Louis, MO 63121-4499.

WG05 15 min 2:33
THE ELECTRONIC SPECTRUM AND MOLECULAR STRUCTURE OF HAsO, THE ARSENIC ANALOG OF HNO

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

WG06 15 min 2:50
THE PFI-ZEKE SPECTROSCOPY STUDY OF HIS$^+$ AND THE IONIZATION ENERGY OF HIS

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

WG07 15 min 3:30
THEORETICAL STUDIES OF ELECTRONIC SPECTRA AND BONDING OF AlCl/AlF(X\^1\Sigma^+, a^3\Pi, A^1\Pi) WITH EXCITED STATES EXHIBITING RECOUPLED PAIR BONDING

JEFF LEIDING, DAVID E. WOON and THOM H. DUNNING, JR., Department of Chemistry, University of Illinois at Urbana-Champaign, Box 86-6, CLSL, 600 South Mathews, Urbana IL, 61801.

WG08 15 min 3:47
ELECTRONIC SPECTROSCOPY OF THE 6p ← 6s TRANSITION IN Au-Ne

ADRIAN M. GARDNER, RICHARD J. PLOWRIGHT, CAROLYN D. WITHERS, TIMOTHY G. WRIGHT, School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom; MICHAEL D. MORSE and W. H. BRECKENRIDGE, Department of Chemistry, 315 South 1400 East, Room 2020, University of Utah, Salt Lake City, Utah 84112.

WG09 10 min 4:04
ELECTRONIC TRANSITIONS AND SPIN-ORBIT SPLITTING OF LANTHANUM DIMER

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

WG10 15 min 4:16
LASER INDUCED FLUORESCENCE SPECTROSCOPY OF COBALT MONOBORIDE

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

WG11 15 min 4:33
HIGH RESOLUTION LASER SPECTROSCOPY OF RHODIUM MONOBROMIDE.

A. G. ADAM, T. F. ALLEN, L. E. DOWNIE, and A. D. GRANGER, Chemistry Department, and Centre for Lasers, and Atomic, and Molecular Sciences, University of New Brunswick, Fredericton, NB, E3B 5A3; and C. LINTON, and D. W. TOKARYK, Physics Department, and Centre for Lasers, and Atomic, and Molecular Sciences, University of New Brunswick, Fredericton, NB, E3B 5A3.

WG12 15 min 4:50
THE VISIBLE SPECTRUM OF IRIDIUM MONOHYDRIDE AND MONODEUTERIDE.

A. G. ADAM, and A. D. GRANGER, Chemistry Department, and Centre for Lasers, and Atomic, and Molecular Sciences, University of New Brunswick, Fredericton, NB, E3B 5A3; and C. LINTON, and D. W. TOKARYK, Physics Department, and Centre for Lasers, and Atomic, and Molecular Sciences, University of New Brunswick, Fredericton, NB, E3B 5A3.

WG13 15 min 5:07
THE VISIBLE SPECTRUM OF ZIRCONIUM DIOXIDE, ZrO\textsubscript{2}

ANH LE AND TIMOTHY C. STEIMLE, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287; VARUN GUPTA AND JOHN P. MAIER, Department of Chemistry, University of Basel, Basel, Switzerland.
SEQUENTIAL OXIDATION OF TRANSITION METAL SUBOXIDE CLUSTER ANIONS

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.
<table>
<thead>
<tr>
<th>Session</th>
<th>Title</th>
<th>Presenters</th>
<th>Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>WH01</td>
<td>REASSIGNMENT OF MILLIMETERWAVE SPECTRUM OF THE HCN INTERNAL ROTATION BANDS OF H$_2$-HCN</td>
<td>Kensuke Harada, Risa Yamanaka, and Keiichi Tanaka</td>
<td>Department of Chemistry, Faculty of Sciences, Kyushu University, Fukuoka, 812-8581 JAPAN.</td>
</tr>
<tr>
<td>WH02</td>
<td>MILLIMETERWAVE SPECTROSCOPY OF THE INTERNAL ROTATION BANDS OF Ne-DCN</td>
<td>Naoko Oyamada, Kensuke Harada, and Keiichi Tanaka</td>
<td>Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashiku, Fukuoka, 812-8581 JAPAN.</td>
</tr>
<tr>
<td>WH03</td>
<td>STUDY OF He$_N$-HCN CLUSTERS USING ROTATIONAL SPECTROSCOPY</td>
<td>Steve Dempster, Oleksandr Sukhorukov, Qi-Yi Lei, and Wolfgang Jäger</td>
<td>Department of Chemistry, University of Alberta, Edmonton, Canada T6G 2G2.</td>
</tr>
<tr>
<td>WH04</td>
<td>MICROWAVE SPECTRA AND STRUCTURES OF H$_2$O···AgF</td>
<td>S. L. Stephens, N. R. Walker, D. P. Tew and A. C. Legon</td>
<td>School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K.</td>
</tr>
<tr>
<td>WH05</td>
<td>INTERNAL ROTATION IN CF$_3$I···NH$_3$ AND CF$_3$I···N(CH$_3$)$_3$ PROBED BY CP-FTMW SPECTROSCOPY</td>
<td>N. R. Walker, S. L. Stephens and A. C. Legon</td>
<td>School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K.</td>
</tr>
<tr>
<td>WH06</td>
<td>INTERNAL MOTION EFFECTS IN THE MICROWAVE SPECTRUM OF ARGON-CIS-1,2-DIFLUOROETHYLENE</td>
<td>Helen O. Leung and Mark D. Marshall</td>
<td>Department of Chemistry, Amherst College, P.O. Box 5000, Amherst, MA 01002-5000.</td>
</tr>
<tr>
<td>WH07</td>
<td>THE MICROWAVE SPECTRUM OF ARGON-VINYL CHLORIDE</td>
<td>Helen O. Leung and Mark D. Marshall</td>
<td>Department of Chemistry, Amherst College, P.O. Box 5000, Amherst, MA 01002-5000.</td>
</tr>
</tbody>
</table>
Intermission

WH08 10 min 3:45
HAOGEN BOND AND INTERNAL DYNAMICS IN CClF₃-H₂O

L. EVANGELISTI, G. FENG and W. CAMINATI, Dipartimento di Chimica "G. Ciamici" dell’Università, Via Selmi 2, I-40126 Bologna, Italy; P. ECIIA, E.J. COCINERO and F. CASTANO, Departamento de Química Fisica, Facultad de Ciencia y Tecnologia, Universidad del Pais Vasco (UPV-EHU), Apartado 644, E-48080 Bilbao, Spain.

WH09 15 min 3:57
WEAK C–H⋯O INTERACTIONS AND H₂O INTERNAL ROTATION IN THE HCCIF₂–H₂O AND HCBrF₂–H₂O DIMERS

REBECCA A. PEEBLES, SEAN A. PEEBLES, BRANDON J. BILLS, LENA F. ELMUTI, DANIEL A. OBENCHAIN, AMELIA J. SANDERS, AMANDA L. STEBER, Department of Chemistry, Eastern Illinois University, 600 Lincoln Ave., Charleston, IL 61920; PETER GRONER, Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110; BROOKS H. PATE, JUSTIN L. NEILL, MATT T. MUCKLE, Department of Chemistry, University of Virginia, McCormick Rd., PO Box 400319, Charlottesville, VA 22904.

WH10 15 min 4:14
CHIRPED-PULSE, FTMW SPECTROSCOPY OF THE LACTIC ACID-H₂O SYSTEM

ZBIGNIEW KISIEL, EWA BIAŁKOWSKA-JAWORSKA, Institute of Physics, Polish Academy of Sciences, Al. Lotnikow 32/46, 02-668 Warszawa, Poland; DANIEL P. ZALESKI, JUSTIN L. NEILL, AMANDA L. STEBER, BROOKS H. PATE, Department of Chemistry, University of Virginia, McCormick Rd., Charlottesville, VA 22904-4319.

WH11 15 min 4:31
STRUCTURE STUDY OF THE CHIRAL LACTIDE MOLECULES BY CHIRPED-PULSE FTMW SPECTROCOPY

DANIEL P. ZALESKI, JUSTIN L. NEILL, and BROOKS H. PATE, Department of Chemistry, University of Virginia, McCormick Rd., P.O. Box 400319, Charlottesville, VA 22904; EWA BIAŁKOWSKA-JAWORSKA and ZBIGNIEW KISIEL, Institute of Physics, Polish Academy of Sciences, Al. Lotnikow 32/46, 02-668 Warszawa, Poland.

WH12 15 min 4:48
THE CHIRPED-PULSE AND CAVITY BASED FTMW SPECTROSCOPY OF THE METHYL LACTATE-WATER AND METHYL LACTATE-DEUTERIUM OXIDE DIMERS

JAVIX THOMAS, OLEKSANDR SUKHORUKOV, WOLFGANG JÄGER, YUNJIE XU, Department of Chemistry, University of Alberta, Edmonton, AB, T6G 2G2, Canada.

WH13 15 min 5:05
THE PURE ROTATIONAL SPECTRUM OF PERFLUOROOCTANONITRILE, C₇F₁₅CN, STUDIED USING CAVITY- AND CHIRPED-PULSED FOURIER TRANSFORM MICROWAVE SPECTROSCOPIES

C. T. DEWBERRY, G. S. GRUBBS II, S. A. COOKE, Department of Chemistry, The University of North Texas, 1155 Union Circle, # 305070 Denton, TX 76203-5017, USA; W. C. BAILEY, Chemistry-Physics Department, Kean University, 1000 Morris Avenue, Union, NJ 07080, USA.
EVIDENCE FOR A NON-PLANAR C=CCC STRUCTURE IN HEXAFLUOROISOBUTENE AND HEXAFLUOROACETONE IMINE: A PURE ROTATIONAL SPECTROSCOPIC STUDY

G. S. GRUBBS II, C. T. DEWBERRY, B. E. LONG, S. A. COOKE, Department of Chemistry, The University of North Texas, 1155 Union Circle, # 305070 Denton, TX 76203-5017, USA; W. C. PRINGLE, Department of Chemistry, Wesleyan University, Hall-Atwater Laboratories, 52 Lawn Ave, Middletown, CT 06459-0180.
WI. MINI-SYMPOSIUM: SPECTROSCOPIC PERTURBATIONS

WEDNESDAY, JUNE 22, 2011 – 1:30 pm
Room: 1015 McPherson Lab

Chair: ROBERT W. FIELD, Massachusetts Institute of Technology, Cambridge, Massachusetts

WI01  INVITED TALK  30 min  1:30
INVISIBLE ELECTRONIC STATES AND THEIR DYNAMICS REVEALED BY PERTURBATIONS

ANTHONY J. MERER, Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan.

WI02  15 min  2:05
INTERNAL AND EXTERNAL PERTURBATIONS IN ELECTRONIC SPECTROSCOPY. THE STARK SPECTRUM OF INDOLE-NH₃⁺

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

Work supported by NSF (CHE-0911117).

WI03  15 min  2:22
NOVEL PATTERNS OF TORSION - INVERSION TUNNELING AND TORSION - ROTATION COUPLING IN THE ν₁₁ CH - STRETCH REGION OF CH₂NH₂

MAHESH B DAWADI, SYLVESTRE TWAGIRAYEZU, C. MICHAEL LINDSAY, and DAVID S. PERRY, Department of Chemistry, The University of Akron, OH 44325-3601; LI-HONG XU, Department of Physics, Centre for Laser, Atomic and Molecular Studies (CLAMS) University of New Brunswick, Saint John, New Brunswick, Canada E2L 4L5.

Present address: U.S. Air Force Research Laboratory, 2306 Perimeter Rd, Eglin AFB, FL 32542-5910

WI04  15 min  2:39
EXTENDED PERMUTATION-INVERSION GROUPS FOR SIMULTANEOUS TREATMENT OF THE ROVIBRONIC STATES OF TRANS-ACETYLENE, CIS-ACETYLENE, AND VINYLIDENE

JON T. HOUGEN, Optical Technology Division, NIST, Gaithersburg, MD 20899-8441, MD, USA; ANTHONY J. MERER, Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan 10617 and Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada V6T 1Z1.

WI05  15 min  2:56
THE VISIBLE SPECTRUM OF Si₃

XIUJUAN ZHUANG, TIMOTHY C. STEIMLE, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287; N. REILLY, D. KOKKIN and M. C. McCARTHY, Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts 02138, USA; J. F. STANTON, Chemistry Department and Biochemistry, U. of Texas, Austin, TX 78712, USA; T. D. CRAWFORD and B. FORTENBERRY, Chemistry Department, Virginia Tech, Blacksburg VA 24061, USA; J. P. MAIER, Department of Chemistry, University of Basel, Basel, Switzerland.
WI06

EXPERIMENTAL CHARACTERIZATION OF THE WEAKLY ANISOTROPIC CN $X^2\Sigma^+ + \text{Ne}$ POTENTIAL FROM IR-UV DOUBLE RESONANCE STUDIES OF THE CN-Ne COMPLEX

JOSEPH M. BEAMES, BRIDGET A. O’DONNELL, MELODIE TING, MARSHA I. LESTER, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104; THOMAS A. STEPHENSON, Department of Chemistry and Biochemistry, Swarthmore College, Swarthmore, PA 19081.

*Research is supported by the Chemistry Division of the NSF

Intermission

WI07

TERAHERTZ SPECTROSCOPY OF HIGH $K$ METHANOL TRANSITIONS

JOHN C. PEARSON*, SHANSHAN YU, HARSHAL GUPTA and BRIAN J DROUIN, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena CA 91109.

*A part of this work was performed at the Jet Propulsion Laboratory, California Institute of Technology under contract with the National Aeronautics and Space Administration. Copyright 2010 © California Institute of Technology. All rights reserved.

WI08

SYMmetry dependence of the ro-vibrionic distributions of the ND$_2$ $A^2A_1$ fragments from the photodissociation of the A states of ND$_3$ and ND$_2$H at 193.3 nm

G. DUXBURY, Department of Physics, SUPA, John Anderson Building, University of Strathclyde, 107 Rottenrow, Glasgow G4 0NG, Scotland, UK; J.P. REID, School of Chemistry, University of Bristol, Bristol BS8 ITS.

WI09

VIBRATIONAL COUPLING PATHWAYS IN THE CH STRETCH REGION OF CH$_3$OH AND CH$_3$OD AS REVEALED BY IR AND FTMW-IR SPECTROSCOPIES

SYLVESTRE TWAGIRAYEZU, XIAOLIANG WANG, AND 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; LI-HONG XU, Department of Physics, Centre for Laser, Atomic and Molecular Studies (CLAMS), University of New Brunswick, Saint John, New Brunswick E2L 4L5, Canada.

WI10

CONFORMATION SPECIFIC ELECTRONIC AND INFRARED SPECTROSCOPY OF ISOLATED [2,2,2]-PARATRICYLCLOPHANE AND ITS MONOHYDRATED CLUSTER

EVAN G. BUCHANAN, JACOB C. DEAN, BRETT M. MARSH , and TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN 47907.

WI11

CONFORMATION-SPECIFIC EFFECTS ON INTERNAL MIXING: INFRARED AND ULTRAVIOLET SPECTROSCOPY OF 1,1-DIPHENYLPROPANE

NATHANAEL M. KIDWELL, EVAN G. BUCHANAN, JACOB C. DEAN, and TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN 47907.
WI12  15 min  5:10
OPTICAL PUMPING AND ELECTRON SPIN RESONANCE OF SINGLE $^{87}$Rb ATOMS ON HELIUM NANODROPLETS

MARKUS KOCH, JOHANNES POMS, ALEXANDER VOLK, and WOLFGANG E. ERNST, Institute of Experimental Physics, TU Graz, Petersgasse 16, 8010 Graz, Austria.

WI13  15 min  5:27
HIGHLY EXCITED STATES OF Cs ATOMS ON HELIUM NANODROPLETS

F. LACKNER, M. THEISEN, M. KOCH, and W.E. ERNST, Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria.
WJ. RADICALS AND IONS
WEDNESDAY, JUNE 22, 2011 – 1:30 pm
Room: 2015 McPHERSON LAB

Chair: GARY E. DOUBERLY, University of Georgia, Athens, Georgia

WJ01 15 min 1:30
RECONCILING EXPERIMENT AND THEORY: THE INTERESTING AND UNUSUAL CASE OF THE HOO Radical

VALERIO LATTANZI, M.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 JOHN F. STANTON, Institute for Theoretical Chemistry, Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX 78712, United States.

WJ02 15 min 1:47
FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF THE HOO Radical

VALERIO LATTANZI, M.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 FILIPPO TAMASSIA, Dipartimento di Chimica Fisica e Inorganica, Università di Bologna, V.le Risorgimento 4, I-40136 Bologna, Italy.

WJ03 15 min 2:04
HIGH RESOLUTION INFRARED SPECTROSCOPY OF THE PO2 Radical

MICHAEL A. LAWSON, KRISTIAN J. HOFFMAN and PAUL B. DAVIES, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, U.K.

WJ04 15 min 2:21
SUBMILLIMETER-WAVE ROTATIONAL SPECTRA OF DNC

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

WJ05 15 min 2:38
HIGH RESOLUTION FOURIER TRANSFORM SPECTROSCOPY OF TRANSIENT SPECIES ON THE FAR INFRARED "AILES" BEAMLINE OF SOLEIL SYNCHROTRON.

M. A. MARTIN-DRUMEL*, O. PIRALI*, D. BALCON*, P. BRECHIGNAC, Institut des Sciences Moléculaires d’Orsay (ISMO), CNRS, Université Paris XI, Orsay, France; M. VERVLOET, P. ROY, SOLEIL Synchrotron, AILES beamline, Saint-Aubin, France.

*ALSO AT: SOLEIL SYNCHROTRON, AILES BEAMLINE, SAINT-AUBIN, FRANCE.

WJ06 15 min 2:55
CALCULATION OF THE TRANSITION DIPOLE MOMENT OF THE \( \tilde{A} \leftarrow \tilde{X} \) ELECTRONIC TRANSITION OF THE C2H5O2 FROM THE PEAK ABSORPTION CROSS-SECTION

DMITRY G. MELNIK, PHILLIP S. THOMAS and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210.
ELECTRONIC SPECTROSCOPY OF COBALT-NEON CATION

J. MOSLEY, S. HASBROUCK, and M. A. DUNCAN, Department of Chemistry, University of Georgia, Athens, GA 30602-2556.

Intermission

ROVIBRATIONAL SPECTROSCOPY OF ALUMINUM CARBONYL CLUSTERS IN HELIUM NANODROPLETS


PYROLYSIS OF ACETALDEHYDE: A FLEETING GLIMPSE OF VINYLIDENE

A.J. VASILIOU, K.M. PIECH, G.B. ELLISON, Department of Chemistry, University of Colorado, Boulder, CO, 80303; A. GOLAN, O. KOSTKO, M. AHMED, Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720; D.L. OSBORN, Sandia National Laboratories, Livermore, CA 94551; J.W. DAILY, Department of Mechanical Engineering, University of Colorado, Boulder, CO 80302; M.R. NIMLOS, Center for Renewable Chemical Technologies and Materials, NREL, Golden, CO 80401; and J.F. STANTON, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712.

SPECTROSCOPIC STUDIES OF THE $\tilde{A} \rightarrow \tilde{X}$ ELECTRONIC SPECTRUM REVEAL BOTH THE STRUCTURE AND DYNAMICS OF $\beta$-HYDROXYETHYLPEROXY RADICAL

MING-WEI CHEN, GABRIEL M. P. JUST, TERRANCE J. CODD, TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus OH 43210; W. LEO MEERTS, Radboud University Nijmegen, Institute for Molecules and Materials, Heyendaalseweg 135, NL-6525 AJ Nijmegen, The Netherlands.

a present address: Lawrence Berkeley National Laboratory, Berkeley, CA 94720

OBSERVATION OF THE $\tilde{A} \rightarrow \tilde{X}$ ELECTRONIC TRANSITION OF THE 2-HYDROXYPROPYL PEROXY RADICAL VIA CAVITY RINGDOWN SPECTROSCOPY

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

VIBRATIONAL SPECTRUM OF THE THIOMETHOXY (CH$_3$S) RADICAL INVESTIGATED WITH INFRARED-VACUUM ULTRAVIOLET PHOTOIONIZATION

HUI-LING HAN, LUNG FU, 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.
CAVITY RING-DOWN SPECTROSCOPY OF THE $1^2 B_1 - \tilde{X}^2 A_1$ TRANSITION OF THE PHENYL RADICAL

KEITH FREEL, J. PARK, M. C. LIN, MICHAEL C. HEAVEN, Department of Chemistry, Emory University, Atlanta, GA 30322.
### RA. MINI-SYMPOSIUM: FUNDAMENTAL PHYSICS

**THURSDAY, JUNE 23, 2011 – 8:30 am**

**Room: 160 MATH ANNEX**

**Chair: NEIL SHAFER-RAY, University of Oklahoma, Norman, Oklahoma**

<table>
<thead>
<tr>
<th>RA01</th>
<th><strong>INVITED TALK</strong> 30 min 8:30</th>
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<tbody>
<tr>
<td><strong>TESTS OF PARITY AND TIME-REVERSAL VIOLATION USING DIATOMIC MOLECULES</strong></td>
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<tr>
<td><strong>D. DeMILLE</strong>*, Physics Department, Yale University, New Haven, CT 06520.</td>
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<td>*This work supported by NSF</td>
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<tr>
<th>RA02</th>
<th>15 min 9:05</th>
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<tr>
<td><strong>A NEW MEASUREMENT OF THE ELECTRON’S ELECTRIC DIPOLE MOMENT USING YbF MOLECULES</strong></td>
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<tr>
<td><strong>J. J. HUDSON, D. M. KARA, I. J. SMALLMAN, B. E. SAUER, M. R. TARBUtT</strong> and E. A. HINDS, Centre for Cold Matter, Blackett Laboratory, Imperial College London, Prince Consort Road, London SW7 2AZ, UK.</td>
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<tr>
<th>RA03</th>
<th>15 min 9:22</th>
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<tbody>
<tr>
<td><strong>SPECTROSCOPY OF THORIUM MONOXIDE, ThO; E(O(^+)),F(O(^+)),-X(^1\Sigma^+) BANDS</strong></td>
<td></td>
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<tr>
<td><strong>FANG WANG AND TIMOTHY C. STEIMLE</strong>, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287; <strong>MICHAEL HEAVEN</strong>, Department of Chemistry, Emory University, Atlanta, GA 30322.</td>
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<th>RA04</th>
<th>10 min 9:39</th>
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<tbody>
<tr>
<td><strong>PERMANENT ELECTRON ELECTRIC DIPOLE MOMENT SEARCH IN THE X(^3\Delta_1) GROUND STATE OF TUNGSTEN CARBIDE MOLECULES</strong></td>
<td></td>
</tr>
<tr>
<td><strong>JEONGWON LEE, JINHAI CHEN, and AARON LEANHARDT</strong>, Department of Physics, University of Michigan, Ann Arbor, MI 48109.</td>
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<th>RA05</th>
<th>10 min 9:51</th>
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<tr>
<td><strong>THEORETICAL STUDY OF THE PbF AND PbO MOLECULES</strong></td>
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<tr>
<td><strong>ALEXANDER N. PETROV</strong>, ANATOLY V. TITOV, MIKHAIL G. KOZLOV, Petersburg Nuclear Physics Institute, Gatchina, Leningrad district 188300, Russia; <strong>KIRILL I. BAKLANOV</strong>, Institute of Physics, Saint Petersburg State University, Saint Petersburg, Petrodvoretz 198904, Russia.</td>
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<td>*This work supported by RFBR Grants No. 09–03–01034</td>
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<tr>
<th>RA06</th>
<th>15 min 10:03</th>
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<tr>
<td><strong>THE EFFECTIVE HAMILTONIAN FOR THE GROUND STATE OF (^{207}\text{Pb}^{19}F) AND NEW MEASUREMENTS OF THE FINE STRUCTURE SPECTRUM NEAR 1.2 (\mu\text{m}).</strong></td>
<td></td>
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<tr>
<td><strong>RICHARD MAWHORTER, BENJAMIN MURPHEY, ALEXANDER BAUM</strong>, Department of Physics and Astronomy, Pomona College, Claremont, CA 91711; <strong>TREVOR J. SEARS</strong>, Chemistry Department Brookhaven National Laboratory, Upton, NY 11973 and Stony Brook University, Stony Brook, NY 11794; <strong>T. ZH. YANG, P. M. RUPASINGHE, C. P. MCRAVEN</strong>, Homer L. Dodge Department of Physics and Astronomy, University of Oklahoma, Norman, OK; <strong>LUKAS D. ALPHEI AND JENS-UWE. GRABOW</strong>, Gottfried-Wilhelm-Liebniz-Universität, Institut für Physikalische Chemie &amp; Elektrochemie, D-30167 Hannover, Germany.</td>
<td></td>
</tr>
<tr>
<td>*Current Address: Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973</td>
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Intermission

RA07 15 min 10:40
A PbF PROBE FOR THE ELECTRON ELECTRIC DIPOLE MOMENT

JOHN MOORE-FURNEAUX, N.E. SHAFER-RAY, Home L. Dodge Department of Physics and Astronomy, University of Oklahoma, Norman OK, 73019.

RA08 10 min 10:57
HIGH RESOLUTION ROTATIONAL SPECTROSCOPY STUDY OF THE ZEEMAN EFFECT IN THE $^2\Pi_{1/2}$ MOLECULE PbF

ALEXANDER BAUM, RICHARD MAWHORTER, and BENJAMIN MURPHY, Department of Physics and Astronomy, Pomona College, Claremont, CA 91711; TREvor J. SEARS, Chemistry Department Brookhaven National Laboratory, Upton, NY 11973 and Stony Brook University, Stony Brook, NY 11794; T. ZH. YANG, P. M. RUPASINGHE, C. P. MCRAVEN, and N. E. SHAFER-RAY, Homer L. Dodge Department of Physics and Astronomy, University of Oklahoma, Norman, OK; LUKAS D. ALPHEI and JENS-UWE. GRABOW, Gottfried-Wilhelm-Liebniz-Universität, Institut für Physikalische Chemie & Elektrochemie, D-30167 Hannover, Germany.

\*Current Address: Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973

RA09 15 min 11:09
STARK SPECTROSCOPY OF PBF MOLECULE

TAO YANG, NEIL SHAFER-RAY, Homer L. Dodge Department of Physics and Astronomy, University of Oklahoma, 440 W.Brooks, NH 100, Norman, OK 73019.

RA10 15 min 11:26
THE PFI-ZEKE SPECTRUM OF HfF$^+$, IN SUPPORT OF FUNDAMENTAL PHYSICS

BEAU J. BARKER, IVAN O. ANTONOV, VLADIMIR E. BONDYBEY, and MICHAEL C. HEAVEN, Department of Chemistry, Emory University, Atlanta, GA 30322.
RB. ATMOSPHERIC SPECIES
THURSDAY, JUNE 23, 2011 – 8:30 am
Room: 170 MATH ANNEX

Chair: BRIAN DROUIN, California Institute of Technology, Pasadena, California

RB01 15 min 8:30
NITROGEN-BROADENED $^{13}$CH$_4$ AT 80 TO 296 K


RB02 15 min 8:47
MEASUREMENT OF CH$_3$D ABSORPTION CROSS SECTIONS, PRESSURE BROADENING, AND SHIFT COEFFICIENTS IN THE 1.65 $\mu$m SPECTRAL REGION BY USING CONTINUOUS AVE CAVITY RING-DOWN SPECTROSCOPY

YONGXIN TANG, SHAOYUE L. YANG, KEVIN K. LEHMANN, Department of Chemistry and School of Medicine, University of Virginia, Charlottesville VA, 22904-4319; D. CHRIS BENNER, Department of Physics, College of William and Mary, Box 8795, Williamsburg, VA 23187-8795.

RB03 15 min 9:04
HIGH-RESOLUTION SPECTROSCOPY AND PRELIMINARY GLOBAL ANALYSIS OF C–H STRETCHING VIBRATIONS OF C$_2$H$_4$ IN THE 3000 AND 6000 CM$^{-1}$ REGIONS

M. A. LORONO GONZALEZ, Department of Chemistry, Universidad de Oriente, Cumaná 6101, Estado Sucre, Venezuela; V. BOUDON, M. LOËTE, Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 5209 CNRS-Université de Bourgogne, 9, Av. A. Savary, BP 47870, F-21078 Dijon Cedex, France; M. ROTGER, M.-T. BOURGEOIS, Groupe de Spectrométrie Moléculaire et Atmosphérique, CNRS UMR 6089, Moulin de la Housse, BP 1039, Cases 16-17, F-51687 Reims Cedex 2, France; K. DIDRICHEN, M. HERMAN, Laboratoire de Chimie quantique et Photophysique, CP160/09, Faculté des Sciences, Université Libre de Bruxelles, 50 ave. Roosevelt, B-1050, Brussels, Belgium; V. A. KAPITANOV, Yu. N. PONOMAREV, A. A. SOLODOV, A. M. SOLODOV, T. M. PETROVA, V.E. Zuev Institute of Atmospheric Optics SB RAS,1, Zuev Square, Tomsk, 634921, Russia.

RB04 15 min 9:21
THE THZ ABSORPTION OF METHYL BROMIDE (CH$_3$Br)

MARLON RAMOS, BRIAN J. DROUIN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099.

RB05 15 min 9:38
IMPACT OF ATMOSPHERIC CLUTTER ON DOPPLER-LIMITED GAS SENSORS IN THE SUBMILLIMETER/TERAHERTZ

IVAN R. MEDVEDEV, Department of Physics, Wright State University, 3640 Colonel Glenn Highway, Dayton, OH 45435, USA; CHRISTOPHER F. NEESE, FRANK C. DE LUCIA, Department of Physics, Ohio State University, 191 West Woodruff Ave., Columbus, OH 43210, USA; GRANT M. PLUMMER, Enthalpy Analytical, Inc., 2202 Ellis Road, Durham, North Carolina 27703, USA.
HIGH RESOLUTION SPECTROSCOPY USING A TUNABLE THZ SYNTHESIZER BASED ON PHOTOMIXING

ARNAUD CUISSET, FRANCIS HINDLE, GAELE MOURET, SOPHIE ELIET, MICKAEL GUINET, ROBIN BOCQUET, Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d’Opale, 189A Ave. Maurice Schumann, 59140 Dunkerque, France.

Intermission

SENSORS ACROSS THE SPECTRUM

CHRISTOPHER F. NEESE, FRANK C. DE LUCIA, Department of Physics, The Ohio State University, 191 W. Woodruff Ave., Columbus, OH 43210 USA; IVAN R. MEDVEDEV, Department of Physics, Wright State University, 3640 Colonel Glenn Hwy, Dayton, OH 45435.

NEW CHIRPED-PULSE THZ FOURIER TRANSFORM TECHNIQUES FOR DETERMINATION OF LINESHAPE PARAMETERS FOR ATMOSPHERIC SPECIES

EYAL GERECHT, KEVIN O. DOUGLASS, DAVID F. PLUSQUELLIC, NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY, OPTICAL TECHNOLOGY DIVISION, GAITHERSBURG, MD 20899.

INFRARED ABSORPTION OF CH$_3$ONO DETECTED WITH TIME-RESOLVED FOURIER-TRANSFORM SPECTROSCOPY

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; JIN-DAH CHEN, Department of Applied Chemistry, National Chiao Tung University, Hsinchu 30010, Taiwan.

TORSIONAL EXCITATION IN O-H STRETCH OVERTONE SPECTRA OF ETHYL HYDROPEROXIDE CONFORMERS

SHIZUKA HSIEH, MA THIDA, MARGARET NYAMUMBO, and R. G. LINCK, Chemistry Department, Smith College, Northampton, MA 01063.

RULES APPLICABLE FOR SPECTROSCOPIC PARAMETERS OF H$_2$O TRANSITIONS INVOLVING HIGH J STATES

Q. MA, NASA/Goddard Institute for Space Studies and Department of Applied Physics and Applied Mathematics, Columbia University, 2880 Broadway, New York, NY 10025; R. H. TIPPING, Department of Physics and Astronomy, University of Alabama, Tuscaloosa, AL 35487.
RC. MICROWAVE
THURSDAY, JUNE 23, 2011 – 8:30 am
Room: 1000 McPHERSON LAB

Chair: SUSANNA WIDICUS WEAVER, Emory University, Atlanta, Georgia

RC01 15 min 8:30
FOURIER TRANSFORM MICROWAVE SPECTRUM OF THE YC₂ (X²A₁) RADICAL

D. T. HALFEN, J. MIN, and L. M. ZIURYS, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.

RC02 15 min 8:47
OBSERVATION OF LOW J TRANSITIONS OF LASER ABLATED ALKALI HALIDES

BROOKE A. TIMP, JAMIE L. DORAN, KENNETH R. LEOPOLD, Department of Chemistry, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN 55455; JENS-UWE GRABOW, Institut für Physikalische Chemie und Elektrochemie, Gottfried-Wilhelm-Leibniz-Universität Hannover, Callinstrae 3A, 30167 Hannover, Germany.

RC03 15 min 9:04
ROTATIONAL SPECTROSCOPY OF ZnCCH (X²Σ⁺) AT MICROWAVE AND MILLIMETER WAVELENGTHS


RC04 15 min 9:21
FOURIER TRANSFORM MICROWAVE SPECTRUM OF MgCCH (X²Σ⁺)

J. MIN, D. T. HALFEN, M. SUN, B. T. HARISS, L. M. ZIURYS, University of Arizona, Deptment of Chemistry and Biochemistry and Steward Observatory, Tucson, AZ-85721; D. J. CLOUTHIER, University of Kentucky, Deptment of Chemistry, Lexington, KY-40506.

RC05 15 min 9:38
A CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTROMETER COMBINED WITH A LASER ABLATION SOURCE

S. MATA, I. PENA, C. CABEZAS, J. C. LÓPEZ, J. L. ALONSO, Grupo de Espectroscopía Molecular (GEM). Edificio Quifima. Laboratorios de Espectroscopía y Bioespectroscopía. Parque Científico. Universidad de Valladolid, 47011 Valladolid. (Spain); B. H. PATE, Department of Chemistry, University of Virginia, Charlottesville. Virginia 22904 (USA).

RC06 15 min 9:55
TECHNIQUES FOR HIGH-BANDWIDTH (≥30 GHz) CHIRPED-PULSE MILLIMETER/SUBMILLIMETER-WAVE SPECTROSCOPY

JUSTIN L. NEILL, AMANDA L. STEBER, BRENT J. HARRIS, and BROOKS H. PATE, Department of Chemistry, University of Virginia, McCormick Rd., P.O. Box 400319, Charlottesville, VA 22904; KEVIN O. DOUGLASS and 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.
Intermission

RC07
PROBING VITAMINE C, ASPIRIN AND PARACETAMOL IN THE GAS PHASE: HIGH RESOLUTION ROTATIONAL STUDIES


RC08
JET COOLED ROTATIONAL STUDIES OF DIPEPTIDES


RC09
CHIRPED-PULSED FTMW SPECTRUM OF VALERIC ACID AND 5-AMINOVALERIC ACID. A STUDY OF AMINO ACID MIMICS IN THE GAS PHASE\(^a\)

RYAN G. BIRD, VANESA VAQUERO, 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).

RC10
STRUCTURE STUDY OF FORMIC ACID CLUSTERS BY CHIRPED-PULSE FTMW SPECTROSCOPY

DANIEL P. ZALESKI, JUSTIN L. NEILL, MATT T. MUCKLE, AMANDA L. STEBER, and BROOKS H. PATE, Department of Chemistry, University of Virginia, McCormick Rd., P.O. Box 400319, Charlottesville, VA 22904; KEVIN O. DOUGLASS, National Institute of Standards and Technology, Optical Technology Division, Gaithersburg, MD 20899.

RC11
A CHIRPED PULSE FTMW STUDY OF THE STRUCTURE OF PHENOL DIMER

AMANDA L. STEBER, JUSTIN L. NEILL, DANIEL P. ZALESKI, and BROOKS H. PATE, Department of Chemistry, University of Virginia, Charlottesville, VA 22904; ALBERTO LESARRI, Departamento Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47011 Valladolid, Spain.

RC12
OBSERVATION OF C−H···π INTERACTIONS: MICROWAVE SPECTRA AND STRUCTURES OF THE CH\(_2\)FX···HCCH (X=F,Cl) WEAKLY BOUND COMPLEXES

LENA F. ELMUTI, DANIEL A. OBENCHAIN, DON L. JURKOWSKI, AMELIA J. SANDERS, REBECCA A. PEEBLES, SEAN A. PEEBLES, Department of Chemistry, Eastern Illinois University, 600 Lincoln Avenue, Charleston, IL 61920; AMANDA L. STEBER, JUSTIN L. NEILL, BROOKS H. PATE, Department of Chemistry, University of Virginia, McCormick Rd., PO Box 400319, Charlottesville, VA 22904.
RD. MINI-SYMPOSIUM: SPECTROSCOPIC PERTURBATIONS
THURSDAY, JUNE 23, 2011 – 8:30 am
Room: 1015 McPHERSON LAB

Chair: THOMAS BERGEMAN, SUNY Stony Brook, Stony Brook, New York

<table>
<thead>
<tr>
<th>RD01</th>
<th>INVITED TALK</th>
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<tr>
<td>SPECTROSCOPIC SIGNATURES OF BOND BREAKING INTERNAL ROTATION IN HCP</td>
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<tr>
<td>MARK S CHILD, Physical and Theoretical Chemistry Laboratory, South Parks Rd, Oxford, OX1 3QZ, UK.</td>
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<th>RD02</th>
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<tr>
<td>PERTURBATION FACILITATED DISPERSED FLUORESCENCE AND STIMULATED EMISSION PUMPING SPECTROSCOPIES OF HCP</td>
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<tr>
<td>HARUKI ISHIKAWA, Department of Chemistry, Graduate School of Science, Kobe University, Nada-ku, Kobe 657-8501, Japan; YASUHIKO MURAMOTO, MASAHITO NAMAI, NAOHIKO MIKAMI, Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan.</td>
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<th>RD03</th>
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<tr>
<td>COLLISIONAL ORIENTATION TRANSFER FACILITATED POLARIZATION SPECTROSCOPY*</td>
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<td>JIANMEI BAI, E.H.AHMED, B. BESER, Y. GUAN, A. M. LYYRA, Temple University; S. ASHMAN, C. M. WOLFE, J. HUENNEKENS, Lehigh University.</td>
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*Funded by NSF PHY 0555608 and PHY 0855502

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<tr>
<th>RD04</th>
<th>10 min</th>
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<tr>
<td>THE $X^1\Sigma^+$ AND $B^1\Pi$ STATES OF LiRb AND PROSPECTS FOR CREATING ULTRACOLD GROUND STATE LiRb MOLECULES</td>
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<tr>
<td>SOURA V DUTTA, ADEEL ALTAF, JOHN LORENZ, D. S. ELLIOTT AND YONG P. CHEN, Purdue University, West Lafayette, IN 47907.</td>
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<th>RD05</th>
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<tr>
<td>OPTICAL STARK SPECTROSCOPY OF CHLORO-METHYLENE, HCCI</td>
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<tr>
<td>XIUIJUAN ZHUANG AND TIMOTHY C. STEIMLE, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287; ZHONG WANG, Math and Sciences Department, Suffolk County Community College, East Campus, Riverhead, NY, 11901.</td>
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Intermission

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<tr>
<td>PHASE SPACE EXPLORATION OF ACETYLENE AT ENERGIES UP TO 13,000 cm$^{-1}$</td>
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<tr>
<td>DAVID S. PERRY, JONATHAN MARTENS, Department of Chemistry, The University of Akron, OH 44325-3601; MICHEL HERMAN, BADR AMYAY, Laboratoire de Chimie quantique et Photophysique, Universite libre de Bruxelles, B-1050, Belgium.</td>
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RD07 15 min 10:37

ACETYLENE DYNAMICS AT ENERGIES UP TO 13,000 cm$^{-1}$

JONATHAN MARTENS, DAVID S. PERRY, Department of Chemistry, The University of Akron, OH 44325-3601; MICHEL HERMAN, BADR AMAYAY, Laboratoire de Chimie quantique et Photophysique, Université libre de Bruxelles, B-1050, Belgium.

RD08 15 min 10:54

THE HIGH RESOLUTION SPECTRUM OF THE Ar–C$_2$H$_2$ COMPLEX


RD09 15 min 11:11

IR EMISSION SPECTROSCOPY OF AMMONIA: LINELISTS AND ASSIGNMENTS

R. HARGREAVES and P. F. BERNATH, Department of Chemistry, University of York, Heslington, York YO10 5DD, UK; N. F. ZOBOV, S. V. SHIRIN, R. I. OVSYANNIKOV and O. L. POLYANSKY, Russian Academy of Sciences, Nizhny Novgorod, Russia; S. N. YURCHENKO, R. J. BARBER and J. TENNYSON, Department of Physics and Astronomy, University College London, London WC1E 6BT, UK.

RD10 15 min 11:28

DIRECT EXCITATION OF THE REACTION COORDINATE: OVERTONE-INDUCED PREDISSOCIATION OF THE HYDROXYMETHYL RADICAL

HANNA REISLER, MIKHAIL RYAZANOV and CHIRANTHA P. RODRIGO, Department of Chemistry, University of Southern California, Los Angeles, CA, 90089-0482.

RD11 15 min 11:45

AUTOIONIZATION BRANCHING RATIOS FOR METAL HALIDE MOLECULES

JEFFREY J. KAY, Lawrence Livermore National Laboratory, Livermore, CA 94550; ROBERT W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.
RE. DYNAMICS
THURSDAY, JUNE 23, 2011 – 8:30 am
Room: 2015 McPHERSON LAB

Chair: MARILYNN JACOX, NIST, Gaithersburg, Maryland

RE01 15 min 8:30
INTER-RING AND HEXYL CHAIN TORSIONAL POTENTIALS IN POLY (3-HEXYLTHIOPHENE) OLIGOMERS: SCALING WITH THE LENGTH OF THE CONJUGATED POLYMER BACKBONE

RAM S. BHATTA, DAVID S. PERRY, Department of Chemistry, The University of Akron, OH 44325-3601; YENENEH YIMER AND MESFIN TSIGE, Department of Polymer Science, The University of Akron, OH 44325-3909.

RE02 15 min 8:47
VIBRATIONAL STATE DEPENDENT LARGE AMPLITUDE TUNNELING DYNAMICS IN MALONALDEHYDE

GRANT BUCKINGHAM AND DAVID J. NESBITT, JILA, National Institute of Standards and Technology and University of Colorado, and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309.

RE03 15 min 9:04
VIBRATIONAL RELAXATION AND CONTROL OF SALICYLIDENE ANILINE

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

RE04 15 min 9:21
DEVELOPMENT OF FEMTOSECOND STIMULATED RAMAN SPECTROSCOPY AS A PROBE OF VIBRATIONAL DYNAMICS

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

RE05 15 min 9:38
VIBRATIONAL DYNAMICS OF TRICYANOMETHANIDE

DANIEL WEIDINGER, CASSIDY HOUCHINS, and JEFFREY C. OWRUTSKY, Code 6111, Naval Research Laboratory, 4555 Overlook Ave SW, Washington, D.C. 20375.

Intermission

RE06 15 min 10:10
PHOTOCHEMISTRY OF HALOGENATED TRANSITION METAL DIANIONS

ALEXANDER N. TARNOVSKY, IGOR L. ZHELDAKOV, EVGENIIA V. BUTAEVA, and ANDREY S. MERESHCHENKO, Department of Chemistry, Bowling Green State University, Bowling Green, OH, 43402.
PHOTOCHEMISTRY OF BROMOFORM AND TRIBROMIDES OF OTHER ELEMENTS IN SOLUTION

ANDREY S. MERESHCHENKO, KANYKEY E. KARABAЕVA, ALEXANDER N. TARNOVSKY, Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403; PATRICK Z. EL-KHOURY, Institute for Surface and Interface Science, University of California Irvine, Irvine, CA 92697; AND SUMAN K. PAL, School of Basic Sciences IIT Mandi, Vallabh Degree College Campus, Mandi 175001, India.

ISOMERIZATION BETWEEN CH₂ClI AND CH₂Cl-I IN CRYOGENIC MATRICES STUDIED ON ULTRAFAST TIMESCALE

THOMAS J. PRESTON, MAITREY A DUTTA, BRIAN J. ESSELMAN, MICHAEL A. SHALOSKI, ROBERT J. MCMAHON, and F. FLEMING CRIM, The University of Wisconsin-Madison Department of Chemistry, 1101 University Avenue, Madison, WI, 53705; AMIABLE KALUME, LISA GEORGE and SCOTT A. REID, Department of Chemistry, Marquette University, Milwaukee, WI, 53233.

ISOMERIZATION OF CH₂Cl-I TO CH₂ClI IN CRYOGENIC MATRICES: A STUDY ON ULTRAFAST TIMESCALE

THOMAS J. PRESTON, MAITREY A DUTTA, BRIAN J. ESSELMAN, MICHAEL A. SHALOSKI, ROBERT J. MCMAHON and F. FLEMING CRIM, The University of Wisconsin-Madison Department of Chemistry, 1101 University Avenue, Madison, WI, 53706; AMIABLE KALUME, LISA GEORGE and SCOTT A. REID, Department of Chemistry, Marquette University, Milwaukee, WI, 53233.

PHOTODISSOCIATION DYNAMICS OF A TRIATOMIC PSEUDO-DIHALIDE: ABSORPTION CROSS SECTION AND DYNAMICS OF SOLVATED ICN

JOSHUA P. MARTIN, QUANLI GU, JOSHUA P. DARR, JILA, Department of Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, CO 80309; ANNE B. McCOY, Department of Chemistry, The Ohio State University, Columbus, OH 43210; and W. CARL LINEBERGER, JILA, Department of Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, CO 80309.

EXCITED-STATE DYNAMICS IN 6-THIOGUANOSINE FROM FEMTOSECOND TO MICROSECOND TIME SCALE

CAO GUO, CHRISTIAN REICHARDT AND CARLOS E. CRESPO-HERNÁNDEZ, Department of Chemistry and the Center for Chemical Dynamics, Case Western Reserve University, 10900 Euclid Avenue, Cleveland, Ohio 44106.
RF. MINI-SYMPOSIUM: THE THz COSMOS
THURSDAY, JUNE 23, 2011 – 1:30 pm
Room: 160 MATH ANNEX

Chair: ERIC HERBST, The Ohio State University, Columbus, Ohio

RF01  INVITED TALK  30 min  1:30
INTERSTELLAR HYDRIDE SPECTROSCOPY WITH HERSCHEL
MARYVONNE GERIN, LERMA, CNRS UMR8112, OBSERVATOIRE DE PARIS & ECOLE NORMALE SUPERIEURE, 24 RUE LHOMOND, 75231 PARIS CEDEX 05, FRANCE; and THE PRISMAS CONSORTIUM.

RF02  15 min  2:05
CHEMICAL HERSCHEL SURVEYS OF STAR FORMING REGIONS (CHESS)
MARTIN EMPRECHTINGER, California Institute of Technology, Pasadena CA 91125 (email: emprecht@caltech.edu).

RF03  15 min  2:22
OBSERVATIONS OF INTERSTELLAR HYDROGEN FLUORIDE AND HYDROGEN CHLORIDE IN THE GALAXY
RAQUEL R. MONJE, DAREK C. LIS, THOMAS G. PHILLIPS, PAUL F. GOLDSMITH, MARTIN EMPRECHTINGER, California Institute of Technology, 1200 E. California Blvd., Pasadena, CA 91125-4700, USA ; DAVID A. NEUFELD, Johns Hopkins University, USA.

RF04  15 min  2:39
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.

RF05  15 min  2:56
INFRARED SPECTROSCOPIC STUDIES 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.

RF06  15 min  3:13
ROTATIONAL SPECTROSCOPY FOR ASTROPHYSICAL APPLICATIONS: THE THz FREQUENCY REGION
CRISTINA PUZZARINI, GABRIELE CAZZOLI, Dipartimento di Chimica "G. Ciamician", Università di Bologna, I-40126 Bologna, Italy.

Intermission
UNRAVELING THE MYSTERIES OF COMPLEX INTERSTELLAR ORGANIC CHEMISTRY USING HIFI LINE SURVEYS

SUSANNA L. WIDICUS WEAVER, MARY L. RADHUBER, JAY A. KROLL, BRETT A. McGUIRE, and JACOB C. LAAS, Department of Chemistry, Emory University, Atlanta, GA 30322; DAREK C. LIS, Department of Physics, California Institute of Technology, Pasadena, CA 91125; and ERIC HERBST, Departments of Physics, Chemistry, and Astronomy, The Ohio State University, Columbus, OH 43210.

PROGRESS TOWARDS THE ROTATIONAL SPECTRUM OF H\textsubscript{3}S AND ITS ISOTOPOLOGUES

BRETT A. McGUIRE, YIMIN WANG, JOEL M. BOWMAN, AND SUSANNA L. WIDICUS WEAVER, Department of Chemistry, Emory University, Atlanta, GA 30303.

ANALYSIS OF NEW DATA SETS PERTAINING TO THE WATER MOLECULE

S. YU, J. C. PEARSON, B. J. DROUIN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA; H. S. P. MÜLLER, S. BRÜNKEN, I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany; M. A. MARTIN-DRUMEL, O. PIRALI, D. BALCON, M. VERVLOET, Ligne AILES – Synchrotron SOLEIL, L’Orme des Merisiers, Saint Aubin, 91192 Gif-sur-Yvette, France; AND L. H. COUDERT, LISA, CNRS/Universités Paris Est et Paris Diderot, 61 Avenue du Général de Gaulle, 94010 Créteil, France.

VIBRATIONALLY HOT HCN IN THE LABORATORY AND IRC+10216

JOHN C. PEARSON\textsuperscript{a}, SHANSHAN YU, HARSHAL GUPTA and BRIAN J. DROUIN, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109.

\textsuperscript{a}A part of this work was performed at the Jet Propulsion Laboratory, California Institute of Technology under contract with the National Aeronautics and Space Administration. Copyright 2010© California Institute of Technology. All rights reserved.

SHOCK-INDUCED MOLECULAR AstroCHEMISTRY IN DENSE CLOUDS


THE LABORATORY AND OBSERVATIONAL STUDY OF 2-BUTANONE AS A TEST FOR ORGANIC CHEMICAL COMPLEXITY IN VARIOUS INTERSTELLAR PHYSICAL ENVIRONMENTS

JAY A. KROLL and SUSANNA L. WIDICUS WEAVER, Department of Chemistry, Emory University, Atlanta, GA 30322; STEVEN T. SHIPMAN, Division of Natural Sciences, New College of Florida, Sarasota, FL 34243.

HIGH RESOLUTION FAR INFRARED FOURIER TRANSFORM SPECTROSCOPY OF THE NH\textsubscript{2} RADICAL.

M. A. MARTIN-DRUMEL, O. PIRALI, D. BALCON, SOLEIL Synchrotron, AILES beamline, Saint-Aubin, France and Institut des Sciences Moléculaires d’Orsay, ISMO, CNRS, Université Paris XI, Orsay, France; M. VERVLOET, SOLEIL Synchrotron, AILES beamline, Saint-Aubin, France.
THE PURE ROTATIONAL SPECTRA OF ACETALDEHYDE AND GLYCOLALDEHYDE ISOTOPOLOGUES MEASURED IN NATURAL ABUNDANCE BY CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTROSCOPY

P. BRANDON CARROLL, BRETT A. McGUIRE, and SUSANNA L. WIDICUS WEAVER, Department of Chemistry, Emory University, Atlanta, GA 30322; DANIEL P. ZALESKI, JUSTIN L. NEILL, and BROOKS H. PATE, Department of Chemistry, University of Virginia, McCormick Rd., P.O. Box 400319, Charlottesville, VA 22904.

THE THZ SPECTRUM OF GLYCOLALDEHYDE

MANUEL GOUBET, THERESE R. HUET, IMANE HAYKAL, LAURENT MARGULES, Laboratoire PhLAM, UMR8523 CNRS-Université Lille 1, F-59655 Villeneuve d’Ascq Cedex, France; OLIVIER PIRALI, PASCALE ROY, Ligne AILES - Synchrotron SOLEIL, L’Orme des Merisiers Saint Aubin, F-91192 Gif-sur-Yvette, France.
RG01 15 min 1:30
VIBRATIONAL SPECTRA OF CRYOGENIC PEPTIDE IONS USING H₂ PREDISSOCIATION SPECTROSCOPY

CHRISTOPHER M. LEAVITT, ARRON B. WOLK, MICHAEL Z. KAMRATH, ETIENNE GARAND, MARK A. JOHNSON, Sterling Chemistry Laboratory, Yale University, PO Box 208107, New Haven, CT 06520; and MICHAEL J. VAN STIPDONK, Department of Chemistry, Wichita State University, 1845 Fairmont Ave, Wichita, KS 67208.

RG02 15 min 1:47
VIBRATIONAL CHARACTERIZATION OF SIMPLE PEPTIDES USING CRYOGENIC INFRARED PHOTODISSOCIATION OF H₂-TAGGED, MASS-SELECTED IONS

MICHAEL Z. KAMRATH, ETIENNE GARAND, PETER A. JORDAN, CHRISTOPHER M. LEAVITT, ARRON B. WOLK, SCOTT J. MILLER, AND MARK A. JOHNSON, Sterling Chemistry Laboratory, Yale University, P.O. Box 208107, New Haven, CT 06520 USA; MICHAEL J. VAN STIPDONK, Wichita State University, Department of Chemistry, 1845 Fairmont Ave, Wichita, KS, USA.

RG03 15 min 2:04
USING AN ORGANIC SCAFFOLD TO MODULATE THE QUANTUM STRUCTURE OF AN INTRAMOLECULAR PROTON BOND: CRYOGENIC VIBRATIONAL PREDISSOCIATION SPECTROSCOPY OF H₂ ON PROTONATED 8-NAPHTHALENE-1-AMINE

ANDREW F. DEBLASE, TIMOTHY L. GUASCO, CHRISTOPHER M. LEAVITT, AND MARK A. JOHNSON, STERLING CHEMISTRY, YALE UNIVERSITY, NEW HAVEN, CT, 06520; THOMAS LECTKA, DEPARTMENT OF CHEMISTRY, JOHNS HOPKINS UNIVERSITY, 3400 NORTH CHARLES STREET, BALTIMORE, MD, 21218.

RG04 15 min 2:21
APPLICATION OF INFRARED MULTIPHOTON DISSOCIATION SPECTROSCOPY FOR THE STUDY OF CHIRAL RECOGNITION IN THE PROTONATED SERINE CLUSTERS: PART II

FUMIE X. SUNAHORI, ELENA N. KITOVA, JOHN S. KLASSEN, AND YUNJIE XU, Department of Chemistry, University of Alberta, Edmonton, Canada T6G 2G2; GUOCHUN YANG, Department of Chemistry, Northeast Normal University, Changchun 130024, Jilin, P.R. China.

RG05 15 min 2:38
ROTATION-VIBRATION SPECTRA OF MALONALDEHYDE OBTAINED WITH FAR-INFRARED SYNCHROTRON RADIATION

D. W. TOKARYK, S. C. ROSS, D. FORTHOMME, J. E. PRESCOTT, Department of Physics and Centre for Laser, Atomic and Molecular Sciences, University of New Brunswick, Fredericton, NB, Canada E3B 5A3; K. M. T. YAMADA, F. ITO, EMTech, AIST, Tsukuba-West, Tsukuba, Ibaraki, Japan.
IR SPECTROSCOPIC AND THEORETICAL STUDY OF NEW PHOTOCHROMIC SYSTEMS BASED ON CYMANTEDINE DERIVATIVES.

B. V. LOKSHIN, M. G. EZERNITSKAYA, Yu. B. BORISOV, E. S. KELBYSHEVA, and N. M. LOIM.
A. N. Nesmeyanov Institute of organoelement compounds of Russian Academy of Sciences, Vavilov street, 28, 119991 GSP-1, Moscow, Russia.

Intermission

VIBRATIONAL ANALYSIS AND VALENCE FORCE FIELD FOR NITROTOLUENES, DIMETHYLANILINES AND SOME SUBSTITUTED METHYLBENZENES

B. VENKATRAM REDDY, Department of Physics, Kakatiya University, Warangal-506 009, A.P., India
Email: bvreddy67@yahoo.com; JAI KISHAN OJHA, Department of Physics, Government Degree College, Mancherial-504 208, A.P., India; G. RAMANA RAO, Department of Physics, Varada Reddy College of Engineering, Ananthasagar, Warangal-506 371, A.P., India.

THE HIGH RESOLUTION SPECTRUM OF JET-COOLED METHYL ACETATE IN THE C=O STRETCH REGION

FUMIE X. SUNAHORI, NICOLE BORHO, XUNCHEN LIU, AND YUNJIE XU, Department of Chemistry, University of Alberta, Edmonton, Canada T6G 2G2.

INFRARED FLUORESCENCE MEASUREMENTS OF GASEOUS BENZENE WITH A NEW HOME-MADE SPECTROMETER

G. FÉRAUD, Y. CARPENTIER, T. PINO, P. PARNEIX, T. CHAMAILLÉ, Institut des Sciences Moléculaires d’Orsay, Université Paris-Sud 11, Orsay, France; E. DARTOIS, Y. LONGVAL, Institut d’Astrophysique Spatiale, Université Paris-Sud 11, Orsay, France; R. VASQUEZ and Ph. BRÉCHIGNAC, Institut des Sciences Moléculaires d’Orsay, Université Paris-Sud 11, Orsay, France.

INFRARED ION-GAIN SPECTROSCOPY AND FRACTIONAL ABUNDANCE MEASUREMENTS OF CONFORMER POPULATIONS

EVAN G. BUCHANAN, JACOB C. DEAN, BRETT M. MARSH, and TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN 47907-2804.

SINGLE-CONFORMATION SPECTROSCOPY OF A DIASTEDEMERIC LIGNIN MONOMER: EXPLORING THE HYDROGEN BONDING ARCHITECTURES OF A TRIOL CHAIN

JACOB C. DEAN, EVAN G. BUCHANAN, ANNA GUTBERLET, WILLIAM H. JAMES III, BIDYUT BISWAS, P. V. RAMACHANDRAN, and TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN 47907.
THE TORSIONAL FUNDAMENTAL BAND OF METHYLFORMATE

M. TUDORIE, Service de Chimie Quantique et Photophysique, Université Libre de Bruxelles, CP 160/09, 50 avenue F.D. Roosevelt, B-1050 Brussels, Belgium; V. ILYUSHIN, Department of Microwave Radiospectrometry, Institute of Radio Astronomy of NASU, Chervonopraporopa 4, 61002 Kharkov, Ukraine; 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; O. PIRALI, P. ROY, Ligne AILES – Synchrotron SOLEIL, L’Orme des Merisiers, F-91192 Gif-sur-Yvette, France; T. R. HUET, Laboratoire de Physique des Lasers, Atomes et Molécules, UMR CNRS 8523, Université Lille 1, 59655 Villeneuve d’Ascq Cedex, France.

A FAR INFRARED SYNCHROTRON-BASED INVESTIGATION OF 3-OXETANONE

ZIQUIU CHEN, JENNIFER VAN WIJNGAARDEN, Department of Chemistry, University of Manitoba, Winnipeg MB R3T 2N2 Canada.

FAR-INFRARED SYNCHROTRON-BASED SPECTROSCOPY OF FURAN: ANALYSIS OF THE $\nu_{14} - \nu_{11}$ PERTURBATION AND THE $\nu_{18}$ AND $\nu_{19}$ LEVELS

D. W. TOKARYK, S. D. CULLIGAN*, Department of Physics and Centre for Laser, Atomic and Molecular Sciences, University of New Brunswick, Fredericton, NB, Canada E3B 5A3; B. E. BILLINGHURST, Canadian Light Source, Inc., 101 Perimeter Road, University of Saskatchewan, Saskatoon, SK, Canada S7N 0X4; and J. A. van WIJNGAARDEN, Department of Chemistry, University of Manitoba, Winnipeg, MB, Canada R3T 2N2.

*Current address: Inorganic Chemistry Laboratory, South Parks Road, University of Oxford, UK OX1 3QR
### RH. MICROWAVE

**THURSDAY, JUNE 23, 2011 – 1:30 pm**

**Room: 1000 McPHERSON LAB**

<table>
<thead>
<tr>
<th>Session</th>
<th>Duration</th>
<th>Time</th>
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<tbody>
<tr>
<td><strong>RH01</strong></td>
<td>15 min</td>
<td>1:30</td>
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<tr>
<td>WAVEGUIDE CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE (CP-FTMW) SPECTRUM OF ALLYL CHLORIDE</td>
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<tr>
<td><strong>ERIN B. KENT, MORGAN N. McCABE, MARIA A. PHILLIPS, BRITTANY P. GORDON and STEVEN T. SHIPMAN, Division of Natural Sciences, New College of Florida, Sarasota, FL 34243.</strong></td>
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<td><strong>RH02</strong></td>
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<td>WAVEGUIDE CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE (CP-FTMW) SPECTRUM OF ORTHOFLUOROTOLUENE</td>
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<tr>
<td><strong>IAN A. FINNERAN and STEVEN T. SHIPMAN, Division of Natural Sciences, New College of Florida, Sarasota, FL 34243.</strong></td>
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<td><strong>RH03</strong></td>
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<tr>
<td>A LOOK AT A SERIES OF ALKYL AND PERFLUOROALKYL BROMIDES AND CHLORIDES</td>
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<tr>
<td><strong>BRITTANY E. LONG, STEPHEN A. COOKE, Department of Chemistry, The University of North Texas, 1155 Union Circle, #305070, Denton, TX 76203-5017, U.S.A.; GARRY S. GRUBBS II, Department of Chemistry, Wesleyan University, Hall-Atwater Laboratories, 52 Lawn Ave., Middletown, CT 06459-0180, U.S.A.</strong></td>
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<td><strong>RH04</strong></td>
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<tr>
<td>METHYL GROUP INTERNAL ROTATION IN THE PURE ROTATIONAL SPECTRUM OF 1,1-DIFLUOROACETONE</td>
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<tr>
<td><strong>G. S. GRUBBS II, S. A. COOKE, Department of Chemistry, The University of North Texas, 1155 Union Circle, #305070 Denton, TX 76203-5017, USA; P. GRONER, Department of Chemistry, University of Missouri-Kansas City, 5100 Rockhill Road, Kansas City, MO 64110.</strong></td>
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<tr>
<td><strong>RH05</strong></td>
<td>15 min</td>
<td>2:38</td>
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<tr>
<td>FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF ALKALI METAL ACETYLIDES</td>
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<tr>
<td><strong>P. M. SHERIDAN, M. K. L. BINNS, Canisius College, Buffalo, NY 14208; J. MIN, M. P. BUCCHINO, D. T. HALFEN, and L. M. ZIURYS, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.</strong></td>
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<td><strong>RH06</strong></td>
<td>15 min</td>
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<tr>
<td>ANALYSIS OF ROTATIONAL STRUCTURE IN THE HIGH-RESOLUTION INFRARED SPECTRA OF THE TRANSHEXATRIENE-1,1-D$_2$ AND -CIS-1-D$_1$ SPECIES</td>
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<tr>
<td><strong>NORMAN C. CRAIG, HANNAH A. FUSON, and HENGFENG TIAN, Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH 44074; THOMAS A. BLAKE, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352.</strong></td>
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ANALYSIS OF THE ROTATIONAL STRUCTURE IN THE HIGH-RESOLUTION INFRARED SPECTRUM OF TRANS-HEXATRIENE-1-\textsuperscript{13}C\textsubscript{1}

NORMAN C. CRAIG and HENGFENG TIAN, Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH 44074; THOMAS A. BLAKE, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352.

Intermission

ROTATIONAL SPECTRUM SPECTRUM AND COUPLED-CLUSTER CALCULATIONS OF SILICON OXYSULFIDE, O=Si=S

S. THORWIRTH, I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany; L. A. MÜCK, J. GAUSS, Institut für Physikalische Chemie, Universität Mainz, 55099 Mainz, Germany; F. TAMASSIA, Dipartimento di Chimica Fisica e Inorganica, Università di Bologna, I-40136 Bologna, Italy; V. LATTANZI, M. 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.

STRUCTRURAL DETERMINATION OF SILACYCLOBUTANE AND SILACYCLOPENTANE USING FOURIER TRANSFORM MICROWAVE (FTMW) AND CHIRPED PULSE FOURIER TRANSFORM MICROWAVE (cp-FTMW) SPECTROSCOPY

ZIQIU CHEN, CODY VAN DIJK AND JENNIFER VAN WIJNGAARDEN, Department of Chemistry, University of Manitoba, Winnipeg MB R3T 2N2 Canada.

ROOM-TEMPERATURE CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE (CP-FTMW) SPECTRUM OF 2-METHYLFURAN

IAN A. FINNERAN and STEVEN T. SHIPMAN, Division of Natural Sciences, New College of Florida, Sarasota, FL 34243.

THE MICROWAVE SPECTRUM OF METHYL VINYL KETONE REVISITED

DAVID S. WILCOX, AMANDA J. SHIRAR, OWEN L. WILLIAMS, BRIAN C. DIAN, Department of Chemistry, Purdue University, West Lafayette, IN, 47907.

HIGH RESOLUTION ROTATIONAL SPECTROSCOPY OF A FLEXIBLE CYCLIC ETHER


THE PURE ROTATIONAL SPECTRA OF THE TWO LOWEST ENERGY CONFORMERS OF \textit{n}-BUTYL ETHYL ETHER

B. E. LONG, G. S. GRUBBS II, S. A. COOKE, Department of Chemistry, The University of North Texas, 1155 Union Circle, # 305070 Denton, TX 76203-5017, USA.
RI THEORY

THURSDAY, JUNE 23, 2011 – 1:30 pm

Room: 1015 McPherson Lab

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

R101 INVITED TALK

30 min 1:30

COMPOSITE APPROACHES FOR AB INITIO SPECTROSCOPY: THE CCN, CCSb, AND HNNO RADICALS

Kirk A. Peterson, J. Grant Hill, James Shearouse, Department of Chemistry, Washington State University, Pullman, WA 99164; Alexander Mitrushchenkov, Laboratoire de Modélisation et Simulation Multi Échelle, Université Paris-Est Marne-la-Vallée, 77454 Marne la Vallée, Cedex 2, France; and Joseph S. Francisco, Department of Chemistry, Purdue University, West Lafayette, IN 47907.

R102

15 min 2:05

EMPLOYING DIFFUSION MONTE CARLO IN THE CALCULATION OF MINIMIZED ENERGY PATHS OF THE CH₃⁺ + H₂ ↔ CH₂⁺ ↔ CH⁺ + H₂ REACTION AND ITS ISOTOPIC VARIANTS

Charlotte E. Hinkle, Anne B. McCoy, Department of Chemistry, The Ohio State University, Columbus, OH 43210.

R103

15 min 2:22

POTENTIAL ENERGY SURFACES OF M+NG, M = K, RB, CS AND NG = HE, NE, AR

L. Blank, David E. Weeks, Engineering Physics Department, Air Force Institute of Technology, 2950 Hobson Way, WPAFB, OH 45433-7765; Gary S. Kedzoria, High Performance Technologies, Inc. 2435 5th St., WPAFB, OH USA 45433-7765.

R104

15 min 2:39

A QUANTUM CHEMICAL STUDY OF XH AND XH₂ (X=Be,C,N,O): 2s² RECOUPLED PAIR BONDING

Lu Xu, D. E. Woon, and T. H. Dunning, Jr., Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

R105

15 min 2:56

COMPUTATIONAL AND SPECTROSCOPIC STUDY OF THE B-N DATIVE BOND IN AMMONIA BORANE

Ashley M. Wright, Gregory S. Tschumper, and Nathan I. Hammer, University of Mississippi, Department of Chemistry & Biochemistry, Oxford, MS 38677.

R106

15 min 3:13

EXCITED STATES IN SOLUTION AT EOM-CCSD LEVEL WITH THE POLARIZABLE CONTINUUM MODEL OF SOLVATION

M. Caricato, Gaussian, Inc., 340 Quinnipiac St., Bldg 40, Wallingford, CT 06492.

Intermission
RI07

EXPLORING TRANSITION METAL CATALYZED REACTIONS VIA AB INITIO REACTION PATHWAYS

HRANT P. HRATCHIAN, Gaussian, Inc., 340 Quinnipiac St., Bldg. 40, Wallingford, CT 06492.

RI08

NON-PRODUCT SMOLYAK GRIDS FOR COMPUTING SPECTRA: HOW AND WHY?

GUSTAVO AVILA and TUCKER CARRINGTON JR., Chemistry Department, Queen's University, Kingston, Ontario K7L 3N6, Canada.

RI09

USING A NON-PRODUCT QUADRATURE GRID TO COMPUTE THE VIBRATIONAL SPECTRUM OF C$_2$H$_4$

GUSTAVO AVILA and TUCKER CARRINGTON JR., Chemistry Department, Queen's University, Kingston, Ontario K7L 3N6, Canada.

RI10

PROGRESS TOWARDS THE ACCURATE CALCULATION OF ANHARMONIC VIBRATIONAL STATES OF FLUXIONAL MOLECULES AND CLUSTERS WITHOUT A POTENTIAL ENERGY SURFACE

ANDREW S. PETIT and ANNE B. McCoy, Department of Chemistry, The Ohio State University, Columbus, OH 43210.

RI11

HOW LIGAND PROPERTIES AFFECT THE FORMATION AND CHARACTERISTICS OF RECOUPLED PAIR BONDS

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

RI12

A QUANTUM CHEMICAL STUDY OF THE STRUCTURE AND CHEMISTRY OF HZnCH$_3$, A TRANSITION METAL COMPOUND WITH 4s$^2$ RECOUPLED PAIR BONDING

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

RI13

THE SEARCH FOR AN OBSERVABLE HELIUM COMPLEX

ADRIAN M. GARDNER, TIMOTHY G. WRIGHT, School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom; COREY J. EVANS, Department of Chemistry, University of Leicester, University Road, Leicester, LE1 7RH, United Kingdom.
**R.J. RADICALS AND IONS**

**THURSDAY, JUNE 23, 2011 – 1:30 pm**

**Room: 2015 McPHERSON LAB**

**Chair: LAURA McCUNN, Marshall University, Huntington, West Virginia**

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**RJ01 15 min 1:30**

DEHYDROGENATION OF ETHYLENE: SPECTROSCOPY AND STRUCTURES OF La(C₂H₂) AND La(C₄H₁₀) COMPLEXES

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

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**RJ02 15 min 1:47**

DEHYDROGENATION AND C-H BOND INSERTION OF PROPENE: La(η²-C₃H₄) AND HLα(η³-C₃H₅)

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

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**RJ03 15 min 2:04**

OBSERVATION OF TWO La(C₃H₂) ISOMERS FORMED BY DEHYDROGENATION OF PROPYNE

DILRUJKSI HEWAGE, MOURAD ROUDJANE, and DONG-SHENG YANG, *Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.*

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**RJ04 15 min 2:21**

VIBRONIC SPECTROSCOPY OF THE PHENYLICYANOMETHYL RADICAL

DEEPALI N. MEHTA, NATHANAEL M. KIDWELL, and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907.*

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**RJ05 15 min 2:38**

SPECTROSCOPIC IDENTIFICATION OF ISOMERIC TRIMETHYLBENZYL RADICALS GENERATED IN CORONA DISCHARGE OF TETRAMETHYLBENZENE

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

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**RJ06 15 min 2:55**

INFRARED SPECTRA OF PRODUCTS OF THE ULTRAVIOLET AND VACUUM ULTRAVIOLET IRRADIATION OF BENZENE TRAPPED IN SOLID NEON

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

---

**Intermission**
INFRARED SPECTROSCOPY OF PROTONATED MIXED BENZENE-WATER CLUSTERS

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

MASS-ANALYZED THRESHOLD IONIZATION AND STRUCTURES OF M₃C₂(M=Sc, La)

LU WU, ROUDJANE MOURAD and D. S. YANG, Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.

VIBRATIONAL AND GEOMETRIC STRUCTURES OF La₃C₂O AND La₃C₂O⁺ FROM MASS-ANALYZED THRESHOLD IONIZATION

ROUDJANE MOURAD, LU WU and D. S. YANG, Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.

AN UNEXPECTED GAS-PHASE BINDING MOTIF FOR METAL DICATION COMPLEXATION WITH PEPTIDES: IRMPD SPECTROSCOPIC STRUCTURE DETERMINATION

ROBERT C. DUNBAR, Chemistry Department, Case Western Reserve Univ., Cleveland, OH 44106; JEFFREY STEILL, Sandia National Laboratory, Livermore, CA; NICOLAS POLFER, Chemistry Department, University of Florida, Gainesville, FL; GIEL BERDEN, FOM Institute for Plasma Physics, Nieuwegein, Netherlands; JOS OOMENS, FOM Institute for Plasma Physics, Nieuwegein, and University of Amsterdam, Netherlands.

SPECTROSCOPIC INVESTIGATION OF ELECTRON-INDUCED PROTON TRANSFER IN THE FORMIC ACID DIMER, (HCOOH)₂

HELEN K. GERARDI, CHRIS M. LEAVITT, ANDREW F. DEBLASE, AND MARK A. JOHNSON, Yale University, Department of Chemistry, New Haven, CT.

VIBRATIONALLY MEDIATED ELECTRON CAPTURE IN THE CO₂(H₂O)₆ ANION

KRISTIN J. BREEN, Sterling Chemistry Laboratory, Yale University, P.O. Box 208107, New Haven, CT 06520; ANDREW F. DEBLASE, Sterling Chemistry Laboratory, Yale University, P.O. Box 208107, New Haven, CT 06520; and MARK A. JOHNSON, Sterling Chemistry Laboratory, Yale University, P.O. Box 208107, New Haven, CT 06520.

INFRARED PREDISSOCIATION SPECTROSCOPY OF H₂-TAGGED DICARBOXYLIC ACID ANIONS

ARRON B. WOLK, Chemistry Laboratory, Yale University, P.O. Box 208107, New Haven, CT 06520; MICHAEL Z. KAMRATH, Chemistry Laboratory, Yale University, P.O. Box 208107, New Haven, CT 06520; CHRISTOPHER M. LEAVITT, Chemistry Laboratory, Yale University, P.O. Box 208107, New Haven, CT 06520; and MARK A. JOHNSON, Chemistry Laboratory, Yale University, P.O. Box 208107, New Haven, CT 06520.
FA. MINI-SYMPOSIUM: THE THz COSMOS

FRIDAY, JUNE 24, 2011 – 8:30 am

Room: 160 MATH ANNEX

Chair: JOHN PEARSON, Jet Propulsion Laboratory, Pasadena, California

FA01

INVITED TALK

30 min 8:30

EXPLORING NEW SPECTRAL WINDOWS WITH THE HERSCHEL SPACE OBSERVATORY

EDWIN A. BERGIN AND THE HEXOS TEAM, Department of Astronomy, University of Michigan (email to: ebergin@umich.edu).

FA02

15 min 9:05

HERSCHEL OBSERVATIONS OF EXTRA-ORDINARY SOURCES (HEXOS): ANALYSIS OF THE HIFI 1.2 THz WIDE SPECTRAL SURVEY TOWARD ORION KL

N. R. CROCKETT, E. A. BERGIN, S. WANG, Department of Astronomy, University of Michigan, 500 Church Street, Ann Arbor, MI 48109, USA; G. BLAKE, M. EMPRECHTINGER, D. LIS, California Institute of Technology, Cahill Center for Astronomy and Astrophysics 301-17, Pasadena, CA 91125 USA; H. GUPTA, J. PEARSON, S. YU, Jet Propulsion Laboratory, Caltech, Pasadena, CA 91109, USA; T. BELL, J. CERNICHARO, Centro de Astrobiología (CSIC/INTA), Laboratorio de Astrofísica Molecular, Ctra. de Torrejón a Alcalá, km 4 28850, Torrejón de Ardoz, Madrid, Spain; S. LORD, Infrared Processing and Analysis Center, California Institute of Technology, MS 100-22, Pasadena, CA 91125; R. PLUME, Department of Physics and Astronomy, University of Calgary, 2500 University Drive NW, Calgary, AB T2N 1N4, Canada; P. SCHILKE, Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, 50937 Köln, Germany; and F. VAN DER TAK, SRON Netherlands Institute for Space Research, PO Box 800, 9700 AV, Groningen, The Netherlands.

FA03

15 min 9:22

DETECTION OF OH+ AND H2O+ TOWARD ORION KL

HARSHAL GUPTA*, JOHN C. PEARSON, SHANSHAN YU, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109; PAUL RIMMER, ERIC HERBST, Departments of Physics, Chemistry, and Astronomy, The Ohio State University, Columbus, OH 43210; EDWIN A. BERGIN, Department of Astronomy, University of Michigan, Ann Arbor, MI 48109; and the HEXOS TEAM, HTTP://WWW.HEXOS.ORG/TEAM.PHP.

* A part of this work was performed at the Jet Propulsion Laboratory, California Institute of Technology under contract with the National Aeronautics and Space Administration. Copyright 2010 © California Institute of Technology. All rights reserved.

FA04

15 min 9:39

IS WATER ICE THE PRECURSOR TO OH+ AND H2O+ IN ORION KL?

PAUL B. RIMMER, Department of Physics, The Ohio State University, Columbus, OH 43210; ERIC HERBST, Departments of Astronomy, Chemistry and Physics, The Ohio State University, Columbus, OH 43210.

Intermission

FA05

15 min 10:10

REACHING THE LINE CONFUSION LIMIT: ANALYSIS OF THE $\lambda=1.3$ mm SPECTRUM OF ORION-KL

MARY L. RADHUBER, JAY A. KROLL, SUSANNA L. WIDICUS WEAVER, 1515 DICKEY DR. ATLANTA, GA 30322.
$^{15}\text{N}/^{14}\text{N}$ RATIO DETERMINATION IN THE ISM WITH HERSCHEL WITH HIGH RESOLUTION SPECTROSCOPY OF NITROGEN RADICALS

L. MARGULÈS, S. BAILLEUX, G. WLODARCZAK, Laboratoire PhLAM, CNRS UMR 8523, Université Lille 1, 59655 Villeneuve d’Ascq Cedex, France; O. PIRALI, M.-A. MARTIN-DRUMEL, P. ROY, Ligne AILES - Synchrotron SOLEIL, L’Orme des Merisiers Saint Aubin, 91192 Gif-sur-Yvette, France; E. ROUEFF, Laboratoire de l’Univers et de ses Théories, Observatoire de Paris-Meudon, 92195, Meudon, France; and M. GERIN, LERMA, CNRS UMR 8112, 24 rue Lhomond, 75231 Paris Cedex 05, France.

THZ SPECTROSCOPY OF $^{13}\text{C}$ ISOTOPIc SPECIES OF A "WEED": ACETALDEHYDE

Sciences Chimiques de Rennes, UMR 6226 CNRS-ENSCR, Avenue du Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France; L. MARGULÈS, and R. A. MOTIYENKO, Laboratoire PhLAM, CNRS UMR 8523, Université de Lille 1, 59655 Villeneuve d’Ascq Cedex, France; and J.-C. GUILLEMIN, Sciences Chimiques de Rennes, UMR 6226 CNRS-ENSCR, Avenue du Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France.

THE ROTATIONAL SPECTRUM OF $^{13}\text{C}_2\text{NH}_2$ UP TO 1 THz

ROMAN A. MOTIYENKO, LAURENT MARGULÈS, Laboratoire PhLAM, CNRS UMR 8523, Université de Lille 1, 59655 Villeneuve d’Ascq Cedex, France; VADIM V. ILYUSHIN, Institute of Radio Astronomy of NASU, Chervonopraporna 4, 61002 Kharkov, Ukraine.

THE EXTENDED SPECTROSCOPIC DATABASE ON FORMAMIDE: PARENT, $^{13}\text{C}$ AND DEUTERATED SPECIES UP TO 1 THz

A. S. KUTSENKO, Institute of Radio Astronomy of NASU, Chervonopraporna 4, 61002 Kharkov, Ukraine; R. A. MOTIYENKO, L. MARGULÈS, Laboratoire PhLAM, CNRS/Université des Sciences et Technologies de Lille 1, Bât. P5, 59655 Villeneuve d’Ascq Cedex, France; J.-C. GUILLEMIN, Sciences Chimiques de Rennes-Ecole Nationale Supérieure de Chimie de Rennes-CNRS, 35700 Rennes, France.

MONTE CARLO MODELING OF GAS-GRAIN CHEMISTRY IN STAR-FORMING REGIONS

A.I. VASYUNIN, E. HERBST, The Ohio State University.

OBSERVATIONS OF INTERSTELLAR HYDROGEN FLUORIDE AND HYDROGEN CHLORIDE IN THE GALAXY

RAQUEL R. MONJE, DAREK C. LIS, THOMAS G. PHILLIPS, PAUL F. GOLDSMITH, MARTIN EM-PRECHTINGER, California Institute of Technology, 1200 E. California Blvd., Pasadena, CA 91125-4700, USA; DAVID A. NEUFELD, Johns Hopkins University, USA.
FB01 15 min 8:30
AUGER ELECTRONS VIA Kα X-RAY LINES OF PLATINUM COMPOUNDS FOR NANOTECHNOLOGICAL APPLICATIONS

SULTANA N. NAHAR, Dept of Astronomy, The Ohio State University, Columbus, OH 43210; SARA LIM, Bio-physics Program, The Ohio State University, Columbus, OH 43210; A.K. PRADHAN, Dept of Astronomy, and Chemical Physics Program, The Ohio State University, Columbus, OH 43210; R.M. PITZER, Dept of Chemistry, The Ohio State University, Columbus, OH 43210.

FB02 15 min 8:47
A QUANTUM CHEMICAL EXPLORATION OF THE SF₆O SERIES (n = 1 − 5): AN ATOM-BY-ATOM APPROACH

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

FB03 10 min 9:04
A COMPUTATIONAL INVESTIGATION OF c-C₃H₂...HX(X = F, Cl, Br) H-BONDED COMPLEXES

PRADEEP R. VARADWAI, ARPITA VARADWAI, GILLES H. PESLHERBE, Centre for Research in Molecular Modeling & Department of Chemistry and Biochemistry, Concordia University, Montreal, QC, Canada.

FB04 15 min 9:16
ELECTRONIC STRUCTURE OF ETHYNYL SUBSTITUTED CYCLOBUTADIENES

FRANK LEE EMMERT III, STEPHANIE J. THOMPSON, and LYUDMILA V. SLIPCHENKO, Department of Chemistry, Purdue University, West Lafayette, IN 47907.

FB05 15 min 9:33
APPLICATIONS OF PATH INTEGRAL LANGEVIN DYNAMICS TO WEAKLY BOUND CLUSTERS AND BIOLOGICAL MOLECULES

CHRISTOPHER ING, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada; CONRAD HINSEN, Centre de Biophysique Moléculaire, CNRS, Rue Charles Sadron, 45071 Orleans, France; JING YANG, PIERRE-NICHOLAS ROY, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

FB06 15 min 9:50
INTERPRETATION OF THE IR/UV SPECTRA OF Ac-Trp-Tyr-NH₂ and Ac-Trp-Tyr-Ser-NH₂ USING MOLECULAR DYNAMICS AND AB INITIO METHODS.ᵃ

JESSICA A. THOMAS and DAVID W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260; ERIC GLOAGUEN, BENJAMIN TARDIVEY, FRANÇOIS PIUZZI, and MICHEL MONS, Laboratoire Francis Perrin, URA 2453 CRNS, Service des Photons, Atomes et Molécules CEA Saclay, Bât 522, 91191 Gif-sur-Yvette Cedex, France.

ᵃWork supported in part by NSF CHE-0911117
Intermission

FB07 15 min 10:30
AB INITIO INVESTIGATION OF THE EXCITED STATES OF NUCLEOBASES AND NUCLEOSIDES

PÉTER G. SZALAY, GÉZA FOGARASI, Eötvös Loránd University, Budapest, Hungary; THOMAS WATSON, AJITH PERERA, VICTOR LOTRICH, ROD J. BARTLETT, Quantum Theory Project, University of Florida, Gainesville, FL.

FB08 15 min 10:47
APPLICATION OF EFFECTIVE FRAGMENT POTENTIAL METHODS TO THE REDOX POTENTIAL OF GREEN FLUORESCENT PROTEIN

DEBASHREE GHOSH, ANNA I. KRYLOV, Department of Chemistry, University of Southern California, Los Angeles, CA 90089 (email to D. G.: debashree.ghosh@gmail.com).

FB09 15 min 11:04
VIBRONIC COUPLING IN ASYMMETRIC DIMERS: GENERALIZATION OF THE FULTON-GOUTERMAN APPROACH

B. NEBGEN and L. V. SLIPCHENKO, Department of Chemistry, Purdue University, West Lafayette, IN 47907.

FB10 15 min 11:21
Post-deadline Abstract
PREDICTION OF FUNDAMENTAL VIBRATIONAL FREQUENCIES AND INFRARED INTENSITIES: A BENCHMARK STUDY

JUANA VÁZQUEZ, MICHAEL E. HARDING, JOHN F. STANTON, Institute for Theoretical Chemistry, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712.

FB11 10 min 11:38
Post-deadline Abstract
VIBRATIONAL CORRECTIONS TO MOLECULAR PROPERTIES: SECOND-ORDER VIBRATIONAL PERTURBATION THEORY VS VARIATIONAL COMPUTATIONS

MICHAEL E. HARDING, JUANA VÁZQUEZ, JOHN F. STANTON, Institute for Theoretical Chemistry, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712, USA; GREGOR DIEZEMANN, and JÜRGEN GAUSS, Institut für Physikalische Chemie, Universität Mainz, Jakob-Welder-Weg 11, D-55128 Mainz, Germany.

FB12 15 min 11:50
Post-deadline Abstract
TDDFT CALCULATIONS OF TRANSIENT IR SPECTRA OF DNA

RYAN M. RICHARD, JOHN M. HERBERT, Department of Chemistry, The Ohio State University, Columbus, OH 43210.
FC. INFRARED/RAMAN
FRIDAY, JUNE 24, 2011 – 8:30 am
Room: 1000 McPHERSON LAB

Chair: MANFRED WINNEWISSE, The Ohio State University, Columbus, OH

FC01 15 min 8:30
NEW METHOD OF FITTING EXPERIMENTAL RO-VIBRATIONAL INTENSITIES TO THE DIPOLE MOMENT FUNCTION: APPLICATION TO HCl

G. LI, P. F. BERNATH, Department of Chemistry, University of York, Heslington, York YO10 5DD; I. E. GORDON, L. S. ROTHMAN, Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge MA 02138, USA.

FC02 15 min 8:47
EXTENSIVE AND HIGHLY ACCURATE LINE LISTS FOR HYDROGEN HALIDES

G. LI and P.F. BERNATH, Department of Chemistry, University of York, Heslington, York YO10 5DD, UK; I.E. GORDON, L.S. ROTHMAN, C. RICHARD, Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge MA 02138, USA; R.J. LE ROY, Department of Chemistry, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada; J.A. COXON, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada; P. HAJIGEORGIOU, Department of Life and Health Sciences, University of Nicosia, 46 Makedonitissas Ave., P.O. Box 24005, Nicosia 1700, Cyprus.

FC03 15 min 9:04
ARE AB INITIO QUANTUM CHEMISTRY METHODS ABLE TO PREDICT VIBRATIONAL STATES UP TO THE DISSOCIATION LIMIT FOR MULTI-ELECTRON MOLECULES CLOSE TO SPECTROSCOPIC ACCURACY?

PÉTER G. SZALAY, Eötvös Loránd University, Budapest, Hungary; FILIP HOLKA, Slovak University of Technology, Trnava, Slovak Republic; JULIEN FREMONT, MICHAEL REY, VLADIMIR G. TYUTEREV, Reims University, Reims, France.

FC04 15 min 9:21
ANALYSIS OF THE VIBRATIONAL SPECTRA OF P₃N₃(OCH₂CF₃)₆ AND P₄N₄(OCH₂CF₃)₈

ADRIAN K. KING, DAVID F. PLANT, PETER GOLDING, Atomic Weapons Establishment, Aldermaston, Berkshire, RG7 4PR, United Kingdom; MICHAEL A. LAWSON and PAUL B. DAVIES, University of Cambridge, Department of Chemistry, Lensfield Road, Cambridge, CB2 1EW, United Kingdom.

FC05 15 min 9:38
GAS PHASE THZ SPECTROSCOPY OF ORGANOSULFIDE AND ORGANOPHOSPHOROUS COMPOUNDS USING A SYNCHROTRON SOURCE

ARNAUD CUISSET, IRINA SMIRNOVA, ROBIN BOCQUET, FRANCIS HNDLE, GAE M. MOURET, DMITRI A. SADOVSKII, Laboratoire de Physico-Chimie de l’Atmosphère, 189A Ave. Maurice Schumann, 59140 Dunkerque, France; OLIVIER PIRALI, PASCALE ROY, Ligne AILES, synchrotron SOLEIL, L’Orme des Merisiers, Saint Aubin, BP 48, 91192 Gif-sur-Yvette, France.

Intermission
FC06  15 min  10:15

HIGH RESOLUTION INFRARED SPECTRA OF SPIROPENTANE, (C₅H₈)


FC07  15 min  10:32

Post-deadline Abstract

COLLISION-INDUCED INFRARED ABSORPTION BY COLLISIONAL COMPLEXES IN DENSE HYDROGEN-HELIUM GAS MIXTURES AT THOUSANDS OF KELVIN

MARTIN ABEL, LOTHAR FROMMOLD, Department of Physics, The University of Texas at Austin, Austin, TX 78712; XIAOPING LI, KATHARINE L. C. HUNT, Department of Chemistry, Michigan State University, East Lansing, MI 48824.

FC08  15 min  10:49

Post-deadline Abstract

ROTATIONALLY-RESOLVED INFRARED SPECTROSCOPY OF THE POLYCYCLIC AROMATIC HYDROCARBON PYRENE (C₁₆H₁₀) IN THE MID-INFRARED 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; BENJAMIN J. McCALL, Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

FC09  10 min  11:06

VIBRATIONAL SPECTROSCOPIC STUDY ON SOME HOFMANN TYPE CLATHRATES: M(2-(1-CYCLOHEXENYL)ETHYLAMINE)₂Ni(CN)₄·2BENZENE (M =Ni AND Cd)

TEKİN İZG, DEPARTMENT OF PHYSICS, ARTS AND SCIENCE FACULTY, İNÖNÜ UNIVERSITY, MALATYA, 44069, TURKEY; CEMAL PARLAK, DEPARTMENT OF PHYSICS, ARTS AND SCIENCE FACULTY, DÜMÜSPİNAR UNIVERSITY, KÜTAHYA, 43100, TURKEY; MUSTAFA SENYEL, DEPARTMENT OF PHYSICS, SCIENCE FACULTY, ANADOLU UNIVERSITY, ESKİŞEHİR, 26470, TURKEY.

FC10  15 min  11:18

Post-deadline Abstract

DETERMINATION OF THE BOND LENGTHS IN MgCCH, CaCCH and SrCCH

D. FORTHOMME, D. W. TOKARYK, C. LINTON, 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, 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.
FD. MINI-SYMPOSIUM: FUNDAMENTAL PHYSICS
FRIDAY, JUNE 24, 2011 – 8:30 am
Room: 1015 McPHERSON LAB

Chair: TREVOR SEARS, Brookhaven National Laboratory, Upton, New York

FD01  INVITED TALK
TIME-DOMAIN MW SPECTROSCOPY: FUNDAMENTAL PHYSICS FROM MOLECULAR ROTATION

JENS-UWE GRABOW, Gottfried-Wilhelm-Leibniz-Universität, Institut für Physikalische Chemie & Elektrochemie, Callinstraße 3A, 30167 Hannover, Germany.

FD02  15 min  9:05
HIGH PRECISION UV MEASUREMENTS IN CO, TOWARDS A LABORATORY TEST OF THE TIME-INVARiance OF $\mu$.

ADRIAN J. DE NIJS, KJELD S.E. EIKEMA, WIM UBACHS and HENDRICK L. BETHLEM, LaserLab, VU University Amsterdam, the Netherlands.

FD03  15 min  9:22
PROSPECTS FOR RAPID DECELERATION OF DIATOMIC MOLECULES WITH OPTICAL BICHROMATIC FORCES

E. E. EYLER and M. A. CHIEDA, Department of Physics, University of Connecticut, Storrs, CT 06269, USA.

FD04  15 min  9:39
DECELERATION AND TRAPPING OF HEAVY DIATOMIC MOLECULES FOR PRECISION MEASUREMENTS


FD05  15 min  9:56
INVESTIGATION OF THE USE OF HE – DIATOMIC VAN DER WAALS COMPLEXES AS A PROBE OF TIME-REVERSAL VIOLATION

JACOB STINNETT, ERIC ABRAHAM, NEIL SHAFER-RAY, Homer L. Dodge Department of Physics, University of Oklahoma, 440 W.Brooks, NH 100, Norman, OK 73019.

Intermission

FD06  15 min  10:30
FREQUENCY COMB VELOCITY MODULATION SPECTROSCOPY

KEVIN C. COSSEL, LAURA C. SINCLAIR, TYLER COFFEY, ERIC CORNELL, 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.
FD07 15 min 10:47
OPTICAL PULSE-SHAPING FOR INTERNAL COOLING OF MOLECULAR IONS

CHIEN-YU LIEN, SCOTT R. WILLIAMS, and BRIAN ODOM, Department of Physics and Astronomy, Northwestern University, 2145 Sheridan Road, Evanston IL 60208.

FD08 Post-deadline Abstract 15 min 11:04
RELATIVISTIC COMBINED PSEUDOPOTENTIAL—RESTORATION METHOD FOR STUDYING MULTITUDE OF PROPERTIES IN HEAVY-ATOM SYSTEMS

ANATOLY V. TITOV, ALEXANDER N. PETROV, LEONID V. SKRIPNIKOV, NIKOLAI S. MOSYAGIN, B.P. Konstantinov Petersburg Nuclear Physics Institute, Gatchina, Leningrad district 188300, Russia.

*This work is supported by the RFBR Grant No. 09–03–01034

FD09 Post-deadline Abstract 15 min 11:21
SPECTROSCOPIC CHARATERIZATION OF ThF AND THE LOW-LYING STATES OF ThF+

BEAU J. BARKER, IVAN O. ANTONOV, and MICHAEL C. HEAVEN, Department of Chemistry, Emory University, Atlanta, GA 30322.

FD10 Post-deadline Abstract 15 min 11:38
LASER SPECTROSCOPY OF THE 4Γ - X 4Φ TRANSITION IN TITANIUM HYDRIDE, TiH

COLAN LINTON, Centre for Laser Atomic and Molecular Sciences and Physics Department, University of New Brunswick, Fredericton, NB E3B 5A3, Canada; SARAH FREY and TIMOTHY C. STEIMLE, Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604.

FD11 Post-deadline Abstract 15 min 11:55
OBSERVATION OF FEMTOSECOND, SUB-ANGSTROM MOLECULAR BOND RELAXATION USING LASER-INDUCED ELECTRON DIFFRACTION

COSMIN I. BLAGA, ANTHONY D. DICHIARA, KAIKAI ZHANG, EMILY SISTRUNK, PIERRE AGOSTINI, LOUIS F. DIMAURO, Department of Physics, The Ohio State University, Columbus, OH 43210; JUNLIANG XU, CHII-DONG LIN, Department of Physics, Kansas State University, Manhattan, KS 66506; and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, OH 43210.
FE. MATRIX/CONDENSED PHASE
FRIDAY, JUNE 24, 2011 – 8:30 am
Room: 2015 McPHERSON LAB

Chair: JAY C. AMICANGELO, Penn State Erie, The Behrend College, Erie, Pennsylvania

FE01 TOWARD A CONTINUOUS-WAVE SOLID HYDROGEN RAMAN LASER FOR MOLECULAR SPECTROSCOPY APPLICATIONS

W. R. EVANS, Department of Physics, University of Illinois at Urbana-Champaign, Urbana, IL 61801; T. MOSE, Department of Chemistry, The University of British Columbia, Vancouver, BC Canada V6T 1Z1; B. J. Mc-CALL, Departments of Chemistry, Physics, and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

FE02 PHOTODISSOCIATION OF FORMIC ACID ISOLATED IN SOLID PARAHYDROGEN

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

FE03 RESONANT TWO-STEP IONIZATION OF Rb AND Cs ATOMS ON HELIUM NANODROPLETS

F. LACKNER, M. THEISEN, and W.E. ERNST, Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria.

FE04 INFRARED AND MICROWAVE-INFRARED DOUBLE RESONANCE SPECTROSCOPY OF METHANOL EMBEDDED IN SUPERFLUID HELIUM NANODROPLETS

PAUL L. RASTON AND WOLFGANG JÄGER, Department of Chemistry, University of Alberta, Edmonton, Alberta T6G-2G2, Canada.

FE05 LASER SPECTROSCOPY OF HYDROGEN PEROXIDE EMBEDDED IN HELIUM NANODROPLETS

CHRISSY J. KNAPP, PAUL L. RASTON, and WOLFGANG JÄGER, Department of Chemistry, University of Alberta, Edmonton, AB, Canada T6G 2G2.

Intermission

FE06 Post-deadline Abstract

PYRIDINE AGGREGATION IN HELIUM NANODROPLETS

PABLO NIETO, MELANIE LETZNER, DANIEL HABIG, TOERSTEN POERSCHKE, SARAH ANGELIQUE GRÜN, KENNY HANKE, GERHARD SCHWAAB and MARTINA HAVENITH, Department of Physical Chemistry II, Ruhr-Universität Bochum, Germany.
FE07

Post-deadline Abstract

IR SPECTROSCOPY STUDY ON THE \((\text{HCl})_n(\text{H}_2\text{O})_m\) AGGREGATION IN HELIUM NANODROPLETS

PABLO NIETO, MELANIE LETZNER, DANIEL HABIG, TOERSTEN POERSCHKE, SARAH ANGELIQUE GRÜN, KENNY HANKE, GERHARD SCHWAAB and MARTINA HAVENITH, Department of Physical Chemistry II, Ruhr-Universität Bochum, Germany.

FE08

Post-deadline Abstract

IR-SPECTROSCOPY OF GLYCINE AND ITS COMPLEXES WITH WATER IN HELIUM NANODROPLETS

M. LETZNER, S. A. GRÜN, G. SCHWAAB and M. HAVENITH, Department of Physical Chemistry II, Ruhr-University Bochum, D-44780 Bochum, Germany.

FE09

Post-deadline Abstract

INELASTIC SCATTERING OF RADICALS FROM A LIQUID SURFACE

MICHAEL ZIEMKIEWICZ and DAVID NESBITT, JILA - UNIVERSITY OF COLORADO, 440 UCB, BOULDER, CO 80309.

FE10

Post-deadline Abstract

QUANTUM CHEMICAL STUDY OF RAMAN SPECTROSCOPY OF SUBSTITUTED BENZENE DERIVATIVES ADSORBED ON METAL SURFACES

DE-YIN WU, ZHONG-QUN TIAN, Dept. of Chemistry, College of Chemistry & Chemical Engineering, & State Key Lab of Physical Chemistry of Solid Surfaces, Xiamen, 361005, Fujian, China.

*Support by NSF of China (Nos. 20973143, 21021002 and 91027009) and National Basic Research Programs (Nos. 2007CB815303 and 2009CB930703) are gratefully acknowledged. Parts of the calculations were performed at the HPC of Xiamen University.

FE11

Post-deadline Abstract

IR-SPECTROSCOPY OF PHENYLRADICALS IN HELIUMNANODROPLETS

D. HABIG, T. POERSCHKE, P. NIETO, G. SCHWAAB and M. HAVENITH, Department of Physical Chemistry II, Ruhr-University Bochum, D-44780 Bochum, Germany.
Welcome
Caroline C. Whitacre, Vice President for Research
The Ohio State University

MA01  40 min  9:00
SPECTROSCOPY AND DYNAMICS OF THE HOCO RADICAL

ROBERT E. CONTINETTI*, BERWYCK L. J. POAD, Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, CA 92093; CHRISTOPHER J. JOHNSON, Department of Physics, University of California San Diego, La Jolla, CA 92093; MICHAEL E. HARDING, JOHN F. STANTON, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712.

The HOCO radical plays a crucial role as the intermediate in the reaction of OH + CO → H + CO₂, yet significant questions regarding its detailed dynamics remain. Through photoelectron and photoelectron-photofragment coincidence spectroscopy on cold HOCO⁻ and DOCO⁻ anions, we have gained new insight into the dynamics of the strongly bound HOCO system. Photoelectron spectra probing the lower region of the deep HOCO well reveal structured spectra that are supported by Franck-Condon simulations, and allow for the reassignment of the electron affinities for both cis- and trans- isomers. Higher in the well, where tunneling from HOCO to H + CO₂ becomes relevant, energy-resolved tunneling lifetimes are inverted to obtain a model barrier to formation of H + CO₂ that is consistent with experimental internal energy distributions. Tunneling lifetimes at the top of the barrier indicate that tunneling can play an important role in this elementary reaction.

*This work supported by the US Department of Energy under grant number DE-FG03-98ER14879
Functional molecules, such as crown ethers and calixarenes, can act as hosts for encapsulating guest species through non-covalent interactions. Applications of crown ethers and calixarenes as molecular receptors, metal cation extraction agents, fluoro-ionophores and phase transfer catalytic media have been previously reported in a number of studies in the literature. One of the important aspects of these host/guest molecular assemblies is their selectivity in the encapsulation of guest species. Two important factors that control this selectivity are: (1) the size and the flexibility of the host cavity and (2) the properties of solvent molecules.

Molecular complexes formed in supersonic jets provide ideal systems for the selective study of the conformational preference and micro-solvated effects under solvent-controlled conditions. This talk will review our spectroscopic and theoretical studies of the structures of dibenzo-18-crown-6-ether (DB18C6), benzo-18-crown-6-ether (B18C6), calix[4]arene (C4A) and their complexes with guest molecules. We apply laser-induced fluorescence (LIF), resonance enhanced two-photon ionization (R2PI) and UV-UV hole-burning (HB) spectroscopy for obtaining electronic spectra and IR-UV doubleresonance and IR photodissociation (IRPD) spectroscopy for the IR spectra. The electronic and IR spectra are compared with the corresponding results obtained by DFT calculations and high-level first principles electronic structure calculations [MP2 and CCSD(T)]. Based on these joint studies we can elucidate the nature of interactions that control the encapsulation of a guest molecular species as well as how the host can adjust its conformation to accommodate a specific guest, leading to the molecular recognition.
ELECTRONIC SPECTROSCOPY OF CARBON CHAINS OF ASTROPHYSICAL RELEVANCE

JOHN P. MAIER, Department of Chemistry, University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland.

Electronic spectra of radicals and ions containing carbon chain skeleton are measured in the laboratory using a number of spectroscopic techniques. The species are selected because of their astrophysical relevance: possessing allowed electronic transitions in the optical range, where absorption measurements through diffuse interstellar clouds have been made. Initial survey spectra are obtained by observation of the absorption of mass-selected species in 6 K neon matrices. Examples of this are the detections of the electronic transitions of protonated coronene and C$_7$H$_7^+$ isomers. This information is then used to search for the relevant transitions in the gas phase using a number of sensitive laser techniques. In the gas phase the species are produced at low temperatures, 20–80 K, using slit jet supersonic expansions through which a discharge runs. The absorptions are detected by cavity ring-down and degenerate four wave mixing methods; the latter approach providing certain advantages. Using a two color degenerate four wave approach both double resonance labeling of rotational levels and mapping of the ground state vibrational manifold is achieved, such as for C$_4$H, X $^2\Sigma^+$. Using a combination of the above techniques the electronic transitions of H$_2$CCC could be identified in the gas phase and these match with two broad diffuse interstellar bands, implying the first identification of such a carrier. Electronic absorptions of mass-selected cations constrained in a 22-pole radio-frequency trap are measured. The vibrational and rotational degrees of freedom are equilibrated to around 20 K by collisions with cryogenically cooled helium. The transition of the ion is then detected by a two color excitation–dissociation scheme. Examples of this are polyacetylene cations, revealing that not only the lowest energy transitions but higher ones are of relevance to astronomical observations. The spectra are also without overlapping features of other species as is encountered in the measurements through discharge plasmas. Comparison of the spectroscopic data on HC$_{2n}$H$^+$ n=2,3 cations with astronomical measurements indicates that magnetic dipole transitions and velocity broadenings in the astronomical data have to be considered.
THEORETICAL STUDIES OF OBSERVABLE TRANSITIONS TO RECOUPLED PAIR BONDED STATES OF SULFUR HALIDE COMPOUNDS: SF/SCl (X^2Π→A^2Σ−), SF2/SCl2 (X^1A1→1^1B1, X^1A1→1^1A2), AND SFCI (X^1A′→A^1A′′)

JEFF LEIDING, DAVID E. WOON and THOM H. DUNNING, JR., Department of Chemistry, University of Illinois at Urbana-Champaign, Box 86-6, CLSL, 600 South Mathews, Urbana IL, 61801.

In previous studies regarding the nature of hypervalent behavior, we identified low-lying excited states of SF(a^1Σ−), SCl(a^1Σ−), SF2(a^3B1,a^3A2), SFCl(a^3A′) and SCl2(a^3B1) that involve recoupled pair bonding (rpb), where the electrons of the S 3p^2 pair are made available to form bonds. While the transitions from the ground states to the quartet states of SF/SCl and the triplet states of SF2/SCl2/SCl2 are spin-forbidden, each of these excited states have analogs with formally spin- and dipole-allowed transitions (except 1^1A2). We performed high level MRCI+Q/aug-cc-pV(Q+d)Z calculations in order to characterize the electronic spectra, spectroscopic constants, and bonding of these species, and made comparisons to available experimental data. We found that excitation into the experimentally known and dipole-forbidden singlet rpb state, SCl2(B^1A2), can explain the well-known photodissociation behavior of SCl2 used to produce SCl(X^2Π) radicals in the laboratory.

a Finally, we have also found a possible system of bond-stretch isomers on the SFCI(A^1A′′) potential energy surface that is analogous to the behavior on the triplet surface reported in our previous study.


BLUE-DETUNED PHOTOASSOCIATION SPECTRUM IN Rb2


We report on the observation of blue-detuned photoassociation as proposed in [1] and references therein. “Blue-detuned” refers to the location of vibrational levels — energetically above the corresponding atomic asymptote. Ultracold ^85Rb atoms in a MOT were photoassociated to levels of the 1^3Πg state a few hundred wavenumbers above the 5S + 5P_{3/2} limit. These transitions were found to be strong even though they occur at short internuclear separations (Rc=10a_0). Levels of the 1^3Πg state spontaneously decay to the a^5Σ^+_{u} state, where they are detected by resonantly enhanced multiphoton ionization with time-of-flight spectroscopy. We have observed most vibrational levels of the 1^3Πg state belonging to all of its spin-orbit components (0^0_g,0^−_g,1_g,2_g). Recent unpublished ab-initio calculations [2] of these potentials show good agreement with the observed vibrational and rotational constants. This work is supported by the NSF, AFOSR, and UConn Research Foundation.

[2] O. Dulieu, private communication
AN ACCURATE NEW POTENTIAL FUNCTION FOR GROUND-STATE Xe₂ FROM UV AND VIRIAL COEFFICIENT DATA

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Determining accurate analytic pair potentials for rare gas dimers has been a longstanding goal in molecular physics. However, most potential energy functions reported to date fail to optimally represent the available spectroscopic data, in spite of the fact that such data provide constraints of unparalleled precision on the attractive potential energy wells of these species. A recent study of ArXe showed that it is a straightforward matter to combine multi-isotopologue spectroscopic data (in that case, microwave, and high resolution UV measurements) and virial coefficients in a direct fit to obtain a flexible analytic potential function that incorporates the theoretically predicted damped inverse-power long-range behaviour. The present work reports the application of this approach to Xe₂, with a direct fit to high resolution rotationally resolved UV emission data for \( v'' = 0 \) and 1,\(^b\) band head data for \( v'' = 0 \) \(-\) 9,\(^c\) and virial coefficient data for \( T = 165 \) – 950 K\(^d\) being used to obtain an accurate new potential energy function for the ground state of this Van der Waals molecule. Analogous results for other rare-gas pairs will also be presented, as time permits.


LASER-INDUCED FLUORESCENCE STUDIES OF THE JET-COOLED ALUMINUM ACETYLIDE RADICAL (AlCCH/AlCCD)

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

Laser-induced fluorescence and single vibronic level (SVL) emission spectra of the \( \tilde{A}^1Π - \tilde{X}^1Σ \) system of aluminum acetylide (AlCCH) and its deuterated isotopologue (AlCCD) have been investigated in the region of 350-317 nm. The radicals were produced in a pulsed electric discharge jet using a precursor mixture of trimethyl aluminum or deuterated trimethyl aluminum in high pressure argon. High resolution spectra of the 0\(_0^0\) and 3\(_0^0\) bands of AlCCH have been recorded and the rotational constants determined for both electronic states. SVL emission spectra from several excited state levels were also recorded and the ground state energy levels have been assigned and fitted. The excited state is complicated by a double Renner-Teller effect involving the \( ν_4 \) (CCH) and \( ν_5 \) (AlCC) bending modes. Our \textit{ab initio} calculations predict \( |ϵ_4| = 0.833 \) and \( |ϵ_5| = 0.432 \) indicating substantial splittings of the bending levels. Progress in assigning the complex vibronic structure in the LIF spectra and fitting it using a Renner-Teller model including both bending modes and the AlC stretching mode will be discussed.

THE ELECTRONIC SPECTRUM OF H₂PO, THE PROTOTYPICAL PHOSPHORYL FREE RADICAL

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The electronic spectrum of the H₂PO radical has been identified by laser-induced fluorescence (LIF) and single vibronic level (SVL) emission techniques. The radical was produced in a pulsed electric discharge jet using a precursor mixture of phosphine (PH₃) and carbon dioxide in high-pressure argon and the \( \tilde{B}^2A' - \tilde{X}^2A' \) electronic transition was detected in the 410-338 nm region. Low resolution LIF and SVL emission spectra of H₂PO and D₂PO have been recorded and the \( a' \) vibrational frequencies have been determined in both states. High-resolution spectra of the 0\(_0^0\) bands of H₂PO and D₂PO, which consist of strong \( a \)-type and weaker \( c \)-type components, were recorded. The spectra have been rotationally analyzed and the excited state molecular structure determined. The spectrum of H₂PO will be discussed in comparison with the spectra of other phosphoryl and arsenyl radicals that have been recently studied in our laboratory.
DETECTION OF THE H$_2$PS FREE RADICAL BY LASER SPECTROSCOPY

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The previously unobserved H$_2$PS free radical has been detected by laser-induced fluorescence (LIF) techniques. H$_2$PS (and D$_2$PS) were produced in a pulsed discharge jet using a precursor gas mixture of Cl$_3$PS vapor and hydrogen (or deuterium) in high pressure argon. Our ab initio predictions of the ground and excited state frequencies and excitation energy are in good agreement with the results obtained by vibrational analysis of the LIF and single vibronic level (SVL) emission spectra. High-resolution spectra of the hybrid $0^0_0$ bands of H$_2$PS and D$_2$PS were analyzed by band contour methods to obtain approximate ground and excited state rotational constants and molecular structures. The electronic transition involves promotion of an electron from the $\pi$ to the $\pi^*$ orbital and is assigned as $\tilde{B}^2A' - \tilde{X}^2A'$. The results will be discussed in comparison to ab initio predictions and the spectra of other X$_2$PS radicals recently studied in our laboratory.

A SPECTROSCOPIC STUDY OF THE LINEAR-BENT ELECTRONIC TRANSITIONS OF JET-COOLED BCl$_2$ AND HBCI

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Laser induced fluorescence (LIF) and single vibronic level emission spectra (SVL) of jet-cooled BCl$_2$ and HBCI have been measured. The radicals were produced in a pulsed electric discharge of a mixture of BCl$_3$/Ar and BCl$_3$/H$_2$/Ar, respectively. The LIF spectra of both radicals are congested due to overlapping bands from the boron and chlorine isotopes. In addition, the ground and first excited states are the two Renner-Teller components of a $2\Pi$ state split by a strong vibronic interaction. The Franck-Condon profile of the $\tilde{A}^2B_1 - \tilde{X}^2A_1$ band system of BCl$_2$ and the $\tilde{A}^2A'' - \tilde{X}^2A'$ system of HBCI are characteristic of linear-bent excitations. Excited state bending progressions have been identified in both species using the LIF-sync scan procedure in which the monochromator is offset by a value corresponding to a ground state fundamental frequency of the target molecule and scanned simultaneously with the dye laser. LIF spectra of individual isotopes can thus be recorded. Ground state vibrational frequencies have been deduced from SVL spectra. The emission spectra for BCl$_2$, are dominated by progressions in the symmetric stretching ($\nu_1$) and bending ($\nu_2$) modes. In the case of HBCI, progressions in the bending ($\nu_2$) and BCI stretching ($\nu_3$) modes were observed.

TWO-DIMENSIONAL (2+n) REMPI SPECTROSCOPY: STATE INTERACTIONS, PHOTOFRAGMENTATIONS AND ENERGETICS OF THE HYDROGEN HALIDES

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Mass spectra are recorded for one-colour (2+n) resonance enhanced multiphoton ionization (REMPI) of HX (X = Cl, Br) as a function of resonance excitation energy to obtain two-dimensional REMPI data. Perturbations due to Rydberg to ion-pair state interactions show as line shifts, ion signal intensity variations as well as band width broadenings depending on rotational quantum numbers, J. The data allow determination of parameters relevant to the nature and strength of state interactions as well as dissociation and ionization processes. Alterations in X$^+$ and HX$^+$ signal intensities prove to be very useful for spectra assignments.

Intermission
OPTICAL STARK SPECTROSCOPY OF THE $\tilde{A}^2\Pi - \tilde{X}^2\Sigma^+$ BAND OF BaOH

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Transitions of the $\tilde{A}^2\Pi - \tilde{X}^2\Sigma^+$ band system of barium monohydroxide, BaOH, were observed and recorded from 11483-11485 cm$^{-1}$ and 12041-12044 cm$^{-1}$. The features were readily identified using the results of the Doppler-limited measurements$^a$. The laser induced fluorescence (LIF) spectrum was analyzed to give optimized field-free excited state parameters. The parameters for the $\tilde{X}^2\Sigma^+$ state were constrained to the previously determined values$^b$. The permanent electric dipole moments for the $\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ states have been determined from the analysis of the optical Stark spectra for the $R_{21}(0.5)$, $Q_{21}(1.5)$, and $R_{2}(0.5)$ lines. The obtained values were $\mu(\tilde{X}^2\Sigma^+)=1.426(38)$ D and $\mu(\tilde{A}^2\Pi)=0.477(7)$ D. The results are compared with predicted values from semi-empirical models and those for CaOH and SrOH$^c$.


LASER INDUCED FLUORESCENCE SPECTROSCOPY OF BORON CARBIDE

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Laser induced fluorescence spectrum of boron carbide (BC) between 490 and 560 nm has been recorded and analyzed. Gas-phase BC molecule was produced by the reaction of B$_2$H$_6$ and CH$_4$ in the presence of magnesium atom from laser ablation process. The (0, 0), (1, 0), and (2, 0) bands of the B$^4\Sigma^+ - X^4\Sigma^-$ transition were recorded and rotationally analyzed. Spectra of both isotopes: $^{10}$BC and $^{11}$BC were observed. Equilibrium molecular constants for the B$^4\Sigma^+$ and X$^4\Sigma^-$ states for both isotopes were determined. A comparison of the determined gas-phase molecular constants with those obtained using matrix isolation spectroscopy and the theoretical calculations will be presented.

Financial support from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. HKU 701008P) is gratefully acknowledged.

IMPROVEMENT OF SPECTROSCOPIC CONSTANTS FOR THE A$^3\Pi_{1u} \leftarrow X^1\Sigma^+_g$ SYSTEM OF Br$_2$

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High-resolution spectroscopy in the near infrared region is very important for frequency standards. We have measured the Doppler limited vibrational-rotational spectrum of ICl$^a$, IBr$^b$, I$_2$$^{c}$ and Br$_2$$^{d}$ by using a titanium sapphire laser, and have reported their spectroscopic constants. The present work presents revised spectroscopic constants for the $X$-state of Br$_2$ which are obtained by performing a combined-isotopologue least-squares fit to all available data for the three isotopic species. We are also attempting to observe the lowest vibrational levels of the $A$-state in order to allow us to determine the potential energy function of this state. Measurements were made at room temperature in the region 13000 – 13700 cm$^{-1}$ and at 150-250°C in the region 11600 – 13000 cm$^{-1}$. Details of these results will be presented.

ACCURATE ANALYTIC POTENTIALS FOR THE $A^3\Pi_1$ AND $X^1\Sigma^+$ STATES OF IBr FROM A COMBINED-ISOTOPOLOGUE DIRECT-POTENTIAL-FIT DATA ANALYSIS

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Iodine monobromide has been studied in various wavelength regions by researchers using diffraction grating, microwave, and high-resolution laser techniques combined with a Fourier transform spectrometer. Differences in predictions generated from parameters for the $A^3\Pi_1$ and $X^1\Sigma^+$ states obtained from some of these studies show that it can be difficult to make reliable predictions outside the data region, especially if one is using conventional Dunham expansions. In the present work, high resolution absorption and laser excitation data for the $X^1\Sigma^+ - A^3\Pi_1$ system of $^{79}$Br and $^{81}$Br, together with earlier microwave, infrared, and fluorescence progression data, are analyzed using a direct-potential-fit (DPF) procedure to obtain accurate analytic potential energy functions for the two states that provide a compact unified description of all of the available data, as well as realistic predictions for the unobserved levels of this species.

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TRANSITION STRENGTHS IN THE VISIBLE ABSORPTION SPECTRUM OF I$_2$: ONE MORE PASS

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The absorption spectrum of I$_2$ is examined anew across the wavelength range 400-850 nm, where there is significant room-temperature absorption in the three overlapped electronic transitions. To better characterize the discrete absorption in the dominant $B - X$ system, spectra are recorded in the 520-640-nm region with high quantitative precision (0.0005 absorbance units) at moderate resolution (0.1 nm) and are analyzed by least-squares spectral simulation, yielding the $B - X$ electronic transition strength $\mu^2$ with unprecedented precision (< 2 percent relative standard error) over most of the studied region. This treatment also yields directly new estimates of the continuous absorption, which support previous assessments of the $A - X$ transition but indicate that the $C - X$ transition is 20 percent weaker than thought. In companion studies, lower resolution (1 nm) spectra and multiple-temperature absorption data from the literature are analyzed as bound-free by quantum spectral simulation, to yield estimates of the small-$R$ potential curve extensions for all three excited states and their $R$-dependent transition moment functions. To increase the precision and range of description of the least-known $C$-state potential, the least-squares analysis is expanded to include quantum simulation of literature data for the $B - C$ predissociation. The result is a $C$-state potential obtained with a precision comparable to that achieved in many discrete spectroscopic studies, over the range where absorption and predissociation occur (2.5-2.9 Å), and extending smoothly to its van der Waals well at 4.3 Å.

The discrete simulation method described here is applicable to any system where the spectrum can be reliably simulated, which must include treatment of the absorption and instrumental lineshapes. The I$_2$ $B - X$ results are directly applicable to the monitoring of I$_2$ in the atmosphere.
We report the photoelectron spectrum of ICN\(^{-}\) to probe transitions to the ground state (X \(^{1}\Sigma^{+}\)) and first 5 excited states (\(^{3}\Pi_2\), \(^{3}\Pi_1\), \(^{3}\Pi_0\), \(^{3}\Pi_{0+}\), and \(^{1}\Pi_1\)) of neutral ICN. We spectroscopically resolve the first 3 excited states and a conical intersection region between the \(^{3}\Pi_{0+}\) and \(^{1}\Pi_1\) states for the first time. The spectra are assigned with the aid of previously published high-level calculations by Morokuma and coauthors\(^{b}\). Our assignments are further verified by comparison to the photoelectron spectra of the dihalides I\(_2\) and IBr\(^{-}\). The poor Franck-Condon overlap between the ground states of the anion and neutral precludes direct observation of the adiabatic electron affinity, EA(ICN). However, through thermochemical cycles involving narrow transitions to excited states, we determine the EA(ICN) to be 1.7\(\pm\)0.1 eV and the dissociation energy, \(D_0\)(ICN\(^{-}\)), to be 0.9\(\pm\)0.1 eV. To our knowledge, the EA(ICN) has not been previously reported in experiment or theory; therefore, this is the first EA(ICN) determination. In addition, we observe at least four spectral peaks with kinetic energies of \(\leq\) 5, 45, 70, and 160 meV that are independent of the photon energy over the 2.6 - 4.1 eV energy range. It appears that these peaks are related to autodetachment from excited anions to the ground electronic state of the neutral. We use a combination of previous calculations by Morokuma et al. and two-dimensional SO-MR-CI scans with a fixed CN distance of the anion potential energy surfaces to aid in an autodetachment mechanism. Support from NSF and AFOSR is gratefully acknowledged.

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NEAR-INFRARED OVERTONE SPECTROSCOPY OF TRITIATED WATER

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The tritiated water molecules (here HTO and T$_2$O) are important isotopomers of water. The spectroscopic information is essential from the viewpoint of the basic science. However, the high-resolution spectroscopic studies of tritiated water were limited probably due to the radioactive nature of tritium. The microwave studies of these species were carried out and the molecular constants of the ground state were determined. $^a$ $^b$ $^c$ $^d$ $^e$ $^f$ For T$_2$O, the $\nu_3$ band was studied.

At 1.3 micron region, overtone and combination bands are expected. In this study we prepared tritiated water of high concentration which is necessary for the near-infrared measurement and carried out frequency modulated near-infrared spectroscopy. Many lines which are not listed in HITRAN were observed. We will report the current status of the analysis.


ASSIGNMENT OF INFRARED AMMONIA SPECTRA

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Global ammonia emissions have more than doubled during the period of industrialisation, largely due to widespread use of intensive agricultural techniques and in particular the use of fertilisers and are are set to double again by 2050. However the ammonia data in the present version of HITRAN is not only missing at key wavelengths, but also have significant problems. HITRAN contains 28 057 $^{14}$NH$_3$ lines of which some 10 % lack full quantum number assignments. Furthermore 1190 of the assigned lines have demonstrably incorrect assignments (for example are parity forbidden); others have incorrect lower state energies or symmetries leading to incorrect predictions of temperature-dependent spectra.

We have undertaken a systematic (re-)analysis of the data in HITRAN. This has been done using both lower state and upper state combination differences starting from a consistent set of lower state energy levels [P. Chen et al, J. Mol. Spectrosc., 236, 116 (2006)] and by using the newly computed variational line list BYTe [S. N. Yurchenko, R. J. Barber, and J. Tennyson, Mon. Not. R. Astron. Soc., in press, (2011)]. Previous errors and misassignments have been corrected and significant progress is being made new assignments.

Comparisons with the BYTe line list suggest that HITRAN is also missing a significant number of important transitions, particular at frequencies above 5000 cm$^{-1}$. 
MODELING VIBRATIONAL STRUCTURE USING HARMONICALLY-COUPLED MORSE OSCILLATORS: A GLOBAL DESCRIPTION OF THE C-H STRETCHES IN METHYL RADICAL AND ITS DEUTERATED ISOTOPOMERS

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Methyl radical has been the subject of numerous theoretical and experimental studies over the past 50 years, including several studies fitting force constants to experimental data. Only recently have high-resolution gas phase data become available for most of the stretches of all four isotopic species: CH$_3$, CH$_2$D, CHD$_2$, and CD$_3$. A harmonically-coupled Morse oscillator model, developed by Halonen and Child for tetrahedral molecules, is used to describe the set of high resolution data for the first time. In this picture, each C-H (or C-D) stretch is modeled as a Morse oscillator and the interactions between the local mode stretches are modeled as harmonic interactions. The C-H and C-D stretches differ only by analytic G-matrix element terms thus making this a three parameter model that describes each of the three stretches for all four isotopic species, where the parameters are the Morse oscillator dissociation energy (D), the range parameter (a), and the harmonic potential coupling constant.


HIGH-RESOLUTION FOURIER TRANSFORM INFRARED SPECTROSCOPY OF SMALL BORON-CONTAINING MOLECULES

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A series of small boron-containing molecules were synthesized in the gas phase using a tube furnace. High-resolution spectra of these species were recorded in either emission or absorption in the mid-infrared region using a Bruker IFS-125HR spectrometer. Our observations contain vibration-rotation bands of BO, the $v_1$ and $v_3$ bands of HBO, the $v_1$ and $v_3$ bands of HBS, the $v_1$ band of FBO, and the $v_1$ band of HBF$_2$. The vibrational bands of HOBO, BF$_2$OH and other boron-containing molecules may also be present. Ab initio calculations were performed at the MRCI level to assist in the vibrational assignments. Preliminary assignments of the spectra for these species will be reported.

INFRARED LINE INTENSITIES FOR FORMALDEHYDE FROM SIMULTANEOUS MEASUREMENTS IN THE INFRARED AND FAR INFRARED SPECTRAL RANGES

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Formaldehyde (H$_2$CO) is an important intermediate compound in the degradation of the volatile organic compounds (VOCs), including methane, in the terrestrial troposphere. Its observation using optical remote sensing in the infrared range relies on the 3.6 and 5.7 μm absorption bands. Band and individual line intensities have been reported in both ranges.

With the present work, we aim to also derive infrared line intensities for formaldehyde, however relying on pure rotation line intensities and the known electric dipole moment to determine the particle density. Indeed, because formaldehyde polymerizes or degrades easily, the gas phase may contain polymerization or degradation products. Spectra of H$_2$CO diluted in 10 hPa of N$_2$ were therefore simultaneously recorded in the 20 – 60 cm$^{-1}$ and 3.6 μm ranges, respectively using a Bruker IFS125HR Fourier transform spectrometer and a tunable diode laser.

Many of the molecules found in space are carbonaceous, that is, they have a carbon backbone in their structure. In addition, many of these molecules carry heteroatoms such as nitrogen and oxygen and also second row elements such as silicon. To date, four silicon-carbon molecules $\text{SiC}_n$ ($n = 1 - 4$) have been detected in space and several more by high-resolution spectroscopic techniques in the laboratory. Owing to their symmetry, many clusters of the form $\text{SiC}_n\text{Si}$ (and linear $\text{C}_n$ chains) are non-polar and hence have no pure rotational spectrum. In an effort to obtain the gas-phase spectra of these clusters in the infrared, we have started a dedicated laboratory program employing diode laser techniques and more recently an optical parametric oscillator-based spectrometer operating at 5 microns, where many carbon- and carbon-silicon chains are expected to exhibit strong infrared-active vibrational modes. Results from new observations of the previously studied $\text{Si}_2\text{C}_3$ and $\text{C}_6$ clusters \textsuperscript{a,b} will be reported.


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\textbf{Intermission}

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HYDROGEN BOND RING OPENING AND CLOSING IN PROTONATED METHANOIL CLUSTERS PROBED BY INFRARED SPECTROSCOPY WITH AND WITHOUT AR TAGGING

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Infrared spectra of protonated methanol clusters $\text{H}^+(\text{MeOH})_n$ ($n=4-7$) in the OH stretching vibrational region were measured with and without Ar tagging. While the spectra of the clusters without Ar are mainly attributed to the linear structures, the cyclic and bycyclic structures are dominant in the Ar tagged clusters. Significant switching of the structural motifs occurs with the Ar attachment, and its origin will be discussed.

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C...H...N HYDROGEN BOND FORMATION IN TRIMETHYLAamine DIMER UPON ONE-PHOTON IONIZATION

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Structures of trimethylamine dimer cluster cations which are generated by the vacuum-ultraviolet photoionization are investigated by a combination of infrared spectroscopic methods and theoretical reaction-pass calculations. In the trimethylamine dimer cluster cation, a proton of a methyl group is shared with the N atom of the other trimethylamine moiety. This is evidence that the methyl group acts as a proton donor in the cation state.
NON-CYCLIC ISOMERS OF (H₂O)₄ IN HELIUM NANODROPLETS: INFRARED SPECTROSCOPY AND AB INITIO CALCULATIONS


Water clusters are assembled via the sequential pick-up of water molecules by helium nanodroplets. Unlike previous infrared spectroscopy experiments of water clusters in helium droplets, one or two Neon atoms are added to the droplets prior to water pick-up. The upstream pick-up of a Neon atom results in several new bands in the infrared spectrum in addition to the bands that correspond to the water monomer, dimer and larger cyclic water complexes. The new spectral features are determined to be signatures of a (H₂O)₄ cluster on the basis of the pick-up cell pressure dependence of the band intensities. A dc electric field is applied to the laser droplet beam interaction region, and these clusters are determined to be polar with permanent dipole moments between 2 and 3 Debye. On the basis of comparisons to CCSD(T) anharmonic frequency calculations, the new bands are assigned to OH stretch vibrations of a non-cyclic 3+1 cluster, which corresponds to a water molecule hydrogen bonded to a trimer ring. The presence of the Neon atom substantially affects the barrier to ring insertion of the fourth water molecule into a preformed cyclic trimer complex. In contrast, no new bands corresponding to open (non-cyclic) trimers or pentamers are observed.


MATRIX ISOLATION FTIR AND AB INITIO STUDIES ON THE CONFORMATIONS OF DIMETHYL AND DIETHYL CARBONATE AND THEIR COMPLEXES WITH WATER

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Dimethyl carbonate (DMC) and diethyl carbonate (DEC) have been studied for their conformations using matrix isolation infrared spectroscopy and ab initio computations. In addition to the above studies, the complexes of the two compounds with water have also been studied. The experiments were corroborated with ab initio calculations at the B3LYP/6-31+G** level. The organic carbonates were trapped in argon and nitrogen matrices using an effusive source maintained at two different temperatures; i.e. room temperature and 170°C. In addition the matrix was also deposited using a supersonic jet source. These experiments were performed to alter the relative population of the various conformations, to aid us in the assignments of the vibrational features. The conformation of DMC corresponding to the global minimum of DMC was found to be a cis-cis conformer where the two methyl groups are found to be at cis position with respect to the carbonyl oxygen. The next higher energy conformer corresponded to a cis-trans structure with a near trans-near trans structure being the highest energy conformer. In our experimental matrix isolation spectra of DMC, we were able to assign features due to the cis-cis and cis-trans conformers. The features of the higher energy cis-trans conformer was confirmed with our experiments using the elevated temperature effusive source and the supersonic source. DEC displays a richer conformational landscape due to the presence of a longer carbon chain. The computational and experimental indicate that the ground state conformer for this compound is one in which carbon attached to oxygen adopts a cis configuration with respect to the carbonyl oxygen, while the terminal carbon adopts an anti conformation. A detailed study of the conformational picture of DEC will be presented. In addition to the above conformational studies, 1:1 hydrogen bonded complexes of DMC and DEC with water were also observed in the matrix, which was corroborated by our computations. Studies of the water complexes of DMC and DEC will also be presented.
Hyperconjugative interactions have received considerable attention because of its importance in determining structure and reactivity in organic compounds. In all these molecules, our studies, as many others in the literature, indicated that the $O - P - O$ and $O - C - O$ segments played a crucial role in conformational preferences. In the case of the organic phosphates, in addition to the $O - P - O$ segments, the $P = O$ group was also found to influence the structures. To address this issue further, it was thought interesting to study the conformations of trimethylphosphite (TMPhite), which lacks a $P = O$ group. A comparison of the conformations of trimethylphosphate (TMP) and TMPhite was expected to highlight the role of the $P = O$ group in the conformational preference of organic phosphates, which is the motivation for the present work.

The conformations of TMPhite were studied using matrix isolation infrared spectroscopy. TMPhite was trapped in a nitrogen matrix using an effusive source maintained at 298 K and 410 K and also a supersonic source. These experiments were designed to enable us to assign the infrared features of the higher energy conformer(s). As a result of these experiments, infrared spectra of the conformations of TMPhite were obtained. The experimental studies were supported by ab initio computations performed at the $B3LYP/6-31++G^{***}$ level. Computations indicated four minima corresponding to conformers with the following symmetries: $C_1$, $C_s$, $C_{1a}$ and $C_3$, given in order of increasing energy. This conformational picture was clearly different from that of TMP, in which the $C_3$ was the lowest energy structure, thereby clearly indicating the role of the $P = O$ group in structural preferences in these systems. We also performed a photochemical insertion of oxygen in TMPhite to produce TMP in the matrix, in an effort to correlate the conformers of the two molecules. These experiments also gave rise to interesting side reactions, where in addition to TMP, we also observed the products where oxygen appeared to be inserted into the $P - O - Me$ moiety. The conformational landscape of the two molecules has also been rationalized using Natural Bond Orbital (NBO) analysis.

Cyclic $\beta$-diketo compounds are known to show markedly different physical and chemical properties compared to their linear counterparts. 1,3-cyclohexanedione, the simplest molecule among the cyclic variants was found to exist exclusively in ketoenolic form in crystal whereas appreciable amount of diketo tautomer was identified in chloroform solution. We have studied this system by means of infrared spectroscopy to elucidate its tautomeric behavior under different environmental as well as thermal conditions ranging from solid argon matrix at 8 K to carbon tetrachloride and chloroform solution at room temperature and low pressure vapor at 330 K. Besides, we have monitored its homodimeric complexes and the effect of weak CH---O hydrogen bonding on the keto-enol tautomeric equilibria. The potential energy surface of the ground electronic state has been computed by means of electronic structure calculation to corroborate the experimental findings.
VIBRON AND PHONON HYBRIDIZATION IN DIELECTRIC NANOSTRUCTURES

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In this talk we present a hybridization scheme for the external and internal vibrations of dielectric nanostructures. This method provides an intuitive understanding of the infrared spectra of nanoparticles through analogy to molecular orbital theory. Using the example of cubic nanoshells composed of carbon dioxide, it is demonstrated how the spectra of complex nanostructures can be understood in terms of their primitive components.4

MH01

MICROWAVE SPECTRA AND STRUCTURES OF H$_4$C$_2$···AgCl AND H$_4$C$_2$···CuCl

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A Balle-Flygare FT-MW spectrometer coupled to a laser ablation source has been used to measure the pure rotational spectra of H$_4$C$_2$···AgCl and H$_4$C$_2$···CuCl. Both molecules are generated via laser ablation (532 nm) of a metal rod in the presence of CCl$_4$, C$_2$H$_4$ and argon and are stabilized by supersonic expansion. Rotational constants ($A_0$, $B_0$, $C_0$) and the centrifugal distortion constant, $D_J$, have been measured for six isotopologues of H$_4$C$_2$···AgCl and five isotopologues of H$_4$C$_2$···CuCl with substitutions at the metal, chlorine and carbon atoms in each case. The spectrum of each molecule is consistent with a C$_{2v}$ structure in which the metal atom interacts with the π-orbital on ethene. The measured rotational constants allow determination of the length of the bond between the metal and chlorine atoms, $r_{MCl}$, and the distance between the metal atom and the centre of the ethene double bond, $r_{MEx}$. Nuclear quadrupole coupling constants have been determined for the chlorine atom in each molecule and also for copper in H$_4$C$_2$···CuCl.

MH02

MICROWAVE SPECTRA AND STRUCTURE OF CF$_3$I···CO

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A Chirped Pulse Fourier transform Microwave spectrometer has been used to measure the pure rotational spectrum of CF$_3$I···CO. This complex is generated by supersonic expansion of a gas sample containing a small percentage of CF$_3$I and CO in argon. The rotational constant $B_0$, centrifugal distortion constants, $\Delta_J$ and $\Delta_{JK}$, and nuclear quadrupole coupling constant for iodine, $\chi_{\alpha\alpha}(I)$, have been determined for each of CF$_3$I···$^{12}$C$^{16}$O, CF$_3$I···$^{13}$C$^{16}$O and CF$_3$I···$^{12}$C$^{18}$O allowing determination of the distance between the two sub-units. The complex is a prolate symmetric top with C$_{3v}$ symmetry.
INTERMOLECULAR INTERACTION BETWEEN CO OR CO2 AND ETHER OR THIOETHER OR PROPYLENE OXIDE IN A COMPLEX, INVESTIGATED BY FOURIER TRANSFORM MICROWAVE SPECTROSCOPY AND ABINITIO CALCULATIONS

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In sharp contrast with the hydrogen bond, which has been well established to be one of the strongest interactions between two atomic and/or molecular species, weak interactions between two closed-shell molecules have not been understood in detail. We have thus carried out a systematic study on complexes shown in the title; examples include the CO-ethylene oxide (EO), CO-ethylene sulfide (ES), CO-dimethyl ether (DME), CO-dimethyl sulfide (DMS), CO2-EO, CO2-ES, CO2-DME, and CO2-propylene oxide (PO) complexes. From their Fourier transform microwave spectra, we determined the $r_s$ structure, the force constant of the van der Waals stretching mode, and the dissociation energy by analyzing the observed rotational and centrifugal distortion constants. We have also carried out ab initio molecular orbital calculations at the level of MP2 with basis sets 6-311++G(d,p) and aug-cc-pVDZ using the Gaussian 09 package. In most cases, the MP2/6-311++G(d,p) calculations yield rotational constants in better agreement with the experimental values, than the other basis set, in other word, the molecular structures calculated using this basis set are close to those experimentally found for the ground state. The estimated bond dissociation energies including the zero-point vibrational energy corrections $\Delta ZPV$ and the basis set superposition errors (BSSE) calculated with the counterpoise correction (CP) are in good agreement with the observed binding energies $E_B$. We have applied an NBO analysis to the complexes to calculate the stabilization energy $\sigma\sigma^*$, which we found are closely correlated with the binding energies $E_B$. We have thus achieved a consistent overview on the intermolecular interaction in the complexes under consideration.

DOES WATER PREFER TO DONATE A PROTON TO AN F OR TO A CI ATOM? - A ROTATIONAL STUDY OF CH3CHClF...H2O

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We measured the molecular beam Fourier transform microwave spectra of six isotopologues of the 1:1 adduct of CH3CHClF with water. The water prefers to form an O-H...F rather than an O-H...Cl hydrogen bond. This is exactly the contrary of what observed in the chlorofluoromethane-water adduct, where a O-H...Cl link was formed. Besides the rotational constants, the quadrupole coupling constants of the chlorine atom have been determined. In addition, information on the internal dynamics has been obtained.

DETERMINATION OF THE STRUCTURE OF THE ARGON CYCLOPENTANONE AND NEON VAN DER WAALS COMPLEXES

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The microwave spectrum of the $^{36}$Ar-cyclopentanone van der Waals complex has been observed and assigned. The rotational constants are $A = 2616.10$ MHz, $B = 1176.62$ MHz, and $C = 1022.089$ MHz. The results of microwave spectra of the seven isotopomers of the argon-40 cyclopentanone and eight isotopomers of the neon-20 (including $^{22}$Ne) cyclopentanone van der Waals complexes in the ground vibrational state have already been reported. The structures of both the argon and neon complexes were determined using extreme Kraitchman analysis. The coordinates of the Ne-20 and Ne-22 isotopologues are nearly equal in the principal axis system of the monomer. Also, the coordinates of the Ar-36 and Ar-40 isotopologues are nearly equal in the principal axis system of the monomer. These results will be discussed in terms of the vibrational averaging in the ground vibrational states of the large amplitude van der Waals vibrations.

IMPROVED DIPOLE MOMENTS FOR ACRYLONITRILE AND PROPIONITRILE

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Previous determinations of the electric dipole moment of acrylonitrile, while in agreement on the total dipole moment, showed an appreciable difference in the value of the smaller $\mu_b$ component.$^a,b$ The value of this component is important for intensity considerations in the THz spectrum of this molecule, which is dominated by $b$-type transitions.$^c$ We decided to update the dipole moment determination of acrylonitrile, and also of propionitrile (ethyl cyanide) by making Stark measurements in supersonic expansion. We used the Stark electrode arrangement developed in our laboratory and the program QSTARK for fitting Stark measurements on resolved nuclear quadrupole hyperfine structure.$^d$ The results for acrylonitrile show a further, significant difference in the value of $\mu_b$, while those for propionitrile, while more precise, are essentially consistent with previous values.$^e$ The evidence from $ab\ initio$ calculations and from relative intensity measurements supporting the current dipole moment determinations is presented.

NOTATION CONFUSION OF SYMMETRY SPECIES FOR MOLECULES WITH SEVERAL LARGE-AMPLITUDE INTERNAL MOTIONS

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The Mulliken convention has become the standard notation for symmetry species (irreducible representations) of point groups for quasi-rigid molecules. No such convention exists for symmetry species of symmetry groups for semi-rigid or non-rigid molecules with large amplitude internal motions (LAMs). As a result, we have a situation where we create notations in a do-it-yourself fashion or adopt them from the literature, sometimes even without proper reference to its derivation or to the character table on which it is based. This may be just a nuisance for those who are comfortable enough with group theory and molecular symmetry groups to figure “it” out, but it represents a real problem for everybody else.

The notation confusion is illustrated with examples from the literature (both old and new) on molecules with two or more LAMs. Most authors use the notation introduced by Myers and Wilson for molecules such as acetone or propane. No universal notation is in use for molecules with two methyl groups but lower overall symmetry. For example, the notation $G_{18}$ is used for one of these groups. As it turns out, different people use the same notation for different groups. This presentation is an attempt to bring some light into the dark and to combat confusion with a call for an anti-confusion convention.

$a$ R. S. Mulliken, Phys. Rev. 43, 279 (1933).

SEMI-EXPERIMENTAL $(r_s/r_e)$ STRUCTURES FOR THE HEAVY ATOM BACKBONES OF TWO MODERATELY LARGE MOLECULES OBTAINED FROM MICROWAVE SPECTROSCOPY AND QUANTUM CHEMICAL CALCULATIONS

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From recent microwave investigations of 1-methyl-4-piperidone and tropinone ground state rotational constants are available for the equatorial conformers of the normal species and the isotopologues with single substitution of all the heavy atoms. Vibration-rotation constants (alphas) were computed with Gaussian 03 (G03) for the B3LYP/cc-pVTZ model and used to convert ground state rotational constants into equilibrium rotational constants. Using the Kraitchman equations ($r_s$ method), the equilibrium ($r_e$) Cartesian coordinates were determined for all the heavy atoms in the principal axis framework. Equilibrium bond lengths and bond angles are compared with those computed with the B3LYP/cc-pVTZ model. We have compared the ground state rotational constants computed with G03, after scaling by factors based on the normal species, with observed values. The agreement is within 0.1% for the full set of constants (0.04% for methyl-piperidone and 0.1% for tropinone). This agreement between experiment and theory is so good that it seems possible to use calculated ground state rotational constants in place of experimental ones for determining $r_s/r_e$ structures for organic molecules of this size.


Intermission
VIBRATIONAL ENERGIES FOR ACRYLONITRILE FROM MM-WAVE TO THZ ROTATIONAL SPECTRA

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The THz rotational spectrum of acrylonitrile has recently been studied in detail. The coverage of the ground state rotational transitions has been extended up to $J = 128$, $K_a = 29$ and it was found that at very high-$J$ there are multiple manifestations of a perturbation between the ground state and the lowest vibrationally excited state, $v_1 = 1$. The perturbation has been successfully fitted and the excited state energy determined at $228.29991(2) \text{ cm}^{-1}$, which turns out to be the largest energy difference between any two neighboring vibrational states of acrylonitrile.

Extensive broadband rotational spectra of acrylonitrile have been recorded at JPL and at OSU and provide coverage from the mm-wave region up to well into the THz. The analysis of these spectra performed with the AABS package allowed identification of a ladder of pairwise perturbations extending from the ground state and connecting all successive low lying vibrational states. A global fit of all of the observed effects is expected to deliver accurate energies for the lowest vibrational states from only the rotational spectrum. The progress made towards achieving this goal is described.

MH10

ROOM-TEMPERATURE CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE (RT-CP-FTMW) SPECTRUM OF PYRIDINE

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The pure rotational spectrum of pyridine has been measured from 10-18 GHz by room-temperature chirped-pulse Fourier transform microwave (RT-CP-FTMW) spectroscopy. The measurement and analysis of the spectrum will be discussed and compared to previous reports. Anharmonic ab initio calculations complemented the spectroscopy and aided in its interpretation. The design and construction of the RT-CP-FTMW spectrometer will be discussed. It is based on a similar design developed in the Pate laboratory at the University of Virginia, but it is less expensive than the original design. Due to its low cost, the RT-CP-FTMW spectrometer is ideally suited for primarily undergraduate institutions (PUIs).

MH11

THE ROTATIONAL SPECTRUM OF BIOMOLECULAR RELATED COMPOUNDS.a

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Chirped pulse Fourier Transform microwave spectroscopy can be used to study either the structure of heavy biomolecular related compounds or the complex landscape of more simple molecules. Protected amino acids are the key to understand how the different interactions between the amino and the carboxylic groups can govern the folding process of peptides to yield either $\alpha$-helix or $\beta$-sheet related structures. In this work, the aromatic amino acid phenylalanine protected in both, amino and carboxylic groups, has been studied revealing its preferential structure and confirming the structure found by Gerhards. D-threoninol is an acyclic diol which can be used as a building block to form a double-helical structure similar to the one from the natural nucleic acids. The result is called acyclic threoninol nucleic acid ($\alpha$TNA), which shows a high compatibility with the DNA strands. Here the conformational preferences of the D-threoninol in gas phase are reported for which several conformers have been found in the molecular beam.

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aWork supported by NSF(CHE-0911117)

Rhodium substitution in molecules is a common practice in bio-organic chemistry in order to modulate physicochemical properties and biological activity of molecules and an increasing number of drugs on the market contain fluorine, the presence of which is often of major importance to modify pharmacokinetics properties and molecular activity. The rationale for such a strategy is that fluorine is generally a stronger electron acceptor than the other halogen atoms and its size is intermediate between that of hydrogen and oxygen. We have studied two fluorinated analogs of 2-phenylethylamine (PEA), the prototype molecule for adrenergic neurotransmitters, namely: 4-Fluoro (4FPEA) and 2-Fluoro-2-phenylethylamine (2FPEA) by Molecular Beam Fourier Transform Microwave Spectroscopy in the frequency range 6-18 GHz and ab initio calculations at the MP2/6-311++G** level. The aim is to obtain information on the spatial arrangement of the ethylamine side chain and the effects of fluorination on the energy landscape. The conformational space is dominated by low energy gauche conformations stabilized by weak interactions between the aminic hydrogens and the electron cloud of the benzene ring and anti conformations higher in energy. In 2FPEA the presence of the fluorine atom almost duplicate the number of possible conformation with respect to 4FPEA. We observed two conformers of 4FPEA and five conformers of 2FPEA which have been classified with the guide provided by accurate ab initio calculations. The identification of the conformational species was helped by the analysis of the quadrupole hyperfine pattern which is greatly influenced by the orientation of the amino group and acts as a fingerprint for each conformation. The orientation of the dipole moment within the principal axis frame and the order of stability of the different conformations are other independent pieces of evidence for the unambiguous assignment and identification of the conformers. The order of stability was found to be altered in both molecules with respect to the prototype PEA molecule, especially in the case of 2FPEA where we observe a stabilization of some of the anti forms and great destabilization of some of the gauche forms. These observations are in agreement with the results of the theoretical calculation and can be rationalized in terms of the effect of the fluorine atom on the electron density of the molecule and in particular on the electron cloud on the benzene ring.

Recently, rotational studies of biomolecules have entered in a new stage with the LA-MB-FTMW experiment. It combines laser ablation with Fourier transform microwave spectroscopy in supersonic jets overcoming the problems of thermal decomposition associated with conventional heating methods. This technique has been successfully applied to the study of monosaccharides. Three conformers of the prototype α-D-glucose and other three for β-D-glucose have been characterized for the first time in the gas phase.

LA-MB-FTMW spectroscopy combines laser ablation with Fourier transform microwave spectroscopy in supersonic jets overcoming the problems of thermal decomposition associated with conventional heating methods. We present here the results on LA-MB-FTMW studies of some neurotransmitters. Six conformers of dopamine, four of adrenaline, five of noradrenaline and three conformers of serotonin have been characterized in the gas phase. The rotational and nuclear quadrupole coupling constants extracted from the analysis of the rotational spectrum are directly compared with those predicted by ab initio methods to achieve the conclusive identification of different conformers and the experimental characterization of the intramolecular forces at play which control conformational preferences.
MI. RADICALS AND IONS
MONDAY, JUNE 20, 2011 – 1:30 pm
Room: 1015 McPHerson LAB

Chair: DMITRY MELNIK, The Ohio State University, Columbus, OH

MI01 10 min 1:30

ISOTOPIC EFFECTS IN CHEMICAL REACTIONS OF SINGLE IONS

JAMES E. GOEDERS, CRAIG R. CLARK, and KENNETH R. BROWN, Georgia Institute of Technology.

Chemical reactions using laser cooled ions are dominated by quantum effects due to their localized nature. Studying isotopic effects allows for the probing of reaction mechanisms and the topography of potential energy surfaces. Previously, single ion experiments involving Mg$^+$ and HD were done utilizing a nondestructive identification method based on the motional modes of the ions.a. Our work focuses on reactions with single atomic calcium ions. A novel method that observes the sideband spectra of the $^2S_{1/2}$ to $^2D_{5/2}$ transition in Ca$^+$ for reaction detection is discussed.


MI02 15 min 1:42

MODELING THE INFLUENCE OF NUCLEAR SPIN IN THE REACTION OF $H_3^+$ WITH $H_2$

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The reaction $H_3^+ + H_2 \rightarrow H_2 + H_3^+$ is among the simplest of bimolecular chemical reactions, and may play an important role in determining the ortho:para ratios of $H_3^+$ and $H_2$ in interstellar environments. Despite its apparent simplicity, the kinetics of this reaction is not well understood, particularly the branching fractions of the proton hop and hydrogen exchange reaction pathways. In this contribution, we present a series of steady state chemical models that show how this reaction can be studied in the laboratory with spectroscopy. Our first model is based entirely on nuclear spin statistics, appropriate for high temperature, low pressure plasmas. This model is then extended to account for the possibility of a small number of three-body collisions which could influence the interpretation of spectroscopic measurements of the $H_3^+ + H_2$ binary reaction. Our final model employs rate coefficients calculated using a microcanonical statistical approach which takes into account energetic restrictions on certain reaction pathways, which may become important at lower temperatures. These models are directly aimed at extracting kinetic information about the $H_3^+ + H_2$ reaction from laboratory spectra of hydrogenic plasmas.

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The fundamental reaction involving H$_3^+$ and H$_2$ has not been well-studied in the laboratory. Typical approaches to studying kinetics using mass spectrometry are ineffective because the products have identical masses to the reactants. Isotopic labeling fundamentally alters the exchange symmetry of this system, and therefore cannot be employed. However, because the two nuclear spin configurations of H$_3^+$ (ortho, $I = 3/2$, and para, $I = 1/2$) and H$_2$ (ortho, $I = 1$, and para, $I = 0$) are linked to specific rotational states by symmetry, spectroscopy is a useful tool for studying this reaction.

We have employed infrared multipass direct absorption spectroscopy to measure transitions in the $\nu_2$ fundamental band of H$_3^+$ using a difference frequency generation laser. Hydrogenic plasmas were produced in a hollow cathode discharge cell, which could be cooled as low as 130 K using liquid nitrogen. To measure the nuclear spin dependence of the H$_3^+$ + H$_2$ reaction, we prepared hydrogen gas enriched up to 99.9% para-H$_2$ using a para-hydrogen converter, and determined the ortho:para ratio of H$_3^+$ formed in the hollow cathode plasma at steady state as a function of both para-hydrogen enrichment and temperature. By utilizing steady state chemical models, we have determined that the ratio of the rates of the proton hop and hydrogen exchange pathways ($\alpha \equiv k_H^E / k^E$) decreases from 1.6 ± 0.1 at 350 K to 0.5 ± 0.1 at 135 K. These results suggest that at lower temperatures, the intermediate (H$_3^+$)* complex lifetime increases, leading to more statistical proton scrambling.

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INFRARED PHOTODISSOCIATION SPECTROSCOPY OF FIRST ROW TRANSITION METAL-CARBONYL CATIONS

ANTONIO D. BRATHWAITE, ALLEN M. RICKS, ZACH D. REED, MICHAEL A. DUNCAN, Department of Chemistry, University of Georgia, Athens, GA 30602-2256.

Transition metal-carbonyl cations are generated in a laser vaporization/supersonic expansion cluster source, mass selected and studied using infrared laser photodissociation spectroscopy. The carbonyl stretching region (2050-2350 cm$^{-1}$) is probed using a tunable infrared OPO/OPA system. Several cluster sizes are investigated and insight into their stability and geometry is obtained. Cu(CO)$_4^+$ has a complete coordination sphere, consistent with 18-electron stability and a tetrahedral structure similar to that of isovalent Ni(CO)$_4$. Ti(CO)$_6^+$ has a complete coordination sphere and does not satisfy the 18-electron rule. DFT calculations are performed and reported to corroborate the experimental data.

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INFRARED PHOTODISSOCIATION SPECTROSCOPY OF METAL ION WATER COMPLEXES

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Metal ion-water complexes are produced in a supersonic expansion cluster source via laser vaporization technique. Infrared photodissociation spectroscopy has been performed in the O-H stretch region. DFT calculations have also been carried out to obtain the structures and vibrational frequencies. Infrared spectra show partially resolved rotational structures which will be analyzed.
VIBRATIONALY DRIVEN ELECTRON TRANSFER IN \( \text{CH}_3\text{NO}_2 \cdot \text{CH}_3\text{I} \) CLUSTERS

BENJAMIN J. KNURR, CHRISTOPHER L. ADAMS and J. MATHIAS WEBER, JILA, NIST and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309.

Excitation of vibrations in species with weakly bound electrons can lead to the loss of electrons by vibrational autodetachment (VAD). If the molecular host of a weakly bound electron is stabilized by solvation, VAD can become energetically disallowed. However, electron transfer can take the role of VAD if the solvent can accept an excess electron. The analog of such a process via electronic excitation is known as charge transfer to solvent and can be seen as distinct absorption bands in the UV spectra of bulk solutions and clusters.

We investigate vibrationally driven charge transfer in \( \text{CH}_3\text{NO}_2 \cdot \text{CH}_3\text{I} \) clusters, initiated by excitation of CH stretching and HCH bending fundamental transitions in the cluster. In the initial configuration, the excess electron is localized on the nitro group of the \( \text{CH}_3\text{NO}_2 \) moiety. Upon excitation and subsequent vibrational relaxation, charge transfer to the \( \text{CH}_3\text{I} \) molecule leads to dissociative attachment of the excess electron and formation of an \( \text{I}^- \) fragment. No other fragments are observed, leading to the conclusion that the charge transfer reaction is the most favorable pathway. The reaction can be shut down by solvation of the cluster ion by two or more Ar atoms, in which case Ar evaporation becomes the only observed channel. Isotopic substitution using \( \text{CD}_3\text{I} \) is used to identify the vibrational modes in the action spectra in concert with calculated infrared spectra of the complex.

PHOTOELECTRON IMAGING OF NITROETHANE, NITROPROPANE AND NITROBUTANE

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We will show high resolution, low-energy photoelectron imaging data on nitroethane, nitropropane, 2-nitropropane and nitrobutane. We obtain new values for the adiabatic electron affinities of these nitroalkanes by comparison of the spectra of bare anions with the spectra of Ar solvated anions, where hot bands are strongly suppressed. For nitroethane, we can quantitatively recover the photoelectron spectrum using Franck-Condon calculations and find an adiabatic electron affinity of \( (192 \pm 6) \) meV. Similar to the case of nitromethane, the main contributions to the Franck-Condon profile come from the vibrational modes involving the nitro group. For nitropropane and nitrobutane, electron affinities are tentatively 223 meV and 238 meV, respectively.

Intermission
Protonated molecular ions of nitrous oxide ($N_2OH^+$) and acrylonitrile ($CH_2CHCNH^+$) have been detected at high spectral resolution in the molecular beam of a Fourier transform microwave spectrometer on the basis of high-level \emph{ab initio} calculations. The ions were synthesized in the throat of a pulsed supersonic nozzle by discharging in a flow of the corresponding precursor gas (either $N_2O$ or $CH_2CHCN$) heavily diluted in $H_2$. Two isomers of $N_2OH^+$ were identified, corresponding to protonation at either the N or O end of NNO. This work contributes precise nitrogen hyperfine coupling constants to existing measurements of ground state NNOH$^+$, and represents the first detection of the higher energy HNNO$^+$ isomer, which is calculated to lie 4.4 kcal/mol above ground. In addition, protonated acrylonitrile has been detected for the first time at high spectral resolution, yielding spectroscopic constants that are in excellent agreement with high-level quantum-chemical calculations. Owing to sizable calculated dipole moments of protonated nitrous oxide and acrylonitrile and the relatively high proton affinities of their neutral counterparts, both cations are plausible candidates for astronomical detection with radio telescopes.

\(^b\)At CCSD(T)/cc-pwCVQZ level of theory with zero-point vibrational effects at CCSD(T)/cc-pVQZ.

The technique of Cavity Enhanced Velocity Modulation Spectroscopy (CEVMS) has recently been developed\(^ab\). By demodulating the detector signal at twice the plasma modulation frequency ($2f$), the velocity-modulated ionic absorption signal can be extracted. Although the concentration-modulated excited neutral molecules are also observed at $2f$, the ion and neutral signals can be distinguished and separated with phase-sensitive demodulation.

The optical cavity provides two major benefits. It increases both the optical path length and the intracavity laser power by a factor of $2 \times \text{Finesse}/\pi$. The multipass advantage allows for much longer path length than was previously possible with unidirectional multipass White cells. The power enhancement combined with perfectly overlapped counterpropagating beams within the cavity allows for sub-Doppler spectroscopy. Although CEVMS showed much potential, its sensitivity was ultimately limited by electronic noise from the plasma interfering with the cavity-locking electronics.

We have further improved upon CEVMS by combining it with Noise Immune Cavity Enhanced Optical Heterodyne Molecular Spectroscopy (NICE-OHMS). The laser is frequency modulated at precisely an integer multiple of the free spectral range of the optical cavity; this allows the heterodyne sidebands to be coupled into the optical cavity. Heterodyne detection of the cavity leak-out is immune to noise in the laser-cavity lock, and $2f$ demodulation further decreases electronic noise in the system and retains ion-neutral discrimination.

The additional level of modulation beyond ordinary CEVMS has the added advantage of enabling the observation of both absorption and dispersion signals simultaneously by using two RF mixers, each driving its own lock-in amplifier. In a single scan, four distinct signals can be obtained: absorption and dispersion for ions and excited neutrals. The technique has been demonstrated in the near-IR for $N_2^+$. 

MI10  
LINE-SHAPE AND SENSITIVITY OF SPECTROSCOPIC SIGNALS OF N$_2^+$ IN A POSITIVE COLUMN COLLECTED USING NOISE IMMUNE CAVITY ENHANCED OPTICAL HETERODYNE VELOCITY MODULATION SPECTROSCOPY

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Challenges to studying gas phase ions include the dilute analyte, Doppler line broadening, and a lack of ion/neutral discrimination. Techniques which provide high sensitivity, sub-Doppler features, and some form of ion/neutral discrimination increase the ability to study gas phase ions. Recently our group has used noise immune cavity enhanced optical heterodyne velocity modulated spectroscopy (NICE-OHVMS) to help overcome each of these challenges.

Using NICE-OHMS to probe a velocity modulated positive column produces a distinctive line shape. The high optical power from and geometry of the cavity saturates optical transitions and allows sub-Doppler Lamb dips to be observed. Depending on sideband frequency (1 or 9 times the free spectral range) the sub-Doppler features are closer together or further apart. The sub-Doppler features can then be used to measure the line-centers with high (∼1 MHz) precision and accuracy using an optical frequency comb.

The Kramers-Kronig relations describe how the absorption and dispersion are related to one another and can be used to obtain the absorption from the dispersion (and vice-versa). Owing to the phase dependent absorption signal produced with heterodyne spectroscopy, both absorption and dispersion signals can be obtained simultaneously. Two RF mixers (one for absorption and one for dispersion), each driving its own lock-in amplifier, are used to obtain a signal for ions and excited neutrals.

We will report a comparison of the sensitivities of several absorbance techniques to study a nitrogenic velocity modulated positive column including: direct absorption, cavity enhanced velocity modulation, heterodyne spectroscopy and NICE-OHMS, and show how the signal-to-noise ratio is increased by using NICE-OHMS.

Future plans for this technique include using a high power cw-OPO in the mid-IR to perform high precision vibrational spectroscopy of ions such as CH$_3^+$.

MI11  
PROGRESS AND RECENT DEVELOPMENTS IN SENSITIVE, COOLED, RESOLVED ION BEAM SPECTROSCOPY (SCRIBES)

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Molecular ions play key roles in many phenomena of chemical interest, from combustion to interstellar chemistry. To better understand the physical and chemical behavior of the ions in such processes, information on their structure, energies, and quantum states must be obtained. High resolution spectroscopy is an effective tool in this endeavor, especially in the investigation of molecular ions of interstellar interest, as spectroscopy is the only tool available to probe the interstellar medium. This technique, however, can be very difficult when applied to molecular ions, due to spectral congestion with neutral species and the low density of ions produced. To circumvent these problems, we are developing a unique way of conducting high resolution spectroscopy on molecular ions called Sensitive, Cooled, Resolved, Ion BEam Spectroscopy (SCRIBES). This technique features ion-neutral discrimination, narrow spectral linewidths from kinematic compression, high signal from cavity-enhanced spectroscopic techniques, and mass sensitivity from Doppler analysis and time-of-flight (TOF) mass spectrometry. The system can also be upgraded with a supersonic expansion ion source to study rotationally cooled molecular ions.

Recent modifications to and insights from the instrument will be presented and discussed. These include exploring different electrode configurations of the presently used cold cathode source, which has led to clarifications into molecular collisions of the gaseous sample before extraction into the ion beam. Mass spectral data of hydrogen samples clearly show the difference between ion extraction by anode and extraction by cathode. Other items to be presented include implementation of highly sensitive spectroscopic techniques, such as Noise Immune Cavity Enhanced Optical Heterodyne Molecular Spectroscopy (NICE-OHMS).
PHOTODISSOCIATION SPECTROSCOPY OF Ca\textsuperscript{+}-H\textsubscript{2}O IN THE TEMPERATURE-VARIABLE ION TRAP

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In the last two decades, developments of infrared spectroscopy and theoretical calculations on gas-phase molecular clusters have revealed detailed solvation structures of various systems, especially of hydrogen-bonded systems. One of the remained problems in studies on microscopic solvation or hydration is a temperature dependence of solvation structures. Lisy and coworkers succeeded in interpreting the hydration structures of alkali metal ions by taking temperature- or entropic effect\textsuperscript{b}. They utilized Ar vaporization to cool down the temperature of clusters.

Another method for controlling temperature of cluster ions is a buffer gas cooling in an ion trap. In the present study, we have measured photodissociation spectra of Ca\textsuperscript{+}-H\textsubscript{2}O in our temperature-variable ion trap\textsuperscript{c}. In the present study, we examined the temperature of the Ca\textsuperscript{+}-H\textsubscript{2}O in the trap by simulating the rotational profile of the 0-0 band of the \( ^2B_1 \rightarrow ^2A_1 \) transition. The observed rotational profile is similar to that reported by Duncan and coworkers\textsuperscript{d}. By changing the trap period from 10 ms to 40 ms, it was confirmed that the trap period of 10 ms is sufficient to get temperature equilibrium in our experimental condition. Details of the experimental results will be presented in the paper.

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HIGH-RESOLUTION IR ACTION SPECTRUM OF C\textsubscript{2}H\textsubscript{2}\textsuperscript{+}

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The method of Laser-Induced-Reactions (LIR), which is described in detail in Schlemmer et al. 2002\textsuperscript{a}, is used to obtain high-resolution infrared spectra of molecular ions. Here, the endothermic reaction \( \text{C}_2\text{H}_2\textsuperscript{+} + \text{H}_2 \rightarrow \text{C}_2\text{H}_3\textsuperscript{+} + \text{H} \) is promoted by ro-vibrational excitation of the parent ion. A spectrum of the \( \nu_3 \) stretching vibration of \( \text{C}_2\text{H}_2\textsuperscript{+} \) is recorded by variation of the wavelength of a home-build OPO (Optical Parametric Oscillator) operating in the 3 micron region. The experiments are carried out in a low temperature 22-pole ion trap where several hundred cold, mass selected parent ions are stored. Typical linewidths of the action spectra are \( 3 \times 10^{-3} \text{ cm}^{-1} \). First spectra for \( \text{C}_2\text{H}_2\textsuperscript{+} \) and their analysis will be presented. Other possible applications of LIR spectroscopy will be discussed.

\textsuperscript{a}S. Schlemmer, E. Lescop, J. von Richthofen, D. Gerlich, and M. Smith, Laser Induced Reactions in a 22-Pole Ion Trap: \( \text{C}_2\text{H}_2\textsuperscript{+} + \text{H}_2 \rightarrow \text{C}_2\text{H}_3\textsuperscript{+} + \text{H} \), \textit{J. Chem. Phys.} \textbf{117}(2006-2075), 2002
MJ01 15 min 1:30

**FLUORESCENCE OF MATRIX-ISOLATED BIACYETYL**

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Matrix-isolated biacetyl (C₄H₆O₂) was irradiated at 514nm and 488nm. Emission was observed throughout the 200-800nm region, including at wavelengths shorter than those of the incident radiation. These are the result of sequential and simultaneous two-photon excitation. Some of the emission comes from the parent while other emission may be attributed to nascent photoproducts. The effects of concentration, matrix, and isotopic substitution on the observed emission will be discussed.

MJ02 15 min 1:47

**EXPERIMENTAL THERMOCHEMISTRY OF GAS PHASE CYTOSINE TAUTOMERS**


Enthalpies of interconversion are measured for the three lowest energy tautomers of isolated cytosine. The equilibrium distribution of tautomers near 600 K is frozen upon the capture of the gas phase species by low temperature helium nanodroplets. The temperature dependence of the gas phase cytosine tautomer populations is determined with infrared laser spectroscopy of the helium solvated species. The interconversion enthalpies obtained from the van’t Hoff relation are 1.14 ± 0.21 and 1.63 ± 0.12 for the C₃¹ ⇌ C₃₂ and C₃₁ ⇌ C₁ equilibria, respectively. C₃₁ and C₃₂ are rotamers of an enol tautomer, and C₁ is a keto tautomer. The interconversion enthalpies are compared to recent CCSD(T) thermochemistry calculations of cytosine tautomers.

MJ03 10 min 2:04

**TAUTOMERS OF CYTOSINE AND THEIR EXCITED ELECTRONIC STATES: A MATRIX ISOLATION SPECTROSCOPIC AND QUANTUM CHEMICAL STUDY**

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We have measured the IR and UV spectra of cytosine in a low-temperature argon matrix. An attempt was made to determine the tautomeric ratios existing in the matrix, making use of the matrix-isolation IR spectrum and computed IR intensities of the tautomers in a least squares fitting procedure. The mole fractions are about 0.22 for oxo(-amino) form, 0.26 and 0.44 for the two rotamers, respectively, of the hydroxy(-amino) form and 0.08 for the (oxo-)imino tautomer. These ratios were then used to simulate the matrix-isolation UV spectrum as a composite of the individual spectra, the latter calculated *ab initio* at high levels of electron correlation theory. The agreement between simulated and experimental UV spectra seems satisfactory. This indicates that, in contrast to the solid state and solution spectra described up to now by the oxo(-amino) form alone, the reproduction of the matrix-isolation UV spectrum needs at least the hydroxy(-amino) and oxo(-amino) forms, and probably also the (oxo-)imino form.
MJ04 15 min 2:16
PULSED JET DISCHARGE MATRIX ISOLATION AND COMPUTATIONAL STUDY OF HALOGEN ATOM COMPLEXES: Br–BrCH₂X (X=H,Cl,Br)

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Halogen atoms are important reactive radicals in the atmosphere, and the reactions of these radicals often proceed through formation of a pre-reactive complex. In this work, pulsed jet discharge matrix isolation spectroscopy and computational methods were used to characterize pre-reactive complexes of halogen atoms with simple halons. Our experiments combined matrix isolation techniques with a pulsed DC discharge nozzle, where a dilute CH₂XBr (X=H,Cl,Br):rare gas sample was gently discharged and the products deposited onto a KBr window. The Br–BrCH₂X (X=H,Cl,Br) complexes were characterized by infrared and electronic spectroscopy, supported by ab initio and Density Functional Theory (DFT) calculations, which shed light on the structure of, bonding in, and binding energy of the complexes.

MJ05 15 min 2:33
PHOTOINDUCED ELECTRON TRANSFER IN THE C₂H₄–Br₂ COMPLEX

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We have used a new dual-nozzle late-mixing scheme for the trapping and interrogation of pre-reactive donor-acceptor complexes to examine photoinduced electron transfer in the prototypical Mulliken donor-acceptor (halogen bonded) π-complex, C₂H₄–Br₂. The charge transfer transition of this band was measured for the first time, and the position and intensity of this band is in excellent agreement with theoretical expectations. Excitation into the intense charge transfer band of the complex leads exclusively to the anti-conformer of the single reaction product, 1,2-dibromoethane, in agreement with the Mulliken theory of electron transfer.

MJ06 15 min 2:50
INFRARED SPECTRA OF THE 2-CHLOROETHYL RADICAL IN SOLID PARA-HYDROGEN

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The reaction of chlorine atoms with ethylene and two of its deuterium isotopomers in solid para-hydrogen (p-H₂) matrices at 3 K has been studied using infrared spectroscopy. Irradiation at 365 nm of a co-deposited mixture of Cl₂, C₂H₄, and p-H₂ at 3 K produces a series of new lines in the infrared spectrum. Several of the new lines are readily assigned to the gauche and trans conformers of 1,2-dichloroethane (CH₂CICH₂Cl) resulting from the addition of two Cl atoms to C₂H₄. Of the remaining lines, a strong line at 664 cm⁻¹ and three weaker lines at 562, 1070, and 1228 cm⁻¹ are concluded to be due to a single carrier based on their behavior upon subsequent annealing to 4.5 K and irradiation at 254 and 214 nm. When the positions and intensities of these lines are compared to the MP2/aug-cc-pVDZ predicted vibrational spectra of the possible species that could result from the addition and abstraction reactions of one Cl atom with C₂H₄, the best agreement is found with the 2-chloroethyl radical (·CH₂CH₂Cl). In order to confirm this assignment, isotopic experiments were performed with C₂D₄ and t-C₂H₂D₂ and the corresponding infrared bands due to the deuterium isotopomers of this radical (·CD₂CD₂Cl and ·CHDCHDCl) have been observed. A final set of experiments were performed following irradiation of the Cl₂/C₂H₄/p-H₂ mixture at 365 nm, in which the matrix was irradiated with filtered infrared light from a globar source, which has been shown to induce a reaction between isolated Cl atoms and matrix H₂ to produce HCl and H atoms. In our experiments, the major products observed were HCl and ethyl chloride (CH₃CH₂Cl) and the possible mechanism of the formation of ethyl chloride will be discussed.

Intermission

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FTIR ISOTOPIC AND DFT STUDIES OF SiC$_5$ TRAPPED IN SOLID Ar

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We report here the first results from a Fourier transform infrared (FTIR) and density functional theory (DFT) study on SiC$_5$. This species has been produced by ablating a rod made of silicon and graphite powder with a Nd:YAG laser and trapping the products in solid Ar at $\sim 15$ K. In the only previous observation of SiC$_5$, McCarthy et al. reported the microwave rotational spectrum$^a$. In the present work, extensive FTIR measurements of vibrational frequencies and isotopic shifts from $^{13}$C enrichment and the naturally occurring $^{29,30}$Si isotopes have been compared with the predictions of density functional theory calculations at the B3LYP/cc-pVDZ level. The excellent agreement between experiment and theory has enabled the assignment of the $\nu_4(\sigma)$ fundamental of linear SiC$_5$ at $936.9 \pm 0.2$ cm$^{-1}$. This information may help in identifying SiC$_5$ in circumstellar and interstellar environments.


FTIR AND DFT STUDIES OF THE MgC$_3^-$ ANION IN SOLID Ar

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This study on MgC$_3^-$ anion is part of an ongoing investigation of the structures and vibrational fundamentals of small metal-carbon clusters using Fourier transform infrared (FTIR) spectroscopy and density functional theory (DFT). In part, these studies are motivated by the potential presence of small metal carbide molecules in astronomical environments. Binary carbon compounds containing silicon and sulfur, including SiC$_2$, SiC$_3$, and SC$_3$, as well as metal-containing molecules such as MgCN and MgCN have already been detected in interstellar space and circumstellar shells. In the present work, the linear MgC$_3^-$ was produced by trapping the products from the dual laser Nd-YAG laser ablation of carbon and magnesium rods in solid Ar at $\sim 12$ K. Measurements of $^{13}$C isotopic shifts confirm the identification of the $\nu_4(\sigma)$ vibrational fundamental at 1797.5 cm$^{-1}$. A second fundamental $\nu_2(\sigma)$, has been tentatively identified at 1190.1 cm$^{-1}$. The results are in very good agreement with the predictions of density functional theory calculations using the B3LYP functional with both the 6-311+G(d) and the cc-pVDZ basis sets. This is the first optical detection of the linear isomer of MgC$_3^-$. 
DIMINISHED CAGE EFFECT IN p-H₂: IR IDENTIFICATION OF INTERMEDIATES IN ADDITION REACTIONS OF CL ATOM WITH UNSATURATED HYDROCARBONS

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We report infrared absorption spectra of several free radicals produced upon reaction of Cl atoms with unsaturated hydrocarbons isolated in solid p-H₂. Cl atoms were produced by in situ photodissociation of Cl₂ isolated in solid p-H₂ at 365 nm. In experiments with the Cl₂/C₆H₆/p-H₂ matrices, intense absorption features at 617.0, 719.8, 956.0, and 1430.5 cm⁻¹ and weaker ones at 577.1, 833.6, 876.8, 833.6, 983.0, 993.5, 1008.0, 1026.4, 1112.5, 1118.5, 1179.0, 1406.5, 1509.4, 2967.2, 3054.3, 3063.4, 3070.9, and 3083.9 cm⁻¹ appeared upon irradiation of the matrix at 365 nm and increased in intensity upon subsequent annealing of the matrix at 4.8 K for a few minutes. By comparison of vibrational wavenumbers and deuterium isotopic shifts predicted with the B3PW91 and MPW1PW91/aug-cc-pVTZ methods, these features are readily assigned to the σ-complex of ClC₆H₆ (chlorocyclohexadienyl radical), rather than the previously proposed π-complex. In experiments with the Cl₂/C₂H₆/p-H₂ matrices, the 1-chloroethyl radicals (CHClCH₃) and chloroethene (C₂H₃Cl) are identified as the main products of the Cl + C₂H₂ reaction in solid p-H₂. The assignments of IR absorption lines at 738.2, 1027.6, 1283.4, 1377.1, 1426.6, 1442.6, and 2861.2 cm⁻¹ to 1-chloroethyl radicals are based on comparison of the observed vibrational wavenumbers and ¹³C- and D-isotopic shifts with those predicted with the B3LYP and MP2/aug-cc-pVDZ methods. These results indicate that the primary products of the addition reaction Cl + C₂H₂, the 2-chlorovinyl radicals, are unstable; they react readily with p-H₂ to form CHClCH₃ and C₂H₃Cl. If time permits, other examples such as Cl + 1, 3-butadien and H + C₆H₆ or C₆H₅Cl will be discussed. These results serve as excellent examples to demonstrate that the diminished cage effect of solid p-H₂ makes production of free radicals via bimolecular reactions feasible.

MOLECULAR HYDROGEN INTERACTIONS WITHIN METAL-ORGANIC FRAMEWORKS

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There is much interest in understanding the details of molecular hydrogen physisorption within highly porous materials that could be used for hydrogen storage applications. Unfortunately, the structures of the most promising materials are too complex for ab initio calculations and DFT models are notoriously unreliable for weak interactions. A new approach based on so-called van der Waals DFT has been proposed for explaining the behavior of molecular hydrogen within metal-organic frameworks. In this talk we will present IR spectra of adsorbed hydrogen within a series of isostructural MOFs containing Mg²⁺ and various first-row transition metal cations. The data clearly show that H₂ binds first at an open metal site, with a large vibrational redshift that correlates with the magnitude of the site binding energy. These spectra show minimal effects due to H₂···H₂ interactions and are significantly different from the recent findings of the Chabal group. After collecting spectra over a wide range of temperature and H₂ pressure, we could only reproduce their experimental observations by exposing samples to moist air, which is well-known to cause occupation of the open metal sites by water. This calls into question the appropriateness of the van der Waals DFT models that were used to support their interpretations. We are hopeful that the spectra we present will inspire improved parametrization of such advanced computational models, or prompt the development of superior ones.

Hydrogen cluster ions are of interest as reactants in astrophysical processes and as simple models for theoretical calculations. In this work, the formation mechanism of $H_4^+$ and its deuterated isotopomers was investigated by varying the experimental conditions required to observe $H_4^+$ isolated in a neon matrix. The $H_4^+$ cluster was formed by mixing $H_2$, $D_2$, and HD gases with neon and depositing the mixtures onto a copper rod cooled by liquid helium. The resulting matrix was then x-irradiated at 60 keV for 30 minutes and electron spin resonance spectra were recorded. Previous studies conducted in our lab have indicated that hydrogen cluster cations can only be formed at extremely low temperatures (2.6 K) and are very sensitive to temperature change. In the current study, the local environment of the deposition region was characterized by investigating the allowable temperature range, the effect of sample gas flow rate, and the need for nearby cold surfaces.
TA01 10 min 8:30
TIME RESOLVED FTIR ANALYSIS OF COMBUSTION OF ETHANOL AND GASOLINE COMBUSTION IN AN INTERNAL COMBUSTION ENGINE

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In order to pursue In Situ measurements in an internal combustion engine, a MegaTech Mark III transparent spark ignition 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 Step-scan equipped Fourier transform spectrometer, temporally resolved infrared spectral data were acquired and compared for combustion in the modified Mark III engine. Measurements performed with the FTIR system provide insight into the energy transfer vectors that precede combustion and also provides an in situ measurement of the progress of combustion. Measurements were performed using ethanol and gasoline.

TA02 10 min 8:42
TIME RESOLVED FTIR ANALYSIS OF TAILPIPE EXHAUST FOR SEVERAL AUTOMOBILES

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The automotive catalytic converter reduces or eliminates the emission of various chemical species (e.g. CO, hydrocarbons, etc.) that are the products of combustion from automobile exhaust. However, these units are only effective once they have reached operating temperature. The design and placement of catalytic converters has changed in order to reduce both the quantity of emissions and the time that is required for the converter to be effective. In order to compare the effectiveness of catalytic converters, time-resolved measurements were performed on several vehicles, including a 2010 Toyota Prius, a 2010 Honda Fit, a 1994 Honda Civic, and a 1967 Oldsmobile 442 (which is not equipped with a catalytic converter but is used as a baseline). The newer vehicles demonstrate both a reduced overall level of CO and hydrocarbon emissions but are also effective more quickly than older units. The time-resolved emissions will be discussed along with the impact of catalytic converter design and location on the measured emissions.
TA03 15 min  8:54
HIGH-RESOLUTION MID-INFRARED SPECTROSCOPY OF DEUTERATED WATER CLUSTERS USING A QUANTUM CASCADE LASER-BASED CAVITY RINGDOWN SPECTROMETER

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The experimental and theoretical study of small water clusters has provided a wealth of information about interactions between water molecules. In order to expand knowledge of these clusters, we have acquired rotationally-resolved infrared spectra of fully deuterated gas-phase water clusters in the intramolecular $D_2O$ bending region near 1200 cm$^{-1}$. To acquire the spectra, we utilized our continuous-wave cavity ringdown spectrometer (cw-CRDS) which is based on a quantum cascade laser (QCL). The clusters were generated in a continuous supersonic expansion from a 150 $\mu$m $\times$ 1 cm slit using argon as the carrier gas. The collected spectra span 1195 to 1200 cm$^{-1}$, and individual rovibrational transitions have a full width at half maximum of $\sim$20 MHz. We will present our analysis of the collected spectra.

TA04 15 min  9:11
MID-IR CAVITY RING-DOWN SPECTROMETER FOR BIOLOGICAL TRACE NITRIC OXIDE DETECTION

VINCENT KAN, AHEMD RAGAB, VITALI STSIAPURA, KEVIN K. LEHMANN, Department of Chemistry and School of Medicine, University of Virginia, Charlottesville VA, 22904-4319; BENJAMIN M. GASTON, School of Medicine, University of Virginia, Charlottesville VA, 22904-4319.

S-nitrosothiols have received much attention in biochemistry and medicine as donors of nitrosonium ion (NO$^+$) and nitric oxide (NO) D physiologically active molecules involved in vasodilation and signal transduction. Determination of S-nitrosothiols content in cells and tissues is of great importance for fundamental research and medical applications. We will report on our ongoing development of a instrument to measure trace levels of nitric oxide gas (NO), released from S-nitrosothiols after exposure to UV light (340 nm) or reaction with L-Cysteine+CuCl mixture. The instrument uses the method of cavity ringdown spectroscopy, probing rotationally resolved lines in the vibrational fundamental transition near 5.2 $\mu$m. The laser source is a continuous-wave, room temperature external cavity quantum cascade laser. An acousto-optic modulator is used to abruptly turn off the optical power incident on the cavity when the laser and cavity pass through resonance.

TA05 15 min  9:28
OFF-AXIS CAVITY RING DOWN SPECTROSCOPY BASED ON A CONTINUOUS-WAVE OPTICAL PARAMETRIC OSCILLATOR

JARI PELTOLA, MIKAEL SILTANEN and LAURI HALONEN, Laboratory of Physical Chemistry, Department of Chemistry, P.O. BOX 55 (A.I. Virtasen aukio 1), FI-00014 University of Helsinki, Finland; MARKKU VAINIO, Laboratory of Physical Chemistry, Department of Chemistry, P.O. BOX 55 (A.I. Virtasen aukio 1), FI-00014 University of Helsinki, Finland and Centre for Metrology and Accreditation, P.O. Box 9, FIN-02151 Espoo, Finland.

Continuous-wave cavity ring down spectroscopy (cw-CRDS) is a sensitive absorption technique for trace gas analysis. Although it is highly sensitivity and relatively fast, ring down repetition rate and spectral resolution are limited by the cavity free spectral range (FSR). Normally, the injected beam is mode matched to the lowest transverse electro-magnetic mode (TEM$_{00}$) of the cavity. Light is coupled into the cavity only when standing wave condition is fulfilled. Scanning of the laser without variation of the cavity length leads to transmission comb where recorded ring down times are separated in frequency by the FSR. Recently Romanini$^a$ et. al. reported an off-axis (OA) CRDS spectrometer operating in the 766 nm region where the FSR of the cavity was reduced by $N = 4$ times from the original. In this re-entrant condition the cavity length is chosen to provide degeneracy of transverse modes. If the injection is adequately off-axis the beam returns to the starting point after $N$ round trips. This divides the FSR to $N$ group of degenerated modes which are equally frequency-spaced. We present an OA-CRDS spectrometer ($N = 4$) based on a continuous-wave optical parametric oscillator (cw-OPO) operating in the mid-infrared region (2.75 - 3.45 $\mu$m). The measurement of formaldehyde (H$_2$CO) using an OA-CRDS spectrometer will be presented.

The OA-ICOS cavity consisted of two 1" high reflectivity spherical mirrors with 1 m radius of curvature, separated by a 0.5-m long quartz coated stainless steel tube. The mirrors reflectivity was > 99.996% at 1435 nm as specified by the manufacturer (Layertec, GmbH). The effective optical path length of the OA-ICOS approach was determined with direct absorption signal intensity of the pure H2O vapor line at 6965.80233 cm\(^{-1}\) and was found to be 1.263 km.

The OH radicals were generated with the help of a 2.45 GHz microwave discharge in water vapor flow under low pressure (1 mbar) to evaluate the developed OA-ICOS performance. The OH radical concentration of 7.28 e+13 OH/cm\(^3\) was determined using calibration with a close H2O absorption line at 6965.80 cm\(^{-1}\). The detection limit, deduced from the signal to noise ratio, was 3.86 e+11 OH/cm\(^3\). Experimental instrument detail and the preliminary measurement results will be presented and discussed.

\(^a\)This work is supported by the IRENI program of the Region Nord-Pas de Calais. The support of the Groupement de Recherche International SAMIA between CNRS (France), RFBR (Russia) and CAS (China) is acknowledged.

\(^b\)thanks the IRENI program for the postdoctoral support.

**Intermission**

**TA07**

CAVITY RINGDOWN LASER ABSORPTION SPECTROSCOPY (CRLAS) of ISOTOPICALLY LABELED ACETYLENE BETWEEN 12,500 - 13,600 cm\(^{-1}\)

CHRISTOPHER J. LUE, MICHAEL N. SULLIVAN, MARK E. DRAGANJAC, and SCOTT W. REEVE, Arkansas Center for Laser Applications and Science and Department of Chemistry and Physics, Arkansas State University, P.O. Box 419, State University, AR 72467.

About five years ago, Arkansas State University created the Arkansas Center for Laser Applications and Science (ArCLAS) with the intention of making it a state-of-the-art facility for laser-based research and optical spectroscopy in the midSouth. Since that time, University and DoD support has lead to the acquisition of numerous laser based spectrometers including a novel three color picosecond system utilized primarily for STIRAP measurements of bulk gas samples. Over the past few months, we have begun collecting near infrared overtone and combination band spectra for the acetylene molecule with a pulsed cavity ringdown laser absorption spectrometer (CRLAS) as part of the STIRAP support effort. Certainly acetylene has been extensively studied by a number of different spectroscopic methods \(^a\). During these CRLAS investigations a \(^{13}\)C\(_2\)H\(_2\) band was discovered which we believe has not been previously reported. Here a complete rovibrational analysis of this band will be presented.

\(^a\)See for example, Michel Herman, Jacques lievin, Jean Vander Auwera, and Alain Campargue, in Global and Accurate Vibration Hamiltonians from High Resolution Molecular Spectroscopy, Advances in Chemical Physics Volume 108, John Wiley and Sons, NY, NY (1999) and references therein.

**TA08**

AUTOMATIC TUNING OF AN ACULIGHT OPTICAL PARAMETRIC OSCILLATOR


We have automated the tuning of a continuous wave, singly resonant optical parametric oscillator (Lockheed-Martin Aculight ARGOS 2400-SF-15). This OPO is capable of producing > 1 Watt of continuously tunable idler output between 2.3 and 3.9 \(\mu\)m. We will discuss a simple algorithm and its implementation that synchronizes the tuning of three separate OPO tuning elements, which allows for several hundred wavenumbers of efficient, automatic, continuous tuning. Continuous feedback from a wavemeter (Bristol Instruments 621A) limits the frequency resolution to ~10 MHz.
TA09 15 min 10:49

PRECISION MEASUREMENT OF CARBON DIOXIDE HOTBAND TRANSITION AT 4.3 MICRON USING A HOT CELL

PEI-LING LUO, JYUN-YU TIAN, HSHAN-CHEN CHEN, Institute of Photonics Technologies, National Tsing Hua University, Hsinchu, Taiwan 30013; YU-HUNG LIEN, JOW-TSONG SHY, Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 30013.

We report a mid-IR spectrometer based on a difference frequency generation (DFG). This tunable CW DFG source covers the spectral range from 2.6 \(\mu\)m to 4.7 \(\mu\)m with an output power of a few mW. The saturation spectrum of the \(^{12}\)C\(^{16}\)O\(_2\) hot band 01\(^1\) 0 - 01\(^0\) P(30) transition is greatly enhanced by using a 40 cm long hot cell. The saturated absorption S/N ratio of over 1000 at 1 Hz bandwidth is achieved. We investigate the linewidth analysis and absolute frequency measurement of this transition. This transition center frequency of 69,267,228.761(15) MHz and the transition linewidth of 3.040(36) MHz are accurately measured.

TA10 15 min 11:06

HIGH PRECISION MID-IR SPECTROSCOPY OF \(^{14}\)N\(^{16}\)O NEAR 4.5 \(\mu\)m

WEI-JO TING, JOW-TSONG SHY, Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 30013, R.O.C.

The sub-Doppler saturation spectrum of the \(^{14}\)N\(^{16}\)O near 4.5 \(\mu\)m is studied 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 45-mm long PPLN (Periodically-Poled Lithium Niobate) crystal. 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 \(\text{N}_2\text{O}\) transition and its frequency is measured by an OFC (Optical Frequency Comb). In this talk, we will report our measurements of the fundamental band of \(\text{N}_2\text{O}\) near 4.5 \(\mu\)m.

TA11 15 min 11:23

MID-IR SATURATION SPECTROSCOPY OF HeH\(^+\) MOLECULAR ION

HSUAN-CHEN CHEN, CHUNG-YUN HSIAO, Institute of Photonics Technologies, National Tsing Hua University, Hsinchu, Taiwan, R.O.C.; JIN-LONG PENG, Center of Measurement Standards, Industrial Technology Research Institute, Hsinchu, Taiwan, R.O.C.; TAKAYOSHI AMANO, Department of Chemistry and Department of Physics and Astronomy, University of Waterloo, Canada; and JOW-TSONG SHY, Department of Physics and Institute of Photonics Technologies, National Tsing Hua University, Hsinchu, Taiwan, R.O.C..

The HeH\(^+\) ion, one of the simplest diatomic molecular ions, plays an important role not only in the quantum mechanical calculations but also, potentially, in the astrophysics. In this report, we demonstrated the first observation of the saturation absorption spectrum of the HeH\(^+\) using a continuous-wave, singly resonant, single frequency and widely tunable optical parametric oscillator in the mid-infrared region. The HeH\(^+\) ions were produced in an ethanol cooled extended negative glow discharge tube at -70 degrees centigrade with flowing mixtures of helium and hydrogen. The negative glow region of discharge was extended by applying an axial magnetic field of 300 gauss. The saturation spectrum of HeH\(^+\) (R(1) transition of \(v=1-0\) band at 90,788 GHz) was observed by scanning the frequency of the pump laser and demodulated at third harmonics by a lock-in amplifier. The investigations of the linewidth and the frequency measurement will be also presented.
STATE OF WATER MOLECULES AND SILANOL GROUPS IN OPAL MINERALS: A NEAR INFRARED SPECTROSCOPIC STUDY OF OPALS FROM SLOVAKIA

MIROSLAV BOBON, Department of Physics, Faculty of Natural Sciences, Constantine the Philosopher University in Nitra, Slovakia; ALFRED A. CHRISTY, Department of Science, Faculty of Engineering and Science, University of Agder, Serviceboks 422, 4604 Kristiansand, Norway; DANIEL KLUVANEK and L’UDMILA IL-LASOVA, Gemological Institute, Faculty of Natural Sciences, Constantine The Philosopher University in Nitra, Slovakia.

Recently near infrared spectroscopy in combination with double derivative technique has been effectively used by Christy [1] to differentiate between free silanol groups and hydrogen bonded silanol groups on silica gel. The method has given some insight into the type of functionalities and their location in silica gel samples. The important information in this respect comes from the overtones of the OH groups of water molecules hydrogen bonded to free silanol groups, and hydrogen bonded silanol groups absorbing in the region 5500- 5100 cm$^{-1}$ region. The approach was adapted to study the state of water and silanol functionalities and their locations in opals from Slovakia.

Twenty opal samples classified into CT and A classes and one quartz sample were used in this work. The samples were crushed using a hydrolic press and powderised. Each sample was then subjected to evacuation process to remove surface adsorbed water at 200 °C and the near infrared spectrum of the sample was measured using a Perkin Elmer NTS near infrared spectrometer equipped with a transflectance accessory. The detailed analysis of the sample was carried out using the second derivative profile of the spectrum. The samples were also heated to 750 °C to study the state of water molecules in Opal minerals.

The results indicate that the opal samples contain 1) surface adsorbed water 2) free and hydrogen bonded silanol groups on the surface 3) Trapped water in the bulk 4) free and hydrogen bonded silanol groups in the cavity surfaces in the bulk. A part of the water molecules found in the bulk of opal minerals are free molecules and the rest are found in hydrogen bonded state to free and hydrogen bonded silanol groups.


C-H STRETCH OVERTONE SPECTRA OF FLUORINATED ETHERS

SHIZUKA HSIEH, Chemistry Department, Smith College, Northampton, MA 01063.

Photoacoustic spectra of some fluorinated ethers at 4-6 quanta of C-H stretch illustrate effects of fluorination on overtone frequencies and intensities.
TB. DYNAMICS
TUESDAY, JUNE 21, 2011 – 8:30 am
Room: 170 MATH ANNEX

Chair: DAVID PERRY, University of Akron, Akron, Ohio

TB01 10 min 8:30
FREE-INDUCTION DECAY SIGNALS USING A VOLTAGE MODULATED QUANTUM CASCADE LASER

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

Pulse modulated, continuously operating, quantum cascade, QC, lasers have been used to probe the infrared spectra of nitrous oxide and nitric oxide. We have extended the method of solving the Maxwell-Bloch equations numerically, which was developed for pulsed QC lasers, to include the dual sweep rate behaviour seen in pulse modulated lasers. Using this approach we have demonstrated that two types of rapid oscillatory signals should be observed, free induction decay signals which occur at the beginning and end of the excitation pulse, and rapid passage induced signals. Rapid passage signals only occur if the frequency swept pulse scans towards the centre frequency of the absorption line. Oscillatory structure may then be observed both during the excitation pulse, and during the relaxation time period required for the laser to reach equilibrium following the end of the excitation pulse.

TB02 15 min 8:42
OBSERVATION OF INFRARED FREE INDUCTION DECAY AND OPTICAL NUTATION SIGNALS FROM NITROUS OXIDE USING A VOLTAGE MODULATED QUANTUM CASCADE LASER

G. DUXBURY and N. LANGFORD, Department of Physics, SUPA, John Anderson Building, University of Strathclyde, 107 Rottenrow, Glasgow G4 0NG, Scotland, UK; J. F. KELLY and T. F. BLAKE, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, PO Box 999, MS K-88, Richland, Washington 99352.

Free induction decay, FID, and rapid passage, RP, signals in nitrous oxide, under both optically thin and optically thick conditions, have been observed using a pulse modulated quantum cascade laser operating at 7.97 μm. The variation in optical depth was achieved by increasing the pressure of nitrous oxide in a long path length multipass absorption cell. This allows the variation of optical depth to be achieved over a range of low gas pressures. Since, even at the highest gas pressure used in the cell, the sweep rate of the QC laser is faster than the collisional reorientation time of the molecules, there is minimal collisional damping allowing a large macroscopic polarisation to develop. The resultant FID signals are enhanced owing to the constructive interference between the field within the gas generated by the pump laser, and the probe laser signal generated by pulse modulation of the continuously operating QC laser. The FID signals obtained at large optical depth have not been observed previously in the mid infrared regions, and unusual oscillatory signals have been observed at the highest gas pressures used.
Using a low power modulated quantum cascade laser, collective coherent effects in the 5 μm spectrum of NO have been demonstrated by the observation of sub- Doppler hyperfine splitting. For nitrous oxide, experiments and model calculations have demonstrated that two main effects occur with chirped pulse modulated quantum cascade (QC) lasers, these are free induction decay signals, and those induced by rapid passage during the chirped modulation pulse. In the open shell molecule, NO, in which both lambda-doubling splitting and hyperfine structure occur, laser field induced coupling between the hyperfine levels of the two lambda-doublet components can induce a large AC Stark effect. This may be regarded as an extension of the types of behaviour observed, using the same apparatus fitted with an 8 μm QC laser, in the closed shell molecule nitrous oxide.

Metastable rare gas atoms are gaining increasing interest for their potential in the development of optically pumped laser systems. Understanding the time evolution of excited rare gas states in a collisional environment is of importance for the possibility of exploiting them as the active laser species. Collisional deactivation rates for excited states of Kr*(4p^55p^1) atoms colliding with ground state Kr (4p^6) and He (1s^2) have been measured by time resolved measurements of the laser induced fluorescence, following state selective excitation at room temperature. Collisional energy transfer for the Kr*(4p^55p^1) + Kr (4p^6) and Kr*(4p^55p^1) + He (1s^2) systems were investigated in a pulsed electrical discharge. Metastable Kr*(4p^55s^1) was generated by electron impact excitation from the ground state. Using a pulsed tunable dye laser these metastable states were pumped to selected upper levels of the 2p_J manifold (Paschen notation) and time-dependent fluorescence decay data from pumped and collisionally populated levels were collected. The total and intramultiplet state-to-state collisional deactivation rate constants were derived from the experimental data and by numerical models. The experimental data were simulated by fitting to numerical solutions of a set of coupled differential equations describing the full collisional relaxation processes. State-to-state rate constants are reported.

Recently it has been proposed that IR/THz double resonance (DR) spectroscopy has potential for remote detection of trace gases at atmospheric pressures. Historically, these techniques have been utilized in the investigation of molecular collision dynamics. Understanding the effects of pressure on the energy dynamics of the system aids in the prediction of signatures in remotes sensing applications. We have performed IR/THz DR spectroscopy on a selection of gases and at a variety of pressures. Energy transfer models are utilized to understand the effects of pressure on these dynamics. Latest results will be presented in the context of remote sensing applications and laboratory studies.
ULTRAFAST STRUCTURAL DYNAMICS OF TERTIARY AMINES UPON ELECTRONIC EXCITATION

XINXIN CHENG, MICHAEL P. MINITTI, SANGHAMITRA DEB, YAO ZHANG, JAMES BUDARZ, PETER M. WEBER, Department of Chemistry, Brown University, Providence, Rhode Island 02912.

The structural response of several tertiary amines to electronic excitation has been investigated using Rydberg Fingerprint Spectroscopy. The 3p Rydberg states are reached by excitation with a 5.93 eV photon while 3s states are populated by electronic relaxation from 3p state. We observe binding energy shifts on ultrafast time scales in all peaks that reflect the structural change of the molecular ion cores. The shifts are in the range of 15 meV to 30 meV, within time scales of less than 500 fs, depending on the specific molecular systems and the nature of the electronic state. In cases where the p states are spectrally separate, the trends of the energy shifts are different for the \( p_z \) and \( p_{xy} \) Rydberg states whereas the \( p_z \) and s states are similar. This suggests that the response of the Rydberg states to structural displacements depends on the symmetry. Very fast binding energy shifts, observed on sub-picosecond time scales, are attributed to the structural adjustment from a pyramidal to a planar structure upon Rydberg excitation. The quantitative values of the binding energy shifts can also be affected by laser chirp, which we model using simulations.

ULTRAFAST STRUCTURAL DYNAMICS OF 1,3-CYCLOHEXADIENE: ELECTRONIC STATE DEPENDENCE

CHRISTINE C. BÜHLER, MICHAEL P. MINITTI, SANGHAMITRA DEB, PETER M. WEBER, Department of Chemistry, Brown University, Providence, Rhode Island 02912; JIE BAO, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

The ultrafast structural dynamics of 1,3-cyclohexadiene has been investigated using structurally sensitive Rydberg electron binding energies. Excitation to the 1B state and the 3p Rydberg state yielded different structural responses. In both experiments, the structural dynamics of the molecular core are reflected by time-dependent shifts of the Rydberg electron binding energy. Structural distortions associated with 3p-excitation cause a dynamical shift in the \( p_z \)- and \( p_{xy} \)-binding energies by 8 and 25 meV/ps respectively, whereas after excitation into 1B more severe structural transformations along the ring-opening coordinate produce binding energy shifts at a rate of 65 meV/ps.

Intermission
PHOTOCHEMISTRY OF BENZYLALLENE: PHOTOCHEMICAL PATHWAYS TO NAPHTHALENE

JOSHUA A. SEBREE, NATHAN KIDWELL, TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN 47907; ALEX NOLAN, ROBERT MCMAHON, Department of Chemistry, University of Wisconsin, Madison WI 53706; TALITHA SELBY, Department of Chemistry, University of Wisconsin Washington County, West Bend, WI 53095; MAREK ZGIERSKI, National Research Council Canada, Ottawa, ON.

Recently, many groups have suggested that the flexible side chain of alkylated benzene rings may play an important role in the formation of fused ring compounds. Here we present the conformer-specific, vibrationally-resolved electronic spectroscopy of benzylallene along with a detailed analysis of the products formed via its ultraviolet photoexcitation. Benzylallene is the minor product of the recombination of benzyl and propargyl radicals. The mass-selective resonant two-photon ionization spectrum of benzylallene was recorded showing an origin at 37483 cm$^{-1}$. UV-UV holeburning showed that only one conformer was present in the expansion and rotational band contour analysis showed the allene unit to be pointing away from the phenyl ring. The photochemistry of benzylallene was carried out by counterpropagating the expansion with a photoexcitation laser. The laser was timed to interact with the gas pulse in a reaction channel to initiate reactions. The reactions were quenched upon exiting the channel. Products were then interrogated using mass-selective resonant two-photon ionization techniques. The UV-Vis spectra of products were compared to literature for identification. Product distributions at various excitation wavelengths were recorded. Using 193 nm light, eight products were observed including two radicals, benzyl and benzylallenyl, and several mass 128 isomers including naphthalene. Photoexciton at the S$_0$-S$_1$ origin of benzylallene yielded only four products including naphthalene. One important note is that at the lower energy excitation, over three times as much naphthalene was observed. A combination of isotopic substitution and calculations has been used in the determination of a mechanism for naphthalene formation.

BIMOLECULAR REACTIONS OF A DIFFERENT COLOR: CH$_3$D + CHLORINE WITH VARIED PHOTOLYSIS WAVELENGTHS

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

We examine the effect varying the collision energy has on the bimolecular reaction of CH$_3$D and chlorine. A Raman shifting cell pumped at 355 nm and filled with either hydrogen or methane gas provides, in discrete steps, light to photolyze Cl$_2$. This imparts between 600 and 2000 cm$^{-1}$ of collision energy to our system. By also adding C-H vibrational overtone excitation, around 6000 cm$^{-1}$, we can compare to previous, fixed-photolysis energy studies from our research group. We seek to elucidate the role translational energy (collision energy) plays in this reactive system.

COMPARATIVE TORSION-INVOLUTION DYNAMICS FOR CH$_3$CH$_2$, CH$_3$OH$_2^+$ AND CH$_3$NH$_2$

RAM S. BHATHA and DAVID S. PERRY, Department of Chemistry, The University of Akron, OH 44325-3601.

A general 2-dimensional torsion-inversion Hamiltonian was developed for methylamine, protonated methanol and ethyl radical. The torsion-involution potential energy surfaces and kinetic parameters were determined from ab initio calculations at CCSD(T)/6-311++G(3df,2p)//MP2/6-311++G(3df,2p). The quantum torsion-involution dynamics were solved for this Hamiltonian, including the dependence of the reduced masses on the inversion coordinates. The manifolds of torsion-involution energy levels are calculated for the three molecular species and are compared with the available experimental and theoretical data. The patterns of the tunneling splittings vary as the inversion and torsional barriers go from low to high in the sequence CH$_3$CH$_2$, CH$_3$OH$_2^+$ and CH$_3$NH$_2$. 
STATE-TO-STATE ROTATIONAL AND VIBRATIONAL ENERGY TRANSFERS FOLLOWING VIBRATIONAL EXCITATION OF \((1010^00^0)\) AND \((0112^00^0)\) IN THE GROUND ELECTRONIC STATE OF ACETYLENE

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

We have examined state-to-state rotational and vibrational energy transfers for the vibrational levels \((1010^00^0)\) and \((0112^00^0)\) of \(\text{C}_2\text{H}_2\) in the ground electronic state at ambient temperature. Measurements were made using a pulsed IR - UV double resonance technique. Total removal rate constants and state-to-state rotational energy transfer rate constants have been characterized for certain even-numbered rotational levels from \(J=0\) to 12 within the two vibrational modes. The measured state-to-state rotational energy transfer rate constants were fit to some energy-based empirical scaling and fitting laws, and the rate constants were found to be best reproduced by the statistical power-exponential gap law (PEGL). The measured rate constants were then further evaluated by a kinetic model which simulated the experimental spectra by solving simultaneous first order differential rate equations. Some rotationally-resolved vibrational energy transfer channels were also observed following excitation of \((1010^00^0)\). The vibrational relaxation channels were found to contribute less than 30% to the total removal rate constants of the measured rotational levels for both of the studied vibrational states.

VIBRATIONAL PREDISSOCIATION DYNAMICS OF THE \((\text{H}_2\text{O})_2\) DIMER

L. C. CH'NG, B. E. ROCHER, A. K. MOLLNER, and H. REISLER, Department of Chemistry, University of Southern California, Los Angeles, CA, 90089.

The state-to-state vibrational predissociation dynamics of the \((\text{H}_2\text{O})_2\) dimer were studied by resonance-enhanced multiphoton ionization (REMPI) and velocity-map imaging (VMI) to obtain pair-correlated product energy distributions. The \(2+1\) REMPI spectra of the \(\text{H}_2\text{O}\) photofragments were recorded via the \(\tilde{C}^1\text{B}_1\ \(000) \leftrightarrow \tilde{X}^1\text{A}_1\ \(000\ and 010\) transition following a vibrational excitation of the dimers bound-OH stretch fundamental. The fragment center-of-mass translational energy (c.m. \(E_T\)) distributions were determined from VMI of selected rotational states of the detected \(\text{H}_2\text{O}\) photofragments. The c.m. \(E_T\) distributions were then converted to pair-correlated \(\text{H}_2\text{O}\) cofragment rotational level distributions. This is the first experiment in which \(\text{H}_2\text{O}\) products with bend \(\nu_2\) excitation were observed by REMPI. The dissociation energy of the dimer was determined from the images with spectroscopic accuracy. The predissociation mechanism of \((\text{H}_2\text{O})_2\) will be discussed and compared with the corresponding hydrogen bonded dimers of an acid (HCl-H\(\text{O}\)) and a base (\(\text{NH}_3\)-H\(\text{O}\)).

DETERMINATION OF THE DISSOCIATION ENERGY OF AMMONIA DIMER: A VIBRATIONAL PREDISSOCIATION STUDY

AMANDA S. CASE, CORNELIA G. HEID, SCOTT. H. KABLE, and F. FLEMING CRIM, Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706.

We have investigated the dynamics of ammonia dimer following initial vibrational excitation in the NH-stretch region using a combination of resonance enhanced multiphoton ionization (REMPI) and velocity-map ion imaging. Upon excitation of either the symmetric \((3331 \text{ cm}^{-1})\), or the antisymmetric \((3427 \text{ cm}^{-1})\) intramolecular NH-stretch vibration, the dimer predissociates into its two constituent monomers. Based on our assignments of the bands in the REMPI-action spectrum, we were able to selectively ionize specific rovibrational states of one of the monomer fragments via \((2+1)\) REMPI, and subsequently image the resulting translational energy distribution. Since both energy and momentum are conserved in the dissociation process, the rovibrational state of the partner fragment is readily deduced. Fitting our energy distributions with a simple model that accounts for all energetically accessible rotational states, we find that the \(\nu_2\) umbrella mode, which is populated up to \(v=3\), is preferentially formed with rotational levels having high \(J\) values. By fitting a series of distributions obtained from probing different rovibrational states in the \(\nu_2 = 2\) manifold, we obtain a dissociation energy of \(660 \pm 20 \text{ cm}^{-1}\) which is consistent across the entire set of measured distributions.
TC. MICROWAVE
TUESDAY, JUNE 21, 2011 – 8:30 am
Room: 1000 McPHERSON LAB

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

TC01 10 min 8:30
EASY-GOING ON-SPECTROMETER OPTIMISATION OF PHASE MODULATED HOMONUCLEAR DECOUPLING SEQUENCES IN SOLID-STATE NMR


A global optimisation scheme for phase modulated proton homonuclear decoupling sequences in solid-state NMR is presented. Phase modulations, parameterised by DUMBO Fourier coefficients, were optimized using a Covariance Matrix Adaptation Evolution Strategies algorithm\textsuperscript{a}. Our method, denoted EASY-GOING homonuclear decoupling, starts with featureless spectra and optimises proton-proton decoupling, during either proton or carbon signal detection. On the one hand, our solutions closely resemble (e)DUMBO\textsuperscript{b} for moderate sample spinning frequencies and medium radio-frequency (rf) field strengths. On the other hand, the EASY-GOING approach resulted in a superior solution, achieving significantly better resolved proton spectra at very high 680 kHz rf field strength.


TC02 15 min 8:42
QUANTUM-CHEMICAL CALCULATIONS OF SPECTROSCOPIC PARAMETERS FOR ROTATIONAL SPECTROSCOPY: THE NEED OF THE INTERPLAY BETWEEN EXPERIMENT AND THEORY

CRISTINA PUZZARINI, Dipartimento di Chimica "G. Ciamician", Università di Bologna, I-40126 Bologna, Italy.

Quantum-chemical calculations are nowadays able to provide very accurate predictions of molecular and spectroscopic properties. The predictive capabilities of such computations take a fundamental role in the field of high-resolution spectroscopy: calculations allow to guide, support and/or challenge the experimental determinations. In the field of rotational spectroscopy, high-level calculations can provide reliable values for the corresponding spectroscopic parameters (mainly, rotational and centrifugal-distortion constants), thus significantly facilitating the assignment of unknown spectra and, if the case, for the hyperfine parameters (nuclear quadrupole-coupling constants, spin-rotation tensors, spin-spin couplings, etc.), essential for the analysis of complex hyperfine structures. Furthermore, calculations can be used to provide information which enable a rigorous interpretation of the obtained spectroscopic parameters. In the present contribution, it will be demonstrated how fruitful is to exploit the interplay of theory and experiment, and the power of such an interplay will be illustrated by a few significant examples.
ROTATIONAL SPECTRUM OF CH₂FI FROM 5 GHZ UP TO 1 THZ: ACCURATE SPECTROSCOPIC AND HYPERFINE PARAMETERS

Cristina Puzzarini, Gabriele Cazzoli, Dipartimento di Chimica "G. Ciamician", Università di Bologna, I-40126 Bologna, Italy; Juan Carlos López, José Luis Alonso, Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47005, Valladolid, Spain; Agostino Baldacci, Alessandro Baldan, Dipartimento di Chimica Fisica, Università "Ca’ Foscari" Venezia, D.D. 2137, I-30123 Venezia, Italy; Stella Stopkowicz, Lan Cheng, Jürgen Gauss, Institut für Physikalische Chemie, Universität Mainz, D-55099 Mainz, Germany.

Guided by theoretical predictions, the rotational spectrum of fluoroiodomethane, CH₂FI, has been recorded and assigned. Three different spectrometers have been employed, a Fourier Transform Microwave spectrometer, a Millimeter/Submillimeter-wave Spectrometer, and a THz spectrometer, thus allowing to record a huge portion of the rotational spectrum, from 5 GHz up to 1 THz, and to accurately determine the ground-state rotational and centrifugal-distortion constants. The hyperfine structure of the rotational spectrum has been investigated by means of the Fourier Transform Microwave spectrometer and the Lamb-dip technique in the millimeter/submillimeter-wave region, thus allowing the determination of the complete iodine quadrupole-coupling tensor and of the diagonal elements of the iodine spin-rotation tensor. Regarding the quantum-chemical calculations, inclusion of relativistic effects turned out to be essential for obtaining reliable and quantitative predictions for experiment, and they have been accounted for either by means of second-order direct perturbation theory or via a spin-free approach based on the Dirac Coulomb Hamiltonian, both in combination with coupled-cluster techniques to treat electron correlation and sufficiently large basis sets.

ANALYSIS OF THE ROTATIONAL SPECTRUM OF HDO IN ITS v₂ = 0 AND 1 VIBRATIONAL STATES UP TO 2.8 THz

Holger S. P. Müller, S. Brünken, C. P. Endres, F. Lewen, I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany; J. C. Pearson, S. Yu, B. J. Drouin, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA; H. Mäder, Institut für Physikalische Chemie, Christian-Albrechts-Universität, 24098 Kiel, Germany.

The rotational and rovibrational spectra of H₂O and its isotopologs, including HDO, are of great importance for atmospheric chemistry, astrophysics, and basic sciences. We recorded rotational spectra of HDO in the ground and first excited bending state from the microwave region up to 2.8 THz. Several spectrometers were employed in Kiel, Köln, and Pasadena. An up-to-date combined analysis with rovibrational data was presented, in which a Hamiltonian based on Euler functions was used to overcome convergence difficulties of the conventional Watson Hamiltonian. The model had been employed previously, e.g., in a related analysis of D₂O spectra with v₂ ≤ 1. Recently, many more data have been obtained in Köln as well as in Pasadena. Including multiple measurements, these add up to about 230 and 100 new transition frequencies in v₂ = 0 and 1, respectively, reaching J = 17/13 and Kₐ = 9/5. In addition, a critically evaluated compilation of IR data was published very recently. Difficulties in reproducing the data within experimental uncertainties prompted a reanalysis of the data starting at small quantum numbers and extending the data set in small portions. At lower quantum numbers, difficulties were due to, e.g., few typographical errors and misassignments. At higher quantum numbers, interactions between v₂ = 0 and 1 as well as between these and higher states (e.g. v₂ = 2/v₁ = 1, which interact through Fermi resonance) are more important. The limitation of the present analysis to the lowest two vibrational states affords some transitions to be excluded from the analysis and causes a truncation of the data set at some values of J and Kₐ.

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TC04 15 min 9:16

ROTATIONAL SPECTROSCOPY OF HD\textsuperscript{18}O

JOHN C. PEARSON\textsuperscript{a}, SHANSHAN YU, HARSHAL GUPTA and BRIAN J. DROUIN, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109.

The recent detection of HD\textsuperscript{18}O in Orion KL\textsuperscript{b} by the Herschel Space Observatory provided a strong motivation to revisit the rotational spectrum in order to obtain more accurate calculations of transition frequencies. Rotational transitions were recorded in the 300 – 2700 GHz frequency range. Analysis of the combined microwave and infrared data sets with an Euler series Hamiltonian\textsuperscript{c} has facilitated determination of a set of precise rotational constants to support precision velocity measurements. The new rotational data also provides a means of evaluating the performance of the MARVEL algorithm used in the recent review of all available HDO data\textsuperscript{d}.

\textsuperscript{a}A part of this work was performed at the Jet Propulsion Laboratory, California Institute of Technology under contract with the National Aeronautics and Space Administration. Copyright 2010 © California Institute of Technology. All rights reserved.

\textsuperscript{b}E. A. Bergin et al., Astron. Astrophys. 521, (L20), 2010.

\textsuperscript{c}H. M. Pickett, J. C. Pearson, and C. E. Miller J. Mol. Spectrosc. 233 (174), 2005.


CHIRPED-PULSE TERAHERTZ SPECTROSCOPY FOR BROADBAND TRACE GAS SENSING

EYAL GERECHT, KEVIN O. DOUGLASS, DAVID F. PLUSQUELLIC, NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY, OPTICAL TECHNOLOGY DIVISION, GAITHERSBURG, MD 20899.

Recently developed solid state sources and heterodyne detectors for the terahertz frequency range have made it possible to generate and detect precise digitally synthesized waveforms at THz frequencies with ultra-low phase noise. The sample gas is polarized using sub-\(\mu\)s chirped THz pulses and both the absorption and the free inductive decay (FID) signals are detected using a mixer amplifier multiplier chain. This approach allows for a rapid broadband multi-component detection with low parts-per-billion sensitivities and high frequency accuracy. Current acquisition time is 30 seconds for 10.6 GHz of bandwidth. Such a system can be configured into a portable, robust, and easy to use sensing platform. A full description of broadband trace gas sensor operating at 540 GHz to 620 GHz will be presented.

Intermission
Knowing the vibrational population distribution of unimolecular fragmentation reaction products can reveal the reaction mechanism. Here, we applied Chirped Pulse Millimeter Wave (CPmmW) spectroscopy, invented by Brooks Pate and co-workers \(^a\), to detect the vibrational population distribution of formaldehyde produced by pyrolysis of methyl nitrite (CH\(_3\)ONO) or ethyl nitrite (CH\(_3\)CH\(_2\)ONO). The pure rotational spectrum contains information about vibrational populations via the known vibration dependence of the rotational constants, which is easily observed in the millimeter-wave spectrum. Only two of six vibrational modes of formaldehyde are significantly populated in both pyrolysis decomposition reactions and in an expansion of pure formaldehyde, suggesting that it is the collisional energy transfer that primarily determines the vibrational population distribution. The non-Boltzmann population distribution among the observed vibrational modes demonstrates non-statistical vibrational energy transfer in formaldehyde. It is in sharp contrast with the equilibrated population distribution measured in OCS and the almost complete vibrational relaxation observed in acetaldehyde.

This work is supported by grants from the US Department of Energy and the ACS Petroleum Research Fund, and the National Science Foundation grant "Organic Radicals in Biomass Decomposition: Mechanisms & Dynamics," (CHE-0848606)


The millimeter/submillimeter spectrum of methylphosphine, CH\(_3\)PH\(_2\) (\(\tilde{X}^1\)A)

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 millimeter/submillimeter spectrum of methylphosphine, CH\(_3\)PH\(_2\) (\(\tilde{X}^1\)A), has been measured using direct absorption techniques. Previously, only the microwave spectrum had been recorded. This molecule was created by the reaction of gas-phase phosphorus and methane or Si(CH\(_3\))\(_4\) in the presence of argon carrier gas and an AC glow discharge. Several transitions have been recorded in the range 280 - 422 GHz in both the \(v = 0\) and \(v = 1\) states each with multiple asymmetry components ranging from \(K_a = 0\) to 16. Several of the \(K_a\) components in the \(v = 0\) state show A/E splittings, while others appear collapsed. The \(v = 1\) state has multiple \(K_a\) components with A/E splittings and is currently being analyzed. The data for the \(v = 0\) state has been fit with an asymmetric top Hamiltonian, including internal rotation interactions, and the spectroscopic constants have been determined. Methylphosphine is the third row analog of methylamine, a known interstellar molecule, and could be a potential interstellar species.
FOURIER TRANSFORM MICROWAVE SPECTRUM OF THE FeCN RADICAL (X^4 \Delta_i) AND CONFIRMATION OF THE GROUND ELECTRONIC STATE

D. T. HALFEN, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ, 85721; M. A. FLORY, CNA, Frankfort, KY; B. J. HARRIS, and L. M. ZIURYS, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ, 85721.

The pure rotational spectrum of the FeCN radical (X^4 \Delta_i) has been measured using Fourier transform microwave (FTMW) techniques in the 4 - 40 GHz frequency range and a laser ablation source. The species was produced using Discharge Assisted Laser Ablation Spectroscopy (DALAS) in a supersonic jet expansion of iron vapor and (CN)2, diluted in argon carrier gas. The fundamental rotational transition, J = 9/2 \rightarrow 7/2 (\Omega = 7/2), was recorded near 36 GHz. Three hyperfine transitions, due to the nitrogen nuclear spin of I = 1, were observed in the spectrum. These data were combined with the previous millimeter/submillimeter measurements of FeCN in a global fit and nitrogen hyperfine constants were determined. These measurements confirm that the ground state of FeCN is X^4 \Delta_i, as suggested by previous millimeter/submillimeter measurements of Flory & Ziurys. Theoretical calculations have predicted that the ground state of this radical is X^6 \Delta_i. In a X^6 \Delta_i state, the J = 9/2 \rightarrow 7/2 transition does not exist in the lowest energy ladder (\Omega = 9/2).

THE PURE ROTATIONAL SPECTRUM OF THE ZnSH RADICAL (X^2 A')

MATTHEW P. BUCCHINO, GILLES R. ADANDE and LUCY M. ZIURYS, Department of Chemistry and Biochemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, Arizona 85721.

The pure rotational spectrum of the ZnSH radical (X^2 A') has been observed in the laboratory for the first time using millimeter/submillimeter direct-absorption methods and Fourier-transform microwave (FTMW) techniques in a frequency range of 4-400GHz. ZnSH was synthesized by reacting zinc vapor with H2S under DC discharge in a Broida-type oven for the millimeter work; in the FTMW studies, the radical was created by discharge assisted laser ablation spectroscopy (DALAS) using 0.5% H2S in Ar and a zinc rod. The K-ladder structure indicates C_s symmetry, and therefore a bent molecule. Spectra of multiple isotopologues have been recorded (^{64}ZnSH, ^{66}ZnSH, ^{68}ZnSH, and ^{64}ZnSD), from which an r_0 structure has been determined. Each K-component consists of spin-rotation doublets with a splitting of 130-140MHz. Proton hyperfine structure was observed in the FTMW data. Rotational, spin-rotation, and hyperfine constants have been determined from a global fit to the data. Although ZnSH and ZnOH are isovalent, there appear to be subtle differences in bonding between the two species.

HYPERFINE SPLITTING AND ROTATIONAL ANALYSIS OF THE DIATOMIC MOLECULE ZINC MONOSULFIDE, ZnS.

DANIEL J. FROHMAN, G. S. GRUBBS II, and STEWART E. NOVICK, Department of Chemistry, Wesleyan University, Hall-Atwater Laboratories, 52 Lawn Avenue, Middletown, CT 06459-0180.

^{67}Zn hyperfine structure has been observed in the diatomic molecule ZnS in the microwave (6-26 GHz) region. The molecule was synthesized by the use of a newly constructed laser ablation source based on the design of Walker and Gerry. Previous rotational studies of this molecule have been performed in the millimeter-wave region (370-471 GHz range). Rotational analyses, including the nuclear electric quadrupole coupling constant, will be discussed and compared with the literature.

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\(^5\)K. A. Walker and M. C. L. Gerry, J. Mol. Spectrosc., 182 (1997), 178

CAVITY AND CHIRPED PULSE ROTATIONAL SPECTRUM OF THE LASER ABLATION SYNTHESIZED, OPEN-SHELL MOLECULE TIN MONOCHLORIDE, SnCl.a

G. S. GRUBBS II, DANIEL J. FROHMAN, STEWART E. NOVICK, Department of Chemistry, Wesleyan University, Hall-Atwater Laboratories, 52 Lawn Avenue, Middletown, CT 06459-0180; and S. A. COOKE, Department of Chemistry, University of North Texas, 1155 Union Circle # 305070, Denton, TX 76203-5017.

The use of laser ablation source-equipped chirped pulse and Balle-Flygare type cavity spectrometers have been utilized to accurately measure multiple isotopologues of the tin monochloride molecule in the $X^2Π_1$ state. The molecule has been synthesized by ablating tin foil in the presence of 0.3% Cl₂ in Ar. Rotational constants, nuclear electric quadrupole coupling constants, and magnetic hyperfine constants for the many isotopologues will be discussed. Although rotational analyses of this molecule have been previously performedb, this is the first high-resolution, microwave study of SnCl.

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aSupport from CHE-1011214

TD. ELECTRONIC
TUESDAY, JUNE 21, 2011 – 8:30 am
Room: 1015 McPHERSON LAB

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

TD01 15 min 8:30
SPECTROSCOPIC CHARACTERIZATION OF Be$_2^+$ X$^2\Sigma_u^+$ AND THE IONIZATION ENERGY OF Be$_2$

I. O. ANTONOV, B. J. BARKER, V. E. BONDYBEY, M. C. HEAVEN, Department of Chemistry, Emory University, Atlanta, GA 30322.

Rotationally resolved spectra for Be$_2^+$ were recorded with PFI-ZEKE technique. Vibrational levels $v^+\leq 0-6$ were observed. The symmetry of the ground state was determined as $^2\Sigma_u^+$. The bond energy was found to be $D_e^+ = 16348(5)$ cm$^{-1}$ and the equilibrium distance $R_e^+ = 2.211(8)$ Å. The ionization energy for Be$_2^+$ was refined at 59824(2) cm$^{-1}$. Comparisons with high-level theoretical calculations indicate that the bonding in Be$_2^+$ is adequately described by MRDCl calculations with moderately large basis sets.

TD02 15 min 8:47
FOURIER TRANSFORM EMISSION SPECTROSCOPY OF THE B$^2\Sigma^+\rightarrow X^2\Sigma^+$ (VIOLET) SYSTEM OF $^{13}$C$^{14}$N

R. S. RAM and P. F. BERNATH, Department of Chemistry, University of York, Heslington, York YO10 5DD.

Emission spectra of the B$^2\Sigma^+\rightarrow X^2\Sigma^+$ transition of $^{13}$C$^{14}$N have been observed at high resolution using the Fourier transform spectrometer associated with the McMath-Pierce Solar Telescope of the National Solar Observatory. The spectra have been measured in the 21000–30000 cm$^{-1}$ region and a total of 52 vibrational bands involving vibrational levels up to $v = 15$ of the ground and excited states have been rotationally analyzed to provide a much improved set of spectroscopic constants. The results of the present analysis should prove useful in the identification of additional $^{13}$C$^{14}$N lines in comets and cool stars, and will help in the determination of the $^{12}$C/$^{13}$C abundance ratio.

The observation of a number of highly-excited vibrational bands of the A$^2\Pi\rightarrow X^2\Sigma^+$ transition as well as a few bands of the B$^2\Sigma^+\rightarrow A^2\Pi$ transition will also be reported.

TD03 15 min 9:04
FOURIER TRANSFORM EMISSION SPECTROSCOPY OF THE E$^2\Pi\rightarrow X^2\Sigma^+$ TRANSITION OF CaH AND CaD

R. S. RAM, K. TERESZCHUK and P. F. BERNATH, Department of Chemistry, University of York, Heslington, York YO10 5DD, UK; I. E. GORDON, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138, USA; K. A. WALKER, Department of Physics, University of Toronto, Toronto, Ont., M5S 1A7, Canada.

The emission spectra of CaH and CaD have been recorded at high resolution using a Fourier transform spectrometer and bands belonging to the E$^2\Pi\rightarrow X^2\Sigma^+$ transition have been measured in the 20100–20700 cm$^{-1}$ region. A rotational analysis of 0–0 and 1–1 bands of both the isotopologues has been carried out. The present measurements have been combined with the previously available pure rotation and vibration-rotation data to provide improved spectroscopic constants for the E$^2\Pi$ state. The constants $\Delta G_{1/2} = 1199.8810(32)$ cm$^{-1}$, $B_e=4.344659(45)$ cm$^{-1}$, $\alpha_e=0.121869(88)$ cm$^{-1}$, $r_e=1.986718$ Å for CaH, and $\Delta G_{1/2}=868.7438(46)$ cm$^{-1}$, $B_e=2.212496(51)$ cm$^{-1}$, $\alpha_e=0.036509(97)$ cm$^{-1}$, $r_e=1.993396(23)$ Å for CaD have been determined. An analysis of the corresponding transitions of SrH and SrD in the 18600–19300 cm$^{-1}$ region will also be reported.
JET-COOLED LASER-INDUCED FLUORESCENCE SPECTROSCOPY OF LARGE SECONDARY ALKOXY RADICALS

JINJUN LIU, MING-WEI CHEN, TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Ave., Columbus, Ohio 43210; W. L. MEERTS, Radboud University, Institute for Molecules and Materials, Heyendaalseweg 135, NL-6525 AJ Nijmegen, The Netherlands.

The \( \tilde{B} \leftarrow \tilde{X} \) laser-induced fluorescence (LIF) spectra of jet-cooled 2-pentoxy and 2-hexoxy have been recorded. The observed rotational and fine structure of the strongest vibronic bands has been simulated with \textit{ab initio} calculated rotational constants for both the \( \tilde{X} \) and \( \tilde{B} \) states, as well as the electron spin-rotation constants of the \( \tilde{X} \) state and the transition dipole moments, which are predicted based on the transferability of these quantities in an "orbital-fixed coordinate system" using iso-propoxy as the reference molecule. It is suggested by \textit{ab initio} calculations that the lowest two electronic (\( \tilde{X} \) and \( \tilde{A} \)) states of secondary alkoxy radicals have a small energy separation on the order of 100 cm\(^{-1}\). The energy ordering of these two nearly degenerate states has been determined by comparing the experimentally determined rotational constants and the transition dipole moments to the predicted ones. Molecular constants derived in fitting the rotational and fine structure of the experimental spectra using an evolutionairy algorithm (EA) enabled unambiguous assignment of the observed vibronic bands to different conformers of 2-pentoxy and 2-hexoxy. Based on the results of these two radicals, the strongest vibronic bands in the LIF spectra of larger secondary alkoxies were also assigned.

HIGH RESOLUTION LASER SPECTROSCOPY OF SrOCH\(_3\)

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, L. E. DOWNIE, W. S. HOPKINS, 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.

The \( \tilde{A}^2E \leftarrow \tilde{X}^2A_1 \) transition of SrOCH\(_3\) was first studied at high resolution by O’Brien et al.\(^a\) using a Broida oven. However lines with typically \( J \leq 20 \) were not observed and congestion prevented them from resolving transitions from the \( \Omega = 1/2 \) component of the upper state. We have studied the \( \tilde{B}^2A_1 \leftarrow \tilde{X}^2A_1 \) and the \( \tilde{A}^2E \leftarrow \tilde{X}^2A_1 \) transitions of SrOCH\(_3\) in a laser ablation molecular jet source, where jet cooling and low Doppler widths greatly simplified the spectra. An optical-optical double resonance technique facilitated definite assignments in a number of the transitions observed. Our analysis of the \( \tilde{A}^2E \leftarrow \tilde{X}^2A_1 \) transition was straightforward, but a perturbation was observed in the \( \tilde{B}^2A_1 \) \( K' = 1 \) \( F_2 \) levels. A satisfactory fit was achieved for the \( \tilde{B}^2A_1 \leftarrow \tilde{X}^2A_1 \) transition when a separate \( B \) parameter was used to fit the perturbed levels.


Intermission
DEVELOPMENT OF BROAD RANGE SCAN CAPABILITIES WITH JET COOLED CAVITY RINGDOWN SPECTROSCOPY

TERRANCE J. CODD, MING-WEI CHEN and TERRY A. MILLER, Laser Spectroscopy Facility, The Ohio State University, Columbus, Ohio 43210.

We have developed a technique for obtaining broad scans, $>100\,\text{cm}^{-1}$, for jet cooled cavity ringdown spectroscopy (CRDS) spectra. Previously the scans of the jet cooled, CRDS apparatus were limited to $<10\,\text{cm}^{-1}$ due to the use of a narrow linewidth radiation source. However, by coupling our jet cooled, CRDS apparatus with a moderate resolution ($\simeq 0.05\,\text{cm}^{-1}$) dye laser we are able to greatly increase our rate of data acquisition thereby gaining the capability to perform broad spectral surveys of jet cooled molecules. As a test of the capabilities of the technique we have scanned the $\tilde{A}$$-\tilde{X}$ transition of NO$_3$ previously reported by Deev et al.$^{a}$ at room temperature. We believe that this will be a very useful technique to search for transitions of cold molecules whose frequencies are not well known and which later can be studied using high resolution methods.


THE JET-COOLED HIGH RESOLUTION $\tilde{A}^2E''-\tilde{X}^2A'_2$ VIBRONIC BANDS OF NO$_3$

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

The $0^2_0^0$, $4^2_0^1$ and $2^2_1^0$ vibronic bands of the $\tilde{A}$ state NO$_3$ absorption spectrum has been successfully observed with our high-resolution, jet-cooled cavity ring-down apparatus. Ground state combination differences$^{bc}$ are used to analyze all four vibronic bands. Rotational transitions of the $4^2_0^1$ band (parallel band) band are assigned including some levels that appear to be doubled. The $4^2_0^0$ band verifies the existence of anomalous doublets in both the $4^2_0^1$ and $4^2_0^0$ bands. The $2^2_1^0$ band is a perpendicular band which has a different band type. Preliminary assignments of this band are utilized for the comprehensive understanding of the structure of NO$_3$ in the $\tilde{A}$ state. Besides the $\nu_2$ and $\nu_4$ vibronic bands, the vibronically forbidden origin band ($0^2_0^0$ band) has also been recorded. The weakly observed $\tilde{A}-\tilde{X}$ origin band structure appears to be different from either the parallel or perpendicular band type and is likely a magnetic dipole transition.

$^a$present address: Lawrence Berkeley National Laboratory, Berkeley, CA 94720
CAVITY RINGDOWN SPECTROSCOPY AND KINETICS OF HO$_2$+HCHO: DETECTION OF THE $\nu_1$ AND $\tilde{A} - \tilde{X}$ BANDS OF HOCH$_2$OO

MATTHEW K. SPRAGUE$^a$, MITCHIO OKUMURA, California Institute of Technology, Division of Chemistry, MC 127-72, Pasadena, CA 91125; and STANLEY P. SANDER, Jet Propulsion Laboratory, California Institute of Technology, MS 183-901, Pasadena, CA 91109.

The reactions of HO$_2$ with carbonyl compounds are believed to be a sink for carbonyl compounds in the upper troposphere and lower stratosphere. These reactions proceed through a hydrogen bond intermediate before isomerizing.$^b$ The reaction of HO$_2$ + formaldehyde (HCHO) serves as a prototype for this class of reactions, forming the isomerization product hydroxymethylperoxy (HOCH$_2$OO, HMP). Previous studies measured the spectrum and kinetics of HMP using either FTIR detection of the end products$^c$ or direct detection of HMP by the unstructured $\tilde{B} - \tilde{X}$ transition.$^d,e$ Despite these studies, considerable uncertainty exists in the rate constant of HMP formation ($k_{\text{HMP}}$). In this talk, we report the first detection of the $\nu_1$ (OH stretch) and $\tilde{A} - \tilde{X}$ electronic spectra of the HMP radical. The OH stretch spectrum is broad and featureless, while the $\tilde{A}(0)-\tilde{X}(0)$ origin and combination band with the OOCO torsion $\tilde{A}(n_{\text{OOCO}}=1)$-$\tilde{X}(0)$ are rotationally resolved. Quantum chemistry calculations have been performed on both the $\tilde{A}$ and $\tilde{X}$ states as a function of the OOCO and HOCO dihedral angles to estimate the $\tilde{A}-\tilde{X}$ transition frequency and to assess the coupling between the two torsional modes. We also present kinetics data showing the rates of production and destruction of HMP.

$^a$Support from the NDSEG Fellowship, California Air Resources Board Contracts 03-333 and 07-730, and NASA Upper Atmosphere Research Program Grants NAG5-11657, NNG06GD88G and NNX09AE21G are gratefully acknowledged


CAVITY RINGDOWN SPECTROSCOPY AND KINETICS OF BUTOXY ISOMERIZATION: DETECTION OF THE $\tilde{A}$-$\tilde{X}$ BAND OF HOCH$_3$HOO

MATTHEW K. SPRAGUE$^a$, MITCHIO OKUMURA, California Institute of Technology, Division of Chemistry, MC 127-72, Pasadena, CA 91125; and STANLEY P. SANDER, Jet Propulsion Laboratory, California Institute of Technology, MS 183-901, Pasadena, CA 91109.

Alkoxy radicals are atmospherically important species, playing a direct role in the HO$_2$ and NO$_x$ cycles that affect tropospheric air pollution. Alkoxy radicals that can form a six membered transition state can isomerize into a hydroxyalkyl radical. In the presence of O$_2$, a rapid association reaction occurs, forming a hydroxyalkyloxynperoxy radical. The $n$-butoxy radical is the smallest alkoxy to undergo isomerization, forming the $\gamma$-hydroxybutyloxynperoxy radical (HOCH$_3$H$_2$OO). Direct detection of HOCH$_3$H$_2$OO opens the door to measuring alkoxy reaction kinetics with higher precision than previous end product studies.$^b$

In this talk, we report the first detection of the $\tilde{A}-\tilde{X}$ electronic spectrum of the HOCH$_3$H$_2$OO radical. The spectrum is similar in shape to the $\tilde{A}$-$\tilde{X}$ spectrum of $n$-butyl peroxy.$^c$ a broad spectroscopic band due to the multiple molecular conformers that are present. We also use the $\tilde{A}$-$\tilde{X}$ band to measure the alkoxy isomerization kinetics relative to the alkoxy radical’s reaction with O$_2$, similar to the previous kinetics studies.

$^a$Support from the NDSEG Fellowship, California Air Resources Board Contracts 03-333 and 07-730, and NASA Upper Atmosphere Research Program Grants NAG5-11657, NNG06GD88G and NNX09AE21G are gratefully acknowledged


STUDY OF PHENYLACETYLENE BY CA VITY RING-DOWN SPECTROSCOPY

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

Cavity ring-down (CRD) measurements have been made on the $S_1(\tilde{A} 1B_2) \leftarrow S_0(\tilde{X} 1A_1)$ absorption spectrum of slit jet-cooled phenylacetylene (PA) in the 279 nm region as a further investigation of the photophysical properties of PA reported by Hosftein et al. The intensities in the new CRD data are compared with those obtained in the old REMPI experiments, and computational models. The results show that the strong bands in the REMPI spectrum are attenuated while the weak bands ($a_1$ modes) remained the same when compared to CRD spectra. The comparison of the simulated spectrum to the CRD and REMPI spectra were satisfactory for most part when the $a_1$ modes were scaled up by a factor of 3.24 and 3.55, respectively, giving evidence of some possible theoretical artifacts. The temperature of the slit jet-cooled PA was found to be in the range of $30\pm5 K$ by comparison with simulations of the rotational structure of the band origin of the $S_1 \leftarrow S_0$ transition. Additionally, many hot bands located near the band origin of this transition have been assigned.

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.

SPECTROSCOPY AND IONIZATION THRESHOLDS OF ISOELECTRONIC 1-PHENYLALLYL AND BENZYLALLENYL RESONANCE STABILIZED RADICALS

JOSHUA A. SEBREE, NATHAN KIDWELL, EVAN BUCHANAN, TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN 47907; MAREK ZGIERSKI, National Research Council Canada, Ottawa, ON.

In recent years it has been proposed that resonance-stabilized radicals (RSRs) may play an important role as intermediates in the formation of polycyclic aromatic hydrocarbons (PAHs). RSRs gain extra stability by delocalizing the unpaired electron through a neighboring conjugated $\pi$-system. Because of this extra stability, RSRs are able to build up in concentration, allowing for the creation of larger, more complex systems through their recombination with other RSRs. Mass-selective two-color resonant two-photon ionization spectra of two RSRs, phenylallyl and benzylallenyl radicals, have been recorded under jet-cooled conditions. These two radicals, while sharing the same radical conjugation, have unique properties. The phenylallyl and benzylallenyl radicals were respectively produced via discharge of trans-$\beta$-methylstyrene and benzylallene in argon prior to supersonic expansion. The $D_0-D_1$ origin of the phenylallyl radical was found at 19204 cm$^{-1}$ and was found to have a strong vertical ionization energy of 6.905(2) eV. By comparison, the benzylallenyl radical has an origin at 19703 cm$^{-1}$ and, while showing similar Franck-Condon activity to phenylallyl, has an IP curve indicative of a large geometry change between the ground state and the ion 7.50(2) eV. Visible-visible holeburning was used to show that each radical exists in one conformer form in the expansion. The CH stretch region of each radical was taken using $D_0$-Resonant Ion Dip Infrared Spectroscopy in a novel four laser experiment. A combination of this and DFT calculations was used to show that each radical exists in a trans geometry.
TE. ATMOSPHERIC SPECIES
TUESDAY, JUNE 21, 2011 – 8:30 am
Room: 2015 McPHERSON LAB

Chair: VINCENT BOUDON, CNRS - Universite de Bourgogne, Dijon, France

TE01  15 min  8:30
LINE PARAMETERS OF CARBON DIOXIDE IN THE 4850 CM$^{-1}$ REGION

D. CHRIS BENNER, V. MALATHY DEVI, EMILY NUGENT, Department of Physics, College of William and Mary, Williamsburg, VA 23187-8795; KEEYOUNG SUNG, LINDA R. BROWN, CHARLES E. MILLER, ROBERT A. TOTH, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109, U.S.A.

The spectral region near 4850 cm$^{-1}$ is used to monitor atmospheric carbon dioxide, but current accuracies of the line intensities and line shape coefficients do not permit carbon dioxide mixing ratios to be obtained to 1 ppm (about one part in 400). To improve the line parameters, we are remeasuring the prominent CO$_2$ bands in this region specifically to characterize the non-Voigt effects of line mixing and speed dependence at room temperature.

The laboratory spectra of air- and self-broadened CO$_2$ have been recorded at a variety of pressures, path lengths, mixing ratios and resolutions (0.005 to 0.01 cm$^{-1}$) with two different Fourier transform spectrometers (the McMath-Pierce FTS at Kitt Peak and a Bruker 125 HR FTS at JPL). The line parameters of some 2000 transitions are being derived by simultaneous multispectrum fitting using a few dozen spectra encompassing a 230 cm$^{-1}$ wide spectral interval. The rovibrational constants for line positions and the band intensities and Herman-Wallis coefficients are being retrieved directly from the spectra, rather than floating positions and intensities individually.

Self and foreign Lorentz widths and pressure shifts are being determined for the stronger bands while non-Voigt coefficients describing line mixing and speed dependence are being obtained for at least one of the strongest bands.

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TE02  15 min  8:47
TOWARDS AN ACCURATE INFRARED LINELIST FOR CO$_2$ AND ISOTOPOLOGUES

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Following the "Best Theory + High-resolution Experimental Data" strategy, we have completed an initial CO$_2$ infrared (IR) line list, denoted Ames-1. A procedure similar to the one used for ammonia$^a$ is adopted to generate a global potential energy surface (PES), including various small corrections such as scalar relativity, extrapolation to the one-particle basis-set limit, and a higher-order correlation correction, followed by refinement using accurate high-resolution laboratory data. We will discuss limitations in the use of HITRAN data for the refinement step. The current PES yields uncertainties of 0.01-0.02 cm$^{-1}$ for $J=0-117$ $^{12}$C$^{16}$O$_2$ energy levels up to 13,845 cm$^{-1}$ above the zero-point level. Comparisons between Ames-1, HITRAN, and CDSD will be presented for room temperature as well as selected higher temperatures. Results for $^{13}$C, $^{14}$C, $^{17}$O, and $^{18}$O isotopologues will be presented, and the accuracy for isotopologues will be discussed. Limitations of the current PES and the Ames-1 line list together with strategies to improve these will be discussed.

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SELF- AND AIR-BROADENING OF $^{12}$C$^{16}$O, $^{13}$C$^{16}$O AND $^{12}$C$^{18}$O AT 2.3 $\mu$m


High resolution (0.005 cm$^{-1}$) absorption spectra of CO and two of its isotopologues ($^{13}$CO and C$^{18}$O) were recorded between 3550 and 5250 cm$^{-1}$ using the Bruker IFS-125HR Fourier transform spectrometer (FTS) located at the Jet Propulsion Laboratory (JPL) and a specially designed and built coolable 20.38 cm long absorption cell$^b$ placed within the sample compartment of the FTS. More than 50 spectra of both pure and air-broadened samples of CO, $^{13}$CO and C$^{18}$O were recorded at various temperatures from 150 K to 298 K, with maximum total pressures up to ~700 Torr. A multispectrum nonlinear least squares spectrum fitting technique$^b$ was used to determine the spectral line shape parameters including speed dependence, Lorentz halfwidth coefficients, pressure-induced shift coefficients, and off-diagonal relaxation matrix element coefficients for line mixing. These line shape parameters were obtained for both self- and air-broadening, and temperature dependences of these parameters were determined where possible. As previously done in studies of CO$_2$,$^c$ rather than retrieving individual line positions and intensities, we constrained them to their theoretical relationships, including Herman-Wallis terms, determining only the band intensities and rovibrational constants. The results are discussed and compared with values reported in the literature.$^d$

4. 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.

MEASUREMENTS OF LINE POSITIONS AND INTENSITIES OF $^{14}$NH$_3$ IN THE 1.5 $\mu$m REGION

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In the atmosphere of outer planets, low mass brown dwarfs, and possibly extrasolar planets, ammonia (NH$_3$) is one of the major opacity sources particularly in the 1.5 $\mu$m region (the $H$-band). However, the spectroscopic information of NH$_3$ in the region is completely missing in the HITRAN database. NH$_3$ has four infrared active fundamental modes, with the well-known inversion doubling for $\nu_2$ band, in addition to the usual vibrational degeneracies. Its strong bands, $\nu_1$, $\nu_3$ and $2\nu_4$, dominate the spectrum at 3 $\mu$m, while their corresponding overtone and combination bands (e.g., $2\nu_1$, $2\nu_3$, $\nu_1+\nu_3$, $\nu_1+2\nu_4$ and $\nu_3+2\nu_4$) are prominent in the 1.5 $\mu$m region. As part of an effort to provide a complete set of NH$_3$ spectroscopic information in the 1.5 $\mu$m region, we are analyzing the laboratory spectra recorded at various temperatures (200 - 299 K) with the McMath-Pierce Fourier transform spectrometer (FTS) on Kitt Peak Observatory in Arizona. Line positions and strengths have been measured from the laboratory spectra, from which lower state energies and quantum assignments are being determined by adopting intensity ratios at two different temperatures and combination differences. A theoretical IR linelist$^a$ built upon the recent HSL-2 potential energy surface (nonadiabatic corrections included) is complementarily used for the quantum assignments. Preliminary results are presented for $\nu_1+\nu_3$, $2\nu_3$, $\nu_1+2\nu_4$ and $\nu_3+2\nu_4$ bands and compared with those from early work available.$^b$

2. Research described in this paper was performed at the Jet Propulsion Laboratory, California Institute of Technology and the Ames Research Center under contracts with National Aeronautics and Space Administration.
The 5-0 overtone band of HCl was recorded using intracavity laser absorption spectroscopy. The experimental conditions provided an effective pathlength of 23.6 km for the 1.81 m long intracavity compartment that contained the HCl gas. Most lines were recorded at 12-22 torr pressure: no noticeable pressure broadening or pressure shifts were observed in the spectra at the HCl pressures used in these experiments. Unblended lines could be determined to an accuracy of better than 0.005 cm$^{-1}$, with a precision of better than 0.002 cm$^{-1}$ as indicated by the fit. Data from the two isotopologues were fit separately and the molecular constants compare favorably with previous literature values.

Intermission

Frequency comb technology has the potential to dramatically improve precision and accuracy in measured spectra, but few applications have yet been reported. One application that can benefit from the high stability of spectrometers referenced to frequency combs is the measurement of spectral line shapes. We have built an absorption spectrometer based on an extended cavity diode laser locked to an Er-fiber-based frequency comb operating near 1550 nm. Here we report the first measurements of line shapes using a frequency comb as a reference. We studied the P(11) line in the ν$_1$ + ν$_3$ combination band of acetylene at 195 739.649 513(8) GHz at several temperatures from 296K down to 175K. This talk focuses on the data taken at 296K. We used a hard collision model (Rautian-Sobel'man) fit to the measurements to determine self- and nitrogen- pressure broadening, pressure shift and Dicke narrowing parameters that are at least 2 orders of magnitude more precise than those reported in previous measurements. We compare these hard collision model results with those of two other widely-used models: the Galatry (soft collision) and the Voigt function. The temperature- and rotational level- dependence of these parameters have been measured and some of the results will be discussed in a separate talk.

Acknowledgements: Acknowledgement is made to the Donors of the American Chemical Society Petroleum Research Fund for partial support of this research. CPM gratefully acknowledges support by DOE EPSCoR grant DOE-07ER46361 for work conducted at the University of Oklahoma. The measurements and analyses were performed under grants NNX09AJ93G and NNX08AO78G from the NASA Planetary and Atmospheres program.

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TE07 15 min 10:27

TEMPERATURE DEPENDENCE OF SELF- and NITROGEN-GAS LINE SHAPE PERTURBATIONS IN THE $\nu_1 + \nu_3$ BAND OF ACETYLENE

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The calibration of remote sensing measurements of the atmosphere of our own and other planetary bodies requires a knowledge of the temperature dependence of spectral line broadening caused by pressure dependent effects. We have extended the frequency comb-referenced measurements of line broadening in the $\nu_1 + \nu_3$ band of acetylene at 296 K, reported elsewhere at this symposium, to include low temperature pressure measurements at 175K, 200K and 240K. Additional data at still lower temperatures is currently being obtained. Line shape parameters for self- and nitrogen- broadening, narrowing and shifts have been determined at these temperatures on the assumption of the hard-collision model. This model was found to be the most appropriate in our earlier 296K data fitting. In addition to its intrinsic value, the temperature dependence of the derived parameters can give insight into the reliability of the physical assumptions of the model, and results of our analysis will be presented at the meeting.

Acknowledgements: Acknowledgement is made to the Donors of the American Chemical Society Petroleum Research Fund for partial support of this research. CPM gratefully acknowledges support by DOE EPSCoR grant DOE-07ER46361 for work conducted while at the University of Oklahoma. The measurements and analyses were performed under grants NNX09AJ93G and NNX08AO78G from the NASA Planetary and Atmospheres program.

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TE08 15 min 10:44

REVISION OF SPECTRAL PARAMETERS FOR THE B- AND $\gamma$-BANDS OF OXYGEN AND THEIR VALIDATION USING ATMOSPHERIC SPECTRA WITH THE SUN AS SOURCE

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Until recently the B ($b^1\Sigma_g^+ (v=1) \rightarrow X^3\Sigma_g^- (v=0)$) and $\gamma$ ($b^1\Sigma_g^+ (v=2) \rightarrow X^3\Sigma_g^- (v=0)$) bands of oxygen in the visible region had not been used extensively in satellite remote sensing. However, these bands (in particular the B-band) are now being considered for future satellite missions. In this light, it is important to make sure that the reference spectroscopic parameters are accurate enough to provide means of deducing important physical characteristics from the atmospheric spectra. The energy levels and intensities currently given for these bands in the HITRAN spectroscopic database a had not been updated for over two decades.

We have collected the best available measured line positions that involve the $b^1\Sigma_g^+$ ($v=1$ and $v=2$) states for the three most abundant isotopologues of oxygen and performed a combined fit to obtain a consistent set of spectroscopic constants. These constants were then used to calculate the line positions. A careful review of the available intensity and line-shape measurements was also carried out, and new parameters were derived based on that review. In particular, line shift parameters that were not previously available were introduced. The new data have been tested in application to high-resolution atmospheric spectra measured with the Fourier transform spectrometers at Park Falls, WI (B-band) and Kitt Peak, AZ ($\gamma$-band) and have yielded substantial improvement. In addition, we report the first direct observation and analysis of the $^{16}\text{O}^{18}\text{O}$ lines in the $\gamma$-band.

ROTATIONAL AND HYPERFINE ANALYSIS OF THE $a^1 \Delta_g \leftrightarrow X^3 \Sigma_g^-$ BAND OF $^{17}$O-CONTAINING ISOTOPOLOGUES OF OXYGEN MEASURED BY CRDS AT ROOM AND LIQUID NITROGEN TEMPERATURES

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The $a^1 \Delta_g \leftrightarrow X^3 \Sigma_g^-$ system of the $^{16}$O$^{17}$O, $^{17}$O$^{18}$O and $^{17}$O$_2$ isotopologues of oxygen was studied by high sensitivity CW-Cavity Ring Down Spectroscopy. The spectra of a $^{17}$O highly enriched sample were recorded at room temperature between 7640 and 7917 cm$^{-1}$ and at liquid nitrogen temperature in the 7876-7893 cm$^{-1}$ region. The magnetic dipole (0-0) band was observed for all three $^{17}$O-containing isotopologues. At liquid nitrogen temperature some of the transitions were observed with partially resolved hyperfine splitting due to the $^{17}$O nuclear spin, allowing determination of the hyperfine constants. The electric quadrupole (0-0) band and the (1-1) magnetic dipole hot band were also observed for the $^{16}$O$^{17}$O and $^{17}$O$_2$ species. The rotational and hyperfine spectroscopic parameters of the $X^3 \Sigma_g^-$ and $a^1 \Delta_g$ states of the three studied isotopologues were derived from global fit of the measured line positions and microwave and Raman measurements available in the literature. The rotational constants of the $a^1 \Delta_g$ (v=0, 1) states of $^{17}$O$_2$ are determined for the first time.

A GLOBAL FIT OF THE $X^3 \Sigma_g^-$, $a^1 \Delta_g$, $b^1 \Sigma_g^+$ AND $B^3 \Sigma_u^-$ STATES OF THE SIX ISOTOPOLOGUES OF OXYGEN

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A global fit of the six isotopologues of the O$_2$ molecule has been carried out, with the purpose to support the current and future Earth remote sensing missions. All previously available experimental data from the following systems were collected and used in the analysis: the microwave transitions in the $X^3 \Sigma_g^-$ and $a^1 \Delta_g$ states, the infrared transitions from the $a^1 \Delta_g \rightarrow X^3 \Sigma_g^-$, $b^1 \Sigma_g^+ \rightarrow X^3 \Sigma_g^-$, and $b^1 \Sigma_g^+ \rightarrow a^1 \Delta_g$ systems, the UV transitions from the $B^3 \Sigma_u^- \rightarrow X^3 \Sigma_g^-$ Schumann-Runge system. For the main $^{16}$O$_2$ isotopologue, experimental data are available for the following vibrational states: $v = 0 - 18$ for $X^3 \Sigma_g^-$, $v = 0 - 1$ for $a^1 \Delta_g$, $v = 0 - 17$ for $b^1 \Sigma_g^+$, $v = 0 - 17$ for $B^3 \Sigma_u^-$. A band by band fit was first carried out for these $^{16}$O$_2$ data to check bad measurements, misassignments and calibration problems. Then all these $^{16}$O$_2$ data were fitted with a Dunham-type model. It was found that most $^{16}$O$_2$ data (98%) could be fitted within 3 times experimental accuracies in the band by band fit; the $X^3 \Sigma_g^-$, $a^1 \Delta_g$, $b^1 \Sigma_g^+$ states could be well reproduced with the Dunham-type model; but the vibrational energies for $v = 0 - 17$ of $B^3 \Sigma_u^-$ could not be fitted well with the Dunham-type mode, probably caused by the known perturbations in this state. A band by band fit has been performed for each of the other five minor isotopologues, and a Dunham-type fit is in progress for these data. Eventually data from all the six isotopologues will be simultaneously fitted with a multi-isotopologue Dunham model. We will present the most recent fitting results to date.
NEW HIGH RESOLUTION OZONE ABSORPTION CROSS SECTIONS

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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 different temperatures. The work is inspired by the more than two decades (1995 - 2020) of the global ozone observations, which are planned to be carried out using current and future atmospheric chemistry instruments (GOME, GOME-2, SCIAMACHY, SAGE II, etc).

New laboratory measurements provide ozone cross-section in the spectral range 230-1000 nm at a spectral resolution of 0.02 nm 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 absolute calibration of relative spectra.

We provide analysis and comparison of the previously available ozone cross-sections databases versus our new dataset and report on the impact of the new data on the ozone retrievals.

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. Release of the new dataset is planned for the summer 2011.

LINE MIXING IN ATMOSPHERIC OZONE

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The modeling of the ozone spectrum and the measurement of relevant spectral line parameters is of significant interest for atmospheric spectroscopy. While line width and shift measurements are easily done at lower pressures, the phenomenon of line mixing can only be observed at atmospheric pressures. We model line mixing parameters as defined by the Rosenkranz method in the 160-270 GHz region using microwave ring-down spectra. These parameters, the challenge of measuring them, and the importance of using a global fit to exclude systematic error will be discussed.
GISBERT WINNEWISER: AN APPRECIATION

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The death of Gisbert Winnewisser in March of this year has robbed us of a peerless spectroscopist and molecular astronomer who made many significant contributions to both subjects. Moreover, Gisbert was a friend and mentor to many of us, who enriched our lives immeasurably. In this brief appreciation, I will discuss some of his many accomplishments.

SCRUTINY OF THE CORE OF THE GALACTIC CENTER BY H$_3^+$ AND CO: GCIRS 3 AND GCIRS 1W

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Out of the over two dozen sightlines toward the Central Molecular Zone of the Galactic center so far observed by infrared spectra of H$_3^+$ and CO, sightlines toward GCIRS 3 and Iota stand out as exceptional since they show cloud components with clear $R(2,2)^J$ absorption indicating that their unstable $(J, K) = (2,2)$ levels are well populated. Those two sightlines toward the Galactic center and Sgr B, respectively, must pass through hot and dense gas. The cloud component at $\sim 60$ km s$^{-1}$ toward GCIRS 3 is particularly intriguing since GCIRS 1W, which is separated from it only by 5":8 (0.23 pc if the same distance to the Galactic center of 8 kpc is assumed), barely shows the $R(2,2)^J$ absorption. The cloud must be compact and this calls for a high ionization rate.

To further study this problem the sightlines toward GCIRS 3 and GCIRS 1W have been observed by VLT under high spectral resolution. The observed $R(3,3)^J$ absorption is extraordinarily deep and the $R(2,2)^J$ absorption is clearly observable at $\sim 60$ km s$^{-1}$ for GCIRS 3 indicating unusually high temperature and high density of the cloud. In contrast, toward GCIRS 1W, the $R(3,3)^J$ absorption is of ordinary depth and the $R(2,2)^J$ absorptions is marginal if any indicating the well known warm and diffuse gas observed toward other regions of the Central Molecular Zone. Their analysis and comparison with radio HCN emission observed in the area will be discussed.


INVESTIGATING THE COSMIC-RAY IONIZATION RATE IN THE GALACTIC ISM WITH H$_3^+$ OBSERVATIONS

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Observations of H$_3^+$ in the Galactic diffuse interstellar medium (ISM) have led to various surprising results, including the conclusion that the cosmic-ray ionization rate ($\zeta$) is variable by over 1 order of magnitude between different diffuse cloud sight lines, with values as high as $8 \times 10^{-16}$ s$^{-1}$, and 3$\sigma$ upper limits as low as $0.7 \times 10^{-16}$ s$^{-1}$. This variation is interesting, as it contradicts the typical assumption that the cosmic-ray spectrum is relatively uniform throughout the Galaxy. Instead, the flux of low-energy cosmic rays responsible for ionizing H$_2$ must be decreased in some regions due to particle propagations effects, and increased in other regions by local acceleration sites. Whether or not acceleration in and propagation from supernova remnants (thought to be the primary accelerators of Galactic cosmic rays) alone can account for such variability remains unknown.

At present, the survey of H$_3^+$ in diffuse clouds consists of observations toward 52 sight lines, with detections in 20 of those. In an attempt to understand variations in the inferred ionization rates, I have studied the environments through which all of these sight lines pass. I have also observed H$_3^+$ in 6 sight lines that probe gas in close proximity to the supernova remnant IC 443. Ionization rates inferred in 2 of these sight lines are about $20 \times 10^{-16}$ s$^{-1}$, indicating a high flux of low-energy particles, but the other 4 sight lines do not show absorption from H$_3^+$, so the high ionization rate and particle flux seems very localized. Combining these results near a supernova remnant to those in the general ISM further enhances the variability seen in the cosmic-ray ionization rate, and requires that the concept of a uniform cosmic-ray spectrum be reviewed.

CAVITY RING DOWN SPECTROSCOPY OF MOLECULAR IONS IN THE 3 $\mu$m REGION

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Ionic complexes may be thought of as intermediates whose potential energy surfaces will provide information on the reaction dynamics of molecule-ion reactions in space. Because ionic complexes possess significantly higher binding energies than their van der Waals analogues, they may survive the intense radiation conditions in space. Candidate complexes include (CO-CO)$^+$, H$_2$-HCO$^+$, H$_2$-HN$_2^+$, H$_2$O-H$_2$O$^+$, N$_2$-N$_2^+$, N$_2$-H$^+$-N$_2$.

An experiment is described in which ionic complexes are created in a continuous plasma jet emanating from a slit-nozzle and characterized with a quadrupole mass spectrometer. Cavity ring down spectroscopy is used to map the potential energy surfaces and to determine molecular parameters. A cw optical parametric oscillator, operating in the 3 $\mu$m region is used as a light source.

Presently, experiments are prepared to record fully resolved spectra of ionic complexes of astrophysical relevance, with a focus on species that may be considered reactive intermediates in ion-molecule reactions in space.
SUBMILLIMETER-WAVE ROTATIONAL SPECTROSCOPY OF H$_2$F$^+$

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Five pure rotational transitions of H$_2$F$^+$ were observed in the 473-774 GHz range with a backward-wave oscillator based submillimeter-wave spectrometer$^a$. The H$_2$F$^+$ ion was generated in an extended negative glow discharge in a gas mixture of hydrogen fluoride generated by heating potassium hydrogen fluoride (HF$_2$K) granular powder at 150°C-160°C and hydrogen in an argon buffer. A simultaneous analysis of the rotational lines with 120 combination differences for the ground state derived from the infrared spectra obtained by Schäfer and Saykally$^b$ and Fujimori et al.$^c$ was carried out to determine the precise molecular constants for the ground state. The rotational transition frequencies that lie below 2 THz were calculated, together with their estimated uncertainties, to facilitate future astronomical identifications. Recently H$_2$Cl$^+$ was detected in NGC 6334I and Sgr B2 with the Heterodyne Instrument for Far-Infrared (HIFI) on board the Herschel Space Observatory$^d$, and HF was also detected in a wide variety of interstellar clouds with the same facility$^e$. The proton affinity of HF is smaller than those of N$_2$ and CO, so the abundance of H$_2$F$^+$ is likely to be low in dense molecular clouds. We will discuss abundances of H$_2$F$^+$ in diffuse molecular clouds, considering various chemical reaction rates.

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DETECTION OF FeCN (X$^4\Delta_i$) IN THE CIRCUMSTELLAR ENVELOPE OF IRC+10216

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A new interstellar molecule, FeCN (X$^4\Delta_i$), has been detected in the envelope of the carbon-rich AGB star, IRC+10216. This work is the first definitive detection of an iron-bearing molecule in the interstellar medium, and is based on newly-measured rest frequencies. Eight successive rotational transitions of this linear free radical in the lowest spin ladder, $\Omega = 7/2$, were observed at 2 and 3 mm using the Arizona Radio Observatory (ARO) 12 m telescope. Three transitions appear as single, unblended features at the 1-2 mK level and exhibit characteristic IRC+10216 line profiles; one had previously been observed with the IRAM 30 m telescope. Two other transitions are partially blended, but exhibit distinct emission at the FeCN frequencies. The remaining transitions are either completely contaminated, or are too high in energy. Comparison of the ARO and IRAM data suggests a source size for FeCN in IRC+10216 of 30\arcsec, indicating an outer shell distribution, as expected for a free radical. The column density derived for FeCN in this object is N$_{tot} = 4.0 \times 10^{11}$ cm$^{-2}$ with a rotational temperature of T$_{rot} = 21$ K The fractional abundance of this molecule is [FeCN]/[H$_2$] = 3x10$^{-10}$, comparable to that of AlNC and KCN in the outer envelope. FeCN is likely formed by gas-phase reactions of Fe$^+$ or neutral iron, which has a significant gas-phase abundance in the outer shell. The detection of FeCN is further evidence that, aside from silicon, metal cyanides/isocyanides dominate the chemistry of refractory elements in IRC+10216.
THE QUEST FOR COMPLEX MOLECULES IN SPACE. SEARCHES FOR CYANIDES RELATED TO n-PROPYL CYANIDE IN SGR B2(N)

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A molecular line survey was carried out with the IRAM 30 m telescope toward the prolific hot core Sgr B2(N) in order to explore its molecular complexity. The entire 3 mm range as well as selected regions at 2 and 1.3 mm were covered. Notable results include the detections of aminoacetonitrile, ethyl formate, n-propyl cyanide, and the singly substituted $^{13}$C isotopologs of vinyl cyanide.

There exists a branched isomer of n-propyl cyanide: iso-propyl cyanide. A search for this isomer in our line survey required a laboratory spectroscopic investigation beforehand. Even though promising emission features have been found for this as well as other, related molecules, there are rather few uncontaminated lines. Overlap by other emission or some absorption features occurs frequently, and uncertainties about the position of the baseline also contribute to considering detections to be inconclusive. Nevertheless, the determination of upper limits or abundances among isomers and related molecules will help to constrain astrochemical pathways.

We will present our results and discuss promising strategies to search for complex molecules in space.

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WHAT MOLECULAR LINES CAN TELL ABOUT EARLY STAGES OF MASSIVE STARS

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Here we present our molecular line investigation of the southern infrared dark clouds (IRDCs). We performed observations of 13 molecular species using the 22-m Mopra radio telescope. In our survey we included in general species which are good tracers of cold and dense gas. Some of them trace the more quiescent gas (e.g. HNC, $N_2H^+$), while others are sensitive to more dynamical processes (HCN, HCO$^+$). We detect SiO emission in some clouds and complicated shapes of the HCO$^+$ emission line profile in all IRDCs, which indicates infall and outflow motions and the beginning of star formation activity, at least in some parts of the IRDCs. Using H$_2$ column densities from our previous investigation, we estimated molecular abundances for all species. We uncovered a tendency for IRDCs to have molecular abundances similar to those in low-mass pre-stellar cores. This similarity may indicate similar chemical composition at the earliest stages of low- and high-mass stars and their close evolutionary status. However, for the $N_2H^+$ and HCO$^+$ species, there is a tendency for higher mean abundances in IRDCs compared with low- mass cores. To find a reason of such behavior, we use chemical models including gas-phase reactions and accretion and desorption onto/from grains. Chemical modeling allows us to study chemical evolution at the early stages of massive stars in more detail and reconstruct the physical conditions and evolutionary status of IRDCs.
In diffuse molecular clouds (environments with high molecular fraction, but low CO abundance), the relative populations of the $J=0$ (para) and $J=1$ (ortho) rotational levels of H$_2$ are often used as a measure of the cloud kinetic temperature, $T_{01}$. Typically, $T_{01}$ is on the order of 50-70 K, but in similar environments, the excitation temperature $T(H_3^+)$ derived from the $(J, K)=(1,0)$ (ortho) and $(1,1)$ (para) rotational levels of H$_3^+$ is 20-40 K. We have extended the number of sight lines in which both $T_{01}$ and $T(H_3^+)$ have been measured from two to five, and in four of the five cases, the two temperatures are discrepant in the same cloud. Using a steady state chemical model based on rate coefficients calculated with a microcanonical statistical approach, we find that the discrepancy between $T_{01}$ and $T(H_3^+)$ likely arises from incomplete thermalization caused by competition between the thermalization reaction H$_3^+ +$H$_2$ $\rightarrow$ H$_2$ + H$_3^+$ and dissociative recombination of H$_3^+$ with electrons.

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There are galactic nuclei that emit high luminosities $L$ $\sim$ 10$^{44}$−$^{46}$ erg s$^{-1}$ including luminosity produced by X-rays from high mass accretion onto the central black holes. These nuclei are called active galactic nuclei (AGNs), and they are accompanied by molecular disks. Observations show high abundances of CN and HCN in the disks; the molecules are proposed to be probes of X-ray dominated regions (XDRs) created by the X-rays from AGNs. We have constructed a spatially-dependent chemical-abundance model of the molecular disk in NGC 1068, a typical AGN-dominated galaxy. Recently, new observations of CN and HCN have been made at much higher spatial resolution, and there are also detections of polyatomic molecules such as HCN, c-C$_2$H$_2$, and C$_2$H. We discuss how these observations and our simulations can help us to better understand the physical conditions, the disk structure, and conditions for star formation within molecular disks, which are still uncertain. We also include a comparison with other types of galaxies such as (ultra-) luminous infrared galaxies.

*b Initial results were presented at the International Symposium on Molecular Spectroscopy 2010, RF05
A STUDY OF HCO\(^+\) AND CS IN PLANETARY NEBULAE

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Millimeter-wave observations have been conducted towards a sample of planetary nebulae (PNe) using the 12-meter and Sub-millimeter telescopes of the Arizona Radio Observatory. HCO\(^+\) was observed in the J=3-2 transition at 1 mm and the J=1-0 transition at 3 mm. CS was observed in the J=5-4, J=3-2, and J=2-1 transitions at 1, 2, and 3 mm, respectively. Both molecules have been detected in NGC 6537 (Red Spider Nebula), K4-47, and M2-48, as well as NGC 6720 (Ring Nebula) and NGC 6853 (Dumbbell Nebula), which are both over 7,000 years old. Although a number of molecular line surveys of circumstellar envelopes have been done and one conducted towards a very young PNe, the molecular content of planetary nebulae is not well characterized. It was previously thought that the high ultraviolet radiation field of the central star would destroy any molecules leftover from the circumstellar envelope; however, molecules clearly exist well into the PNe stage. These data are currently being analyzed and molecular abundances being determined, which will be compared to those seen in diffuse interstellar material. The implications of these observations will be discussed in relation to the molecular content of diffuse clouds and the origins of the diffuse interstellar bands.

THE ARO 1 mm SURVEY OF THE OXYGEN-RICH ENVELOPE OF SUPERGIANT STAR NML CYGNUS

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Although a number of molecular line surveys of carbon-rich circumstellar envelopes (CSE) have been performed, only one oxygen-rich CSE, that of VY Canis Majoris (VY CMa), has been studied in depth. The Arizona Radio Observatory (ARO) 1 mm survey of VY CMa showed a very different and interesting chemistry dominated by sulfur- and silicon-bearing compounds as well as a number of more exotic species. A similar survey of the oxygen rich star NML Cygnus (NML Cyg) from 215 to 285 GHz is currently under way using the ARO Sub-millimeter Telescope. Initial observations show that this circumstellar envelope appears to be as chemically rich as that of VY CMa. Molecules including \(^{12}\)CO, \(^{13}\)CO, \(^{12}\)CN, \(^{13}\)CN, HCN, HCO\(^+\), CS, SO\(_2\), SiO and \(^{30}\)SiO have been observed in NML Cyg. Line profiles of this source also suggest that there may be multiple outflows and that the circumstellar envelope is not spherically symmetric. Current results will be presented.

WATER COLLISIONS WITH NORMAL AND PARAHYDROGEN

BRIAN J. DROUIN, JOHN C. PEARSON, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099; LAURENT WIESENFELD, ALEXANDRE FAURE, UJF-Grenoble 1/CNRS, Institut de Planétologie et d’Astrophysique de Grenoble (IPAG) UMR 5274, Grenoble, F-38041, France.

Previous pressure broadening results for the normal hydrogen/water system displayed a dramatic reduction in the broadening at low temperature. Theoretical predictions, the basis for which are calculated collisional excitation rates, indicated stronger excitation, with a steady increase in the broadening as the temperature drops. Due to this disagreement, concerns were raised about the stability of the the ortho/para hydrogen ratio (OPR) in the apparatus\(^1\). The development of a modified injector, as well as improved optics and a parahydrogen generator, have enabled these concerns to be thoroughly investigated for the 556 GHz transition of water. The modified injector has been shown to eliminate the bias between gas and cell temperature. The improved optics allow much better signal-to-noise ratios with smaller amounts of water. Furthermore, a reduction of water injected into the system was found to be critical to stabilize the OPR, which was verified to be dependent upon several system variables. Preparation of parahydrogen in an exterior vessel was useful for testing the OPR stability and full data sets of both parahydrogen and normal hydrogen water broadening at 556 GHz have been collected. The newest results show good qualitative agreement with theory, with the dramatic decreases of broadening at low temperature no longer evident. Other water transitions near 1 THz are also under investigation. We will discuss the new experimental procedures, the experimental results and compare with recent theoretical work.

LOW TEMPERATURE LINESHAPE OF HYDROGEN DEUTERIDE

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

Hydrogen deuteride, HD, is the simplest and most abundant deuterium-bearing molecule in the universe. It has been detected in numerous astronomical sources, and is a primary target of SOFIA. Imaging instruments utilize relatively broad frequency windows to detect the faint FIR emission or absorption of this molecule, but high spectral resolution instruments such as GREAT will resolve the velocity structure of HD in the ISM as well as expose pressure-broadened profiles in planetary atmospheres. The only previous Doppler resolved FIR work on HD was done with a TuFIR spectrometer¹ utilizing a room temperature sample at relatively high pressure. The development of a 2.5-2.7 THz multiplier chain at JPL has enabled us to examine the lineshape of J = 1 ← 0 HD in detail under extreme environmental conditions in a cryogenically cooled absorption chamber. The low temperatures achieved, near 18 K, allow a maximal absorption coefficient for this very weak dipole, and therefore low pressures can be investigated with high fidelity. At the lowest pressures the linewidth is directly determined by Doppler broadening. However, increased pressures of HD or parahydrogen initially cause motional narrowing, allowing sub-Doppler line measurements. At modestly higher pressures the pressure broadening profile dominates. A significant lineshift is observed at elevated pressures of HD, and the best center frequency is thus determined from a linear regression of the pressure dependence of this quantity. The rest frequency of 2674986.094(25) MHz determined is nearly an order of magnitude more accurate than the previous measurement¹ of 2674986.66(15) MHz, and within one standard deviation of a purely ab initio² value, 2674986.134(240) MHz.


A QUANTUM CHEMICAL INVESTIGATION OF THE STABILITY AND CHEMISTRY OF THE ANIONS OF CO AND H₂CO IN ASTROPHYSICAL ICES

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

Electrons may either be deposited on interstellar icy grain mantles from the gas phase, or they may be produced in situ via photoionization. It is energetically favorable for electrons to bind to species in the ice to form anions. Similarly, anions may be formed within icy grain mantles from chemical processes such as proton transfer from an acid to a base. To understand the fate of electrons in astrophysical ices and the potential impact of anions on gas-grain chemistry, we explored the behavior of two common and important interstellar molecules – CO and formaldehyde (H₂CO) – when they interact with an electron in ice. Neither CO nor H₂CO bind an electron in the gas phase. In astrophysical ices, however, quantum chemical calculations indicate that the anions of CO and H₂CO are stabilized by interacting with the polarized field provided by water ice and are bound with respect to CO and H₂CO. We then investigated whether CO⁻ and H₂CO⁻ are stable with respect to subsequent chemical reactions and sought to identify vibrational spectroscopic features that might be useful for experimentalists to identify these anions in the laboratory. In our theoretical investigations reported here, we studied CO⁻ + nH₂O and H₂CO⁻ + mH₂O in clusters containing from 2 to 17 water molecules using B3LYP/6-31+G** and MP2/6-31+G** calculations. The calculations show that in smaller water clusters, both CO⁻ and H₂CO⁻ are stabilized by water molecules. However, in larger clusters, both anions can undergo barrierless reactions in which a proton is transferred from a nearby water molecule, forming radicals such as HCO or H₂COH and hydroxide anion (OH⁻). Since HCO and H₂COH are precursors to H₂CO and CH₃OH, electron-induced anion chemistry in ices may contribute to the observed abundances of important astromolecules. In addition to the structures and energetics of these clusters, we will also provide theoretical predictions of spectroscopic features that might be detected in the laboratory or interstellar medium.
Using 12 newly found bright dust-embedded stars distributed from 140 pc West to 120 pc East of Sgr A*, we have observed spectra of $\text{H}_3^+$ and CO in the Central Molecular Zone of the Galactic center. Sightlines toward the 12 stars have been observed at the Gemini South Observatory on Cerro Pachon, Chile, and those for 2 of the stars at the Subaru Telescope on Mauna Kea Hawaii. This has extended our previous longitudinal coverage by a factor of 7. Although complete coverage of various transitions have yet to be made for some stars, almost all sightlines showed high total column densities of $\text{H}_3^+$ and highly populated $(J, K) = (3, 3)$ metastable level, demonstrating the prevalence of the warm and diffuse gas previously observed from the center to 30 pc East and high ionization rate in the environment. A few sightlines did not show strong $\text{H}_3^+$ absorptions. It remains to be seen whether this is due to the radial and transverse location of the stars or lack of $\text{H}_3^+$.

While the velocity profiles of $\text{H}_3^+$ toward stars from the center to 30 pc East are similar apart from subtle variations, the velocity profiles of the wider regions vary greatly. A remarkable similarity has been noted between the velocity profile of $\text{H}_3^+$ toward a star nicknamed Iota and those of $\text{H}_2\text{O}^+$ and $^{13}\text{CH}^+$ observed toward Sgr B2 by the HIFI instrument of the Herschel Space Observatory. Although all these ions exist in diffuse environment, this is surprising since $\text{H}_3^+$ favors environments with high $\text{H}_2$ fraction $f(\text{H}_2)$ while $\text{H}_2\text{O}^+$ and $\text{CH}^+$ favors low $f(\text{H}_2)$. Also the peak of Sgr B2 and Iota are separated by 17 pc. Possible interpretations of this will be discussed.
TG01 15 min 1:30
FREQUENCY AND TIME DOMAIN STUDIES OF TOLUENE

ADRIAN M. GARDNER, ALISTAIR M. GREEN, JULIA A. DAVIS, KATHARINE L. REID and TIMOTHY G. WRIGHT, School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom.

Nanosecond zero kinetic energy (ZEKE) and picosecond slow electron velocity map imaging (SEVI) photoelectron spectroscopic techniques have been employed in order to investigate the vibrational levels in the ground electronic state of the toluene cation. Vibrationally-resolved photoelectron spectra have been obtained following the preparation of a range of vibrational intermediate levels in the $S_1$ electronic state. Evidence for intramolecular vibrational energy redistribution (IVR) has been observed at low $S_1$ vibrational energies.

TG02 15 min 1:47
HYDROGEN-BOUND COMPLEXES OF TROPOLONE: GATEWAYS FOR THE INTERROGATION OF MULTIPLE PROTON-TRANSFER EVENTS

DEACON J. NEMCHICK, KATHRYN CHEW, JOHN E. WOLFF, and PATRICK H. VACCARO, Department of Chemistry, Yale University, P.O. Box 208017, New Haven, CT 06520-8107 USA.

Tropolone (TrOH) serves as a model system for the study of coherent proton-transfer processes, where a potential barrier of finite height hinders the symmetric exchange of a lone hydron between hydroxylic (proton-donating) and ketonic (proton-accepting) oxygen centers. This talk will discuss ongoing efforts to build upon the known structural and dynamical properties of tropolone so as to explore related multiple proton-transfer events that are mediated by successive formation and breaking of several hydrogen bonds. Of particular interest are weakly-bound complexes created in situ under "cold" molecular-beam conditions by docking amphoteric ligands (e.g., HF and HCOOH) into the reaction cleft of the TrOH substrate. Such species have the tantalizing possibility of undergoing double proton transfer, with resulting tunneling-induced bifurcation of rovibronic features reflecting the intrinsic vibrational and/or electronic specificity of the attendant unimolecular transformation. Spectroscopic studies of several hydrogen-bound TrOH complexes through use of the richly structured $\tilde{A}^1B_2 \rightarrow \tilde{X}^1A_1(\pi^* \leftarrow \pi)$ absorption system will be presented, with complementary quantum-chemical calculations serving to guide the assignment and interpretation of observed spectral patterns.

TG03 15 min 2:04

**ROTATION-TUNNELING ANALYSIS OF EXCITED-STATE PROTON TRANSFER IN DEUTERATED TROPOLONE**

**KATHRYN CHEW, DEACON J. NEMCHICK, JOHN E. WOLFF, and PATRICK H. VACCARO, Department of Chemistry, Yale University, P. O. Box 208107, New Haven, CT 06520-8107 USA.**

The origin band of the $\tilde{A}^1B_2 - \tilde{X}^1A_1 (\pi^* \rightarrow \pi)$ absorption system in monodeuterated tropolone (TrOD) has been probed with rotational resolution by applying polarization-resolved degenerate four-wave mixing (DFWM) spectroscopy under ambient, bulk-gas conditions. Judicious selection of polarization geometries for incident and detected electromagnetic waves alleviated intrinsic spectral congestion and facilitated dissection of overlapping transitions, thereby enabling refined rotational-tunneling parameters to be extracted for the $\tilde{A}^1B_2 (\pi^* \pi)$ manifold. A pronounced 2.14(5) cm$^{-1}$ bifurcation of rovibronic features is measured for the zero-point level of electronically excited TrOD, reflecting the presence of a substantial potential barrier along the O-$\cdot$D$\cdot$O $\leftrightarrow$ O$\cdot$D$\cdot$O reaction coordinate and representing nearly a ten-fold decrease in magnitude over the analogous tunneling-induced splitting for the parent (TrOH) isotopolog. The dependence of hydron-migration dynamics on internal degrees of freedom will be discussed in light of donor-acceptor displacements incurred by $\pi^* \rightarrow \pi$ electron promotion and structural effects accompanying selective isotopic modification of the tropolone molecular framework.

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TG04 15 min 2:21

**LASER SPECTROSCOPIC STUDY ON STRUCTURES OF 3n-CROWN-n (n = 4, 5, 6) COMPLEXES WITH PHENOL**

**RYOJI KUSAKA and TAKAYUKI EBATA, Department of Chemistry, Graduate School of Science, Hiroshima University, Higashi-Hiroshima, 739-8526, Japan.**

Structures of 3n-crown-n (n = 4, 5, 6) complexes with phenol in supersonic jets have been studied by laser induced fluorescence (LIF), UV-UV hole-burning (UV-UV HB), and IR-UV double resonance (IR-UV DR) spectroscopy. The size-dependence of the structures and the interaction working between the crowns and phenol will be discussed based on the analysis of the electronic transitions and IR spectra in the region of the OH and CH stretching vibrations with the aid of DFT (M05-2X/6-31+G*) calculation.

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TG05 15 min 2:38

**HIGH RESOLUTION STARK SPECTROSCOPY OF MODEL DONOR-ACCEPTOR AMINOBENZONITRILES IN THE GAS PHASE.$^a$**

**ADAM J. FLEISHER, CASEY L. CLEMENTS, RYAN G. BIRD, DAVID W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260; LEONARDO ALVAREZ-VALTIERRA, División de Ciencias e Ingenierías, Universidad de Guanajuato, Campus León, León, Gto. 37150, Mexico.**

Electronic communication between donor-acceptor systems is prevalent in many chemical processes. Unfortunately, an accurate description of the changes in molecular geometry responsible for intramolecular charge transfer (ICT) is difficult to ascertain. Reported here are the $S_0$, $L_a$, and $L_b$ electronic state structures and dipole moments of two model ICT systems, 4-(1H-pyrrol-1-yl)benzonitrile (PBN) and 4-(1-pyrrolidinyl)benzonitrile (PDBN), as measured by rotationally resolved electronic spectroscopy. As was observed for phenylpyrrole,$^a$ the unsaturated rings of PBN become collectively more planar following excitation with UV light, in support of the planar ICT model. However, in PDBN the twist/inversion angle between rings is nearly zero in both the ground and excited electronic states. The unperturbed dipole moments measured here, taken in conjunction with available solvatochromism data, provide an estimate for the polarization, dispersion, and charge transfer contributions to solvent-mediated excited state stabilization.

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**TG06** 15 min 2:55

ROTATIONALLY RESOLVED ELECTRONIC SPECTROSCOPY OF BIOMOLECULES IN THE GAS PHASE. MELATONIN.

JOHN T. YI, and DAVID W. PRATT, University of Pittsburgh, Department of Chemistry, Pittsburgh, PA 15260, USA; CHRISTIAN BRAND, MIRIAM WOLLENHAUPT, and MICHAEL SCHMITT, Heinrich-Heine-Universität, Institut für Physikalische Chemie I, 40225 Düsseldorf, Germany; W. LEO MEERTS, Radboud University Nijmegen, Institute for Molecules and Materials, Heyendaalseweg 135, NL-6525 AJ Nijmegen, The Netherlands.

Rotationally resolved electronic spectra of the A and B bands of melatonin have been analyzed using an evolutionary strategy approach. From a comparison of the ab initio calculated structures of energy selected conformers to the experimental rotational constants, the A band could be shown to be due to a gauche structure of the side chain, while the B band is an anti structure. Both bands show a complicated pattern due to a splitting from the three-fold internal rotation of the methyl rotor in the N-acetyl group of the molecules. From a torsional analysis we additionally were able to determine the barriers of the methyl torsion in both electronic states. The electronic nature of the lowest excited singlet state could be determined to be $^1L_b$ (as in the chromophore indole) from comparison to the results of ab initio calculations.

**TG07** 15 min 3:12

VIBRONIC SPECTROSCOPY OF JET-COOLED 1,4-PHENYLENE DIISOCYANIDE

DEEPAI N. MEHTA, ANNA K. GUTBERLET, and TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN 47907.

This talk will present results of a gas phase, jet-cooled vibronic spectroscopy study of 1,4-PDI. A fluorescence excitation spectrum spanning the range 35,500-44,100 cm$^{-1}$ (226.5-281.5 nm) has been recorded, as well as a resonant two photon ionization excitation and UV hole-burning spectrum, in the region of 35,500-36,500 cm$^{-1}$. The $S_0$-$S_1$ origin is a weak band located at 35,566 cm$^{-1}$. The spectrum in the $S_1$ region is dominated by vibronic coupling to the $S_2$ state. Dispersed fluorescence spectra will be presented that uncover and characterize the vibronic coupling. We have also located the $S_0$-$S_2$ origin 5687 cm$^{-1}$ above the $S_0$-$S_1$ origin. Evidence will be presented for the coupling of the $S_2$ levels with nearby $S_1$ levels and for internal conversion from $S_2$ to $S_1$ on the timescale of the fluorescence.

**Intermission**

**TG08** 15 min 3:45

EXCITED STATE DYNAMICS OF 7-AZAINDOLE HOMODIMER IN FROZEN NITROGEN MATRIX

MOITRAYEE MUKHERJEE, BIMAN BANDYOPADHYAY, SHEETAMA KARMAKAR and TAPAS CHAKRABORTY, Physical Chemistry Department, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India.

In a fluid medium (liquid or gas), the doubly hydrogen bonded dimer of 7-azaindole (7AI) undergoes tautomerization via simultaneous exchange of two H-atoms/protons between the two moieties upon UV excitation to lowest excited singlet state. The excited dimer emits exclusively visible fluorescence from tautomeric configuration, and no UV fluorescence is detected from the locally excited state. We show here for the first time that this generic excited state dynamics of 7AI dimer is totally altered if the species is synthesized and confined in frozen nitrogen at 8 K. The dimer has been found to emit only from the locally excited state, and the photophysical channel leading to excited state tautomerization is completely blocked. The formation of the centrosymmetric dimer in nitrogen matrix is ensured by recording the FTIR spectrum of the dimer before initiating the photophysical measurements. The details of our findings and interpretation of the measured data will be presented in the talk.
EXCITED STATE PERTURBATIONS OF 7-AZAINDOLE MEDIATED THROUGH MICRO-SOLVATION.\textsuperscript{a}

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

7-azaindole readily forms water clusters when seeded into a molecular beam. Interestingly, the addition of water considerably perturbs the excited state of 7-azaindole: the electronic origin of 7-azaindole(H\textsubscript{2}O) is shifted drastically to lower energy, 1290 cm\textsuperscript{-1}, relative to the origin of the bare molecule; furthermore, recent evidence indicates that 7-azaindole(H\textsubscript{2}O) is of \textit{L\textsubscript{a}} character, contrary to the bare molecule.\textsuperscript{b} In this work, high resolution electronic spectra of 7-azaindole(H\textsubscript{2}O) were measured in the presence of an external electric field, as a means to study water induced changes in the electronic distribution of 7-azaindole. Furthermore, the \textit{L\textsubscript{a}}/\textit{L\textsubscript{b}} character of the excited state of 7-azaindole(H\textsubscript{2}O) was examined by recording similar spectra of isotopically labeled species.

\textsuperscript{a}Work supported by NSF(CHE-0911117)

CHIROPTICAL SPECTROSCOPY IN THE VAPOR PHASE

PRIYANKA LAHIRI, BENJAMIN D. LONG, KENNETH B. WIBERG, and PATRICK H. VACCARO, Department of Chemistry, Yale University, P.O. Box 208107, New Haven, CT 06520-8107 USA.

Electromagnetic radiation propagating through an isotropic chiral medium experiences a complex index of refraction that differs in both real (in-phase) and imaginary (in-quadrature) parts for the right-circular and left-circular polarization states that define the helicity basis. The resulting phenomena of circular birefringence (CB) and circular dichroism (CD) lead to observable effects in the form of dispersive rotation and absorptive elliptization for an impinging beam of plane-polarized light, which commonly are measured under conditions of nonresonant and resonant excitation, respectively. This talk will discuss ongoing efforts designed to elucidate the provenance of electronic optical activity under complementary solvated and isolated conditions, with the latter vapor-phase work made possible by our continuing development of Cavity Ring-Down Polarimetry (CRDP).\textsuperscript{a} Molecules of interest include the rigid bicyclic ketone (1\textit{R},4\textit{R})-norbornene, where the spatial arrangement of distal alkene and carbonyl moieties gives rise to extraordinarily large specific rotation (CB) parameters that are predicted incongruously by different quantum-chemical methods; the monoterpenic constitutional isomers (\textit{S})-2-carene and (\textit{S})-3-carene, which display surprisingly distinct chiroptical properties; and conjugated ketones such as (\textit{S})-verbenone, where CD probes of weak \pi* \rightarrow \textit{n} absorption bands have been performed at vibronic resolution. The disparate nature of gas-phase and condensed-phase optical activity will be highlighted, with complementary \textit{ab initio} calculations serving to elucidate the structural, chemical, and electronic origins of observed behavior.

THE ROLE OF $\pi\sigma^*$ STATE IN INTRAMOLECULAR CHARGE TRANSFER OF 4-(DIMETHYLAMINO)-BENZONITRILE AND RELATED MOLECULES

TAKASHIGE FUJIWARA, Department of Physics, The Ohio State University, Columbus OH 43210; MAREK Z. ZGIERSKI, Steacie Institute for Molecular Science, National Research Council of Canada, Ottawa, K1A 0R6 CANADA; EDWARD C. LIM, Department of Chemistry and The Center for Laser and Optical Spectroscopy, The University of Akron, Akron OH 44325-3601.

The solvent-polarity dependence and temporal characteristics of the transient absorption of 4-(dimethylamino)benzonitrile, DMABN, and 4-(dimethylamino)benzethyne, DMABE, demonstrate the presence of the $\pi\sigma^*$-state absorption at about 700 nm and the $\pi\pi^*$ (LE)-state absorption at about 520 nm and 450 nm. The rise and decay times of the $\pi\sigma^*$-state transient differ from those of the $\pi\pi^*$-state transients in both compounds. Moreover, the peak position of the $\pi\sigma^*$-state absorption is blue-shifted and more intense in acetonitrile as compared to $n$-hexane, whereas the band positions of the $\pi\pi^*$-state absorptions are essentially the same in the two solvents. For DMABN in acetonitrile, the rise time ($\sim$ 4.3 ps) of the twisted intramolecular charge transfer (TICT)-state transient at 330 nm is identical to the decay time of the $\pi\sigma^*$-state transient. The 4.8 ns decay time of the TICT-state absorption of DMABN is longer than the 2.9 ns decay time of the intramolecular charge-transfer (ICT) fluorescence, indicating that the fluorescent ICT state differs from the TICT state observed in transient absorption. These results are consistent with the presence of a low-lying $\pi\sigma^*$ state in DMABN (and DMABE), and the role the $\pi\sigma^*$ state plays in the formation of the TICT state of DMABN.

ULTRAFAST DYNAMICS IN NITRO- AND (ORGANOPHOSPHINE)GOLD(I)-POLYCYCLIC AROMATIC HYDROCARBONS

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

Femtosecond UV/Vis broadband transient absorption was used to investigate the excited-state dynamics in nitronaphthalenes and (organophosphine)gold(I) naphthalenes. Both groups of compounds display similar dynamics. Following excitation with UV light the compounds undergo fast and efficient intersystem crossing to the triplet manifold with a lifetime between 0.1 and 0.3 ps. Once in the triplet manifold, internal conversion occurs from the receiver triplet state to the lowest-energy triplet state ($T_1$). Vibrational cooling in the $T_1$ state then proceeds with a lifetime between 3 and 11 ps, which depends on the substituent on the naphthalene moiety. Quantum chemical calculations including solvent effects are used to substantiate the interpretation of the experimental results. Comparisons between the naphthalene derivatives and the previously studied pyrene-containing derivatives$^{[1,2]}$ will be discussed.

2-aminopurine is a structural isomer of adenine that is widely used as a fluorescence probe in DNA because its fluorescence lifetime and quantum yield respond sensitively to local DNA duplex conformation and neighboring microenvironment. Despite its broad utilization in biochemical and biophysical studies, there is ongoing debate about the mechanism by which fluorescence is quenched in 2-aminopurine in different solvents. Establishing the excited-state relaxation pathways that lead to fluorescence quenching is essential for a meaningful interpretation of the experimental data in terms of local structure and dynamics. In this contribution, the excited state dynamics in 2-aminopurine ribonucleoside is investigated by using broad-band transient absorption spectroscopy in different solvents. Excitation is performed at 320 nm and the spectral evolution is monitored in the spectral region from 330 nm to 700 nm. Three exponential functions are required to fit globally the transient absorption signals from femtosecond to microsecond time scale. The first lifetime is assigned to solvent relaxation dynamics in the excited singlet state. The singlet state population then bifurcates to two different decay channels. The first channel is the well-documented fluorescence emission while the second channel is assigned to intersystem crossing to the triplet manifold. The extent of participation of this nonradiative decay channel depends sensitively on the polarity and hydrogen bonding ability of the solvent. The triplet state population decays back to the ground state in hundreds of nanoseconds and is quenched by molecular oxygen. Our results unequivocally show that the excited-state dynamics in 2-aminopurine is more complex than previously thought.
TH. MINI-SYMPOSIUM: SPECTROSCOPIC PERTURBATIONS

TUESDAY, JUNE 21, 2011 – 1:30 pm
Room: 1000 McPHERSON LAB

Chair: CAROLINE CHICK JARROLD, Indiana University, Bloomington, Indiana

TH01

Journal of Molecular Spectroscopy Review Lecture

PERTURBATIONS I HAVE KNOWN AND LOVED

ROBERT W. FIELD, Department of Chemistry, MIT, Cambridge, MA.

A spectroscopic perturbation is a disruption of a $^1\Sigma^+ - ^1\Sigma^+$-like regular pattern that can embody level-shifts, extra lines, and intensity anomalies. Once upon a time, when a band was labeled “perturbed,” it was considered worthless because it could at best yield molecular constants unsuited for archival tables. Nevertheless, a few brave spectroscopists, notably Albin Lagerqvist and Richard Barrow, collected perturbations because they knew that the pattern of multiple perturbations formed an intricate puzzle that would eventually reveal the presence and electronic symmetry of otherwise unobservable electronic states. There are many kinds of patterns of broken patterns. In my PhD thesis I showed how to determine absolute vibrational assignments for the perturber from patterns among the observed values of perturbation matrix elements. When a $^3\Pi$ state is perturbed, its six ($\Omega$, parity) components capture a pattern of level shifts and intensity anomalies that reveals more about the nature of the perturber than a simple perturbation of the single component of a $^1\Sigma$ state. In perturbation-facilitated OODR, a perturbed singlet level acts as a spectroscopic doorway through which the entire triplet manifold may be systematically explored. For polyatomic molecule vibrations, a vibrational polyad (a group of mutually perturbing vibrational levels, among which the perturbation matrix elements are expected to follow harmonic oscillator scaling rules) can contain more components than a $^3\Pi$ state and intrapolyad patterns can be exquisitely sensitive not merely to the nature of an interloper within the polyad but also to the eigenvector character of the vibronic state from which the polyad is viewed. Variation of scaled polyad interaction parameters from one polyad to the next, a pattern of patterns, can signal proximity to an isomerization barrier. Everything in Rydberg-land seems to scale as $n^{*-3}$, yet a trespassing valence state causes all scaling and propensity rules go out the window.

TH02

VIBRONIC PERTURBATIONS IN THE ELECTRONIC SPECTRUM OF BeC

BEAU J. BARKER, IVAN O. ANTONOV, MICHAEL C. HEAVEN, Department of Chemistry, Emory University, Atlanta, GA 30322; RICHARD DAWES, Department of Chemistry, Missouri University of Science and Technology, Rolla, MO 65409.

Electronic spectra for BeC have been recorded over the range 30,500-40,000 cm$^{-1}$. Laser ablation and jet-cooling techniques were used to obtain rotationally resolved data. The vibronic structure consists of a large number of bands with erratic energy spacings. Two-color photoionization threshold measurements were used to show that the majority of these features originated from the ground state zero-point level. The rotational structures are mostly consistent with the bands of $^3\Pi$-X$^3\Sigma^-$ transitions. Theoretical calculations indicate that the erratic vibronic structure results from strong interactions between the four lowest energy $^3\Pi$ states. Adiabatic potential energy curves were obtained from dynamically weighted MRCI calculations. Diabatic potentials and coupling matrix elements were then reconstructed from these results, and used to compute the vibronic energy levels for the four interacting $^3\Pi$ states. The predictions were sufficiently close to the observed structure to permit assignment of the main features. Bands originating from the low-lying $^5\Sigma^-$ state were also identified, yielding a $^5\Sigma^-$ to X$^3\Sigma^-$ energy interval of 2200±50 cm$^{-1}$.
PERTURBATIONS IN THE SPECTRA OF HIGH RYDBERG STATES: CHANNEL INTERACTIONS, STARK AND ZEEMAN EFFECTS

CHRISTA HAASE, MARTIN SCHÄFER, STEPHEN D. HOGAN and FRÉDÉRIC MERKT, Laboratorium für Physikalische Chemie, ETH-Zürich, 8093 Zürich, Switzerland.

Rydberg states of principal quantum number $n \gg 50$ have been prepared by irradiation of an atomic beam of xenon with vacuum ultraviolet (VUV) radiation. Narrowband submillimeter-wave (THz) radiation was then used to record spectra of transitions from these Rydberg states to higher or lower-lying Rydberg states. The transitions were detected by selective field ionization and recording either the electrons or the ions, the latter offering the advantage of mass selection.

Rydberg states of high principal quantum number are extremely sensitive to their environment, which can be exploited to characterize the experimental conditions under which the spectroscopic measurements are carried out. The high resolution achieved in the experiments (better than 100 kHz) enabled the study of the spectral lineshapes and line positions in dependence of weak electric (down to below 100\,\mu V/cm) and magnetic fields (down to a few \mu T), and of the density of Rydberg atoms and ions generated in the experimental volume. The experiments rely on the use of a pulsed, broadly tunable, laser-based source of THz radiation for survey scans, and of a phase- and frequency-stabilized submillimeter-wave backward-wave oscillator-based radiation source for precision measurements.

To illustrate the use of these sources, we present the results of the spectroscopic investigations of the hyperfine structure of $^{129}$Xe Rydberg states in spectral regions where s-d interactions are expected to play a role.


DATA AND ANALYSIS OF SPIN-ORBIT COUPLED $A^1\Sigma_u^+$ AND $b^3\Pi_u$ STATES OF Cs$_2$

ANDREY V. STOLYAROV, Department of Chemistry, Moscow State University, GSP-2 Leninskie gory 1/3, Moscow 119992, Russia; THOMAS H. BERGEMAN, Department of Physics and Astronomy, State University of New York, Stony Brook, New York 11794-3800.

Following work with various collaborators on analogous states of Na$_2$, NaRb, KRb, NaCs, KCs, RbCs and Rb$_2$, we have recently completed a study of the $A^1\Sigma_u^+$ and $b^3\Pi_u$ states of Cs$_2$, based on experimental data obtained in Orsay, Temple University, Innsbruck and Riga. Potentials and spin-orbit coupling functions were fit to the data using both a coupled-channel approach and the discrete variable representation method. As with other species, the goal has been to accurately characterize the energy level structure to facilitate experiments in which cold ground state molecules are produced from cold atoms or Feshbach resonance dimers by stepwise excitation and decay, and also to facilitate excitations to higher lying states. For Cs$_2$, second-order spin-orbit shifts become significant, and since these are typically difficult to obtain experimentally, \textit{ab initio} calculations provided estimates. We will display the excellent quality of the fits to the experimental data, including a modeling of the $b^3\Pi_{1u} - A^1\Sigma_u^+$ fine structure interval and \Lambda-doubling effect in the $b^3\Pi_{1u}^\pm$ state.

\footnote{Support by RFBR is gratefully acknowledged}
SPECTROSCOPIC SIGNATURES OF ISOMERIZATION IN THE S1 STATE OF C2H2

J. H. BARABAN, A. H. STEEVES, R. W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA; J. F. STANTON, Institute for Theoretical Chemistry, Departments of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712; A. J. MERER, Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan.

Spectroscopic signatures of isomerization between the cis and trans conformers of the S1 state of acetylene have been studied using a reduced dimension Discrete Variable Representation (DVR) calculation. The calculated rovibrational level structure yields insight into puzzling aspects of the $\tilde{A} \leftarrow \tilde{X}$ band spectrum, including patterns that reveal the effects of the low-barrier cis-trans conformational change. Large anharmonicities in modes that project along the minimum energy isomerization path are discussed in the context of the isomerization barrier shape. New high-sensitivity Laser Induced Fluorescence (LIF) spectra have also been recorded in the region of the expected transition state energy in order to detect weak transitions into severely predissociated states, uncovering levels that are in accord with the DVR predictions.

EVIDENCE OF PERTURBATIONS ON THE S1 SURFACE OF ACETYLENE FROM PATTERNS IN STIMULATED EMISSION PUMPING SPECTRA

G. BARRATT PARK, JOSHUA H. BARABAN, ADAM H. STEEVES, and ROBERT W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

Stimulated Emission Pumping (SEP) spectra from the $3^4$ level of S1 acetylene to the $N_B = 10$ polyad of S0 contain evidence of an unexpected interference effect. S0 intrapolyad intensity distributions are as a rule governed solely by the fractionation of the (single) bright state. However, the intensity distribution in the SEP spectrum observed from $3^4$ deviates from the expected pattern. Reduced dimension DVR calculations on the S1 surface predict a three-state interaction involving one of the S1 interloper bands. According to the calculation, this cis interloper state engenders an indirect coupling between the trans $2^13^16^2$ and $3^4$ zero order states, causing the eigenstates to lie substantially farther apart than one might expect, and lending intensity to the cis $3^16^1$ interloper band that appears between them. These predictions agree quite well with the experimental observations. The intensity distribution in the SEP spectrum observed from $3^4$ seems to contain an interfering combination of the bright state patterns seen in the $2^13^2$ and the $3^2B^2$ spectra. This type of indirect effect can yield much information about state mixing, and is particularly interesting in this case since its effects on the level structure cannot reasonably be accounted for by effective Hamiltonian models that rely solely on polyads.

Intermission
TH07 15 min 3:45

THE GERADE RYDBERG STATES OF MOLECULAR HYDROGEN

DANIEL SPRECHER 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.

High-resolution spectroscopic investigations of molecular Rydberg states at different values of the principal quantum number \( n \) enable one to study the interaction between the Rydberg electron and the molecular ion core. With increasing \( n \) values, the electron motion gradually decouples from the motion of the molecular ion core. The decoupling is accompanied by very characteristic perturbations of the spectral patterns and by spin-rovibronic channel interactions which provide extremely detailed information on the electron-ion system.

We present the results of a combined experimental and theoretical investigation of the s, p, d, and f Rydberg states of molecular hydrogen. Experimentally, high-resolution laser and millimeter-wave spectra of Rydberg states with principal quantum numbers between 30 and 60 have been recorded with a precision of better than 100 kHz. Theoretically, multichannel quantum defect theory has been employed to analyze the spectra: first, eigenquantum defect functions were determined \textit{ab initio} in R-matrix calculations; second, the eigenquantum defect functions were refined until agreement with the experimental data was reached. The s and d Rydberg states of ortho-H\(_2\) are particularly interesting because pronounced, but also subtle, effects caused by the hyperfine structure and by doubly excited states can be studied in considerable detail. The talk will present several examples of interesting and so far unobserved types of perturbations and uncoupling phenomena.

TH08 15 min 4:02

ROTATIONALLY RESOLVED SPECTROSCOPY OF THE ELECTRONICALLY EXCITED C AND D STATES OF ArXe AND KrXe

LORENA PITICCO, MARTIN SCHÄFER, and FRÉDÉRIC MERKT, ETH Zürich, Laboratorium für Physikalische Chemie, Wolfgang-Pauli-Strasse 10, 8093 Zürich, Switzerland.

Rotationally resolved (1+1') resonance-enhanced two-photon ionization spectra of the D and C ← X \( 0^+ \) band systems of several isotopomers of ArXe and KrXe were recorded using a narrow-bandwidth VUV laser system\(^a\) at a resolution of 0.01 cm\(^{-1}\) in the wave number range from 77000 cm\(^{-1}\) to 77400 cm\(^{-1}\). The analysis of the rotational structures enabled the characterization of the dissociation of the \( \Omega = 1 \) states of ArXe and KrXe\(^c\). In the case of Rg\(^{129}\)Xe and Rg\(^{131}\)Xe (Rg=Ar, Kr), the hyperfine structure could also be resolved and provided new information on these states, and on the nature of the perturbations\(^{d,e}\). Model potentials for the perturbing and perturbed excited states were constructed in an attempt to rationalize the spectroscopic data. The spectra of the C and D states of ArXe and KrXe reveal strong perturbations\(^{(c-e)}\), and are subject to slow predissociation.

TH09 15 min 4:19

ANALYSIS OF STRONGLY PERTURBED $1^1\Pi - 2^3\Sigma^+ - b^3\Pi$ STATES OF THE KRb MOLECULE

J. T. KIM, Department of Photonic Engineering, Chosun University, Gwangju, 501-759, Korea; Y. LEE, Department of Chemistry, Mokpo National University, Jeonnam 534-729, Korea; B. KIM, Department of Chemistry, KAIST, Daejeon, 305-701, Korea; D. WANG, Department of Physics, The Chinese University of Hong Kong, Shatin, Hong Kong; W. C. STWALLEY, P. L. GOULD, and E. E. EYLER, Department of Physics, University of Connecticut, Storrs, CT 06269, USA.

An important goal of recent ultracold molecule research is to produce molecules in the lowest rovibronic state, $v'' = 0, J'' = 0$, of the $X^1\Sigma^+$ ground electronic state. Here, stimulated Raman transfer pathways to the lowest rovibronic state through strongly perturbed intermediate levels, starting from the $a^3\Sigma^+$ state, are determined by observing the intermediate states using a combination of molecular beam and ultracold molecule experiments. By using such spectra, the vibrational levels of strongly perturbed states such as the $1^1\Pi - 2^3\Sigma^+ - b^3\Pi$ states could be rapidly assigned. Vibrational assignments for the $1^1\Pi$ state match well with those of Kasahara, et al. Several $\Omega = 0^+$ and $2$ levels of the $2^3\Sigma^+$ and $b^3\Pi$ states, all of which are forbidden from the $X^1\Sigma^+$ state, were observed and assigned. This new spectroscopic combination allows one to unravel complex and highly perturbed spectra and determine optimal routes for stimulated Raman transfer of molecules formed near dissociation by photoassociation or magnetoassociation to the lowest rovibronic levels of the $X^1\Sigma^+$ ground electronic state.

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TH10 15 min 4:36

OBSERVATION OF THE SYSTEM $(1)^1\Sigma^+_u-(1)^3\Pi_u$ of SR$_2$ BY FOURIER TRANSFORM SPECTROSCOPY AND ITS ANALYSIS

A. STEIN, H. KNÖCKEL, and E. TIEMANN, Institut für Quantenoptik, Leibniz Universität Hannover, Welfengarten 1, 30167 Hannover, Germany.

Ultracold Sr atoms are presently actively discussed for applications on an optical frequency standard. Thus any influence on the reproducibility and accuracy of the intercombination transitions $^1S-^3P$ must be thoroughly investigated, and molecular data which involve the atomic singlet and triplet states are of great interest. This motivated us to study the system $(1)^1\Sigma^+_u-(1)^3\Pi_u$ by Fourier transform spectroscopy in high resolution.

Sr$_2$ is prepared in a heatpipe and fluorescence is excited by different laser sources in a wide spectral range. About 700 levels were measured for which the absolute energies and the rotational quantum numbers are precisely known, applying the detailed data on the ground state of Sr$_2$ (A. Stein, et al., Eur. Phys. J. D 57, 171 (2010)). Spectra were observed for three isotopologues. The low lying part of the state $(1)^1\Sigma^+_u$ is mainly unperturbed, thus offers the advantage for a unique start of the analysis of the energy range where the two states overlap and the spectra show perturbations by the strong spin-orbit interaction everywhere. We will report about the present status of observations and analysis, which finally should deliver the diabatic potential curves of both states and their interaction functions. This result will open the doorway from the singlet ground state to the triplet manifold by laser excitation and thus will also be very important for production schemes of ultracold Sr$_2$, trapped in an optical trap.
A NEW ANALYSIS OF A VERY OLD SPECTRUM: THE HIGHLY PERTURBED $A^2\Pi_i - X^2\Pi_i$ BAND SYSTEM OF THE CHLORINE CATION (Cl$_2^+$)

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

Although the $A^2\Pi_i - X^2\Pi_i$ band system of the chlorine cation has been known since 1928 and has been studied by many investigators, no satisfactory vibrational assignment has been achieved due to substantial vibronic perturbations. In the present work, laser-induced fluorescence and single vibronic level (SVL) emission spectra of the jet-cooled chlorine cation (Cl$_2^+$) have been investigated in the region of 500-312 nm. The cation was produced in a pulsed electric discharge jet using a precursor mixture of 10% chlorine gas in high pressure argon. The spectrum has been extended further to the red than previously known and the 1-0 band has been identified. The 0-0 band was undetectable due to a very small Franck-Condon factor for this transition. Due to efficient cooling in the supersonic expansion, no hot bands and no transitions from the $X^2\Pi_1$ spin-orbit component were observed in our coldest spectra. Chlorine isotope shifts and the number of nodes in the SVL emission spectra were used as diagnostics in assigning the vibrational quantum numbers. SVL emission spectra of $^{35}$Cl$^+$ and $^{37}$Cl$^+$ terminated on levels up to $v''=15$ and these data were used to determine $\omega''_e = 645.0(1)$ and $\omega_e x''_e = 2.927(7)$ cm$^{-1}$. High resolution spectra of the 1-0 and 2-0 bands of $^{35}$Cl$^+$ and $^{37}$Cl$^{37}$Cl$^+$ have been recorded and rotationally analyzed, yielding $r''_e = 2.2287(7)$ and $r''_0 = 1.8944(3)$ Å.

PROBING THE ELECTRONIC STRUCTURE OF THE NICKEL MONOHALIDES: SPECTROSCOPY OF THE LOW-LYING ELECTRONIC STATES OF NiX (X=Cl,Br,I)

LLOYD MUZANGWA, VICTORIA AYLES, SILVER NYAMBO AND SCOTT A. REID, Department of Chemistry, Marquette University, Milwaukee, WI 53233.

Laser induced fluorescence and single vibronic level emission spectroscopy has been used to probe five low-lying electronic states ($X^2\Delta_{3/2}$, $A^2\Delta_{5/2}$, $X^2\Pi_{1/2}$, $A^2\Delta_{3/2}$ and $B^2\Sigma^+_1$) of NiX (X=Cl,Br,I) that arise from the 3d$^9$ configuration of Ni$^+$. In this work, term energies and a complete set of vibrational parameters were derived for all five electronic states of the target molecules, and these are compared with recent high level ab initio calculations. Pertubations among these states were examined, and the data set derived in this work affords a detailed analysis of periodic trends in the Nickel monohalide series.

LASER-INDUCED FLUORESCENCE SPECTROSCOPY ON ROTATIONAL DISTRIBUTION OF HfF PHOTOIONS

MATT GRAU, HUANQIAN LOH, TYLER YAHN, RUSSELL STUTZ, JILA, NIST and University of Colorado, and Department of Physics, University of Colorado, Boulder, Colorado 80309-0440; ROBERT W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139; and ERIC A. CORNELL, JILA, NIST and University of Colorado, and Department of Physics, University of Colorado, Boulder, Colorado 80309-0440.

As a step towards measuring the electron electric dipole moment$^a$, we produce a sample of HfF$^+$ using a two-color excitation. We promote HfF from $X^2\Delta_{3/2}$ to an isotope and parity-selective intermediate state, and then to one of many highly perturbed Rydberg states from which it autoionizes to the vibrational ground state of HfF$^+$. We measure the population of the rotational states of HfF$^+$ using laser-induced fluorescence and find that only a small number of states are populated, with most of the population in $J < 4$. Additionally, we see a strong propensity for autoionization to preserve the parity of the molecule, with one parity populating even $J$ levels and the other populating odd $J$. Using polarized light to prepare the Rydberg molecules in various orientations, and then probing the ion with LIF, we see that a polarization of $m_J$ sublevels also survives autoionization.

PERTURBATIONS IN THE GROUND ELECTRONIC STATE ROTATIONAL SPECTRUM OF TRANSITION-METAL CONTAINING MOLECULES

D.T. Halfen, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721; R. W. Field, Department of Chemistry, MIT, Cambridge, MA 02139; and L. M. Ziurys, Department of Chemistry, Department of Astronomy, and Steward Observatory, University of Arizona, Tucson, AZ 85721.

Transition-metal containing molecules, in general, have a high density of electronic states even in the energy region of the electronic ground state. Often the pure rotational spectrum of these species exhibits perturbations caused by low-lying excited states. Examples of these perturbations include irregular spin-orbit, fine structure, and hyperfine patterns. A good example of a molecule exhibiting some of these perturbations is VCl$^\text{+}$. This species has a $^4\Sigma^-$ ground state, but has unusually large spin-spin splittings. These perturbations indicate that the ground state is interacting with the excited $^4\Pi$, and/or $^2\Pi$, states. A deperturbation analysis of the rotational spectrum of VCl$^\text{+}$ is currently underway, and the results of this analysis will be presented.
TI. INFRARED/RAMAN
TUESDAY, JUNE 21, 2011 – 1:30 pm
Room: 1015 McPHERSON LAB

Chair: GEOFFREY DUXBURY, University of Strathclyde, Glasgow, Scotland, UK

TI01 15 min 1:30

INFRARED SPECTRA OF COMPLEXES CONTAINING ACETYLENE-d2

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

Infrared spectra of the C_2D_2 dimer in the monomer ν_3 region (∼2439 cm^{-1}) are observed by direct absorption using a rapid-scan tuneable diode laser spectrometer to probe a pulsed supersonic slit-jet expansion. We analyze the perpendicular K = 1-0 and 0-1 subbands of the vibrational mode involving the C_2D_2 monomer located at the top of the T-shaped dimer, but miss the parallel band involving the stem monomer vibration due to limited laser coverage. The results are consistent with previous work on acetylene dimers, but perturbations are much less evident than in the analogous infrared spectrum of C_2H_2.

As expected, the tunneling splitting in the excited state (8 MHz) is much smaller than in the ground state (424 MHz). In the same region, we observe the H-bonded isomer of the C_2D_2-C_2H_2 dimer. This has not previously been observed, even though microwave spectra of almost every other conceivable deuterated isotopologue are known.

In addition to these acetylene dimers, our spectra also contain bands arising from impurities in the gas mixture which we assign to the C_2D_2-nitrogen and C_2D_2-water complexes.

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TI02 15 min 1:47

HIGH RESOLUTION OVERTONE SPECTROSCOPY OF ACETYLENE VAN DER WAALS COMPLEXES


The latest upgrades and results from the FANTASIO+ set-up (for ‘Fourier trANsform, Tunable, diode and quadrupole mAss spectrometers interfaced to a Supersonic expansIOn’) are presented. Thanks to the improvements of the calibration (better than ±1 × 10^{-3} cm^{-1} accuracy) and the ring-down time (130 μs), the spectrum of C_2H_2-N_2 around 6500 cm^{-1} was recorded as well as absorption bands due to combined excitations of intra and intermolecular modes of C_2H_2-Ar, C_2H_2-CO_2 and C_2H_2-N_2O. A hot absorption band of the van der Waals complex C_2H_2-Ar was also observed. The first analyses of these spectra will be presented.

Along the development of the FANTASIO+ set-up, a new injection system to probe samples liquid at STP conditions, and a pulse injector are currently under implementation. Those upgrades will allow the study of organic and prebiotic molecules and a better cooling of the gas in the expansion, respectively. The first results will also be presented.

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HIGH RESOLUTION OVERTONE SPECTROSCOPY OF THE ACETYLENE VAN DER WAALS DIMER, $^{12}$C$_2$H$_2$$_2$

K. DIDRICHE, C. LAUZIN, T. FOLDES, D. GOLEBIOWSKI, 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; C. LEFORESTIER, ACTMM-CC 15.01, Institut Charles Gerhardt, 34095 Montpellier, France.

CW-cavity ring down spectroscopy was used to record in a free jet expansion the spectrum of the absorption band in (12$\text{C}_2\text{H}_2$)$_2$ with origin at 6547.6 cm$^{-1}$. It is a perpendicular band and corresponds to 2CH excitation in the hat unit of the T-shaped dimer. Calibration (better than $\pm 1 \times 10^{-3}$ cm$^{-1}$ accuracy) and ring-down time (130 $\mu$s) were improved compared to a previous contribution $^a$, and a line-by-line analysis was undertaken. Three series of lines were identified involving levels with A1$^+$, E$^+$ and B1$^+$ tunneling symmetries, confirming the spectral and symmetry analyses reported in the literature for the 1CH excitation band $^b$. 164 vibration-rotation-tunneling lines were assigned in the $K_a^\prime - K_a^\prime\prime = 2 - 3, 0 - 1, 2 - 1$ and 4 - 3 sub-bands and effective rigid rotor vibration-rotation constants were obtained by simultaneously fitting 1CH and 2CH lines from the same symmetry series. Perturbations affecting the $K_a$ stacks, in particular, are reported. The tunneling frequency in 2CH is estimated to be $\nu_{\text{tunn.}}^{2\text{CH}} = 270$ MHz for the $K_a = 0$ stack. The rotational temperature is determined to be 23 K from relative line intensities and the half lifetime of the dimer in the 2CH hat state is estimated to 1 ns from individual line widths.


$^b$Fraser et al., J. Chem. Phys. 1988, 89, 6028-6045

THE WEAKLY–BOUND CO$_2$–ACETYLENE COMPLEX: FUNDAMENTAL AND TORSIONAL COMBINATION BAND IN THE CO$_2$ $\nu_3$ REGION

C. LAUZIN, Laboratoire de Chimie quantique et Photophysique, CP160/09 Faculté des Sciences, Université Libre de Bruxelles (U.L.B.), Ave. Roosevelt, 50 B-1050 Brussels, Belgium; J. NOROOZ OLIAAE, M. REZAEI, N. MOAZZEN-AHMADI, Department of Physics and Astronomy, University of Calgary, Calgary, AB T2N 1N4, Canada.

Infrared spectrum of the weakly-bound CO$_2$–C$_2$H$_2$ complex in the region of the CO$_2$ $\nu_3$ fundamental band ($\sim$ 2349 cm$^{-1}$) is observed in a pulsed supersonic slit jet expansion using a tunable diode laser probe. Two bands are observed and analyzed: the fundamental (C–O asymmetric stretch) and a combination involving the intermolecular torsional (out-of-plane bend) vibration. The resulting torsional frequency is 44.385(10) cm$^{-1}$. This represents the first observation of an intermolecular frequency for carbon dioxide-acetylene complex. A comparison between the results obtained here and those previously reported for N$_2$O–C$_2$H$_2$ complex $^a$ is discussed.

HIGH RESOLUTION INFRARED AND MICROWAVE SPECTRA OF NH₃-HCCH AND NH₃-OCS COMPLEXES: STUDIES OF WEAK C-H···N HYDROGEN BOND AND ELECTRIC MULTIPOLe INTERACTIONS

XUNCHEN LIU, YUNJIE XU, Department of Chemistry, University of Alberta, Edmonton, Canada, T6G 2G2.

C-H···N weak hydrogen bond is of much current interest. We report the first high resolution infrared spectroscopic study of a prototypical C-H···N bonded system, i.e. NH₃-HCCH, at the vicinity of the ν4 band of NH₃. The spectrum has been recorded using an infrared spectrometer equipped with an astigmatic multipass cell aligned for 366 passes and a room temperature external cavity quantum cascade laser at the 6 μm region. The perpendicular band spectrum of symmetric top rotor observed is consistent with the previous microwave and infrared studies at 3 μm. We also extended the previous microwave measurement to higher J and K.

For the related NH₃-OCS complex, microwave spectrum of J up to 6 and infrared spectrum at the vicinity of the ν4 band of NH₃ have been recorded and analyzed for the first time. Comparison has been made with the previously studied isoelectronic complexes such as NH₃-N₂O and NH₃-CO₂. The source of the difference will be discussed with the aid of ab initio calculations.

Sequential solvation of propylene oxide (C₃H₆O), an prototypical chiral molecule, with water has been investigated using high resolution infrared spectroscopy and ab initio methods. In a number of low resolution studies, the vibrational and vibrational circular dichroism spectral features at the water bending vibration region had been shown to be highly sensitive to the water solvation structures around propylene oxide in aqueous solution. The current study aims to provide quantitative information about solvation of a chiral molecule with water molecules at the molecular level and to provide the experimental benchmarks for calculations of vibrational frequencies in these larger molecular complexes. The high resolution infrared spectra of the propylene oxide-water complexes have been measured using a pulsed jet infrared spectrometer equipped with a room temperature external cavity quantum cascade laser and an astigmatic multi-pass cell. At least 6 bands have been observed from 1650 to 1680 cm⁻¹. Based on the previous microwave spectroscopic studies, these bands have been assigned to the blue-shifted water bending (ν₂) vibration modes associated with both the syn- and anti- conformers of the binary (C₃H₆O-H₂O) and ternary (C₃H₆O-(H₂O)₂) complexes. This report shows the power of high resolution infrared spectroscopy to study multi-conformers of relatively large organic molecule complexes produced in a jet expansion.

Intermission
FIRST INFRARED SPECTRA OF CN-RARE GAS AND CN-H2/D2 COMPLEXES VIA IR-UV FLUORESCENCE DEPLETION SPECTROSCOPY

BRIDGET A. O’DONNELL, MELODIE TING, JOSEPH M. BEAMES, and MARSHA I. LESTER, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323.

In this study, an IR-UV fluorescence depletion scheme is employed to record rotationally resolved IR spectra in the CN overtone region of CN-Ne, CN-Ar, and CN-H2/D2 using previously reported B-X electronic transitions. The resulting IR spectra are fit to yield band origins and rotational constants for the lower and upper states. The band origins for all four species are shifted only slightly from the CN monomer overtone stretch, which reflects the weak nature of the van der Waals interactions. In the case of CN-Ar and CN-D2, the derived rotational constants are consistent with equilibrium distances from ab initio potential energy surfaces. However, for CN-Ne and CN-H2, Coriolis coupling between nearby hindered rotor states complicates the rotational analysis. Ongoing work using an alternate IR-UV double-resonance technique will help elucidate the nature of the interaction and the average configuration of the ground states of the four species.

aResearch is supported by the Chemistry Division of the National Science Foundation

CARBON DIOXIDE CLUSTERS: (CO2)6 TO (CO2)13

A.R.W. MCKELLAR, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, ON K1A 0R6, Canada; J. NOROOZ OLIABEE, M. DEHGANY, and N. MOAZZEN-AHMADI, Department of Physics and Astronomy, University of Calgary, 2500 University Dr., N.W., Calgary, AB T2N IN4, Canada.

We recently reported assignments of specific infrared bands in the CO2 ν3 region (∼2350 cm⁻¹) to (CO2)6, (CO2)7, (CO2)9, (CO2)10, (CO2)11, (CO2)12, and (CO2)13. Spectra are obtained by direct absorption using a rapid-scan tuneable diode laser spectrometer to probe a pulsed supersonic slit-jet expansion and assignments are facilitated by recent calculations of Takeuchi based on the Murthy potential. (CO2)6 is a symmetric top with S6 point group symmetry which can be thought of as a stack of two planar cyclic trimers. (CO2)13 is also an S6 symmetric top, and consists of a single CO2 monomer surrounded by a slightly distorted icosahedral cage. The remaining clusters are asymmetric tops without symmetry. Here we report additional CO2 cluster results. Calculations based on the SAPT-s potential indicate that the structure of (CO2)10 may be slightly different from that given by Takeuchi/Murthy. An additional band is observed for each of (CO2)13 and (CO2)10. A feature observed at 2378.2 cm⁻¹ is assigned as a (CO2)6 parallel combination band involving the sum of a fundamental and a low-lying intermolecular vibration. Most significantly, two bands are assigned to a second isomer of (CO2)6. This is also a symmetric top, but now with S4 symmetry. The two symmetric hexamer isomers observed spectroscopically correspond well with the lowest energy structures given by both the SAPT-s and Murthy intermolecular potentials.

THEORETICAL AND EXPERIMENTAL STUDY OF THE ROVIBRATIONAL SPECTRA OF CO$_2$-(para-H$_2$)-He TRIMERS

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Clusters of p-H$_2$ had been predicted to exhibit superfluid behavior twenty years ago, but direct observation of this phenomenon was elusive until our recent work combining experimental measurements and theoretical simulations of the non-classical rotational inertia and superfluid response of p-H$_2$ clusters doped with CO$_2$. However, the size-dependent superfluid response of those clusters reached a maximum at $N = 12$, and the clusters become frozen at larger $N$. It is therefore interesting to examine the effect of adding helium atoms to a pure p-H$_2$ shell around a CO$_2$ chromophore, and to investigate their effect on the superfluid response of CO$_2$-(p-H$_2$)$_N$ for $N > 12$. This will help us understand the role of helium as a ‘second solvent’ species, and help explain experiments that had been presented as evidence of superfluidity of doped hydrogen clusters embedded in helium nanodroplets.

Exact quantum calculation of infrared and microwave spectra for dopant molecules attached to two pure He atoms or two pure p-H$_2$ molecules, respectively, have been reported by Wang and co-workers and by Li et al. To date, however, no such calculations have been reported for mixed p-H$_2$/He solvent species. The present paper therefore extends such work to the case of one p-H$_2$ and one He atom attached to one CO$_2$ dopant molecule. Three-dimensional p-H$_2$ and helium densities in the body-fixed frame are presented, and compared with those for the analogous CO$_2$-(He)$_2$ and CO$_2$-(p-H$_2$)$_2$ trimers.

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SPECTROSCOPIC OBSERVATION OF CS$_2$ DIMER

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Infrared spectra of the CS$_2$ dimer are observed in the region of the CS$_2$ $\nu_3$ fundamental band ($\sim 1535$ cm$^{-1}$) using a tuneable diode laser spectrometer. The weakly-bound complex is formed in a pulsed supersonic slit-jet expansion of a dilute gas mixture of carbon disulfide in helium. Contrary to the planar slipped-parallel geometry previously observed for (CO$_2$)$_2$, (N$_2$O)$_2$ and (OCS)$_2$, the CS$_2$ dimer exhibits a cross-shaped structure with $D_{2d}$ symmetry. Two bands were observed and analyzed: the fundamental (C–S asymmetric stretch) and a combination involving this mode plus an intermolecular vibration. In both cases, the rotational structure corresponds to a perpendicular ($\Delta K = \pm 1$) band of a symmetric rotor molecule. The intermolecular center of mass separation (C–C distance) is determined to be 3.539(7) Å. Thanks to symmetry, this is the only parameter required to characterize the structure, if the monomer geometry is assumed to remain unchanged in the dimer. From the band centers of the fundamental and combination band an intermolecular frequency of 10.96 cm$^{-1}$ is obtained, which we assign as the torsional bending mode. This constitutes the first high resolution spectroscopic investigation of CS$_2$ dimer.
Infrared spectra of carbon disulfide trimer formed in a pulsed supersonic slit-jet expansion are obtained via direct absorption of a tuneable diode laser in the region of the CS$_2$ $\nu_3$ fundamental band ($\sim$ 1535 cm$^{-1}$). Two bands sharing the same lower state were assigned to (C$^{32}$S$^{2}$)$_3$. These correspond to the two infrared active vibrations (a parallel and a perpendicular band) of the constituent CS$_2$ asymmetric stretches. The weaker perpendicular band is centered at 1524.613 cm$^{-1}$. It is shifted by $-10.74$ cm$^{-1}$ with respect to the free CS$_2$ monomer. The parallel band which is significantly stronger is centered at 1545.669 cm$^{-1}$. It has a vibrational shift of $+10.31$ cm$^{-1}$. The transitions with $K \neq 3n$ and those with $J = odd$ and $K = 0$ in the ground state are absent in both bands. This rigorously establishes that this isomer of carbon disulfide trimer has $D_3$ symmetry. Thanks to the symmetry, only two parameters, the C-C distance and the angle between a monomer axis and the plane containing the C atoms, are required to fully define the structure of the trimer. These were determined to be 3.811 Å and 61.8°, respectively. In addition, a parallel band corresponding to a single $^{34}$S substitution was observed around 1544.46 cm$^{-1}$. Results from this band are in complete agreement with those of the two bands for (C$^{32}$S$^{2}$)$_3$.

Infrared spectra of weakly bound Rg–CS$_2$ (Rg = He, Ne, and Ar) clusters formed in a pulsed supersonic slit-jet expansion have been recorded by exciting the CS$_2$ $\nu_3$ fundamental band ($\sim$ 1535 cm$^{-1}$) using a tuneable diode laser. Spectra were well fitted to a conventional semi-rigid asymmetric rotor Hamiltonian. The He–CS$_2$ spectrum was assigned to an a-type band, while spectra of Ne–CS$_2$ and Ar–CS$_2$ were well described by b-type bands, indicating a/b axis switching in transition from the He–CS$_2$ complex to the Ne–CS$_2$ and Ar–CS$_2$ complexes. The results show that the complexes have vibrationally averaged T-shaped structures. The determined structural parameters along with the observed vibrational shifts are $R = 3.81, 3.57$ and 3.71 Å, $\theta = 80.0, 86.9$ and 86.4° and $\Delta \nu = 0.171, 0.181$ and 0.067 cm$^{-1}$ for He–CS$_2$, Ne–CS$_2$ and Ar–CS$_2$, respectively. Here, $R$ is the distance between the rare gas and the carbon atom, $\theta$ is the the angle between $R$ and and the CS$_2$ axis and $\Delta \nu$ is the vibrational shift with respect to the free CS$_2$ monomer.
A SEMICLASSICAL DIRECT POTENTIAL FITTING SCHEME FOR DIATOMICS

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For decades the standard procedure for obtaining diatomic potential curves from spectroscopic data involved fitting the data to expressions for the vibrational energy $G_\nu$ and rotational constant $B_\nu$ as functions of the vibrational quantum number $\nu$, and then employing the RKR method to compute potential curves from these. Within the first-order semiclassical formalism of RKR, this “inversion” procedure is exact. However, the resulting potentials are limited in their quantum mechanical reliability, as has been demonstrated frequently by using the numerical Numerov method to compute the quantal properties of the potentials and comparing these with the starting spectroscopic information. A particularly troubling region is the repulsive wall of the potential near dissociation, where RKR curves often show unphysical wiggles and flares. Such behavior has generally been attributed to limitations inherent in the $G_\nu/B_\nu$-to-potential construct; by extension, such limitations are similarly responsible for some of the RKR-quantal disparities in other regions of the potential.

In recent years this procedure has begun to be replaced by methods in which the potential curves are the directly fitted quantities in the least-squares analysis of the data, and the so-derived potentials often match the precision of the input data. The question naturally arises, how good might semiclassical methods be in a similar approach? Since the semiclassical calculations are two orders of magnitude faster than the quantal, they might be better than RKR for obtaining approximate potentials and could aid in deciding matters such as best functional forms and appropriate numbers of adjustable parameters. In this paper I will discuss tests of a semiclassical direct potential fitting method.

UNEXPECTED PROPERTIES OF THE MORSE OSCILLATOR

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Analytical solutions for the Morse oscillator are used to evaluate $\langle V \rangle_n$ and $\langle T \rangle_n$. For all bound states $\langle V \rangle_n = \frac{\hbar \omega_c}{2} \left( n + \frac{1}{2} \right)$. This result is identical to the result that is obtained for the harmonic oscillator with the same quadratic force constant. Consequently, all of the anharmonicity in the energy of the quantum states of a Morse oscillator is incorporated in $\langle T \rangle_n$. This finding is tested for realistic diatomic potential functions for Ar-Xe, Be$_2$ and the $E-$state of Li$_2$. Analysis of $\langle V \rangle_n/\left( n + \frac{1}{2} \right)$ for these systems shows that this quantity is well approximated by $\omega_c/2$ over large ranges of $n$. Implications of this result to polyatomic systems and for vibration to translation collisional energy transfer are discussed.\textsuperscript{a}

VIBRATIONAL DYNAMICS AROUND THE CONICAL INTERSECTION RESULTING FROM THE \( ^\ddagger \text{TJ05} \rightarrow \text{TJ05} \) TRANSITION

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While model Hamiltonian approaches have provided considerable qualitative understanding regarding the nature of vibronic coupling and, especially, its effect on the electronic spectra of the nitrate radical, the parametrizations heretofore applied have been rather simplistic. As a result, while patterns of energy levels and appearance of “forbidden” spectral features are satisfactorily reproduced, the absolute position of the levels has not been calculated accurately enough to allow meaningful comparisons with those based on experimental assignments. In recent years, the machinery has been developed and applied to rather routinely make quite accurate calculations of level positions in strongly coupled systems (to, say, 20 cm\(^{-1}\) per quantum of excitation). Such calculations, which have been carried out for systems such as BNB, the formyloxyl radical (HCO\(_2\)) and low-lying excited electronic states of propadienylidene (H\(_2\)C=C=C\(_3\)), have now been completed for NO\(_3\). The spectra obtained from the corresponding model Hamiltonian, which explicitly treat the coupling between the ground \( ^\ddagger \text{A}_1 \) and \( ^\ddagger \text{B}_2 \) electronic states, and use a fairly elaborate parametrization of the corresponding diabatic surfaces, are presented and discussed.

EFFECT OF JAHN-TELLER AND SPIN-ORBIT COUPLING ON \( \tilde{X}^2 \text{E} \) INFRARED SPECTRUM OF \( \text{CH}_3\text{O} \)

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The \( \tilde{X} \) state is doubly degenerate for the \( \text{CH}_3\text{O} \) radical in its highest symmetry, for geometries belonging to \( C_{3v} \) point group. The symmetry is lowered and the degeneracy removed by displacements along asymmetric modes of vibration due to Jahn-Teller coupling between electronic and vibrational degrees of freedom. Spin-orbit coupling plays an important role as well, by removing degeneracy at high symmetry and partially quenching Jahn-Teller coupling at displaced geometries or lower symmetries. In this work, we examine the effect of Jahn-Teller and Spin-Orbit coupling on the infrared spectrum of the \( \tilde{X} \) surface. The selection rules combine symmetries of vibrational and electronic degrees of freedom and are less straightforward. We calculate a 9-D dipole moment surface for \( x, y \) and \( z \) components using \textit{ab initio} methods. The components of the vibronic dipole moment operator, obey transformation properties belonging to different symmetry species of the \( C_{3v} \) point group and we use group-theoretical arguments to impose constraints on the allowed terms in its functional form, similar to that used in construction of the vibronic Hamiltonian [1]. We construct the dipole moment surface solely using geometries of \( C_{s} \) symmetry in a diabatic vibronic representation, using the two electronic states as diabatic basis. We fit only the \( x \) and \( z \) components for the two diabatic states and derive the rest of the dipole operator based on constraints imposed by three-fold symmetry. The merits and limitations of such an approach will be discussed. The vibronic states are calculated using a 9-D quartic force field as described in [1], where both Jahn-Teller and spin-orbit coupling are included. The Davidson and Lanczos iterative methods are used to calculate the transitions between the ground vibronic to the higher levels in the infrared spectrum and the calculated transitions are compared to experimental data.


VIBRATIONAL DYNAMICS AROUND THE CONICAL INTERSECTION RESULTING FROM THE \( \tilde{A} \rightarrow \tilde{X} \) LASER INDUCED FLUORESCENCE OF THE METHOXY (\( \text{CH}_3\text{O} \)) RADICAL

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

The results of a theoretical calculation of the spectra associated with the laser induced fluorescence \( \tilde{A}^2 \text{A}_1 \rightarrow \tilde{X}^2 \text{E} \) of both the methoxy molecule and \( \text{CH}_3\text{O} \) are presented and discussed. The form of the vibronic dipole moment is determined by symmetry and the corresponding dipole expansion coefficients are calculated using \textit{ab initio} methods. The calculated spectra include states up to 3000 cm\(^{-1}\) above the zero point energy. We describe how the various features of the spectrum are related to coordinate dependent terms in the dipole expansion as well as the spin-orbit couplings, Jahn-Teller couplings, and vibrational anharmonicities.
BREAKING THE SYMMETRY IN JAHN-TELLER ACTIVE MOLECULES BY ASYMMETRIC ISOTOPIIC SUBSTITUTION: SPLITTING THE ZERO-POINT VIBRONIC LEVEL.

DMITRY G. MELNIK, JINJUN LIU, TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210; ROBERT F. CURL, Department of Chemistry and Rice Quantum Institute, Rice University, Houston, Texas 77005.

Analysis and understanding of the vibronic spectra of Jahn-Teller active molecules have been challenging tasks due to the complex interaction patterns between vibronic levels even if the density of vibronic states is not too high. An example of a spectral feature that draws attention is the splitting of the ground vibronic level, as reported for degenerate electronic states of asymmetrically deuterated C$_6$H$_6$, C$_5$H$_5$, CH$_4$, and most recently, the methoxy isotopologues, CH$_2$DO and CHD$_2$O. Understanding such splittings plays a crucial role for the analysis of the vibronic spectra of these species. We have developed a simplified model emulating vibronic interactions involving a single doubly-degenerate vibrational mode and one totally symmetric mode in a degenerate electronic state. The extension of this model to more complex, realistic cases and comparison with experiment and quantum chemical calculations will also be presented.

AN ALGEBRAIC METHOD FOR EXPLORING QUANTUM MONODROMY AND QUANTUM PHASE TRANSITIONS IN NON-RIGID MOLECULES

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A simple algebraic Hamiltonian has been used to explore the vibrational and rotational spectra of the skeletal bending modes of HCNO, BrCNO, NCNCS, and other “floppy” (quasi-linear or quasi-bent) molecules. These molecules have large-amplitude, low-energy bending modes and champagne-bottle potential surfaces, making them good candidates for observing quantum phase transitions (QPT). We describe the geometric phase transitions from bent to linear in these and other non-rigid molecules, quantitatively analysing the spectroscopy signatures of ground state QPT, excited state QPT, and quantum monodromy. The algebraic framework is ideal for this work because of its small calculational effort yet robust results. Although these methods have historically found success with tri- and four-atomic molecules, we now address five-atomic and simple branched molecules such as CH$_3$NCO and GeH$_3$NCO. Extraction of potential functions is completed for several molecules, resulting in predictions of barriers to linearity and equilibrium bond angles.
Recent years have seen increasing interest in the structure and dynamics of molecular clusters formed when a chromophore molecule such as CO₂, OCS or N₂O is solvated by number of He atoms and/or para-H₂ molecules. A key experimental probe of their behaviour is the shift of a chromophore’s vibrational transition frequency which occurs when the solvent species are attached to it. Such shifts are driven by the changes in the solvent-chromophore interaction potential upon vibrational excitation of the probe molecule. While ‘conventional’ supermolecule calculations can often provide realistic predictions of such changes in the potential well and repulsive wall region, they become increasingly unreliable for describing the weak interactions at long range where most of the solvent species in a large cluster are located. It is therefore important to have accurate relative-orientation and monomer-stretching dependent long-range $C_6$, $C_8$ and $C_{10}$ dispersion coefficients to incorporate into the models for the interaction potential and for its dependence on the chromophore’s vibrational state. This paper describes how those coefficients can be obtained from calculated monomer dipole, quadrupole, and octupole polarizabilities for imaginary frequencies, and by making use of the Casimir-Polder relation and angular momentum coupling to extract orientation-dependent quantities. The calculations are performed using a modified version of the ACES2 program system which allows the calculation of dipole, quadrupole and octupole polarizabilities at the EOM-CCSD level, and of static multipole moments using CCSD(T) calculations and adequate basis sets. For each relevant level of the chromophore, vibrational averaging is performed by calculating the imaginary frequency polarizabilities at judiciously chosen geometries and performing a numerical integration using the free-molecule vibrational wavefunction. Subsequent work will involve merging this long-range part of the potential with a short-range part obtained from ‘conventional’ CCSD(T) calculations and using it in PIMC simulations of cluster behaviour.

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Intermission
Spectral characterization of astrophysical objects cool enough to form molecules in their atmospheres (cool stars, extrasolar planets and planetary discs) requires considerable amount of fundamental molecular data. The existing molecular line lists (with some exceptions) are however not sufficiently accurate and complete. We present a new (five years) European Union project ExoMol aimed at bridging this gap: ExoMol will generate comprehensive line lists for all molecules likely to be observable in exoplanet atmospheres in the foreseeable future. This is a huge undertaking which will mean providing in excess of \(10^{11}\) spectral lines for a large variety of molecular species.

The physics of molecular absorptions is complex and varies between different classes of absorbers. The project will therefore be divided into following topics (a) diatomic, (b) triatomics, (c) tetratomics, (d) methane and (e) larger molecules. Each of which will require special techniques will be required in each case. The majority of diatomic systems to be tackled are open shell species involving a transition metal atom; the opacity is provided by the transitions between the many low lying electronic states of the system. The calculation of rotation-vibration line lists for closed-shell triatomic systems is now relatively straightforward provided enough care is taken in deriving the potential energy surface. For \(\text{H}_2\text{S}\) calculations are in progress: the unusual properties of the dipole moment will also require careful treatment. Accurate rotation-vibration line lists for hot tetratomic molecules such as ammonia, acetylene, hydrogen peroxide and formaldehyde, are at the very limit of what is computationally possible at present. These will be computed either by direct calculation of the full line list, such as our hot ammonia line list BYTe developed recently [S. N. Yurchenko, R. J. Barber, and J. Tennyson, Mon. Not. R. Astron. Soc., in press (2011)], or by use of high accuracy vibrational calculations onto which the rotational structure will be grafted using ideas developed from the standard perturbation theory approach to molecular spectroscopy. Tests for acetylene suggest that this latter approach, although intrinsically less accurate, is still able to give reliable results [A. Urru, I. N. Kozin, G. Mulas, B. J. Braams, and J. Tennyson, Mol. Phys., 108, 1973 (2010)]. Data from this project can be accessed at www.exomol.com.

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**Using Diffusion Monte Carlo to Probe the Rotationally Excited States of \(\text{H}_3^-\) and Its Isotopologues**

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\(\text{H}_3^-\) and \(\text{D}_n^+\) are among the most abundant polyatomic ions in the universe.\(^a\) Moreover, the deuterated isotopologues are thought to play a key role in the astrochemical reactions governing the H/D fractionation of “metallic” species in the interstellar medium.\(^b\) An accurate quantum mechanical treatment of these species, as well as any reactions involving them, requires a methodology capable of capturing their large fluxionality as well as the constraints, due to particle exchange symmetries, on their physically allowed rovibrational states. Diffusion Monte Carlo (DMC) has been shown to be a highly successful technique for treating quantum zero-point effects of very floppy molecules and clusters and our group has recently developed a fixed-node DMC methodology capable of including the effects of rotational excitation.\(^c\) Here, we report the results of DMC calculations of the rotationally excited states of \(\text{H}_3^+\) and its isotopologues. In particular, comparison with converged variational calculations involving states with \(J \leq 20\) provides the most thorough test yet of the range of quantum states over which the assumptions underlying our rotationally excited state DMC methodology can be reliably applied. Finally, the implications of this work on our overall goal of using DMC based methodologies to map out the energetics of the reaction of \(\text{H}_3^-\)\(\text{D}_n^+\) with HD will be discussed.

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\(^a\)T. R. Geballe and T. Oka, Science 312, 1610 (2006)
COMPUTATIONAL HIGH-FREQUENCY OVERTONE SPECTRA OF THE WATER AMMONIA COMPLEX

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(email to elina.salli@helsinki.fi).

We have computed vibrational high-frequency overtone spectra of the water ammonia complex, $\text{H}_2\text{O} - \text{NH}_3$, and its isotopomers. The cluster has been modelled as two independently vibrating monomer units. Our internal coordinate Hamiltonians for each monomer unit have been constructed using exact gas phase kinetic energy operators. The potential energy and dipole moment surfaces have been calculated with the explicitly correlated coupled cluster method CCSD(T)-F12A and valence triple zeta VTZ-F12 basis around the equilibrium geometry of the complex. The vibrational eigenvalues are calculated variationally. The eigenfunctions obtained are used to compute the relative absorption intensities.

In $\text{H}_2\text{O} - \text{NH}_3$, water molecule acts as the proton donor and its symmetry is broken. The hydrogen bonded $\text{OH}_b$ bond oscillator undergoes a large redshift and intensity enhancement compared to the free hydrogen bond. Broken degeneracy of the asymmetric vibrations, quenched inversion splittings, and blueshift of the symmetric bend are the most visible changes in the ammonia unit.

Our vibrational model is anharmonic. Therefore, we have been able to calculate not only high-frequency fundamentals but also overtones and combination levels that for this complex have not been detected experimentally. The calculated fundamentals agree well with matrix isolation and helium droplet measurements except for the bonded $\text{OH}_b$ stretching of the water unit where our model overestimates the clustering induced shift. The same has previously been seen in the bonded $\text{OH}_b$ stretch of the water dimer and is probably due to the couplings with the low-frequency modes.


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We have studied the vibrational O–H stretching and H–O–H angle bending spectrum of the water trimer computationally around the cyclic minimum energy structure. We obtain the energies and intensities of the fundamental and overtone transitions. Earlier we have modeled the water trimer as three individually vibrating monomer units. In this work we have improved our previous model by including the potential energy coupling between the three hydrogen bonded O–H stretching modes. An internal coordinate Hamiltonian is constructed for each water unit using a kinetic energy operator, which is exact within the Born-Oppenheimer approximation for a triatomic molecule. The potential energy coupling terms between the hydrogen bonded O–H stretching modes are added in the model. The O–H distances and the H–O–H bending angles are used as the vibrational coordinates. The potential energy grid is calculated using the finite differences method. The dipole moment surface is calculated using the finite differences method. The vibrational problem has been solved with the variational method with a harmonic oscillator basis for all the vibrational coordinates. We calculate the transition intensities using the wavefunctions obtained from the variational calculation.
COLLISION INDUCED VELOCITY CHANGES FROM MOLECULAR DYNAMIC SIMULATIONS. APPLICATION TO THE SPECTRAL SHAPE OF THE Q(1) RAMAN LINES OF H$_2$/H$_2^*$

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Collision induced velocity changes for pure H$_2$ have been computed from classical dynamic simulations. The results have been compared with the Keilson-Storer\(^a\) model from four different points of view. The first involves various autocorrelation functions associated with the velocity. The second and third give more detailed information, and are time evolutions of some conditional probabilities for changes of the velocity modulus and orientation and the collision kernels themselves. The fourth considers the evolutions, with density, of the half widths of the Q(1) lines of the isotropic Raman (1-0) fundamental band and of the (2-0) overtone quadrupole band. These spectroscopic data enable an indirect test of the models since velocity changes translate into line-shape modifications through the speed dependence of collisional parameters and the Dicke narrowing of the Doppler contribution to the profile. The results indicate that, while the KS approach gives a poor description of detailed velocity-to-velocity changes, it leads to accurate results for the correlation functions and spectral shapes, quantities related to large averages over the velocity. It is also shown that the use of collision kernels directly derived from MDS lead to an almost perfect prediction of all considered quantities (correlation functions, conditional probabilities, and spectral shapes). Finally, the results stress the need for very accurate calculations of line-broadening and -shifting coefficients from the intermolecular potential to obviate the need for experimental data and permit fully meaningful tests of the models.


EFFECTIVE POTENTIAL APPROACH TO THE SIMULATION OF LARGE PARA-HYDROGEN CLUSTERS AND DROPLETS

**Jing Yang** and **Pierre-Nicholas Roy**, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

The quantum simulation of large molecular system is a formidable task. We explore the use of effective potentials based on the Feynman path centroid variable in order to simulate large quantum clusters at a reduced computational cost. This centroid can be viewed as the “most classical” variable of a quantum system. Earlier work has shown that one can use a pairwise centroid pseudo-potential to simulate the quantum dynamics of hydrogen in the bulk phase at 25 K and 14 K.\(^a\) Bulk hydrogen, however, freezes below 14 K and we rather focus on nanodroplets in the very low temperature regime in order to study the superfluid behaviour of hydrogen. The calculation of the effective potential will be discussed along with its use in the context of molecular dynamics simulations. Centroid structural properties will be presented and compared to the results of path integral Monte Carlo simulations. We will present an approach for de-convoluting centroid structural properties in order to obtain real space results for hydrogen clusters of a wide range of sizes. The extension of the approach to the treatment of confined hydrogen will be discussed.


SIMULATION STUDIES OF THE VIBRATIONAL DYNAMICS OF para-HYDROGEN CLUSTERS


This paper discusses the construction and application of reduced-dimensional potential energy surfaces for use in performing simulation of para-hydrogen clusters. Simple spherical averaging and ‘adiabatic-hindered-rotor’ averaging\(^a\) treatments of the angular degrees of freedom are considered and compared. The resulting one-dimensional surface is used in quantum Monte Carlo simulations of para-hydrogen clusters of varying sizes. Energetic, and structural properties are computed and compared to previously published results, and vibrational frequency shifts are predicted and compared to available experimental measurements.

MIXED CLUSTERS OF H\textsubscript{2} AND H\textsubscript{2}O: INSIGHTS FROM THEORY AND SIMULATIONS

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Water-hydrogen clusters are of considerable interest for both fundamental and practical reasons; in particular, a better understanding of their nature has implications in astrophysics and in the field of hydrogen storage. The present research investigates the quantum dynamics of water-hydrogen clusters based on a new interaction potential, exact bound-state calculations, and Feynman Path Integral simulations. We first discuss the development of a reduced-dimension effective potential for the water-hydrogen interaction. The quality of this potential is assessed by comparing the results of exact dimer and trimer bound-state calculations performed using the full-dimension and reduced-dimension surfaces both with each other and with experimental rovibrational spectra. We then perform Path Integral Monte Carlo and Path Integral Molecular Dynamics simulations of larger clusters using this newly developed effective potential, focusing on the quantum delocalization effects of para-hydrogen and its superfluidity in the presence of water as the size of the hydrogen clusters grow. Spectroscopic observables will be computed and compared to available experiments. This work is a prelude to an exploration of the possible impact of these quantum effects on the behaviour of nano-scale water clathrates.
WA. PLENARY

WEDNESDAY, JUNE 22, 2011 – 8:30 am
Room: AUDITORIUM, INDEPENDENCE HALL

[Box: Chair: MALCOLM CHISHOLM, The Ohio State University, Columbus, Ohio]

WA01  40 min  8:30
THE ATMOSPHERIC CHEMISTRY EXPERIMENT, ACE: LATEST RESULTS

P. F. BERNATH, Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK.

ACE (also known as SCISAT) is making a comprehensive set of simultaneous measurements of numerous trace gases, thin clouds, aerosols and temperature by solar occultation from a satellite in low earth orbit. A high inclination low earth orbit gives ACE coverage of tropical, mid-latitudes and polar regions. The primary instrument is a high-resolution (0.02 cm$^{-1}$) infrared Fourier Transform Spectrometer (FTS) operating from 750–4400 cm$^{-1}$ that measures the vertical distribution of trace gases, and the meteorological variables of temperature and pressure. Aerosols and clouds are being monitored using the extinction of solar radiation by two filtered imagers as well as by their infrared spectra. Although now in its eighth year, the ACE-FTS is still operating nominally. An short introduction and overview of the ACE mission will be presented (see http://www.ace.uwaterloo.ca for more information and reprints of published papers). Science results discussed will include the observation of organic molecules associated with air pollution, greenhouse gases (including CO$_2$) and aerosols. ACE retrievals are dependent on line parameters and absorption cross sections measured in the laboratory; the talk will highlight the spectroscopic aspects of the ACE mission including the need for non-Voigt lineshape functions.

WA02  40 min  9:15
CHASING NONEXISTENT COMPOUNDS WITH LASERS: ELECTRONIC SPECTROSCOPY OF MAIN GROUP TRANSIENT MOLECULES, FREE RADICALS, AND IONS

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One of the important contributions of the science of high resolution molecular spectroscopy has been the identification and characterization of new molecules in the gas phase, whether they exist in the laboratory, in extreme terrestrial environments, or in outer space. Despite the innovative efforts of many dedicated spectroscopists, one can still easily visualize a large number of novel small molecules that remain to be discovered and investigated. In this talk I will review the efforts of our group in recent years to study the electronic spectra of some new, and some not so new but still challenging species, concentrating primarily on those that are made up of main group elements. The target molecules have been produced in a pulsed electric discharge at the exit of a supersonic jet, often using novel precursors which we have had to synthesize in the laboratory. Conventional laser-induced fluorescence as well as wavelength resolved emission, stimulated emission pumping, fluorescence depletion and LIF sync-scan techniques have been used to detect the species of interest. Examples of diatomic and polyatomic transient molecules, free radicals, and ions that we have recently explored will be discussed.

Intermission
WA03 40 min 10:20

WATCHING CONFORMATIONS OF BIOMOLECULES: A MICROWAVE SPECTROSCOPY APPROACH


The combination of laser ablation with Fourier transform microwave spectroscopy in supersonic jets (LA-MB-FTMW) has made possible the gas-phase study of solid biomolecules with high melting points. In the experiment, solids are efficiently vaporized by a high-energy laser pulse, supersonically expanded into a evacuated Fabry-Perot cavity and characterised by their rotational spectra. Recent improvements such as the use of picosecond pulse lasers, new ablation nozzles and the extension of the range of the spectrometers to low frequency have notably increased the sensitivity of our experimental setup. To date different α-, β- and γ-amino acids have been studied using this technique, making possible the characterization of their preferred conformations and gaining insight in the role of intramolecular interactions. Even in conformationally challenging systems the different rotamers of such biomolecules can be identified by rotational spectroscopy as can be illustrated by the assignment of six low-energy conformers in cysteine and aspartic acid, seven in serine and threonine, and nine in γ-amino butyric acid (GABA). In all cases the low-energy conformers have been conclusive identified from their experimental rotational and 14N quadrupole coupling constants. The spectra of neurotransmitters and of the nucleic acid bases uracil, thymine, cytosine and guanine have also been studied and their preferred conformers or tautomeric forms determined. The complexes between amino acids and nucleic acid bases with water have also been investigated to obtain information on the possible changes induced in the conformational or tautomeric preferences by the addition of solvent molecules.

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WA04 40 min 11:05

POLAR MOLECULES IN THE QUANTUM REGIME

DEBORAH S. JIN, JUN YE, JILA, NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY AND UNIVERSITY OF COLORADO, BOULDER, CO 80309-0440, USA.

Quantum gas of ground-state polar molecules opens the door to a wide range of scientific explorations. Novel molecular interactions, chemical reactions in the quantum regime, exotic quantum phase transitions, and strongly correlated states of matter are among a few prominent examples to be studied. We present recent experimental progresses at JILA, including the production of a high phase-space density gas of polar molecules in the absolute rovibrational ground state, coherent manipulation of the nuclear spin state, and the observation of barrier-less chemical reactions at ultralow temperatures. We control the reaction rate with the quantum mechanical wave functions of the molecules. Long-range and anisotropic dipolar interactions are observed in the thermodynamics of the molecular gas and we control inelastic and elastic collision rates by varying the molecular dipole moment in the laboratory frame and by confining molecules in two-dimensional optical traps.
WF01  15 min  1:30
INTERSTELLAR NITRILE CHEMISTRY AS REVEALED BY CHIRPED-PULSE FTMW SPECTROSCOPY

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Nitriles make up a significant fraction of the known interstellar species, in part because their large dipole moments allow for easier detection. The presence of several nitriles in rich interstellar sources makes them a class of molecules that can be used to test proposals for molecule formation in the interstellar medium. We have performed a screening of the laboratory nitrile chemistry produced in a pulsed discharge source using the high abundance interstellar species CH$_3$CN and H$_2$S. The reaction products are identified by broadband rotational spectroscopy in a chirped-pulse FTMW spectrometer. We compare laboratory yields with column densities in Sagittarius B2(N) for several nitriles. We also describe the common lineshapes. So far 25 discharge-induced species, of which 18 are known interstellar molecules, have been identified in the laboratory spectrum. Because the column densities found in the GBT PRIMOS survey of Sgr B2(N) are similar to what is seen in laboratory relative population analysis, it seems to suggest the conditions created by the discharge nozzle may be similar to those found in the interstellar medium. Radicals of CH$_3$CN and H$_2$S are produced in high abundances and can explain many of the observed product species. These comparisons suggest that radical chemistry may dominate nitrile formation in some interstellar sources.

WF02  15 min  1:47
3-D SUBMILLIMETER SPECTROSCOPY OF ASTROPHYSICAL ‘WEEDS’ – CONTINUED ANALYSIS

SARAH M. FORTMAN, IVAN R. MEDVEDEV, CHRISTOPHER F. NEESE, and FRANK C. DE LUCIA, Department of Physics, 191 W. Woodruff Ave., The Ohio State University, Columbus, OH 43210-1106 USA.

In this presentation we report on the latest enhancements of the temperature resolved 3-dimensional spectroscopic technique and the recent results obtained. We have continued the analysis in the 210-270 GHz and 560-650 GHz spectral regions of the astrophysical weeds CH$_3$OH, CH$_3$CN, CH$_3$CHO, CH$_3$OCH$_3$, C$_2$H$_5$CN, C$_2$H$_7$CN, CH$_3$OCHO and SO$_2$. Our analysis includes a detailed comparison of the intensities of the quantum mechanical assignments and the experimental intensities to determine the completeness of each molecule as a function of temperature.
PERFORMANCE OF THE NEW 0.4 mm RECEIVER (602-720 GHz) AT THE SUB-MILLIMETER TELESCOPE OF THE ARIZONA RADIO OBSERVATORY


A new 0.4 mm receiver has been commissioned for general use at the Sub-millimeter Telescope (SMT) of the Arizona Radio Observatory (ARO) on Mt. Graham, Arizona. The receiver architecture is dual linear polarization with 4 GHz of instantaneous IF bandwidth from 4-8 GHz and a frequency range of 602-720 GHz. The elemental mixers are double sideband (DSB) SIS junctions provided by the Space Research Organization of the Netherlands (SRON). These are the same devices used for Band 9 of the Atacama Large Millimeter Array (ALMA). Receiver equivalent noise temperatures range from 75 to 90 K (DSB) and the system temperatures are typically around 2,000 K with water vapor levels in the atmosphere less than or equal to about 2 mm. Main beam efficiencies at 690 GHz using Jupiter and Saturn as sources have been found to be 61 and 52 percent respectively. The performance of the SMT and receiver system at this wavelength, in terms of pointing, baseline stability, and beam shape, is excellent. Observations during the 2011 season have resulted in the detection of the CO (6-5) transition at 691 GHz in a young planetary nebula, NGC 6537 (Red Spider Nebula), with an intensity of 650 mK. The HCN (8-7) transition at 708 GHz was also observed towards R Leonis and in NML Cygnus, both with line intensities of about 100 mK.

HIGHLY ACCURATE QUARTIC FORCE FIELDS, VIBRATIONAL FREQUENCIES, AND SPECTROSCOPIC CONSTANTS FOR CYCLIC AND LINEAR C₃H₃⁺ INCLUDING ¹³C AND DEUTERIUM ISOTOPOLOGUES

TIMOTHY J. LEE, MS 245-1, NASA Ames Research Center, Moffett Field, CA, 94035; XINCHUAN HUANG, SETI Institute, 189 Bernardo Ave, Suite 100, Mountain View, CA, 94043; and PETER R. TAYLOR, Victorian Life Sciences Computation Initiative and Department of Chemistry, University of Melbourne, Vic 3010, Australia.

High levels of theory have been used to compute quartic force fields (QFFs) for the cyclic and linear forms of the C₃H₃⁺ molecular cation, referred to as c-C₃H₃⁺ and l-C₃H₃⁺. Specifically the singles and doubles coupled-cluster method that includes a perturbational estimate of connected triple excitations, CCSD(T), has been used in conjunction with extrapolation to the one-particle basis set limit and corrections for scalar relativity and core correlation have been included. The QFFs have been used to compute highly accurate fundamental vibrational frequencies and other spectroscopic constants using both 2nd-order perturbation theory and exact variational methods to solve the nuclear Schrödinger equation. Agreement between our best computed fundamental vibrational frequencies and recent infrared photodissociation experiments is reasonable for most bands, but there are a few exceptions. Possible sources for the discrepancies are discussed. Fundamental vibrational frequencies and spectroscopic constants for ¹³C and deuterium isotopologues will also be presented. It is expected that the fundamental vibrational frequencies and spectroscopic constants presented here for c-C₃H₃⁺ and l-C₃H₃⁺ are the most reliable available for the free gas-phase species. It is hoped that these will be useful in the assignment of future high-resolution laboratory experiments or astronomical observations.
A SEARCH FOR HYDROXYLAMINE (NH$_2$OH) TOWARDS IRC+10216, ORION-S, ORION(KL), SGRB2(N), SGRB2(OH), W51M AND W3(IRS5)

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Over 50 molecular species containing nitrogen have been detected in the gas phase towards various astronomical environments. A number of chemical models have tried to reproduce the observed abundances of N-bearing species in the various environments of the ISM and CSM with limited success. Recently, there has been an interest in hydroxylamine (NH$_2$OH) because of its possible role in the formation of amino acids in space.

a, b Implications of amino acid formation in space and detections of possible precursor species would have a profound impact on our pursuit of understanding the prebiotic molecular origins of life. However, hydroxylamine has yet to be detected in the gas phase in the interstellar medium. A recent gas-grain model by Garrod et al. (2008) suggests that NH$_2$OH is formed through radical recombination on grain surfaces and predicts an abundance ratio range of NH$_2$OH/H$_2$ between $1.2 \times 10^{-6}$ - $3.5 \times 10^{-7}$; thus, suggesting that NH$_2$OH should be within the detectable limits of existing radio receivers. Here we present the search for hydroxylamine towards seven different sources: IRC+10216, Orion-S, Orion(KL), SgrB2(N), SgrB2(OH), W51M, and W3(IRS5) at 2mm wavelengths using archival data from the NRAO 12m telescope. Hydroxylamine is not confirmed toward any region and upper limits to the total column density were determined for each source. The implications of these upper limits of NH$_2$OH to both the gas phase and grain surface models will also be discussed.

\cite{VBlagojevic2003}
\cite{JLSnow2007}
\cite{RTGarrod2008}
\cite{AJRemijan2008}
\cite{BarryETurner2008}


A SEARCH FOR INTERSTELLAR CARBON-CHAIN ALCOHOL HC$_4$OH IN THE STAR FORMING REGION L1527

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We have made a sensitive search for the rotational transitions of carbon-chain alcohol HC$_4$OH with the frequency range from 21.2 to 46.7 GHz in the star forming region L1527 in Taurus with rich carbon-chain chemistry. The incentive of this observation was a laboratory detection of HC$_4$OH by the microwave spectroscopy. Despite achieving an rms of several mK in antenna temperature by the 45m telescope at Nobeyama Radio Observatory, the search for HC$_4$OH was negative, leading to a 5 sigma upper limit corresponding to the column density of $4 \times 10^{12}$ cm$^{-2}$ based on the excitation temperature of 12.3 K. The upper limit indicates that the [HC$_3$OH]/[HC$_4$-CN] ratio is less than 1.0. The ratio suggests that the cyanide species with carbon-chain structure is dominant in comparison with the hydroxyl one in L1527, which can be the opposite case of saturated compounds, e.g. CH$_3$OH and CH$_3$CN, in hot cores and dark clouds.

\cite{MitsunoriAraki2018}


LABORATORY SUBMILLIMETER SPECTROSCOPY AS A PROBE OF METHANOL PHOTODISSOCIATION

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Radical-radical addition reactions on the ice surfaces of interstellar grains lead to the formation of many complex organic molecules in the interstellar medium. Methanol photodissociation is the dominant source of the three organic radicals CH$_3$O, CH$_2$OH, and CH$_3$. Recent chemical models show that changes to the methanol photodissociation branching ratios directly impact the relative abundances of many complex organics, most notably methyl formate and its structural isomers glycolaldehyde and acetic acid. Neither the condensed-phase nor the gas-phase methanol photodissociation branching ratios required for these models have been quantified in the laboratory. Interpretation of the results from condensed-phase measurements rely upon the use of complicated chemical networks that offer only a limited view of the chemistry and often lead to difficulty in obtaining more than semi-quantitative results. However, gas-phase measurements enable independent, quantitative monitoring of each dissociation channel. We are therefore studying the methanol photodissociation mechanism using submillimeter spectroscopy to directly detect the gas-phase photodissociation products. Here we will present our progress toward the quantification of the gas-phase methanol photodissociation branching ratios, and will discuss these results in the context of interstellar organic chemistry.

NEW ACETYLENE $^{12}$C$_2$H$_2$ MEASUREMENTS USING SOLEIL SYNCHROTRON

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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.

A recent study using SOLEIL synchrotron AILES beamline will be presented in the spectral region around 100 cm$^{-1}$. This work is the continuation of a previous one (D. Jacquemart, L. Gomez, N. Lacome, J.-Y. Mandin, O. Pirali and P. Roy. JQSRT 2010:111;1223-33) for which absolute line intensities of the intense $\nu_5-\nu_4$ band have been measured. In the present work a White-type cell has been used to reach an absorption path of 150 meters. With such an absorption path, several weaker bands have been observed and studied in term of absolute line intensities. Analysis of high resolution spectra using the FIR beam AILES of the synchrotron required a special care to the modelization of the apparatus function. The knowledge of the optical weighting of the apparatus function is crucial to measure accurate line parameters especially when using a synchrotron beam.
The rotational spectrum of $n$-butyl cyanide ($C_4H_9CN$) was measured between 75 and 130 GHz using a novel all-solid-state spectrometer with a total absorption path of 44 m. In the course of the analysis of the spectrum, about 3000 transitions were assigned and a full set of quartic centrifugal distortion parameters with some sextic and octic terms could be determined for each of the three known conformers (anti-anti, anti-gauche(methyl end) and gauche(CN end)-anti). The work was motivated by the fact that $n$-butyl cyanide is likely to be found in interstellar hot core environments. This is indicated by the discovery of $n$-propyl cyanide ($C_3H_7CN$), the next smaller alkyl cyanide, in the ISM. The increased accuracy of the model, which will be additionally extended by future laboratory measurements around 200 GHz, may now be employed for a prediction of the spectrum up to 300 GHz with a feasible uncertainty for astronomic line surveys. Furthermore, there are two less abundant conformers, cis-gauche-gauche and trans-gauche-gauche, which have not yet been detected in the rotational spectrum. Due to the increased sensitivity of the new spectrometer, it seems possible now for the first time to identify their spectroscopic fingerprints in the recorded data.

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The linear carbon chain radicals have been topic of a series of spectroscopic studies. The hexatriynyl radical $C_6H$ (and deuterated equivalent $C_6D$), a member of the linear $C_nH$ series, has attracted renewed interest in recent years after the astronomical identification of its chemically related anion $C_6H^-$. Precise spectroscopic parameters for the $11_{11} \mu^2 \Sigma$ levels of both $C_6H$ and $C_6D$ are determined for the first time, and the spectroscopic parameters for the $B^2 \Pi$ $0^0_{00}$ states are also improved. The Renner-Teller interaction is also discussed to estimate the excitation energies of the low-lying $11_{11} \mu^2 \Sigma$ vibronic states.

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Intermission
PROSPECTIVE WORK FOR ALMA: THE MILLIMETERWAVE AND SUBMILLIMETERWAVE SPECTRUM OF DEUTERATED GLYCOLALDEHYDE

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Glycoaldehyde, a sugar-related interstellar prebiotic molecule has been detected in two star-forming regions, Sgr B2(N)b,c and G31.41+0.31b,d. The detection of this new species increases the list of Complex Organic Molecules detected in the ISM and adds a further level to the chemical complexity present in space. For many years, astronomers have been struggling to understand the origin of such high chemical complexity in the ISM. The study of deuteration may provide crucial hints.

In this context, we have measured in the laboratory the spectra of the deuterated isotopologues of glycoaldehyde: CH$_2$OD-CHO, CHDOH-CHO, CH$_2$OH-CDO and CHDOH-CDO. Previous laboratory work on the D-isotopologues was restricted to less than 26 GHzf. New spectra between 150 and 630 GHz were measured in Lille with a solid-state submillimetre-wave spectrometer.

This work is supported by the contract ANR-08-BLAN-0225 and by the Programme National de Physico-Chimie du Milieu Interstellaire (PCMI-CNRS).

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THE MICROWAVE SPECTRUM OF PARTIALLY DEUTERATED SPECIES OF DIMETHYL ETHER

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Dimethyl ether is a molecule of astrophysical interest spectroscopically well characterized. It is one of the simplest molecules with two methyl groups undergoing large amplitude internal rotations. Due to deuterium enrichment in the interstellar medium, one can reasonably expect that partially deuterated species of dimethyl ether might be detected. However, there are no spectroscopic results about the microwave spectrum of such species. A theoretical calculation of the rotation-torsion energy levels of the partially deuterated species of dimethyl ether has been undertaken aided by ab initio calculations. The approach accounts for the complicated torsion-rotation interactions displayed by this molecule and for the fact that deuteration leads to changes of the bidimensional internal rotation effective potential energy surface. Due to zero-point energy contributions from the 19 small amplitude vibrational modes, this surface no longer displays $G_{36}$ symmetry. Rotation-torsion energy levels are computed treating the two angles of internal rotation as active coordinates and evaluating Hamiltonian matrix elements with the help of Gaussian quadrature.

It is hoped that the present results will allow us to understand the microwave spectrum of the mono deuterated species CH$_3$DOCH$_3$ which has been recorded in Lille with the new sub millimeter wave spectrometer (150–950 GHz) based on harmonic generation of solid-state sources.

aThis work is supported by ANR-08-BLAN-0054, ANR-08-BLAN-0225, and by the PCMI French program.
PROSPECTIVE WORK FOR ALMA: THE MILLIMETERWAVE AND SUBMILLIMETERWAVE SPECTRUM OF $^{13}$C-
GLYCOLALDEHYDE

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Glycolaldehyde has been identified in interstellar sources. The relative abundance ratios of the three isomers (acetic acid) : (glycolaldehyde) : (methylformate) were estimated. The detection of $^{13}$C$_1$ and $^{13}$C$_2$ isotopomers of methylformate has been recently reported in Orion, as a result of the detailed laboratory spectroscopic study. Therefore the spectroscopy of the $^{13}$C isotopomers of glycolaldehyde is investigated in laboratory in order to provide data for an astronomical search. The instrument ALMA will certainly be a good instrument to detect them. Up to now, only the microwave spectra of $^{13}$CH$_2$OH-CHO and of CH$_2$OH-$^{13}$CHO have been observed several years ago in the 12-40 GHz range.

Spectra of both species are presently recorded in Lille in the 150-950 GHz range with the new submillimetre-wave spectrometer based on harmonic generation of a microwave synthesizer source, using only solid-state devices, and coupled to a cell of 2.2 m length. The absolute accuracy of the line positions is better than 30 KHz. The rotational structure of the ground state and of the three first excited vibrational states has been observed. Two $^{13}$C enriched samples were used. The analysis is in progress.

This work is supported by the Programme National de Physico-Chimie du Milieu Interstellaire (PCMI-CNRS) and by the contract ANR-08-BLAN-0054.

EXPERIMENTAL ELECTRONIC SPECTROSCOPY OF TWO PAHs: NAPHTHALENE AND 2-METHYL NAPHTHALENE

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The presence of polycyclic aromatic hydrocarbons (PAHs) in the interstellar medium (ISM) was suggested in the mid-80s. Since then, their important role in the physico-chemical evolution of the ISM has been confirmed. Interstellar PAHs have been in particular proposed as possible carriers of some Diffuse Interstellar Bands (DIBs). These absorption bands are seen in the spectra of reddened stars from the visible to the near infrared and constitute a major astrophysical issue. Our purpose is to obtain electronic spectra of gas phase PAHs which will be used to probe their participation to the interstellar extinction curve from the visible (DIBs) to the UV (bump). For this goal PAH cations represent an excellent set of target species. A new way of forming PAH$^+\cdot$Ar$_n$ clusters cations has been implemented in the experimental set-up ‘ICARE’ at ISMO (Orsay) giving us the capability to measure the electronic spectra of cold PAH cations in the gas phase through the Ar tagging trick. Two molecules have been investigated in this way: naphthalene (C$_{10}$H$_8$) and 2- methyl naphthalene (C$_{11}$H$_{10}$). Clusters of naphthalene and (or 2-methyl-naphthalene) with Ar atoms are first formed in a supersonic jet, before being hit by a 281 nm laser beam which photo-ionizes the clusters which are then injected in a molecular beam through a skimmer. A tunable laser beam crossing downstream photo-dissociates the cations. The bare PAH fragments are detected using a Time-Of-Flight spectrometer while scanning the visible laser wavelength from 470 to 690 nm.
We present the first detailed analysis of the Tetradecad region of methane $^{12}CH_4$ from 2.1 to 1.6 μm (4800 to 6250 cm$^{-1}$)\textsuperscript{a}. New high resolution FTIR spectra measured in a collisional cooling cell at 80 K and at room temperature have allowed us to perform many new assignments. All assigned lines of $^{12}CH_4$ in the 0–6200 cm$^{-1}$ region have been included in a global fit, extending our previous analysis covering all levels up to and including the Octad (i.e. up to 4800 cm$^{-1}$\textsuperscript{b}). In the end, 3012 line positions and 1387 intensities of 45 individual subbands were modeled up to $J=14$. The root mean square deviations were 0.023 cm$^{-1}$ for line positions and 13.86 % for line intensities in the Tetradecad region itself. Although this study is still preliminary, it is already sufficient to characterize the stronger bands throughout the whole of the Tetradecad polyad. The analysis and present success substantially improves our understanding of the methane spectra needed to interpret planetary atmospheres.

\textsuperscript{a}This work is part of the ANR contract “CH$_4$Titan” (ref: BLAN08-2_321467). Part of the research described here was also carried out at the Jet Propulsion Laboratory, under a contract with the National Aeronautics and Space Administration. Our work is also supported by the Swiss National Science Foundation.

THE $4v_3$ SPECTRAL REGION OF METHANE

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The near infrared bands of methane were first observed in the outer planets and Titan where atmospheric ray paths are long. 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. The band models generally used in the 890 nm spectral region of methane do not provide transmissions that are multiplicative, so scattering and inhomogeneous atmospheres cannot be properly treated using this approach.

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.$^a$ Simulations of the methane spectrum for outer planet atmospheres using our positions, intensities and lower state energies reveal a surprising amount of spectral structure at high resolution. This structure carries a great deal of atmospheric information.$^b$


$^b$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. Partial Support for the work at Bridgewater College was provided from an AAS Small Research Grant.
APPROXIMATE THEORETICAL MODEL FOR THE FIVE ELECTRONIC STATES ($\Omega = 5/2, 3/2, 3/2, 1/2, 1/2$) ARISING FROM THE GROUND $3d^9$ CONFIGURATION IN NICKEL HALIDE MOLECULES AND FOR ROTATIONAL LEVELS OF THE TWO $\Omega = 1/2$ STATES IN THAT MANIFOLD

JON T. HOUGEN, Optical Technology Division, NIST, Gaithersburg, MD 20899-8441, USA.

An effective Hamiltonian for a non-rotating diatomic molecule containing only crystal-field and spin-orbit operators has been set up to describe the energies of the five spin-orbit components that arise in the ground electronic configuration of the nickel monohalides. The model assumes that bonding in the nickel halides has the approximate form Ni$^+$X$^-$, with an electronic $3d^9$ configuration plus closed shells on the Ni$^+$ moiety and a closed shell configuration on the X$^-$ moiety. Least-squares fits of the observed five spin-orbit components of the three lowest electronic states in NiF and NiCl are then carried out in terms of the three crystal field parameters $C_0, C_2, C_4$ and the spin-orbit coupling constant $A$. Following this, the usual effective Hamiltonian $B(J-L-S)^2$ for a rotating diatomic molecule is used to derive expressions for the unusually large $\Omega$-type doubling parameter $p$ in the two $\Omega = 1/2$ states in the $3d^9$ manifold. These expressions show (for certain sign conventions) that the sum of the two $p$ values should be $-2B$, but that their difference can vary between $-10B$ and $+10B$. The theoretical magnitudes for $p$ are in good agreement with the two observed $p$ values for both NiF and NiCl, but the signs are not. The experimental signs can be brought into agreement with the theoretical signs by a fairly massive change in +/- parity assignments in the NiF and NiCl literature. The last part of the talk will focus on the theoretical and experimental implications of these parity changes.

OBSERVATION OF $\Omega = 1/2$ STATES IN NiH THROUGH COLLISIONALLY INDUCED FLUORESCENCE

C. RICHARD, P. CROZET, A. J. ROSS, Université Lyon 1; CNRS; LASIM UMR 5579, 43 Bd du 11 novembre 1918, F-69622 Villeurbanne, France; D. W. TOKARYK, Department of Physics and Center for Laser, Atomic, and Molecular Sciences, University of New Brunswick, Fredericton, Canada E3B 5A3.

Fourier transform spectra of collisionally induced fluorescence following isotopically selective laser excitation of NiH at $\sim 550$ nm has allowed us to locate an exited $\Omega' = 1/2$ state of NiH lying 17900 cm$^{-1}$ above the electronic ground state. We identify this as $v = 0$ of a $^2\Pi_{1/2}$ state, originating from the Ni$^+$ $3d^84s^1$ $^2F$ configuration, from the ab initio studies published by Zou and Liu in 2007. Emission from the [17.9]0.5 state occurs to $v'' = 0$ and 1 of the $^2\Sigma^+$ and $^2\Pi_{1/2}$ low-lying ligand field states, locating hitherto elusive $^2\Pi_{1/2}$ f parity levels to within 0.01 cm$^{-1}$. Collisionally induced fluorescence following laser excitation at lower energies has been recorded in the presence of a magnetic field (0.7 - 1 Tesla), at Doppler resolution. The partially resolved Zeeman patterns have been used to derive effective Landé factors $g_J$ for the $v = 0$ and 1 levels of the low-lying $\Omega'' = 5/2$ and $3/2$ states ($^2\Delta$ and $^2\Pi$ states from Ni$^+$ $3d^9$). These are compared with predictions from a revised fit of zero-field energy levels, now including the new observations concerning the $\Omega'' = 1/2$ states.

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NEW BANDS OF NICKEL FLUORIDE IN THE NEAR INFRARED BY INTRACAVITY LASER ABSORPTION SPECTROSCOPY

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

Several new electronic transitions of NiF with red-degraded bandheads near 12896 and 13497 cm$^{-1}$ were recorded and analyzed. All bands have a common lower level: namely, $v=0$ of the $A^2\Delta_{5/2}$ state. The observed $^{58}\text{NiF}$ and $^{60}\text{NiF}$ isotopologue splitting in each band suggests tentative assignments as the (3,0) and (2,0) vibrational bands of the $[12.6]\Omega=5/2-\Sigma$ transition and the (2,0) band of a new $[13.1]\Omega=5/2-\Delta$ transition of NiF. Results of the analysis will be presented. The gas phase NiF molecules were produced using a nickel-lined hollow cathode in an argon-based electric discharge with a small amount of SF$_6$.

INTRACAVITY LASER ABSORPTION SPECTROSCOPY OF PLATINUM FLUORIDE IN THE NEAR INFRARED

LEAH C. O’BRIEN, KAITLIN WOMACK, Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026-1652; JAMES J. O’BRIEN, MEREDITH REDDICK, REBECCA STEINBERG, Department of Chemistry and Biochemistry, University of Missouri, St Louis, MO 63121-4499.

Two new bands of PtF have been recorded in the near-infrared with rotational resolution using intracavity laser absorption spectroscopy. Red-degraded bandheads are observed at 12523 and 13079 cm$^{-1}$, and they are identified as the (0,0) and (1,0) bands of a new electronic transition based on the observed isotopologue splitting in the bands. 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 SF$_6$.

THE ELECTRONIC SPECTRUM AND MOLECULAR STRUCTURE OF HAsO, THE ARSENIC ANALOG OF HNO

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

The previously unknown, closed shell transient species HAsO has been observed in the 525 - 665 nm region by laser-induced fluorescence (LIF) spectroscopy. HAsO and its deuterated isotopologue were produced in a pulsed discharge jet using a precursor mixture of AsH$_3$ and CO$_2$ in high pressure argon. Vibrational analysis of low-resolution LIF and single vibronic level (SVL) emission spectra has established the $\nu_2$ and $\nu_3$ vibrational frequencies in both states. High resolution spectra of the 0$^0_0$ bands of both HAsO and DAsO have been recorded and rotationally analyzed, proving that the observed electronic transition is $\tilde{A}^1\Pi' - \tilde{X}^1\Pi$. Effective molecular structures for the ground and excited states have been determined from the rotational constants of the two isotopologues. The HAsO angle decreases upon electronic excitation in contradiction to the geometry change predicted using Walsh’s angular orbital correlation diagrams. Reasons for this anomalous behavior will be discussed.

THE PFI-ZEKE SPECTROSCOPY STUDY OF HfS$^+$ AND THE IONIZATION ENERGY OF HfS

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

Spectroscopic data for the ground and low-lying states HfS$^+$ have been obtained using the technique of pulse field ionization - zero electron kinetic energy (PFI-ZEKE) spectroscopy. PFI-ZEKE spectra were recorded for the levels $X^2\Sigma^+\ (v=0-18)$, $^2\Delta_{5/2}\ (v=0-8)$ and $^2\Delta_{3/2}\ (v=0-3)$. Assignments of the electronically excited states of HfS$^+$ are based on CCSD(T) and DFT calculations with SDB-aug-cc-pVTZ basis set. Rotationally resolved spectra were recorded for the $X^2\Sigma^+\ (v=0)$ state using single rotational line excitation of the intermediate state. The ionization energy for HfS, term energies and molecular constants for the ground and low-lying states of HfS$^+$ will be reported.
**Intermission**

WG07 15 min 3:30

THEORETICAL STUDIES OF ELECTRONIC SPECTRA AND BONDING OF AlCl/AlF(\( \chi^1 \Sigma^+ \), \( \alpha^3 \Pi \), \( \alpha^1 \Pi \)) WITH EXCITED STATES EXHIBITING RECOUPLED PAIR BONDING

JEFF LEIDING, DAVID E. WOON and THOM H. DUNNING, JR., Department of Chemistry, University of Illinois at Urbana-Champaign, Box 86-6, CLSL, 600 South Mathews, Urbana IL, 61801.

Ground electronic state rotational lines of AlCl and AlF have been observed in the circumstellar envelope of IRC +10216, and electronic transitions of AlF have been observed in sunspot umbra. We have performed high-level \textit{ab initio} MRCI+Q and RCCSD(T) calculations with large correlation consistent basis sets up to augmented sextuple zeta quality including core-valence correlation effects on the ground state (\( \chi^1 \Sigma^+ \)) and two lowest excited states (\( \alpha^3 \Pi \), \( \alpha^1 \Pi \)) of AlF and AlCl. Theoretical spectroscopic constants as well as vibrational and rotational spectra will be presented and compared with experiment. We will also discuss the nature of the bonding in these states. The excited states are formed via recoupled pair bonds, in which the Al 3s pair of electrons is decoupled to allow one of its electrons to recouple with a halogen to form a bond.

WG08 15 min 3:47

ELECTRONIC SPECTROSCOPY OF THE 6p ← 6s TRANSITION IN Au-Ne

ADRIAN M. GARDNER, RICHARD J. PLOWRIGHT, CAROLYN D. WITHERS, TIMOTHY G. WRIGHT, School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom; MICHAEL D. MORSE and W. H. BRECKENRIDGE, Department of Chemistry, 315 South 1400 East, Room 2020, University of Utah, Salt Lake City, Utah 84112.

Electronic spectra of the Au-Ne complex have been recorded for the first time in the vicinity of the atomic Au 6p ← 6s transition.\(^a\) A structured spectrum was observed near the Au \( ^2 \)P\(_{3/2} \) ← \( ^2 \)S\(_{1/2} \) transition, however, the complex spectrum expected near the Au \( ^2 \)P\(_{1/2} \) ← \( ^2 \)S\(_{1/2} \) transition was not observed. This is rationalized using high level \textit{ab initio} calculations.


WG09 10 min 4:04

ELECTRONIC TRANSITIONS AND SPIN-ORBIT SPLITTING OF LANTHANUM DIMER

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

Lanthanum dimer (La\(_2\)) was studied by mass-analyzed threshold ionization (MATI) spectroscopy and a series of high-level multi-configuration \textit{ab initio} calculations (CASSCF, CASPT2, and MRCI). The MATI spectrum exhibits three band systems originating at 39044, 40312, and 40862 cm\(^{-1}\), respectively. Above the band origin, the first band system displays a vibrational progression of \( \sim 232 \) cm\(^{-1}\), and the other two show vibrational progression with the same interval of \( \sim 240 \) cm\(^{-1}\). Below the band origin, the three systems exhibit the same vibrational interval of \( \sim 207 \) cm\(^{-1}\). These band systems are assigned to three electronic transitions from the ground state of La\(_2\) to the low-lying electronic states of La\(_2^+\): \( ^2 \Sigma_g^+ ← ^1 \Sigma_g^+ \), \( ^2 \Pi_{u,1/2} ← ^1 \Sigma_g^+ \), and \( ^4 \Pi_{u,3/2} ← ^1 \Sigma_g^+ \). The spin-orbit splitting in the \( ^4 \Pi_u \) ion state is 550 cm\(^{-1}\). In addition, the electronic states and bonding of La\(_2\) will be compared with those of Sc\(_2\) and Y\(_2\).
LASER INDUCED FLUORESCENCE SPECTROSCOPY OF COBALT MONOBORIDE

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

Laser induced fluorescence spectrum of cobalt monoboride (CoB) in the visible region between 465 and 560 nm has been observed. CoB molecule was produced by the reaction of laser ablated cobalt atom and diborane (B₂H₆) seeded in argon. Over twenty five vibronic bands have been recorded, and both Co¹⁰B and Co¹¹B isotopic species have been observed and analyzed. Preliminary analysis of the rotational lines showed that the observed vibronic bands belong to two categories namely: the \( \Omega' = 2 - \Omega'' = 2 \) and the \( \Omega' = 3 - \Omega'' = 3 \) transitions, which indicated the ground state of CoB is consistent with an assignment of a \( ^3\Delta_i \) state predicted from ab initio calculations. Unresolved hyperfine structure arising from the Co nucleus (I = 7/2) causes a broadening of spectral lines. This work represents the first experimental investigation of the spectrum of the CoB molecule. Financial support from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. HKU 701008P) is gratefully acknowledged.

HIGH RESOLUTION LASER SPECTROSCOPY OF RHODIUM MONOBROMIDE.

A. G. ADAM, T. F. ALLEN, L. E. DOWNIE, and A. D. GRANGER, Chemistry Department, and Centre for Lasers, and Atomic, and Molecular Sciences, University of New Brunswick, Fredericton, NB, E3B 5A3; and C. LINTON, and D. W. TOKARYK, Physics Department, and Centre for Lasers, and Atomic, and Molecular Sciences, University of New Brunswick, Fredericton, NB, E3B 5A3.

The rhodium monobromide molecule, RhBr, has been created in our laser ablation pulsed jet apparatus by ablating a rhodium target rod in the presence of 1% CH₃Br seeded in He. A low-resolution survey spectrum from 415 to 850 nm indicated the presence of a number of bands belonging to RhBr. Thirteen of these band systems, mainly in the blue spectral region, have been recorded at high resolution with our cw dye laser. In addition, dispersed fluorescence spectra have been obtained for these bands. Not all of the bands have been fully analyzed to date, however, from those analyzed, the RhBr ground state has been determined to have \( \Omega = 2 \) consistent with the isovalent RhCl molecule which has a \( ^3\Pi_2 \) ground state\(^a\). Vibrational and rotational analysis yields the following ground state parameters for the two isotopologues, Rh⁷⁹Br and Rh⁸¹Br: \( \omega'' = 260 \text{ cm}^{-1} \), \( B''(\text{Rh}⁷⁹\text{Br}) = 0.0655 \text{ cm}^{-1} \), and \( B''(\text{Rh}⁸¹\text{Br}) = 0.0646 \text{ cm}^{-1} \). Further ground and excited state parameters will be presented at the conference.


THE VISIBLE SPECTRUM OF IRIDIUM MONOHYDRIDE AND MONODEUTERIDE.

A. G. ADAM, and A. D. GRANGER, Chemistry Department, and Centre for Lasers, and Atomic, and Molecular Sciences, University of New Brunswick, Fredericton, NB, E3B 5A3; and C. LINTON, and D. W. TOKARYK, Physics Department, and Centre for Lasers, and Atomic, and Molecular Sciences, University of New Brunswick, Fredericton, NB, E3B 5A3.

Iridium-containing moieties are prevalent in asymmetric catalytic systems. For this reason, diatomic Ir containing species have been the subject of both theoretical and experimental studies. We have investigated IrH/D using our laser ablation molecular jet apparatus. After searching from 380 - 820 nm, eight rotationally-resolved bands for both IrH and IrD were observed. The spectra were determined to belong to several \( ^3\Phi_4 - X^3\Phi_1 \) transitions. No other spin-orbit components were observed in either the excited or ground states. A global fit of the bands was performed for each molecule. The molecular parameters have been compared with those of the valence isoelectronic molecules, CoH and RhH. Ground state vibrational frequencies have been determined, from dispersed fluorescence spectra, to be \( \Delta G_{1/2} = 2140(11) \text{ cm}^{-1} \) for IrH and \( \omega''_e = 1609(2) \text{ cm}^{-1} \) and \( \omega_e x''_e = 19.3(5) \text{ cm}^{-1} \) for IrD. The ground state bond length of IrH was determined to be 1.603 Å somewhat in agreement with the theoretical prediction of 1.565 Å of Dai and Balasubramanian\(^a\).

THE VISIBLE SPECTRUM OF ZIRCONIUM DIOXIDE, ZrO₂

ANH LE AND TIMOTHY C. STEIMLE, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287; VARUN GUPTA AND JOHN P. MAIER, Department of Chemistry, University of Basel, Basel, Switzerland.

Zirconia (ZrO₂) is an important material with applications in microelectronics, catalysis, and ceramics. Previously the photo-electron spectrum⁴⁻⁵ of the ZrO₂ anion and the pure rotation spectrum of the neutral⁶ have been recorded and analyzed. Here we present the first observation of the visible spectrum of ZrO₂ via laser induced fluorescence (LIF) and resonance enhanced multi-photon ionization (REMPI). The LIF spectrum was recorded between 17000-18900 cm⁻¹ at a resolution of 0.2 cm⁻¹ using pulsed dye laser excitation and tentatively analyzed to give harmonic vibrational parameters ω₁, ω₂, and ω₃ for the A¹B₂ state of 495(1) cm⁻¹, 150(3) cm⁻¹ and 1045(4) cm⁻¹, respectively. Dispersed fluorescence spectra of thirteen bands were recorded and analyzed to give harmonic vibrational parameters ω₁, ω₂, and ω₃ for the X¹A₁ state of 898 (1) cm⁻¹, 287(3) cm⁻¹ and 808(4) cm⁻¹, respectively. The radiative lifetimes of numerous bands have been measured and analyzed. Franck-Condon factors were calculated and used to model the REMPI and excitation spectra. A comparison with TiO₂ is made⁷.

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WG14 15 min 5:24

SEQUENTIAL OXIDATION OF TRANSITION METAL SUBOXIDE CLUSTER ANIONS

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.

Photoelectron spectroscopy and DFT calculations are used to study the evolution of the molecular properties of metal suboxide clusters as they are sequentially oxidized toward bulk stoichiometry. The spectra of group 6 tri-metal suboxide anions with three to six oxygen atoms reflect a shift from direct metal-metal bonding to metal-oxo-metal bonding motifs. Additionally, multiple energetically competitive structures are predicted for the most reduced species.
REASSIGNMENT OF MILLIMETERWAVE SPECTRUM OF THE HCN INTERNAL ROTATION BANDS OF H$_2$-HCN

KENSUKE HARADA, RISA YAMANAKA, and KEIICHI TANAKA, Department of Chemistry, Faculty of Sciences, Kyushu University, Fukuoka, 812-8581 JAPAN.

The H$_2$-HCN complex is a weakly bound molecular complex and we have reported the pure rotational transitions of H$_2$-HCN in the MMW region. According to the results, ortho- and para-H$_2$ complexes have different structures in the ground state, H$_2$ is attached to the nitrogen and hydrogen end of HCN, respectively, for ortho- and para-H$_2$ complexes and the $\Sigma$ symmetry has been confirmed for both species.

We also reported the MMW spectroscopy of $j=1$-0 internal rotation band of H$_2$-HCN in 2006, where $j$ is the quantum number for the HCN internal rotation. Although we assigned most of intense lines to the $\Sigma_1 - \Sigma_0$ and $\Pi_1 - \Sigma_0$ bands of (ortho)H$_2$-HCN, some intense lines are unidentified. To confirm their assignments, we performed the MMW-MMW double resonance spectroscopy in the present study and came to the conclusion that our previous assignments of $\Sigma_1 - \Sigma_0$ and $\Pi_1 - \Sigma_0$ bands should be changed, and then all of the intense lines are finally assigned to the $\Pi_1 - \Sigma_0$ ($R_0$, $R_1$, $R_2$, $Q_1$, $Q_2$, and $P_2$) and $\Sigma_1 - \Sigma_0$ ($R_0$, and $P_2$) bands.

The band origins of the $\Sigma_1 - \Sigma_0$ and $\Pi_1 - \Sigma_0$ bands of (ortho)H$_2$-HCN newly determined are 187 and 165 GHz, respectively. They are larger than those of Ne-HCN (133 and 107 GHz) but comparable with those of Ar-HCN (165 and 182 GHz, their order is reversed) indicating that the potential anisotropy of (ortho)H$_2$-HCN is larger than that of Ne-HCN but comparable with that of Ar-HCN. The mean square amplitudes of HCN for excited states ($57^\circ$ and $51^\circ$ for $\Sigma_1$ and $\Pi_1$), given by the analysis of hyperfine structure of the nitrogen nucleus, are much larger than that ($33^\circ$) of the ground $\Sigma_0$ state.

A plenty of weak lines in the 100-300 GHz region are still unassigned, possibly due to the higher internal rotation bands of ortho-H$_2$ complex, such as the $\Delta_1 - \Pi_0$ band, as well as the fundamental bands ($\Sigma_1 - \Sigma_0$ and $\Pi_1 - \Sigma_0$) of para-H$_2$ complex. Analysis of these weak bands and survey in the region with pure para-H$_2$ sample are now in progress.

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MILLIMETERWAVE SPECTROSCOPY OF THE INTERNAL ROTATION BANDS OF Ne-DCN

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

In 2005, we reported the MMW spectrum of internal rotation bands \((j=1-0\) and \(2-1)\) of Ne-HCN to analyzed the intermolecular potential energy surface (PES) between Ne and HCN, where \(j\) denotes the quantum number for the HCN internal rotation. In the present study, we have extended our observation to the Ne-DCN deuterated complex in the MMW region (78-175 GHz), and assigned the several DCN internal rotation bands such as the \(j=1-0\) fundamental band (\(\Sigma_1^1-\Sigma_0^0\) and \(\Pi_1^1-\Sigma_0^0\)) and the \(j=2-1\) hot band (\(\Sigma_2^2-\Sigma_1^1\), \(\Pi_2^2-\Sigma_1^1\), \(\Pi_2^2-\Pi_1^1\), and \(\Delta_2^2-\Pi_1^1\)) for the \(^{20}\)Ne-DCN and \(^{22}\)Ne-DCN complexes. In total, 69 and 12 lines have been assigned to the \(^{20}\)Ne-DCN and \(^{22}\)Ne-DCN. The intermolecular stretch band between Ne and DCN, however, was not observed in this frequency region. Analysis shows that the \(\Sigma_1^1\) and \(\Pi_1^1\) sublevels for \(j=1\) state are located at 134 and 105 GHz, respectively, above the \(j=0\) ground state (\(\Sigma_0^0\)), while the \(\Sigma_2^2\), \(\Pi_2^2\), and \(\Delta_2^2\) sublevels of \(j=2\) state are located at 286, 276, and 257 GHz with different order from that for the normal species.

The observed MMW frequencies for Ne-DCN were analyzed with two dimensional (\(\theta - R\)) PES freezing the freedom in DCN moiety. The PES given by CCSD(T) level \(\text{ab initio}\) calculation was modified by adding sixteen extra parameters and fitted to the observed frequencies of internal rotation bands of both \(^{20}\)Ne and \(^{22}\)Ne species. The \(\theta - R\) PES thus fitted has a global minimum in the linear configuration (Ne-\(\cdots\)D–C–N) with a well depth of 64.1 cm\(^{-1}\), and a saddle point located in the anti-linear configuration (D–C–N-\(\cdots\)Ne) by 18.4 cm\(^{-1}\) higher than the global minimum. The \(j=0\) ground vibrational state is located by 4.8 cm\(^{-1}\) higher than the saddle point. The PES is anisotropic because the center-of-mass distance between Ne and DCN changes much along the minimum energy path, 4.230, 3.477, and 4.020 Å in the linear, T-shaped, and anti-linear forms, together with their energies. The PES estimated for Ne-DCN is very similar to that of Ne-HCN, but the global minimum is by 1.1 cm\(^{-1}\) deeper than that of Ne-HCN, due to the frozen model of the HCN/DCN moiety and also our observation is quite limited to the bottom of PES, e.g. highest observed state (\(\Sigma_2^2\)) is still 30 cm\(^{-1}\) below the dissociation limit.

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STUDY OF He\(_N\)-HCN CLUSTERS USING ROTATIONAL SPECTROSCOPY

STEVE DEMPSTER, OLEKSANDR SUKHORUKOV, QI-YI LEI, and WOLFGANG JÄGER, Department of Chemistry, University of Alberta, Edmonton, Canada T6G 2G2.

In previous studies of He\(_N\)-molecule clusters it was observed that the rotational constants begin to increase with increasing number of helium atoms, \(N\), at a certain critical cluster size. This non-classical behaviour is attributed to a decoupling of helium density from the rotational motion of the probe molecule and signifies the onset of microscopic superfluidity. It is still debated, however, how this trend can be correlated to, for example, the moment of inertia of the probe molecule or the anisotropy of the helium-molecule interaction potential energy surface. For this study, He\(_N\)-HCN clusters were chosen to investigate the phenomenon of microscopic superfluidity for a light rotor system, and to shed light on the relationship between quantum solvation and the molecular properties of the probe molecule. In this presentation, recent experimental results obtained for He\(_N\)-HCN clusters along with several of its isotopologues, i.e. He\(_N\)-DCN, He\(_N\)-H\(^{13}\)CN, He\(_N\)-D\(^{13}\)CN, He\(_N\)-HC\(^{15}\)N, with \(N=1\) to 6 are highlighted. The experimental results, in particular the cluster rotational constants, \(B\), are compared to several theoretical predictions.
MICROWAVE SPECTRA AND STRUCTURES OF H₂O···AgF

S. L. STEPHENS, N. R. WALKER, D. P. TEW 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···AgF. Generation is via laser ablation (532 nm) of a silver rod in the presence of SF₆, argon, a low partial pressure of H₂O and the molecules are stabilized by supersonic expansion. The spectra of eight isotopologues have been measured. Rotational constants, B₀ and C₀, and the centrifugal distortion constant, ΔJ, have been determined. Isotopic substitutions are available at the silver, oxygen and hydrogen atoms. The spectra are consistent with a linear arrangement of oxygen, silver and fluorine atoms and the structure is either Cᵥ 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.

INTERNAL ROTATION IN CF₃I···NH₃ AND CF₃I···N(CH₃)₃ PROBED BY CP-FTMW SPECTROSCOPY

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

The pure rotational spectra of CF₃I···NH₃ and CF₃I···N(CH₃)₃ have been measured by chirped-pulse, Fourier transform microwave (CP-FTMW) spectroscopy between 7 and 18.5 GHz. Both molecules are generated by supersonic expansion of a gas sample containing a small percentage of each precursor in a balance of argon. The spectra of both complexes are consistent with Cᵥ prolate symmetric top structures. The observed spectrum of CF₃I···NH₃ displays evidence for internal rotation of NH₃ about the principal axis. More than one hundred transitions of CF₃I···NH₃ have been assigned to the internal rotor A state allowing rotational, centrifugal distortion constants and a nuclear quadrupole coupling constant for the iodine atom to be determined for this state. Measurements performed using a Balle-Flygare FTMW spectrometer further allow determination of a nuclear quadrupole coupling constant for the ¹⁴N nucleus. Many transitions in the spectrum of the CF₃I···¹⁵NH₃ isotopologue have also been measured and the length of the halogen bond between the iodine and nitrogen atoms has been determined. Measurements of hyperfine components in nine different J″ ← J′ transitions of CF₃I···N(CH₃)₃ have allowed assignment of the spectrum of this complex to determine rotational, centrifugal distortion and nuclear quadrupole coupling constants.

INTERNAL MOTION EFFECTS IN THE MICROWAVE SPECTRUM OF ARGON-CIS-1,2-DIFLUOROETHYLENE

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Using the results of Fourier transform microwave spectroscopy, we have recently completed a comprehensive study of protic acid-fluoroethylene complexes. The structures obtained for these species, specifically the length of the hydrogen bonding interaction, the deviation of this bond from linearity, and the contribution from a secondary interaction between the electron rich portion of the acid and a hydrogen contained in the fluoroethylene moiety, have been interpreted in terms of changes in the nucleophilicity of the fluorine atoms caused by an increasing degree of fluorine substitution. Our work included complexes with all the possible mono-, di-, and tri-substituted fluoroethylenes, with the exception of cis-1,2-difluoroethylene. In the course of seeking to observe the complex of this species with HF, a rich spectrum due to complexes with the argon carrier gas has been observed. Most notably, all c-type transitions observed for Ar-cis-1,2-difluoroethylene are doubled, while a-type lines are not and b-type lines are absent. This suggests that the complex is interconverting between two equivalent, non-planar, symmetric structures on the timescale of the experiment, a conclusion that is supported by ab initio calculations. Comparisons will be made with previously observed Ar-fluoroethylene complexes.
Through the systematic comparison of the structures of a series of complexes formed between protic acid and fluorine substituted ethylenes, we have been able to observe how tuning the properties of the functional groups (F and H atoms) in ethylene using additional F atoms causes these groups to compete or cooperate with each other in intermolecular interactions. A necessary step for expanding our work in the next natural direction by examining the effects of the less electronegative, but more polarizable Cl atom is the determination of the structures of protic acid-vinyl chloride complexes. Since the rich microwave spectrum of Ar-vinyl chloride has not previously been reported, it is essential to first characterize this rare gas complex. We have observed strong $b$-type and weak $a$-type transitions for both $^{35}\text{Cl}$ and $^{37}\text{Cl}$ versions of this species, all of which appear to be doubled. Although $ab\text{ initio}$ calculations suggest a sufficiently large value of $\mu_c$, $c$-type lines remain elusive. Indeed, these same calculations reveal the presence of several minima on the interaction potential energy surface, which may provide an explanation.

The pure rotational spectra of $\text{CF}_3^{35}\text{Cl}-\text{H}_2\text{O}$, $\text{CF}_3^{37}\text{Cl}-\text{H}_2\text{O}$, $\text{CF}_3^{35}\text{Cl}-\text{H}_2^{18}\text{O}$, $\text{CF}_3^{35}\text{Cl}-\text{OD}$, $\text{CF}_3^{35}\text{Cl}-\text{D}_2\text{O}$ isotopologues have been investigated by pulsed supersonic-jet FT-microwave spectroscopy. We assigned the $m = 0$ and $m = 1$ (for the first 2 isotopologues) states and the spectra, for all, are characteristic of a symmetric top of evenly spaced band. A substitution analysis was made for the $m = 0$ state of the dimers with $\text{H}_2^{18}\text{O}$ and $\text{D}_2\text{O}$. Ab initio calculation (MP2 level of electron correlation and 6-311++G** basis set) have been carried out in order to obtain information about the structure and relative stability. The interaction between the subunits occurs via C-Cl···O($\text{H}_2\text{O}$) halogen bond.
WEAK C–H···O INTERACTIONS AND H₂O INTERNAL ROTATION IN THE HCCIF₂–H₂O AND HCBrF₂–H₂O DIMERS

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The polarity of the C-H bond involved in a weak C-H···X interaction may be tuned by introducing different combinations of halogen substituents on the carbon atom. In this study, the structures of the HCCIF₂–H₂O and HCBrF₂–H₂O dimers have been studied by rotational spectroscopy and theoretical methods, with the hope of observing weak C-H···O interactions. Ab initio calculations (MP2/6-311++G(2d,2p)) predict cyclic structures for both dimers, with a C-H···O and an O-H···X (X = Cl or Br) interaction present in each complex. Fourier-transform microwave spectroscopic investigations of both species have confirmed that this structural motif is present, although the experimental results display some significant differences from the theoretical predictions.

The spectra of both HCCIF₂–H₂O and HCBrF₂–H₂O were doubled due to internal rotation of the water molecule within the weak complex (with the higher frequency state about three times the intensity of the lower frequency state, as expected for exchange of equivalent hydrogen nuclei). Ab initio potential energy scans have been performed to estimate the barrier to rotation of the water molecule in both dimers, and for HCCIF₂–H₂O a global fit using ERHAM has also provided an experimental determination of the energy difference between the tunneling states (16.0(4) GHz) and barrier to rotation (195(5) cm⁻¹). Remarkably, the more intense higher frequency transitions belong to the lower energy B internal rotation state.

CHIRPED-PULSE, FTMW SPECTROSCOPY OF THE LACTIC ACID-H₂O SYSTEM

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The previous study of the rotational spectrum of lactic acid in supersonic expansion revealed rather temperamental behaviour of signal intensity suggestive of considerable clusterization. Lactic acid samples contain an appreciable amount of water so that the presence of clusters with water, as well as lactic dimers is suspected. Several, mainly computational, studies of such species have already been published.

Investigation of the chirped-pulse rotational spectrum of a heated lactic acid (LA) sample diluted in Ne carrier gas allowed unambiguous assignment of the LA-H₂O, LA-(H₂O)₂, and LA-(H₂O)₃ species. In addition, the rotational spectrum of the AaT conformer of lactic acid has been assigned. This conformer involves an intramolecular hydrogen bond to the hydroxyl of the carboxylic group and it has been estimated to be less stable by ca 10 kJ/mol than the most stable SsC conformer. The evidence for the assignment and a discussion of the derived properties for the new species are presented.

WH11 15min 4:31
STRUCTURE STUDY OF THE CHIRAL LACTIDE MOLECULES BY CHIRPED-PULSE FTMW SPECTROSCOPY

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Lactide is a six member cyclic diester with two chiral centers that forms from lactic acid in the presence of heat and an acid catalyst. It can form either a homo-chiral (RR) structure with both methyl groups equatorial or a hetero-chiral (RS) structure where one methyl group is equatorial and the other methyl group is axial. Structurally lactide is similar to lactic acid dimer; however, the kinked ring is covalently bonded and two waters are lost. And unlike lactic acid dimer, which has a very small dipole moment, the dipole moment of lactide is on the order of 3 Debye. Here the microwave spectra of the highly rigid homo- and hetero-chiral lactides are presented, which were first assigned in a heated lactic acid spectrum where the chemistry took place in the reservoir nozzles. Further isotopic information from a commercial sample of predominately homo-chiral lactide was obtained leading to a Kraitchman substitution structure of the homo-chiral lactide. Preliminary results of the cluster of homo-chiral lactide with one water molecule attached are also presented.

WH12 15min 4:48
THE CHIRPED-PULSE AND CA VITY BASED FTMW SPECTROSCOPY OF THE METHYL LACTATE-W ATER AND METHYL LACTATE-DEUTERIUM OXIDE DIMERS

JAVIX THOMAS, OLEKSANDR SUKHORUKOV, WOLFGANG JÄGER, YUNJIE XU, Department of Chemistry, University of Alberta, Edmonton, AB, T6G 2G2, Canada.

The delicate competition between the inter- and intramolecular hydrogen-bonding in the complex consisting of a chiral alpha-hydroxy ester, methyl lactate, and water, has been studied using rotational spectroscopy and high level ab initio calculations. Extensive ab initio calculations have been performed to locate all possible low energy conformers of the methyl lactate-water contact pair and five lowest energy conformers have been identified. The most stable conformer forms a seven membered ring with two intermolecular hydrogen bonds: one between the alcoholic hydroxy group of methyl lactate and the oxygen of the water molecule and the other between the hydrogen of water and the oxygen of the carbonyl group. Broadband scans for the rotational spectra of these conformers have been carried out using a newly built chirped-pulse FTMW instrument and the final frequency measurements with a cavity based FTMW instrument. Spectral assignments have been made for the lowest energy conformer of methyl lactate-H₂O and D₂O. The hyperfine splitting and the source of the splitting will be discussed.

WH13 15min 5:05
THE PURE ROTATIONAL SPECTRUM OF PERFLUOROOCTANONITRILE, C₇F₁₅CN, STUDIED USING CA VITY- AND CHIRPED-PULSED FOURIER TRANSFORM MICROWAVE SPECTROSCOPIES

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Fourier transform rotational spectroscopy has been used to collect the spectrum of perfluorooctanoneitrile. The spectrum was weak and only one conformer was observed. The assigned spectrum currently consists of both a- and b-types transitions spanning J = 8 to 40. The rotational constants are small, A = 681.37155(18) MHz, B = 126.116097(48) MHz, and C = 124.284824(49) MHz. The spectroscopic constants together with quantum chemical calculations have been used to identify the structure of the observed conformer. Notably the helical nature of the perfluoro alkyl chain is fully in evidence. Further calculations confirm that the nitrogen quadrupole coupling tensor is such that nitrogen hyperfine splitting will not be observable at the high J transitions recorded in our experiments. Spectroscopic constants and a discussion of the molecular structure will be presented.
The pure rotational spectra of the parent and all $^{13}$C isotopologues of hexafluoroisobutene, $(\text{CF}_3)_2\text{C}=\text{CH}_2$, have been recorded using chirped pulse Fourier transform microwave spectroscopy. The spectra observed consist of only $b$-type transitions all of which are doubled by between $\approx 1$ MHz to $60$ MHz. This doubling phenomena may be rationalized by the assumption that the methylene carbon is slightly out of the plane formed by the remaining carbons, similar to that observed in methylene cyclobutane$^a$. For the parent species 235 transitions have been fitted simultaneously using rotational constants, centrifugal distortion constants, the Coriolis coupling constant $F_{ac}$, and the vibrational energy spacing $\Delta E_{01}$. The results are compared to those recently obtained for the related species hexafluoroacetone imine, $(\text{CF}_3)_2\text{C}=\text{NH}$.

INVITED TALK

INVISIBLE ELECTRONIC STATES AND THEIR DYNAMICS REVEALED BY PERTURBATIONS

ANTHONY J. MERER, Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan.

Sooner or later everyone working in the field of spectroscopy encounters perturbations. These can range in size from a small shift of a single rotational level to total destruction of the vibrational and rotational patterns of an electronic state. To some workers perturbations are a source of terror, but to others they are the most fascinating features of molecular spectra, because they give information about molecular dynamics, and about states that would otherwise be invisible as a result of unfavorable selection rules. An example of the latter is the essentially complete characterization of the \( ^3A_2 \) state of \( \text{SO}_2 \) from the vibronic perturbations it causes in the \( ^3B_1 \) state. The \( S_1 \)-trans state of acetylene is a beautiful example of dynamics in action. The level patterns of the three bending vibrations change dramatically with increasing vibrational excitation as a result of the vibrational angular momentum and the approach to the isomerization barrier. Several vibrational levels of the \( S_1 \)-cis isomer, previously thought to be unobservable, can now be assigned. They obtain their intensity through interactions with nearby levels of the trans isomer.

INTERNAL AND EXTERNAL PERTURBATIONS IN ELECTRONIC SPECTROSCOPY. THE STARK SPECTRUM OF INDOLE-NH\(_3\),\(^a\)

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

Hydrogen bond pairs involving the chromophore indole have been extensively studied in the gas phase. Here, we report new rotationally resolved data on the indole-NH\(_3\) hydrogen bond pair in the absence and presence of an electric field. The electronic origin of this complex recorded at high resolution reveals two overlapping spectra, a consequence of NH\(_3\) internal rotation. The barrier to internal rotation is predicted by theory to be below 20 cm\(^{-1}\) in the ground state, therefore requiring a revision of the standard rigid rotor Hamiltonian. Conducting the experiment in the presence of an applied electric field further perturbs the already congested spectrum, but allows for the permanent dipole moments of the complex to be measured. Efforts to understand the unique perturbations that arise from both internal (molecular frame) and external (laboratory frame) sources will be discussed.

\(^a\)Work supported by NSF (CHE-0911117).
NOVEL PATTERNS OF TORSION - INVERSION TUNNELING AND TORSION - ROTATION COUPLING IN THE ν_{11} CH - STRETCH REGION OF CH$_3$NH$_2$

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The high-resolution infrared spectrum of CH$_3$NH$_2$ has been recorded using slit-jet absorption spectroscopy in the ν_{11} asymmetric CH-stretch region (2965 to 3005 cm$^{-1}$) with resolution of 0.003 cm$^{-1}$. The 580 lines, assigned by ground state combination differences, represent 27 subbands with |K'| ≤ 2 for the A, B, E$_1$ and E$_2$ symmetries. Several of the observed subbands are split by perturbations. The analysis of spectrum shows that the patterns of the torsion-inversion tunneling splittings are qualitatively different from the ground state. In addition, the low - J splittings between |K'| = ±|K'| and −|K'| are greatly reduced relative to the ground state in both the E$_1$ and the E$_2$ species, indicating that torsion-rotation coupling is suppressed in the ν_{11} CH-stretch excited state.

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EXTENDED PERMUTATION-INVERSION GROUPS FOR SIMULTANEOUS TREATMENT OF THE ROVIBRONIC STATES OF TRANS-ACETYLENE, CIS-ACETYLENE, AND VINYLIDENE

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The electronic ground state potential surface of acetylene (HCCH) has a minimum at the linear conformation, but the excited electronic states may have potential minima at a variety of nonlinear equilibrium shapes. This work is concerned with the group theoretical ideas necessary to treat simultaneously the symmetry properties of rovibronic states associated with three different planar acetylene equilibrium configurations, namely trans bent acetylene, cis bent acetylene, and vinylidene (H2C=C). We make use of three different kinds of groups: (i) point groups, (ii) permutation-inversion (PI) groups, and (iii) extended PI groups. The PI group is G$_4$ or G$_8$, depending on whether C-H bond breaking is impossible (no bent acetylene ↔ vinylidene interconversion), or possible. The extended PI groups are G$_4^{(2)}$ and G$_8^{(2)}$, respectively, when the only large amplitude motions are the CCH bends at each end of the molecule, and G$_4^{(8)}$ and G$_8^{(8)}$, respectively, when internal rotation is added as a third large amplitude motion. Applied to acetylene, the results indicate that there will be no splittings of the rovibronic levels unless CH bond breaking occurs. Even without bond breaking, however, states of the cis and trans isomers just below their interconversion barrier will show $\Sigma$staggering$\Sigma$ in their $K$-structures, i.e., a given vibrational level will have three tunneling components at slightly different energies: one component will have levels with $K = 4n$ only (where n is an integer), a second component will have levels with $K = 4n + 2$ only, and the third will have only odd-$K$ levels. New experimental results for the S$_1$-cis electronic state of acetylene are reviewed, and are found to be consistent with the group theory in so far as comparison is possible.
THE VISIBLE SPECTRUM OF Si$_3$

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We report the first recording of the visible spectrum of gas-phase Si$_3$. A cold molecular beam sample was produced by skimming the output of a pulsed discharge source. The 545–490 nm spectral region was examined using both mass-selected REMPI and pulsed dye laser excitation with LIF detection. Dispersed fluorescence and lifetime measurements of numerous bands were recorded. The spectrum has an origin at 18600 cm$^{-1}$ and a progression in the symmetric stretch with a harmonic frequency of 445 cm$^{-1}$. The bands are assigned to the $^2A''_1$–$^2A'_2$ transition of the $D_3h$ isomer based upon new and previous predictions. A vibrational progression observed in the dispersed fluorescence having a spacing of 505 cm$^{-1}$ is in agreement with previous ZEKE studies. An additional vibrational progression observed in dispersed fluorescence having a spacing of 173 cm$^{-1}$ is in agreement with the bending frequency for the $^2A_1$ state of the $C_{2v}$ isomer estimated from the pure rotational spectrum.


EXPERIMENTAL CHARACTERIZATION OF THE WEAKLY ANISOTROPIC CN $^2\Sigma^+$ + Ne POTENTIAL FROM IR-UV DOUBLE RESONANCE STUDIES OF THE CN-Ne COMPLEX

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A fluorescence based IR-UV double resonance technique is used to obtain rotationally resolved infrared spectra of the CN-Ne van der Waals complex in the CN stretch overtone region. Several hindered rotor combination bands are observed, with the spectra displaying evidence of Coriolis coupling in both line intensities and positions of the closely spaced vibrationally excited states. A deperturbation analysis is performed through modification of the rotational Hamiltonian to generate accurate rotational constants and account for the shifted line positions and band shapes observed. The energy spacings between hindered rotor states are used to deduce information on the anisotropic CN $X^2\Sigma^+$ + Ne intermolecular potential from which radially averaged anisotropy terms ($V_{10}$ and $V_{20}$) are extracted. The angular potential is compared to that produced by ab initio calculations using MRCI+Q extrapolated to the complete one-electron basis set limit. Experiment and theory are in excellent agreement, both indicating a nonlinear CN-Ne (X) minimum energy configuration and nearly free-rotor behavior. Similar studies on CN-Ar and CN-H$_2$ are currently in progress and analogous data analysis is ongoing.

$^a$Research is supported by the Chemistry Division of the NSF
TERAHERTZ SPECTROSCOPY OF HIGH $K$ METHANOL TRANSITIONS

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Methanol is one of the primary sources of line confusion in warm star-forming regions. Herschel has detected rotational transitions in $v_t = 0, 1, 2$ with rotational quantum numbers up to $J > 35$. The Herschel observations are clearly beam diluted on the hottest regions. Since ALMA will not suffer from similar beam dilution it is likely that significantly more methanol states are quickly detected. Since the existing detections largely span the previously analyzed space of laboratory data, a program of THz measurements of methanol has been undertaken to identify higher $K_a$ states and to connect the $v_t = 2$ manifold more completely to the rest of the available data with microwave accuracy. During the course of this work it became possible to directly compare TuFIR, FTIR, Laser Sideband, Quantum Cascade Laser, and conventional millimeter-wave spectroscopy. It has also been possible to assess the strengths and weakness of the rho-axis method (RAM) Hamiltonian in extrapolation for methanol.

A part of this work was performed at the Jet Propulsion Laboratory, California Institute of Technology under contract with the National Aeronautics and Space Administration. Copyright 2010 © California Institute of Technology. All rights reserved.

SYMMETRY DEPENDENCE OF THE RO-VIBRONIC DISTRIBUTIONS OF THE ND$_2$ $A^2A_1$ FRAGMENTS FROM THE PHOTODISSOCIATION OF THE A STATES OF ND$_3$ AND ND$_2$H AT 193.3 NM

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A rotational and vibrational analysis has been made of the ND$_2$ $A^2A_1-\tilde{X}^2B_1$ emission spectrum produced from the ultraviolet laser induced dissociation of both jet cooled and room temperature deuterated ammonia, ND$_3$, and di-deutero ammonia, ND$_2$H. The pattern of the strong features in the emission spectra is very different in the fragmentation of ND$_3$ and ND$_2$H, with a much wider range of angular momentum states being observed from the photolysis of the predissociative state of the unsymmetrical parent ND$_2$H. The analysis is based upon the earlier studies of the electronic spectrum of ND$_2$, and model calculation based upon the stretch-bender Renner-Teller Hamiltonian. The spectra consist of two types, transitions from a narrow distribution of high angular momentum states in the photolysis of ND$_3$ and ND$_2$H, and in the photolysis of ND$_2$H strong emission from threshold states to three high energy regions of the $\tilde{X}^2B_1$ state. The threshold states are in the third bending level, $v_2'=3$, of the ND$_2$ $A^2A_1$ state, and have no angular momentum about the axis of least moment of inertia, $K_a = 0$. 
VIBRATIONAL COUPLING PATHWAYS IN THE CH STRETCH REGION OF CH$_3$OH AND CH$_3$OD AS REVEALED BY IR AND FTMW-IR SPECTROSCOPIES

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Infrared spectra of jet-cooled CH$_3$OD and CH$_3$OH in the CH stretch region are observed by coherence-converted population transfer Fourier transform microwave-infrared (CCPT-FTMW-IR) spectroscopy (E torsional species only) and by slit-jet single resonance spectroscopy (both A and E torsional species, CH$_3$OH only). Previously, we reported$^a$ the analysis of $\nu_3$ symmetric CH stretch region (2750–2900 cm$^{-1}$), and the present work extends the analysis to higher frequency (2900–3020 cm$^{-1}$). The overall observed spectra contain 17 interacting vibrational bands for CH$_3$OD and 28 for CH$_3$OH. The signs and magnitudes of the torsional tunneling splittings are deduced for three CH fundamentals ($\nu_3$, $\nu_9$, $\nu_2$) of both molecules and are compared to a model calculation and to ab initio theory. The number and distribution of observed vibrational bands indicate that the CH stretch bright states couple first to doorway states that are binary combinations of bending modes. In the parts of the spectrum where doorway states are present, the observed density of coupled states is comparable to the total density of vibrational states in the molecule, but where there are no doorway states, only the CH stretch fundamentals are observed. A time-dependent interpretation of the present FTMW-IR spectra indicates a fast ($\sim 200$ fs) initial decay of the bright state followed by second, slower redistribution ($\sim 1–3$ ps). The qualitative agreement of the present data with the time-dependent experiments of Iwaki and Dlott$^b$ provides further support for the similarity of the fastest vibrational relaxation processes in the liquid and gas phases.


CONFORMATION SPECIFIC ELECTRONIC AND INFRARED SPECTROSCOPY OF ISOLATED [2,2,2]-PARA-TRICYLCLOPHANE AND ITS MONOHYDRATED CLUSTER

EVAN G. BUCHANAN, JACOB C. DEAN, BRETT M. MARSH, and TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN 47907.

[2,2,2]-Para-tricyclophane (TCP) is a highly symmetric macrocycle containing three para-substituted phenyl rings linked by ethyl bridges. Therefore, TCP affords a unique opportunity to explore the coupling between three electronic chromophores isolated in supersonic expansion. Furthermore, the three phenyl rings create an electron rich macrocyclic cavity capable of forming a $\pi$-hydrogen bond to a single water molecule. Resonant two-photon ionization and UV-UV hole-burning spectroscopy proved that the monomer population resides in a single conformer. Its vibronic spectrum shows unusual activity in the first 150 cm$^{-1}$ due to the close, intermingled set of three excited states. Resonant ion-dip infrared (RIDIR) spectroscopy was carried out in the alkyl and aromatic CH stretch regions to probe the conformations of the three ethyl linkages. Dispersed fluorescence spectra served to probe the electronic energy transfer between the three phenyl rings, which is rampant already at low energies. In the TCP-H$_2$O complex, RIDIR spectroscopy is used to characterize the $\pi$ H-bonding of H$_2$O in the TCP cavity.
CONFORMATION-SPECIFIC EFFECTS ON INTERNAL MIXING: INFRARED AND ULTRAVIOLET SPECTROSCOPY OF 1,1-DIPHENYLPROPANE

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Over the past few years, our group has studied a series of flexible bichromophores (e.g. Diphenylmethane) in which the degree of symmetry or asymmetry between the two UV chromophores is dictated by the position and type of substitution on the two rings. These studies provided fundamental insight into the vibronic coupling between the close-lying, intermingled excited states. Here, we present a study of the vibronic spectroscopy of 1,1-Diphenylpropane (DPP), in which the two phenyl rings are unsubstituted, but the alkyl chain itself is long enough to interact differently with the two rings, leading to an asymmetry in the local environments in which the two rings move. In this talk, we will discuss the results of single- and double-resonance spectroscopy methods applied to DPP, providing single-conformation UV spectra in the region of the $S_0\rightarrow S_1$ and $S_0\rightarrow S_2$ transitions. To this end, the LIF, R2Pi and UV-UV holeburning spectra were recorded for DPP, identifying a single conformation under the isolated-molecule conditions of a jet-cooled environment. Dispersed fluorescence provided information on the vibronic make-up of the $S_1$ and $S_2$ states and on the degree to which these coupled states are shifted by introducing the propyl chain asymmetry. Furthermore, results from IR-UV holeburning, RIDIRS and infrared-ion gain spectroscopy (IR-IGS) in the alkyl and aromatic CH stretch regions provided further evidence for our assignments. Analogous data on 1,1-Diphenylethane will also be discussed.

OPTICAL PUMPING AND ELECTRON SPIN RESONANCE OF SINGLE $^{87}$Rb ATOMS ON HELIUM NANODROPLETS

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Our recent development of electron spin resonance (ESR) spectroscopy on superfluid helium nanodroplets (HeN) provides a sensitive tool to investigate interactions between a surface located alkali-metal atom and an ESR silent species inside the droplet. Highest sensitivity is expected for alkali-metal atoms with large hyperfine coupling. We present hyperfine resolved ESR spectra of single $^{87}$Rb (hyperfine constant $a_{HFS} = 3417 \text{ MHz}$) atoms isolated on HeN. In accordance with our previous work on $^{85}$Rb ($a_{HFS} = 1012 \text{ MHz}$) we find a droplet size dependent increase of $a_{HFS}$ between 400 and 450 ppm, due to the electronic perturbation by the helium environment. The process of optical pumping and of optical detection on HeN is investigated in detail in order to optimize the ESR signal. A simple model for optical pumping on HeN is presented, which agrees well with the experimental results.

HIGHLY EXCITED STATES OF Cs ATOMS ON HELIUM NANODROPLETS

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Cs atoms on the surface of helium nanodroplets have been excited to high lying nS (n = 8-11), nP (n = 8-11), and nD (n = 6-10) levels. A two-step excitation scheme via the $^6\text{P}_{1/2}(^2\Pi_{1/2})$ state using two cw lasers was applied. This intermediate state has the advantage that a large fraction of the excited Cs atoms does not desorb from the helium nanodroplets. An absorption spectrum was recorded by detecting laser induced fluorescence light from the $^6\text{P}_{3/2}\rightarrow^6\text{S}_{1/2}$ transition. The pseudo-diatomic model for helium nanodroplets doped with single alkali-metal atoms holds for the observed spectrum. An investigation of spectral trends shows that the $^n\text{D}(\Delta)\rightarrow^6\text{P}_{1/2}(^2\Pi_{1/2})$ (n’ > 9) transitions are lower in energy than the corresponding free-atom transitions. This indicates that the Cs*–HeN potential becomes attractive for these highly excited states.

Our results suggest a possibility of generating an artificial super-atom with a positive ion core inside a helium nanodroplet and the electron outside, which will be subject to future experiments.

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RECONCILING EXPERIMENT AND THEORY: THE INTERESTING AND UNUSUAL CASE OF THE HOOO RADICAL

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The HO$_3$ radical, which can be considered a weakly bound OH–O$_2$ complex that consists of two important open-shell species, has been the subject of many theoretical studies. The first high-resolution spectroscopic work was carried out several years ago through rotational analysis\(^a\), work which firmly established the existence of the cis isomer, and an initial determination of its molecular structure. More recently, high-level coupled-cluster quantum chemical calculations\(^b\) have revealed large discrepancies between the theoretical and experimental structures for this important atmospheric radical. To better understand the origin of this disagreement, extensive isotopic spectroscopy of HOOO has been performed using Fourier Transform microwave spectroscopy and microwave-millimeter double resonance techniques. The results of these experiments will be presented along with new calculations of the rotation-vibrational coupling constants.


FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF THE HOSO RADICAL

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Molecules closely-related to SO$_2$ are of considerable interest because of the important role this triatomic or its surrogates play in the atmospheric and combustion chemistry of sulfur-containing compounds. Previous coupled-cluster quantum chemical calculations\(^a\) of the [HSO$_2$] potential energy surface conclude that a cis-isomer is the ground state, the trans isomer is a transition state, and that a $C_2$v HSO$_2$ isomer lies considerably higher in energy ($\sim 20$ kcal/mol). Using Fourier Transform microwave spectroscopy, the rotational spectrum of the cis-HOSO radical has been precisely characterized for the first time by applying a DC discharge to a mixture of water and sulfur dioxide heavily diluted in neon. The fundamental rotational transition was detected near 17 GHz, in good agreement (within $\sim 1\%$) of the calculated value derived from the equilibrium structure\(^b\). Microwave-microwave double resonance techniques have been used to extend the dataset to higher frequencies and to provide confirmation of the spectroscopic assignments.

HIGH RESOLUTION INFRARED SPECTROSCOPY OF THE PO\(_2\) RADICAL

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The infrared absorption spectrum associated with the asymmetric stretching fundamental of PO\(_2\) (\(v_3\)) has been measured using high resolution tunable diode laser spectroscopy. The free radical was formed in large concentrations in a fast-flow system by reacting white phosphorus vapour with atomic oxygen. More than 700 new lines have been assigned between 1290 and 1350 cm\(^{-1}\). Data was combined with infrared and LMR lines, obtained from previous studies and simultaneously fitted using the CALPGM suite. The precise constants derived definitively exclude a series of unassigned transitions from belonging to the \(v_3\) fundamental band and potential assignments for that series are discussed.

SUBMILLIMETER-WAVE ROTATIONAL SPECTRA OF DNC

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Spectroscopic investigations of DNC have been less extensive than those for HNC. See Brünken et al.\(^a\) and Bechtel et al.\(^b\) for relevant references. In the present investigation, rotational transitions of DNC have been observed in the submillimeter-wave region in an extended negative glow discharge in a gas mixture of CD\(_4\) and N\(_2\). The dissociative recombination reaction of DCND\(^+\) with electrons is thought to be a dominant channel to produce DNC in highly excited vibrational states; the rotational lines in levels up to (008) are observed. The rotational and centrifugal distortion constants are determined for these states along with those for the (100) state. The measurement accuracy is high enough to determine some higher order vibration-rotation interaction constants. The least-squares fits were straightforward except for (004), (006), and (008), where very small but significant perturbations were found.

A striking isotope effect was observed on the vibrational temperature in this investigation. The vibrational temperature for the \(v_3\) mode for DNC is as high as 4000 K and the rotational transitions are observable in states up to (008), while the corresponding temperature is about 1500 K for HNC. The vibrational temperature for the \(v_1\) mode is about 1000 K for DNC and about 1300 K for HNC. The bending vibrational mode is not excited, and the vibrational temperature for the \(v_2\) mode is only about 400 K. The origin of this conspicuous excitation of the \(v_3\) mode of DNC is not obvious. However, it should be closely related to mechanism of the dissociation of HCNH and DCND. Apparently the difference in the masses of the departing H/D is a factor causing this difference, but the vibrational temperature for \(v_3\) of DCN is not particularly high, about 1000 K. When the D atom departs from the D-C side, apparently the C-N vibration is highly excited. On the other hand, when the D-N bond is broken, not much excitation of the C-N vibration occurs.

HIGH RESOLUTION FOURIER TRANSFORM SPECTROSCOPY OF TRANSIENT SPECIES ON THE FAR INFRARED "AILES" BEAMLINE OF SOLEIL SYNCHROTRON.

M. A. MARTIN-DRUMEL\textsuperscript{a}, O. PIRALI\textsuperscript{a}, D. BALCON\textsuperscript{a}, P. BRECHIGNAC, Institut des Sciences Moléculaires d’Orsay (ISMO), CNRS, Université Paris XI, Orsay, France; M. VERVLOET, P. ROY, SOLEIL Synchrotron, AILES beamline, Saint-Aubin, France.

Numbers of transient species have already been identified in cold and hotter sources of the interstellar medium. In a context of extensive far infrared (FIR) astrophysical observations (Herschel, ALMA, SOFIA, ...), we developed several experiments to record high resolution spectra of transient species using the Bruker IFS 125 FT interferometer associated to the bright FIR continuum extracted by the "AILES" beamline of SOLEIL.

Despite physical limitations in the FIR, emission spectroscopy is an efficient technique to observe pure rotational transitions of excited molecules and radicals in that spectral range. The emission from a radio frequency discharge is collected by a single off-axis parabolic mirror and focused onto the entrance iris of the FT. Due to the S/N ratio, gas temperature and pressure broadening, FIR spectra were recorded at 0.004 cm\(^{-1}\) resolution.

Absorption spectroscopy benefits at AILES from the strong brilliance of the synchrotron radiation allowing a large improvement in sensitivity. For this purpose, we developed a multipass absorption DC discharge cell to record spectra of transient species. A set of mirrors placed in a White-type arrangement allows an absorption path length of 24 meters. Thanks to the relatively long path length of the cell and the synchrotron radiation source, this absorption technique appears to be sensitive and allows the use of the highest resolution of the FT (R=0.001 cm\(^{-1}\)).

We will present the results obtained with those two complementary techniques on several molecules (H\(_2\)O, HCN and NH\(_3\)) and radicals (OH, NH\(_2\), C\(_3\), CH) from the MIR to the FIR.

\textsuperscript{a}ALSO AT: SOLEIL SYNCHROTRON, AILES BEAMLINE, SAINT-AUBIN, FRANCE.
\textsuperscript{b}O. Pirali, M. Vervloet Chemical Physics Letters 423, 376-381 (2006)

CALCULATION OF THE TRANSITION DIPOLE MOMENT OF THE \textit{\tilde{A}} ← \textit{\tilde{X}} ELECTRONIC TRANSITION OF THE C\(_2\)H\(_5\)O\(_2\) FROM THE PEAK ABSORPTION CROSS-SECTION

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

With the advent of sensitive spectroscopic techniques such as cavity ring-down spectroscopy (CRDS), the \textit{\tilde{A}} ← \textit{\tilde{X}} electronic transition of the organic peroxy radicals becomes an attractive analytical tool to study such species which play crucial roles in atmospheric and combustion chemistry. Since both the \textit{\tilde{X}} and \textit{\tilde{A}} states are bound, the electronic transition between them bears structural information on the both states and therefore the \textit{\tilde{A}} ← \textit{\tilde{X}} absorption is highly species-selective. To utilize this selectivity in quantitative studies, the accurate knowledge of the absorption properties must be known. The electronic transition moment, |\(\mu_e|\textsuperscript{2}\), is the key piece of information that allows one to calculate absorption spectra of the radicals over wide range of the experimental conditions.

Additionally, the experimentally obtained values of the |\(\mu_e|\textsuperscript{2}\) for \textit{\tilde{A}} ← \textit{\tilde{X}} transition in organic peroxy radicals provide a benchmark for quantum chemical calculations of the electronic structure of these species.

In this work we obtain the value for |\(\mu_e|\textsuperscript{2}\) for the G-conformer of ethyl peroxy radicals using their experimentally measured peak absorption cross-section in the room-temperature spectra and the results of quantum chemical calculations of the vibrational structure and the high resolution CRDS study of the rotational structure of these species. The results of this analysis will be compared to the calculated values, and the major sources of errors will be discussed.
ELECTRONIC SPECTROSCOPY OF COBALT-NEON CATION

J. MOSLEY, S. HASBROUCK, and M. A. DUNCAN, Department of Chemistry, University of Georgia, Athens, GA 30602-2556.

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 13529 cm\(^{-1}\). A progression of fifteen 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 (\(\omega_e=113\) cm\(^{-1}\), \(\omega_x=4.76\) cm\(^{-1}\)) were determined, and the electronic cycle leads to a ground state binding energy (D\(_0\)=933 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. Resolved rotational structure in the (0,0) transition gives the excited and ground state bond lengths.

Intermission

ROVIBRATIONAL SPECTROSCOPY OF ALUMINUM CARBONYL CLUSTERS IN HELIUM NANODROPLETS


Helium nanodroplet isolation and a tunable quantum cascade laser are used to probe the fundamental CO stretch bands of Aluminum Carbonyl complexes, Al-(CO)_n (n \leq 5). The droplets are doped with single aluminum atoms via the resistive heating of an aluminum wetted tantalum wire. The downstream sequential pick-up of CO molecules leads to the rapid formation and cooling of Al-(CO)_n clusters within the droplets. Near 1900 cm\(^{-1}\), rotational fine structure is resolved in bands that are assigned to the CO stretch of a \(^2\Pi_{1/2}\) linear Al-CO species, and the asymmetric and symmetric CO stretch vibrations of a planar C\(_{2v}\) Al-(CO)_2 complex in a \(^2\Pi_1\) electronic state. Bands corresponding to clusters with n \geq 3 lack resolved rotational fine structure; nevertheless, the small frequency shifts from the n=2 bands indicate that these clusters consist of an Al-(CO)_2 core with additional CO molecules attached via van-der-Waals interactions. A second n=2 band is observed near the CO stretch of Al-CO, indicating a local minimum on the n=2 potential consisting of an “unreacted” Al-CO-(CO) cluster. The linewidth of this band is \(~0.5\) cm\(^{-1}\), which is over 50 times broader than transitions within the Al-CO band. The additional broadening is consistent with a homogeneous mechanism corresponding to a rapid vibrational excitation induced reaction within the Al-CO-(CO) cluster to form the covalently bonded Al-(CO)_2 complex. For the n=1,2 complexes, CCSD(T) calculations and Natural Bond Orbital (NBO) analyses are carried out to investigate the nature of the bonding in these complexes. The NBO calculations show that both \(\pi\) “back” donation (from the occupied aluminum p-orbital into the \(\pi\) antibonding CO orbital) and \(\sigma\) donation (from CO into the empty aluminum p-orbitals) play a significant role in the bonding, analogous to transition metal carbonyl complexes. The large redshift of the CO stretch vibrations is consistent with this bonding analysis.
PYROLYSIS OF ACETALDEHYDE: A FLEETING GLIMPSE OF VINYLIDENE

A.J. VASILLOU, K.M. PIECH, G.B. ELLISON, Department of Chemistry, University of Colorado, Boulder, CO, 80303; A. GOLAN, O. KOSTKO, M. AHMED, Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720; D.L. OSBORN, Sandia National Laboratories, Livermore, CA 94551; J.W. DAILY, Department of Mechanical Engineering, University of Colorado, Boulder, CO 80302; M.R. NIMLOS, Center for Renewable Chemical Technologies and Materials, NREL, Golden, CO 80401; and J.F. STANTON, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712.

The thermal decomposition of acetaldehyde has been studied in a heated silicon carbide “microtubular reactor”, with products monitored by both photoionization mass spectrometry and matrix-isolation Fourier transform infrared spectroscopy. A well-known, and observed, route of decomposition occurs when the weakest C-C bond is broken; this process leads to methyl and formyl radicals. In addition to this, we find evidence for two additional channels: CH$_3$CHO $\rightarrow$ H$_2$CCO (ketene) and CH$_3$CHO $\rightarrow$ C$_2$H$_2$ (acetylene), reactions that also generate molecular hydrogen and water, respectively. This talk focuses on the last pathway, which proceeds via vinyl alcohol. Evidence is presented that the high temperature unimolecular dehydration of vinyl alcohol proceeds by two mechanisms; one of these is a (1,2) elimination that directly yields acetylene, and the other is a (1,1) elimination that necessarily accesses the vinylidene isomer of C$_2$H$_2$ as an intermediate.

SPECTROSCOPIC STUDIES OF THE $\tilde{A}$--$\tilde{X}$ ELECTRONIC SPECTRUM REVEAL BOTH THE STRUCTURE AND DYNAMICS OF $\beta$-HYDROXYETHYLPEROXY RADICAL

MING-WEI CHEN, GABRIEL M. P. JUST*, TERRANCE J. CODD, TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210; W. LEO MEERTS, Radboud University Nijmegen, Institute for Molecules and Materials, Heyendaalseweg 135, NL-6525 AJ Nijmegen, The Netherlands.

The jet-cooled $\tilde{A}$--$\tilde{X}$ origin band absorption spectra of the G$_1$G$_2$G$_3$ conformer of four $\beta$-hydroxyethyl-peroxy ($\beta$-HEP) isotopologues, $\beta$-HEP (HOCH$_2$CH$_2$OO), $\beta$-DHEP (DOCH$_2$CH$_2$OO), $\beta$-HEP-d$_4$ (HOCD$_2$CD$_2$OO), $\beta$-DHEP-d$_4$ (DOCD$_2$CD$_2$OO), have been recorded by a cavity ringdown apparatus with a laser source linewidth $\sim$70 MHz in the near IR region. The spectra of all four isotopologues have been analyzed and successfully simulated with an evolutionary algorithm, confirming the cyclic structure of the conformer responsible for the observed origin band. In addition, rotational constants in both the $\tilde{X}$ and $\tilde{A}$ states and the orientation of the transition dipole moment have been determined. The broadened linewidth of the absorption spectrum ($\Delta\nu > 2$ GHz) is due to the shortened lifetime of the $\tilde{A}$ state following its internal conversion back to the $\tilde{X}$ state. The variation of lifetime with deuteration suggests that the hydroxyl hydrogen is involved and the process likely occurs along the reaction path for conversion between the peroxy and peroxide isomers.

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OBSERVATION OF THE $\tilde{A}$ - $\tilde{X}$ ELECTRONIC TRANSITION OF THE 2-HYDROXYPROPYL PEROXY RADICAL VIA CAVITY RINGDOWN SPECTROSCOPY

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

Alkyl peroxy radicals are key intermediates in the atmospheric oxidation and low temperature combustion of hydrocarbons. In the past decade our group has obtained and analyzed the $\tilde{A}$ - $\tilde{X}$ spectra of a series of saturated and unsaturated organic peroxy radicals using cavity ringdown spectroscopy (CRDS). We have recently extended our investigations of peroxy radicals to include OH substituted peroxy radicals. Hydroxy peroxy radicals are key intermediates in the OH mediated oxidation of unsaturated hydrocarbons in the atmosphere and we recently reported the study of $\beta$-hydroxyethylperoxy radical (HOCH$_2$HOO). We have now made preliminary observation of the $\tilde{A}$ - $\tilde{X}$ spectrum of the 2-hydroxypyropyl peroxy radical. With the aid of ab initio and DFT calculations we hope to obtain a conformer specific assignment of the bands.

We produced methylthio (or thiomethoxy, CH$_3$S) radicals by photodissociation of CH$_3$SH in a supersonic jet at 248 nm. The CH$_3$S$^+$ ions were subsequently produced with the 1+1 IR-VUV photoionization and detected with the time-of-flight (TOF) technique. The IR spectrum of CH$_3$S was obtained on tuning the wavelength of the IR laser in the range 2780–3280 cm$^{-1}$ while monitoring the intensity of the CH$_3$S$^+$ signal; the frequency of the VUV laser was maintained at 134.8 nm, 200 cm$^{-1}$ below the ionization threshold of CH$_3$S (IE = 9.225 eV). This technique has an advantage over other IR-absorption techniques because its mass selectivity eliminates interferences from the precursor and other photolysis products such as H$_2$CS, CH$_3$, or CH$_3$SS. Absorption bands near 2820, 2904, and 3215 cm$^{-1}$ were observed and tentatively assigned as transitions from the ground vibrational state to the $1^1A_1$, $4^1A_1$, and $5^16^2$ states, respectively. These bands are in agreement with those reported for CH$_3$S produced via in situ photolysis of CH$_3$SH, CH$_3$SCH$_3$, and CH$_3$SSCH$_3$ isolated in solid p-H$_2$.\(^1\) A new band near 2970 cm$^{-1}$ that is consistent with that observed in photoelectron spectrum\(^2\) might be assigned to the transition from the ground vibrational state to the $a_1$ component of the $5^16^2$ state.


In hydrocarbon combustion chemistry, the phenyl radical is believed to be a key intermediate in processes that lead to the formation of polycyclic aromatic hydrocarbons (PAH's) and soot. The radical is also of significance in atmospheric chemistry, interstellar chemistry, and environmental health. The detection and characterization of this highly reactive intermediate species in PAH formation reactions can help with the elucidation of mechanisms. However, the low concentrations associated with these radicals require special techniques to study them. This study combines an electrical discharge to produce radicals, a jet expansion to cool them immediately after production, and cavity ring-down spectroscopy (CRDS) for detection. We report absorption spectra for the $1^2B_1 \rightarrow \tilde{X}^2A_1$ transition of the phenyl radical at a rotational temperature near 15 K. Rotational constants and vibrational frequencies for the $0^1_0^0$, $9^1_{10}$, and $10^1_{11}$ bands are reported. Homogeneous line broadening was evident with a width indicative of an excited state lifetime of 80 ps. These results show the effectiveness of our system for studying relatively large reactive intermediates.
RA. MINI-SYMPOSIUM: FUNDAMENTAL PHYSICS
THURSDAY, JUNE 23, 2011 – 8:30 am
Room: 160 MATH ANNEX

Chair: NEIL SHAFER-RAY, University of Oklahoma, Norman, Oklahoma

RA01
INVITED TALK
30 min 8:30

TESTS OF PARITY AND TIME-REVERSAL VIOLATION USING DIATOMIC MOLECULES

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Our group is pursuing several experiments to study violations of discrete symmetries such as parity ($P$-) and time-reversal ($T$-). These effects arise due to particle physics phenomena at very high energy scales, yet can give rise to observable effects in precision spectroscopic measurements. Our experiments all use the structure of diatomic molecules to dramatically amplify the signals due to $P$- and $T$-violation, relative to previous experiments using atoms for similar purposes. This talk will focus on two of our experiments. The ACME project$^b$ seeks to measure the permanent electric dipole moment of the electron, a $P$- and $T$-violating effect predicted in many extensions to the Standard Model of particle physics (e.g. Supersymmetric theories). ACME uses ThO molecules, delivered from a newly-developed type of cryogenic molecular beam source,$^c$ to simultaneously provide high statistical sensitivity and unprecedented rejection of systematic errors. The ZOMBEY experiment$^d$ seeks to measure $P$-violating effects in free radicals, with the goal to determine properties of the electroweak force that are inaccessible to accelerator-based measurements. This talk will describe the concepts and methods of these experiments, highlighting the crucial role of molecular spectroscopy in optimizing their performance.

$^a$This work supported by NSF

RA02
15 min 9:05

A NEW MEASUREMENT OF THE ELECTRON’S ELECTRIC DIPOLE MOMENT USING YbF MOLECULES

J. J. HUDSON, D. M. KARA, I. J. SMALLMAN, B. E. SAUER, M. R. TARBUTT and E. A. HINDS, Centre for Cold Matter, Blackett Laboratory, Imperial College London, Prince Consort Road, London SW7 2AZ, UK.

Using a beam of YbF molecules, we have made an improved measurement of the electron’s electric dipole moment. We present our new result and discuss how we plan to reduce the statistical and systematic uncertainties in future measurements.
SPECTROSCOPY OF THORIUM MONOXIDE, ThO; E(O+),F(O+),-X 1Σ+ BANDS

FANG WANG AND TIMOTHY C. STEIMLE, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287; MICHAEL HEAVEN, Department of Chemistry, Emory University, Atlanta, GA 30322.

Thorium monoxide, ThO, has recently attracted interest as a possible venue for the determination of the electric dipole moment of the electron, $d_e$. Here we report on the results of an optical Stark study of the $E(O^+)-X 1Σ^+ (1,0)$ band and the field-free study of the $F(O^+)-X 1Σ^+ (0,0)$ band. A supersonic molecular beam of ThO was generated using a laser ablation technique and probed using laser excitation spectroscopy. The determined values for the permanent electric dipole moments, $μ_{el}$, for the $E(O^+)-X 1Σ^+ (v=1)$ and $X 1Σ^+ (v=0)$ vibronic states were determined to be $3.534 ± 0.010$ D and $2.782 ± 0.012$ D, respectively. The dispersed laser induced fluorescence resulting from the excitation of the $E(O^+)-X 1Σ^+ (1,0)$ and $F(O^+)-X 1Σ^+ (0,0)$ bands have been recorded and the results are compared to Franck-Condon predictions. The radiative lifetimes for the $E(O^+)-X 1Σ^+ (1,0)$ band $F(O^+)-X 1Σ^+ (0,0)$ bands were determined.

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PERMANENT ELECTRON ELECTRIC DIPOLE MOMENT SEARCH IN THE X 3Δ1 GROUND STATE OF TUNGSTEN CARBIDE MOLECULES

JEONGWON LEE, JINHAI CHEN, and AARON LEANHARDT, Department of Physics, University of Michigan, Ann Arbor, MI 48109.

We are developing an experiment to search for the permanent electric dipole moment (EDM) of the electron using the valence electrons in the $X 3Δ_1$ ground state of Tungsten Carbide (WC) molecules. Currently, we are detecting the molecules by Laser Induced Fluorescence spectroscopy at ~75 cm downstream of a pulsed ablation beam source. We have a detection rate of ~10 $^{183}$W $^{12}$C molecules/second in $X 3Δ_1$, $v^*=0$, $J^*=1$ state with geometric detection efficiency of 0.004. A continuous WC molecular beam is under development. Additionally, preliminary measurements of the $^{183}$W $^{12}$C hyperfine structure will be presented.
THEORETICAL STUDY OF THE PbF AND PbO MOLECULES

ALEXANDER N. PETROV, ANATOLY V. TITOV, MIKHAIL G. KOZLOV, Petersburg Nuclear Physics Institute, Gatchina, Leningrad district 188300, Russia; KIRILL I. BAKLANOV, Institute of Physics, Saint Petersburg State University, Saint Petersburg, Petrodvortsy, 198904, Russia.

Planned experiments to search for the simultaneous violation of the time-reversal invariance (T) and space parity (P) have motivated interest to the theoretical study of the PbF and PbO molecules. In this work we use the configuration interaction method with the generalized relativistic effective core potential for calculation of the spin-rotational Hamiltonian for the ground $^2\Pi_{1/2}$ and the first excited $^3\Sigma^+_1$ states of the PbF including PT-odd and P-odd terms. In particular, we have obtained hyperfine constants on the $^{207}$Pb nucleus. For the $^2\Pi_{1/2}$ state $A_\perp = -6859.6$ MHz, $A_\parallel = 9726.9$ MHz and for the $^3\Sigma^+_1$ state $A_\perp = 1720.8$ MHz, $A_\parallel = 3073.3$ MHz. Our values are in good agreement with recent experimental data. The effective electric field on the electron, which is required for interpretation of the results of the planned experiment in terms of eEDM is found to be $3.3 \times 10^{10}$V/cm. The same method was used for calculation of the PbO molecule. The main goal is to clarify role of interaction with the nearest electronic state $^3\Sigma^+_u$ on the hyperfine structure and magnetic properties of the $a(1)^3\Pi^+_u$ state of PbO. The accounting for this contribution leads to the difference between $g$-factors of the $J = 1$ $\Omega$-doublet levels, $\Delta g = 37 \times 10^{-4}$, which is in good agreement with the experimental data $\Delta g = 30(8) \times 10^{-4}$. The contribution of this interaction rapidly grows with $J$. For $J = 30$ the difference of $g$-factors of $\Omega$-doublet states reaches 100%; for hyperfine constants it reaches 18%. These differences also depend on the electric field, and for $E = 11$ V/cm for $^{207}$PbO the difference in $g$-factors turns to zero. The latter is important for suppressing systematic effects in the electron electric dipole moment search experiment.

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THE EFFECTIVE HAMILTONIAN FOR THE GROUND STATE OF $^{207}$Pb$^{19}$F AND NEW MEASUREMENTS OF THE FINE STRUCTURE SPECTRUM NEAR 1.2 $\mu$m.

RICHARD MAWHORTER, BENJAMIN MURPHEY, ALEXANDER BAUM, Department of Physics and Astronomy, Pomona College, Claremont, CA 91711; TREVOR J. SEARS, Chemistry Department Brookhaven National Laboratory, Upton, NY 11973 and Stony Brook University, Stony Brook, NY 11794; T. ZH. YANG, P. M. RUPASINGHE, C. P. MCRAVEN, N. E. SHAFER-RAY, Homer L. Dodge Department of Physics and Astronomy, University of Oklahoma, Norman, OK; LUKAS D. ALPEHJ AND JENS-UWE. GRABOW, Gottfried-Wilhelm-Liebniz-Universität, Institut für Physikalische Chemie & Elektrochemie, D-30167 Hannover, Germany.

We have measured rotational transitions in the ground, $X_1 2^2\Pi_{1/2}$, electronic state of naturally occurring isotopomers of PbF in a supersonic free jet Fourier transform microwave spectrometer. The data for $^{207}$Pb$^{19}$F is particularly interesting because it is a candidate for a future experimental e-EDM measurement. To fit the data for this species to the measurement precision, the nuclear spin-spin dipolar interaction and a second term that can be equivalently viewed as a centrifugal distortion correction to the familiar Frosch and Foley hyperfine coupling terms, or an $\Omega$– dependent correction to the nuclear spin-rotational coupling terms are required, in addition to the standard terms. To characterize the higher $X_2 2^1\Pi_{3/2}$ component of the ground state of PbF, we are attempting a direct measurement of transitions between the two components in a slit jet-cooled sample using a frequency comb-referenced extended cavity diode laser. This spectrum was originally detected in a hot source by Fourier transform near-infrared spectroscopy, but low–J transitions were unresolved at that time.

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Intermission
A PbF PROBE FOR THE ELECTRON ELECTRIC DIPOLE MOMENT

JOHN MOORE-FURNEAUX, N.E. SHAFER-RAY, Home L. Dodge Department of Physics and Astronomy, University of Oklahoma, Norman OK, 73019.

A molecule in a state of total angular momentum \( F \) has a familiar \( 2F + 1 \) degeneracy. In the presence of a pure magnetic field, each magnetic sub-level \( M_F \) acquires its own energy, fully lifting each magnetic sub-level \( M_F \). In the presence of a pure electric field, quantum states with non-zero magnetic quantum numbers \( |M_F| \) remain doubly degenerate. This fact is well established by Stark spectroscopy and is a consequence of time-reversal symmetry. In 1950, Purcell and Ramsey pointed out that time-reversal symmetry could be broken by the existence of an electric dipole moment of the electron. Over the last 60 years, the interest in such a symmetry breaking dipole moment has increased, in part because it may explain the matter-antimatter asymmetry of the Universe, and in part because it could help to differentiate between competing fundamental models of Physics. If large enough, such a dipole moment could lead to an observable lifting of the degeneracy between \( +M_F \) and \(-M_F\) states of a molecule in a pure electric field. We report on progress toward searching for an electric dipole moment by an optical quantum beat experiment utilizing the \( X_1 \ ^2\Pi_{1/2} \) state of PbF molecule.

HIGH RESOLUTION ROTATIONAL SPECTROSCOPY STUDY OF THE ZEEMAN EFFECT IN THE \(^2\Pi_{1/2}\) MOLECULE PbF

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Motivated by the ongoing search for the CP-violating electron electric dipole moment (e-EDM), rotational spectra of the radicals \(^{207}\text{Pb}^{19}\text{F}\) and \(^{208}\text{Pb}^{19}\text{F}\) were measured using a supersonic jet Fourier transform microwave spectrometer. Zeeman splitting was examined for \(^{207}\text{Pb}^{19}\text{F}\) and \(^{208}\text{Pb}^{19}\text{F}\) \( J = 1/2 \) and \( J = 3/2 \) transitions using three pairs of Helmholtz coils capable of generating magnetic fields up to \( \sim 4 \) Gauss. Transitions were observed with 0.5 kHz accuracy over a range of \( 2 - 26.5 \) GHz. Zeeman splittings as small as 6 kHz were able to be resolved. The observation of these field dependent spectra allowed for the determination of the two body-fixed g-factors, \( G_\parallel \) and \( G_\perp \), of the electronic wave function. The final values obtained compare reasonably well with recently calculated values and will be reported at the meeting. The precise determination of the body fixed g-factors is an important step in a possible future e-EDM experiment using either the \(^{207}\text{Pb}^{19}\text{F}\) or \(^{208}\text{Pb}^{19}\text{F}\) molecule.

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. Work by N. E. Shafer-Ray was performed with support from the National Science Foundation award NSF-0855431. J.-U. Grabow acknowledges funding from the Deutsche Forschungsgemeinschaft and the Land Niedersachsen. RJM and ALB appreciate the support of a Sontag Research Fellowship from Pomona College.

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STARK SPECTROSCOPY OF PbF MOLECULE

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In 1950 Purcell and Ramsey (Phys. Rev. 78, 807-807, 1950) suggested that the electron may have an electron’s electric dipole moment (e-EDM). Such a dipole moment could influence the Stark spectra of heavy diatomic molecules. The lead mono-fluoride (PbF) molecule has a large dipole moment combined with closely spaced levels of opposite parity. This feature reduces the magnitude of the external electric field required to become sensitive to the e-EDM. A multi-photon ionization technique pseudo-continuous-REMPI (pc-REMPI) is utilized for Stark spectroscopy of PbF molecule. We analyze data in terms of an spin-rotational Hamiltonian to determine the dipole moment of the PbF molecule. The results will compare to the theoretical ones and some implications of measuring e-EDM are discussed.

THE PFI-ZEKE SPECTRUM OF HfF+, IN SUPPORT OF FUNDAMENTAL PHYSICS

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The HfF+ cation has been identified as a molecule with favorable properties for investigation of the dipole moment of the electron. The ion is predicted to have a $^1\Sigma^+$ ground state, but the state of greatest interest is the low-lying $^3\Delta_1$ state, which correlates with Hf$^+(6s5d)F^-$. A high internal electric field may be generated when the $\Omega=1$ state is polarized by a modest external field. In the present work, spectroscopic data for the ground and low-lying states HfF$^+$ have been obtained using the technique of pulse field ionization - zero electron kinetic energy (PFI-ZEKE) spectroscopy. Sequential two-photon excitation was used, with the first photon set to excite a transition near 28593 cm$^{-1}$. This previously unreported band was used as it is at slightly less than half of the ionization energy (IE), and therefore not subject to one-color, two-photon ionization. PFI-ZEKE spectra were recorded for the levels $X^1\Sigma^+ (v=0-6)$, $^3\Delta_1 (v=0-3)$, $^3\Delta_2 (v=0-3)$, and $^3\Delta_3 (v=0,1)$. Rotational resolution was achieved using single rotational line excitation of the intermediate state. The IE for HfF$^+$ was found to be 59477 cm$^{-1}$. Term energies and molecular constants for the ground and low-lying states of HfF$^+$ will be reported.
RB01 15 min 8:30

NITROGEN-BROADENED $^{13}$CH$_4$ AT 80 TO 296 K


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 were recorded using temperature-controlled absorption cells installed in the sample compartment of a Bruker IFS-125HR Fourier Transform spectrometer (FTS) at the Jet Propulsion Laboratory (JPL). Analysis of these spectra using multispectrum fitting has determined half widths, pressure-induced shifts, line mixing parameters and their temperature dependences for transitions belonging to a number of P- and R-branch J-manifolds. The analysis examined in detail the temperature-dependence of N$_2$-broadened half width and pressure-induced shift coefficients over the entire temperature range from 80 K to 296 K. The results are compared with other published measurements of N$_2$- and air-broadened methane parameters.

RB02 15 min 8:47

MEASUREMENT OF CH$_3$D ABSORPTION CROSS SECTIONS, PRESSURE BROADENING, AND SHIFT COEFFICIENTS IN THE 1.65 $\mu$m SPECTRAL REGION BY USING CONTINUOUS AVE CAVITY RING-DOWN SPECTROSCOPY

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Quantitative spectroscopy of CH$_3$D in the near-IR is of importance for an ongoing project to build an instrument to measure the H/D isotopic ratio of methane gas. Continuous-wave cavity ring-down spectroscopy (CRDS) has been used to examine the absorption cross sections, the pressure-broadening and pressure-shift coefficients at around 1652 nm. The absorption cross sections of CH$_3$D were quantified in the wavenumber region between 6046 and 6060 cm$^{-1}$. The maximum peak is located at 6055.17 cm$^{-1}$, which gives $(8.58 \pm 0.37) \times 10^{-21}$ cm$^2$/molecule at the total pressure of ~ 8.2 Torr of the N$_2$ buffer gas. By using the small step size of the laser wavenumber scan, we measured the pressure-broadening effects, and the pressure-shift effects, on CH$_4$ and CH$_3$D absorption lines. The N$_2$, O$_2$ and CO$_2$ pressure broadening coefficients of CH$_3$D are 0.058, 0.054 and 0.049 cm$^{-1}$/atm, respectively, at the wavenumber we employed. Under the experimental conditions we used, N$_2$ and O$_2$ have very similar pressure broadening effects, and their effects on CH$_3$D is very similar to those of CH$_4$. At the wavenumber we employed, the same values of N$_2$ and O$_2$ pressure-shift coefficient , - 0.012 cm$^{-1}$/atm, and a little higher value of CO$_2$, - 0.013 cm$^{-1}$/atm, were found.
Ethylene is a naturally occurring compound in ambient air that affects atmospheric chemistry and global climate. The \( \text{C}_2\text{H}_4 \) spectrum is available in databases only for the 1000 and 3000 cm\(^{-1}\) ranges. In this work\(^a\), the ethylene absorption spectrum was measured in the 6030-6250 cm\(^{-1}\) range with the use of a high resolution Bruker IFS 125HR Fourier-spectrometer and a two-channel opto-acoustic spectrometer with a diode laser. As a secondary standard of wavelengths, the methane absorption spectrum was used in both cases. A preliminary analysis was realized thanks to the tensorial formalism developed by the Dijon group that is implemented in the XTDS software package\(^b\). We considered the two combination bands \( \nu_5 + \nu_9 \) and \( \nu_5 + \nu_{11} \) as an interacting dyad. Parameters for the \( \nu_9/\nu_{11} \) dyad were fitted simultaneously from a re-analysis of previously recorded supersonic expansion jet FTIR data, while parameters for the \( \nu_5 = 1 \) Raman level were taken from literature. More than 600 lines could be assigned in the 6030-6250 cm\(^{-1}\) region (and also 682 in the 2950–3150 cm\(^{-1}\) region) and effective Hamiltonian parameters were fitted, including Coriolis interaction parameters. The dyad features are globally quite well reproduced, even if there are still problems at high \( J \) values.


The possibility of monitoring Methyl Bromide is of interest for both environmental and health concerns. It has an ozone depletion potential of 0.2% and falls under regulations of the Clean Air Act. Neurological effects from long term exposure may result from its major use as a pesticide. Recent improvements in microwave limb sounding at mm & submm wavelengths have resulted in retrievals of Methyl Chloride from atmospheric spectra. It is conceivable that Methyl Bromide would also be measurable by this technique. In an effort to extend and improve the previous work, the THz spectrum of Methyl Bromide has been measured at JPL. We used an isotopically enriched \( ^{13}\text{CH}_3\text{Br} \) (90%) sample and recorded spectra from 750–1200 GHz. Our assignment covers the \( \text{CH}_3^{79}\text{Br}, \text{CH}_3^{81}\text{Br}, ^{13}\text{CH}_3^{79}\text{Br} \) and \( ^{13}\text{CH}_3^{81}\text{Br} \) isotopologues with \( J < 66 \) and \( K < 17 \) for the ground vibrational state. We plan to assign vibrational satellites and investigate possible perturbations near \( K = 12 \) in the ground state.
This paper will discuss the implications of spectral interference from atmospheric constituents on the performance of spectroscopic point sensors in the submillimeter/terahertz (SMM/THz) spectral range. Spectral clutter can be a limiting factor for spectroscopic sensors, especially where high sensitivity and specificity are required. The most abundant atmospheric gases are either transparent or have spectra that are very sparse in the SMM/THz. For SMM/THz sensors that utilize continuous wave (cw) electronic techniques the clutter limit for the detection of common target gases is in the ppt (1 part in $10^{12}$) or lower range. This warrants absolute specificity of molecular identification with probability of false alarm well below $10^{-10}$. Moreover, the low clutter limit demonstrated for cw electronic systems in the SMM/THz is independent of system size and complexity.

High Resolution Spectroscopy Using a Tunable THz Synthesizer Based on Photomixing

Optical heterodyning, also known as photomixing, is an attractive solution as a single device able to cover the entire frequency range from 300 GHz to 3 THz. As the THz frequency is extracted from the difference frequency of two lasers, the accuracy with which the generated frequency is known is directly determined by the frequency accuracy of the lasers. In order to fully characterize the spectral fingerprint of a given molecule, an accuracy approximately one order of magnitude finer than the Doppler linewidth is required, around 100 kHz for smaller polar compounds. To generate accurate cw-THz the frequency spacing of the modes of a Frequency Comb (FC) has been employed to constrain the emission frequency of a photomixing source. Two phase locked loops are implemented coherently locking the two cw-lasers (CW1 and CW2) to different modes of the FC. Although this solution allows accurate generation of narrowband THz the continuous tuning of the frequency presents some obstacles. To overcome these difficulties a system architecture with a third cw-laser (CW3) phase locked to CW2 has been implemented. The beatnote between CW2 and CW3 is free from the FC modes therefore the PLL frequency can be freely scanned over its entire operating range, in our case around 200 MHz. The most of polar compounds may be studied at high resolution in the THz domain with this synthesizer. Three different examples of THz analysis with atmospheric and astrophysical interests will be presented:

- The ground and vibrationally excited states of H$_2$CO revisited in the 0.5-2 THz frequency region
- The rotational dependences of the broadening coefficients of CH$_3$Cl studied at high J and K values
- The molecular discrimination of a complex mixture containing methanol and ethanol.

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A resurgence of interest in spectroscopic sensors has been fueled by increases in performance made possible by technological advancements and applications in medicine, environmental monitoring, and national security. Often this research is technology driven, without enough consideration of the spectroscopic signatures available to be probed. We will compare several current spectroscopic sensors across the electromagnetic spectrum, with an eye towards the fundamental spectroscopic considerations important at each wavelength.

We will discuss the implementation of the recently developed Chirped-Pulse Fourier Transform THz spectrometer for the measurement of important atmospheric species. We will discuss how the method is used to obtain high-precision and high-sensitivity measurements of shapes, intensities, and broadening parameters directly from the rotational free induction decay signal. The current system measures a bandwidth of 10.6 GHz in a single measurement step with a resolution of 20 kHz and achieves high sensitivity in 30 seconds. Measurements of nitrous oxide, OCS, and other atmospheric species in the HITRAN database will be presented.

A step-scan Fourier-transform spectrometer coupled with a 6.4-m multipass absorption cell was employed to detect time-resolved infrared absorption spectra of reaction intermediates produced upon UV irradiation of a flowing mixture of CH$_3$SSCH$_3$ and NO$_2$ in CO$_2$. Irradiation of CH$_3$SSCH$_3$ at 248 nm produces CH$_3$S radicals that subsequently react with NO$_2$. Under a total pressure of 100 Torr, we observed bands near 1560 cm$^{-1}$, assignable to mainly the N=O stretching mode of CH$_3$SONO, with a small contribution from CH$_3$SNO$_2$. Calculations with density-functional theory (B3LYP/aug-cc-pVTZ and B3P86/aug-cc-pVTZ) predicted the geometry, vibrational wavenumbers, and rotational parameters of CH$_3$SONO and CH$_3$SNO$_2$. Based on these predicted rotational parameters, the simulated absorption band agrees satisfactorily with experimental results. Under a total pressure of 16 Torr, bands near 1560 and 1260 cm$^{-1}$ are assigned to NO$_2$ asymmetric and symmetric stretching modes of CH$_3$SNO$_2$, respectively; the former is overlapped with the N=O stretching mode of CH$_3$SONO. An additional band near 1070 cm$^{-1}$ is assigned to the S=O stretching mode of CH$_3$SO, reported previously as a secondary product in the reaction of CH$_3$S + O$_2$.$^a$ Reaction of CH$_3$S + NO$_2$ at high pressure clearly yields CH$_3$SONO, rather than CH$_3$SNO$_2$, as a major product.

TORSIONAL EXCITATION IN O-H STRETCH OVERTONE SPECTRA OF ETHYL HYDROPEROXIDE CONFORMERS

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Photoacoustic spectra at 3-6 quanta of O-H stretch show features attributed to torsion about the O-O bond and to distinct contributions from two conformers. Laser-induced fluorescence detection of OH radicals demonstrates unimolecular dissociation from some vibrationally and torsionally excited states.

RULES APPLICABLE FOR SPECTROSCOPIC PARAMETERS OF H₂O TRANSITIONS INVOLVING HIGH J STATES

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Two basic rules applicable for H₂O transitions involving high J states have been discovered. The origins of these rules are quantum properties of H₂O rotational states with their J values above certain boundaries. As a result, for transition lines involving high J states in individually defined groups, all their spectroscopic parameters (i.e., the transition wavenumber, intensity, pressure broadened half-width, pressure-induced shift, and temperature exponent) must follow these rules. One can use these rules to screen spectroscopic data provided by databases and to identify possible errors. In addition, by using extrapolation methods within the individual groups, one is able to predict spectroscopic parameters for lines involving very high J states. The latter are required in developing high-temperature molecular spectroscopic databases such as HITEMP.
FOURIER TRANSFORM MICROWAVE SPECTRUM OF THE YC$_2$ ($X^2A_1$) RADICAL

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The pure rotational spectrum of YC$_2$ ($X^2A_1$) in the range 4 - 40 GHz has been measured using Fourier transform microwave (FTMW) techniques. The species was produced using Discharge Assisted Laser Ablation Spectroscopy (DALAS) in a supersonic jet expansion of yttrium vapor and HCCH or CH$_4$, diluted in argon carrier gas. Three rotational transitions ($N = 1 \rightarrow 0$, $2 \rightarrow 1$, and $3 \rightarrow 2$) have been recorded each exhibiting fine structure and hyperfine splittings due to the yttrium nuclear spin of $I(^{89}$Y) = 1/2. The data have been analyzed with a case (b) asymmetric top Hamiltonian, and rotational, fine, and hyperfine constants have been determined. The spectrum of this species was previously measured by PPMODR methods, and our data have refined the spectroscopic constants. Measurements of the $^{13}$C isotopologues are currently underway to establish a precise structure for YC$_2$.

OBSERVATION OF LOW J TRANSITIONS OF LASER ABLATED ALKALI HALIDES

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Pulsed nozzle Fourier transform microwave spectroscopy has been used to observe low J transitions (J = 1 $\leftarrow$ 0 and J = 2 $\leftarrow$ 1) of several alkali halides produced by 532 nm laser ablation of pressed pellets. Spectra were readily located using predictions based on literature constants derived from higher J transitions but improvements of 10 to 100 kHz in spectral line positions are obtained. The additional accuracy could prove useful for astrophysical identification. The $^{41}$K isotopologue of KBr has been observed for the first time. Ablation of a mixed pellet of KCl and NaBr produces spectra of NaCl, indicating exchange between species produced by the ablation event. Aspects of the new experimental apparatus will be reported.

ROTATIONAL SPECTROSCOPY OF ZnCCH ($X^2\Sigma^+$) AT MICROWAVE AND MILLIMETER WAVELENGTHS

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The pure rotational spectrum of ZnCCH ($X^2\Sigma^+$) has been measured using Fourier transform microwave (FTMW) and direct absorption millimeter/submillimeter methods in the frequency range of 7-260 GHz. This is the first study of ZnCCH by any spectroscopic technique. In the FTMW system, the molecule was synthesized using discharge assisted laser ablation spectroscopy (DALAS) from a mixture of 0.05% acetylene in argon and the ablation of a zinc rod. In the millimeter-wave spectrometer, the radical was created from the reaction of zinc vapor, produced in a Broida-type oven, with HCCH in a DC discharge. Spectra of the main isopologue, $^{64}$ZnCCH, as well as $^{68}$ZnCCH, $^{69}$ZnCCH, ZnCCD and Zn$^{13}$C$^{13}$CH have been recorded. The data have been analyzed with a $^2\Sigma$ Hamiltonian and rotational, spin-rotation and H, D and $^{13}$C hyperfine parameters have been determined. The structure is being calculated based on the rotational constants and will be presented. Interpretation of the hyperfine constants will also be discussed.
FOURIER TRANSFORM MICROWAVE SPECTRUM OF MgCCH (X^2Σ^+)

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The pure rotational spectrum of MgCCH (X^2Σ^+) in the frequency range of 9-40 GHz has been measured using Fourier transform microwave (FTMW) methods. The molecule was synthesized using discharge assisted laser ablation spectroscopy (DALAS) from a mixture of 0.1% acetylene in argon and the ablation of a magnesium rod. From these data, the hydrogen hyperfine parameters have been determined for the first time, as well as refinement of the rotational and spin-rotational constants, combined with previous millimeter-wave spectra measured by the Ziurys group.

A CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTROMETER COMBINED WITH A LASER ABLATION SOURCE

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The design of a chirped-pulse Fourier transform microwave spectrometer CP-FTMW combined with a laser ablation LA source is presented. The spectrometer is capable of measuring the 6.5-18 GHz region. Rotational spectra of solid samples of proline (m.p. 228 °C) and alanine (m.p. 290 °C) vaporized by laser ablation has been recorded. Four low-energy conformers of proline and two in alanine have been detected. ^13C species of alanine in their natural abundance have been also observed. The performance of this spectrometer is compared to a LA-MB-FTMW spectrometer.

TECHNIQUES FOR HIGH-BANDWIDTH (\geq 30 GHz) CHIRPED-PULSE MILLIMETER/SUBMILLIMETER-WAVE SPECTROSCOPY

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Due to the increased availability of active multiplier chains for converting microwave pulses into the millimeter/submillimeter with reasonably high power (\geq 1 mW), chirped pulses with high phase stability and complete arbitrary waveform generator (AWG) frequency agility can be created and employed for high-sensitivity molecular spectroscopy, as demonstrated at the Symposium in the past few years.a,b The bandwidths of multiplier chains, however, can exceed the current limitations on digitizer bandwidth. Therefore, in order to obtain \geq 30 GHz spectra in 1 ms or less, techniques are being developed in which a two-channel AWG creates both the chirped pulses for molecular irradiation and a local oscillator pulse for heterodyne detection. These approaches reduce the digitizer bandwidths to 500 MHz or less to collect a high-bandwidth spectrum. A single instrument design can be used to measure both absorption and emission spectra, only requiring that the AWG pulses are changed. Due to the phase stability of the pulse generation and detection, coherent time-domain signal averaging can be performed to enhance sensitivity as desired. Preliminary results from prototype instruments designed at UVa and NIST will be presented, with sensitivity, frequency accuracy, and measurement speed comparisons to current millimeter/submillimeter-wave spectrometers.

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Intermission
A solid sample of Vitamin C (m.p. 190 °C) vaporized by laser ablation has been investigated in gas phase and characterized through their rotational spectra. Two spectroscopy techniques have been used to obtain the spectra: a new design of broadband chirped pulse Fourier transform microwave spectroscopy with in-phase/quadrature-phase-modulation passage-acquired-coherence technique (IMPACT) and conventional laser ablation molecular beam Fourier transform microwave spectroscopy (LA-MB-FTMW). Up to now, two low-energy conformer have been observed and their rotational constants determined. Ab initio calculations at the MP2/6-311++G (d,p) level of theory predicted rotational constants which helped us to identify these conformers unequivocally. Among the molecules to benefit from the LA-MB-FTMW technique there are common important drugs never observed in the gas phase through rotational spectroscopy. We present here the results on acetyl salicylic acid and acetaminophen (m.p. 136 °C), commonly known as aspirin and paracetamol respectively. We have observed two stable conformers of aspirin and two for paracetamol. The internal rotation barrier of the methyl group in aspirin has been determined for both conformers from the analysis of the A-E splittings due to the coupling of internal and overall rotation.

Rotational spectra of Gly-Pro and Pro-Gly dipeptides have been examined with laser ablation molecular beam Fourier transform microwave (LA-MB-FTMW) spectroscopy. Three conformers for Gly-Pro and one for Pro-Gly have been unequivocally identified in the supersonic expansion by the comparison of the experimental rotational and $^{14}$N (I=1) nuclear quadrupole coupling constants with those predicted by ab initio methods. The quadrupole hyperfine structure of two $^{14}$N nuclei has been totally resolved and it allows to experimentally characterize the main intramolecular forces which stabilize the assigned conformers. The biomimetic molecule Ac-Ala-NH$_2$ has been also studied. The C$_7$ and C$_5$ peptide conformations (intramolecularly hydrogen-bonded seven- or five-membered cycle, respectively) have been unequivocally identified in the supersonic expansion. The ability to identify peptide conformations suggest that it soon may be possible to explore the structures of larger peptides using LA-MB-FTMW spectroscopy.

Microwave studies of the structural and dynamical properties of several organic acids and their water complexes have been described by a number of research groups. Here we continue this theme by the study of valeric acid and 5-aminovaleric acid, 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. Their structures and water complexes were determined and will be compared to other amino acids.

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**Research Papers**

1. **PROBING VITAMINE C, ASPIRIN AND PARACETAMOL IN THE GAS PHASE: HIGH RESOLUTION ROTATIONAL STUDIES**

2. **JET COOLED ROTATIONAL STUDIES OF DIPEPTIDES**

3. **CHIRPED-PULSED FTMW SPECTRUM OF VALERIC ACID AND 5-AMINOVALERIC ACID. A STUDY OF AMINO ACID MIMICS IN THE GAS PHASE**
   - Ryan G. Bird, Vanesa Vaquero, 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.

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**Notes**

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STRUCTURE STUDY OF FORMIC ACID CLUSTERS BY CHIRPED-PULSE FTMW SPECTROSCOPY

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The large bandwidths and high sensitivity afforded by chirped-pulse FTMW spectrometers allow for the detection of large molecules (10+ heavy atoms) and their isotopomers in natural abundance. With the isotopic information, an experimental structure can be obtained by using Kraitchman’s equations. Clusters of carboxylic acids are of interest because of the different possibilities for hydrogen bonding that lead to the formation of larger clusters. The first study of formic acid clusters by microwave spectroscopy was presented by Bauder and the formic acid dimer with one water molecule complexed was identified. Previously the formic acid trimer cluster was reported where the third formic acid attaches itself to the already formed formic acid dimer. Here we present the full heavy atom and partial deuterium Kraitchman substitution structure of formic acid trimer. In addition we have identified two new nonplanar formic acid clusters - formic acid pentamer and the cluster of formic acid trimer with one water molecule attached. For the latter, two tunneling states with an energy splitting of 178 MHz are observed for the normal species and $^{13}$C isotopomers. Candidate structures and the difficulty of modeling these clusters by electronic structure theory will be discussed.

A CHIRPED PULSE FTMW STUDY OF THE STRUCTURE OF PHENOL DIMER

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Phenol dimer has been studied extensively and is considered a benchmark molecular complex for ab initio theory due to a long range dispersion interaction between the rings as well as an intermolecular hydrogen bond. Previously, the structure had been determined using RCS and high resolution UV measurements; however, several assumptions were integrated into the structure because a full isotopically substituted structure could not be determined. In this study, the rotational spectrum of the dimer as well as $^{13}$C and $^{18}$O isotopologue spectra that were seen in natural abundance were obtained using chirped pulse Fourier transform microwave spectroscopy (CP-FTMW). The structure was determined using both linear least squares fitting ($r_0$ structure) and the Kraitchman substitution analysis ($r_s$ structure). Ab initio calculations were performed for the dimer using MP2/cc-pVTZ cp, B3LYP/6-31G(d,p), M06-2X/6-31G(d,p), and M06-2X/6-311++G(d,p), while CCSD calculations are currently under way. Changing the level of theory and the basis set dramatically changes the structure. The MP2 calculation underestimates the hinge angle (C-O-O-C dihedral angle), while the B3LYP overestimates it. The M06-2X calculations seem to give the best cost-to-benefit ratio when compared to the $r_s$ structure, but they show poorer agreement with increasing basis set size.

RC10 15 min 11:21

RC11 15 min 11:38
With an interest in characterizing C−H···π interactions, CH$_2$F$_2$···HCCH and CH$_2$ClF···HCCH have been examined by Fourier-transform microwave (FTMW) spectroscopy. These interactions involve the π bond in acetylene acting as a hydrogen bond acceptor to both hydrogen atoms of CH$_2$FX. In addition, there is a secondary contact between one hydrogen atom from acetylene and the X atom in the halomethane (X=F in CH$_2$F$_2$, X=Cl in CH$_2$ClF).

Initial assignments for the most abundant isotopologues of both species were completed using the chirped-pulse FTMW spectrometers at the University of Virginia (CH$_2$ClF···HCCH) and at Eastern Illinois University (CH$_2$F$_2$···HCCH). Rotational constants obtained from experiment are in good agreement with those of the most stable orientations predicted by ab initio calculations at the MP2/6-311++G(2d,2p) level. Multiple isotopically substituted species for each complex were measured using a Balle-Flygare cavity FTMW spectrometer at Eastern Illinois University. Spectroscopic parameters for all observed isotopologues will be presented, and a comparison of the C−H···π interactions in these and related complexes will be discussed.
INVITED TALK

SPECTROSCOPIC SIGNATURES OF BOND BREAKING INTERNAL ROTATION IN HCP

MARK S CHILD, Physical and Theoretical Chemistry Laboratory, South Parks Rd, Oxford, OX1 3QZ, UK.

Changes in the eigenvalue structure in the vicinity of a saddle-point on the potential energy surface are illustrated by semiclassical and quantum mechanical studies on model potential energy surfaces for HCP. The following points are addressed:

(a) The connection between classical periodic orbits and Fermi resonance polyads, and the breakdown of the polyad model as the bending frequency tunes out of 2:1 resonance with the CP stretch a.

(b) The observation of 'quantum mondromy' in the underlying spherical pendulum model, and its influence of the values of the spectroscopic vibration-rotation parameters, as the H atom approaches the P end of the molecule b.

(c) A possible formulation of the spectroscopic theory at the saddle point in terms of spherical pendulum eigenstates, and the nature of the relevant matrix elements c.

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PERTURBATION FACILITATED DISPERSED FLUORESCENCE AND STIMULATED EMISSION PUMPING SPECTROSCOPIES OF HCP

HARUKI ISHIKAWA, Department of Chemistry, Graduate School of Science, Kobe University, Nada-ku, Kobe 657-8501, Japan; YASUHIKO MURAMOTO, MASAHITO NAMAI, NAOHIKO MIKAMI, Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan.

Perturbations among molecular rovibronic levels provide us with mainly two benefits. Perturbations themselves are characteristic features of structure and dynamics of molecules. We have been investigating dynamics of highly excited vibrational levels of HCP in the $\tilde{X}$ $^1\Sigma^+$ state by dispersed fluorescence (DF) and stimulated emission pumping (SEP) spectroscopies of the $\tilde{C}$ $^1A' - \tilde{X}$ $^1\Sigma^+$ transition a.

In the case of $\tilde{X}$ $^1\Sigma^+$ HCP, its vibrational dynamics is well described by the Fermi resonance between the bend and the CP stretch modes. Based on the analysis of the Fermi resonance, we have succeeded in revealing the change in character of the bending motion in highly excited vibrational levels. In addition, perturbations enable us to explore rovibrational levels into much wider region that cannot be accessed under limits of selection rules.

Jacobson and Child showed that the Coriolis interaction becomes very strong in the highly excited levels near and above the CPH barrier b. For the experimental confirmation of their prediction, the observation of the $v_{\text{CH}} \neq 0$ and the $\ell'' \neq 0$ levels are necessary. However, due to the selection rules and the Franck-Condon selectivity, only the $v_{\text{CH}} = 0$ and the $\ell'' = 0$ levels had been observed. In the course of our study, we have found a perturbed level in the $\tilde{C}$ state. In general, a very clear even-$v_2$ progression appears in the DF spectra of HCP. However, in the DF spectra measured by using the perturbed level as the intermediate both the odd- and even-$v_2$ levels are observed. Moreover, several $v_{\text{CH}} = 1$ levels are observed in the spectra. The perturbation-facilitated DF and SEP spectroscopies are very powerful tools to exploring the highly excited vibrational levels of HCP. Details of the perturbation-facilitated DF and SEP spectroscopies are presented in the paper.

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We present a spectroscopic study of the X state of the Rb$_2$ and Cs$_2$. Since spectral congestion makes it difficult to find isolated pump transitions for heavy molecules such as Rb$_2$ and Cs$_2$, this technique significantly enlarges the range of rotational levels that can be observed per vibrational level. Collisional satellite lines with $\Delta J$ up to 58 were observed in the Rb$_2$ polarization experiment. In the Cs$_2$ experiment, due to weaker Franck-Condon factors, collisional satellite lines with $\Delta J_{max}$ equals to 12 were observed. Collisional orientation transfer in polarization spectroscopy was first observed with buffer gas pressure of several hundred Torr. The high pressure led to loss of spectral resolution from collisional broadening. Only 1 to 3 Torr of argon buffer gas pressure was used in our experiments to obtain spectra with much higher resolution. Among the six types of possible probe signals, we assigned and analyzed the signals from the V type excitation scheme. The data was used in the global deperturbation analysis of the A-b complex of both Rb$_2$ and Cs$_2$.

We present a spectroscopic study of the $X^1\Sigma^+$ and $B^1\Pi$ states of LiRb and prospects for creating ultracold ground state LiRb molecules. LiRb molecules were formed in a heat-pipe oven and spectroscopic measurements of the laser induced fluorescence (LIF) were performed. LIF to the first 45 vibrational levels of the $X^1\Sigma^+$ state (covering more than 98% of the potential well depth) was observed. We also studied the excitation to the $B^1\Pi$ state with high resolution excitation spectroscopy. The values of vibrational, rotational and other spectroscopic constants for both $X^1\Sigma^+$ and $B^1\Pi$ states will be presented in addition to their dissociation energies. Measurements aimed to probe perturbations in the $B^1\Pi$ state due to other nearby states will be discussed. The use of such spectroscopic information in finding efficient photoassociation pathways for the production of ultracold LiRb molecules will also be discussed. This work is supported by the NSF grant number CCF0829918.

The optical spectrum of chloro-methylene, HCCl, has been studied for more than 40 years by both conventional and laser-based spectroscopy. Surprisingly, numerous visible bands have yet to be characterized, due in part to known perturbations. Since spectral congestion makes it difficult to find isolated pump transitions for heavy molecules such as Rb$_2$ and Cs$_2$, this technique significantly enlarges the range of rotational levels that can be observed per vibrational level. Collisional satellite lines with $\Delta J$ up to 58 were observed in the Rb$_2$ polarization experiment. In the Cs$_2$ experiment, due to weaker Franck-Condon factors, collisional satellite lines with $\Delta J_{max}$ equals to 12 were observed. Collisional orientation transfer in polarization spectroscopy was first observed with buffer gas pressure of several hundred Torr. The high pressure led to loss of spectral resolution from collisional broadening. Only 1 to 3 Torr of argon buffer gas pressure was used in our experiments to obtain spectra with much higher resolution. Among the six types of possible probe signals, we assigned and analyzed the signals from the V type excitation scheme. The data was used in the global deperturbation analysis of the A-b complex of both Rb$_2$ and Cs$_2$.

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**RD03**

**COLLISIONAL ORIENTATION TRANSFER FACILITATED POLARIZATION SPECTROSCOPY**

JIANMEI BAI, E.H.AHMED, B. BESER, Y. GUAN, A. M. LYYRA, Temple University; S. ASHMAN, C. M. WOLFE, J. HUENNEKENS, Lehigh University.

Collisional orientation transfer facilitated V-type double-resonance polarization spectroscopy technique was applied to study the A-b complex of Rb$_2$ and Cs$_2$. Since spectral congestion makes it difficult to find isolated pump transitions for heavy molecules such as Rb$_2$ and Cs$_2$, this technique significantly enlarges the range of rotational levels that can be observed per vibrational level. Collisional satellite lines with $\Delta J$ up to 58 were observed in the Rb$_2$ polarization experiment. In the Cs$_2$ experiment, due to weaker Franck-Condon factors, collisional satellite lines with $\Delta J_{max}$ equals to 12 were observed. Collisional orientation transfer in polarization spectroscopy was first observed with buffer gas pressure of several hundred Torr. The high pressure led to loss of spectral resolution from collisional broadening. Only 1 to 3 Torr of argon buffer gas pressure was used in our experiments to obtain spectra with much higher resolution. Among the six types of possible probe signals, we assigned and analyzed the signals from the V type excitation scheme. The data was used in the global deperturbation analysis of the A-b complex of both Rb$_2$ and Cs$_2$.

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**RD04**

**THE $X^1\Sigma^+$ AND $B^1\Pi$ STATES OF LiRb AND PROSPECTS FOR CREATING ULTRACOLD GROUND STATE LiRb MOLECULES**

SOURAV DUTTA, ADEEL ALTAF, JOHN LORENZ, D. S. ELLIOTT AND YONG P. CHEN, Purdue University, West Lafayette, IN 47907.

We present a spectroscopic study of the $X^1\Sigma^+$ and $B^1\Pi$ states of LiRb. LiRb molecules were formed in a heat-pipe oven and spectroscopic measurements of the laser induced fluorescence (LIF) were performed. LIF to the first 45 vibrational levels of the $X^1\Sigma^+$ state (covering more than 98% of the potential well depth) was observed. We also studied the excitation to the $B^1\Pi$ state with high resolution excitation spectroscopy. The values of vibrational, rotational and other spectroscopic constants for both $X^1\Sigma^+$ and $B^1\Pi$ states will be presented in addition to their dissociation energies. Measurements aimed to probe perturbations in the $B^1\Pi$ state due to other nearby states will be discussed. The use of such spectroscopic information in finding efficient photoassociation pathways for the production of ultracold LiRb molecules will also be discussed. This work is supported by the NSF grant number CCF0829918.

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**RD05**

**OPTICAL STARK SPECTROSCOPY OF CHLORO-METHYLENE, HCCI**

XIUJUAN ZHUANG AND TIMOTHY C. STEIMLE, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287; ZHONG WANG, Math and Sciences Department, Suffolk County Community College, East Campus, Riverhead, NY, 11901.

The optical spectrum of chloro-methylene, HCCl, has been studied for more than 40 years by both conventional and laser-based spectroscopy. Surprisingly, numerous visible bands have yet to be characterized, due in part to known perturbations. Furthermore, the permanent electric dipole moment, $\mu_{el}$, for any state has yet to be determined. Here we report on the field-free and optical Stark spectrum of the $A^1\Pi''$ (000)- $X^1\Sigma^+$ (000) band system. A cold molecular beam sample was produced by skimming the output of a pulsed discharge source and the spectrum recorded at a resolution of approximately 30 MHz via LIF detection. The field-free spectrum was analyzed to produce an improved set of spectroscopic parameters for the $A^1\Pi''$ (000) state. The Stark induced shifts were analyzed to determine the values of the $\alpha$-component of $\mu_{el}$ for the $X^1\Sigma^+$ (000) state of 0.498(8)D. Small perturbations in the $A^1\Pi''$ (000) state will be described.

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PHASE SPACE EXPLORATION OF ACETYLENE AT ENERGIES UP TO 13,000 cm$^{-1}$

DAVID S. PERRY, JONATHAN MARTENS, Department of Chemistry, The University of Akron, OH 44325-3601; MICHEL HERMAN, BADR AMYAY, Laboratoire de Chimie quantique et Photophysique, Université libre de Bruxelles, B-1050, Belgium.

The rotation-vibration Hamiltonian of acetylene is known in detail up to 13,000 cm$^{-1}$ in the electronic ground state, allows the calculation of time-dependent dynamics for postulated excitations of certain bright states. Three different measures of phase space exploration are examined including the participation number, Gruebele’s dispersion, and the Shannon entropy. The time scales for phase space exploration span the range from 20 fs to 10 ps. The volume of phase space explored by the dynamics increases with energy and the rotational quantum number, $J$, reaching about 90% of the (GOE) statistical limit at 12,000 cm$^{-1}$ and $J = 100$. At low and intermediate $J$, the extent of phase space exploration is reduced for the local bender and counter-rotator bright states as compared to their normal mode counterparts. However, the phase space exploration of the local mode CH stretch state is similar to that of the corresponding normal mode vibration. These calculations shed light on the applicability of the energy randomization assumption that is at the heart of the Rice-Rampsberger-Kassel-Marcus (RRKM) theory of unimolecular reactions.

ACETYLENE DYNAMICS AT ENERGIES UP TO 13,000 cm$^{-1}$

JONATHAN MARTENS, DAVID S. PERRY, Department of Chemistry, The University of Akron, OH 44325-3601; MICHEL HERMAN, BADR AMYAY, Laboratoire de Chimie quantique et Photophysique, Université libre de Bruxelles, B-1050, Belgium.

The rotation-vibration Hamiltonian of acetylene is known in detail up to 13,000 cm$^{-1}$ in the electronic ground state and allows the calculation of time-dependent dynamics for postulated excitations of certain bright states. The spectroscopic Hamiltonian, derived by Herman$^a$, includes four types of off-diagonal interactions: vibrational $l$-resonances, rotational $l$-resonances, anharmonic coupling, and Coriolis coupling. At high energies, hundreds of states may be coupled in each polyad and the rate and extent of intramolecular vibrational redistribution (IVR) increase substantially with rotational excitation. As each coupling mechanism becomes active, a hierarchical, sequential flow of probability through the different regions of phase space occurs on timescales ranging from 20 fs to 10 ps. As the energy is increased from one polyad to the next, the dynamics of similar bright states are similar; however, the dynamics depend critically on the nature of the bright state excited within a given polyad. The rotationally-mediated dynamics of the local CH stretch, the local bender and counter-rotator bright states are qualitatively similar to their normal mode counterparts.

We present high resolution intensity-calibrated linelists of ammonia (NH$_3$) at high temperatures obtained from Fourier transform emission spectra recorded using a tube furnace. Individual calibrated linelists are presented for 12 temperatures (300 – 1300°C in 100°C intervals and 1370°C). Each linelist covers the 800–2200 cm$^{-1}$ range and includes the majority of the $\nu_2$ bending mode and the complete $\nu_4$ mode regions. We also demonstrate the useful technique of obtaining empirical lower state energies from spectra at different temperatures. We expect our hot NH$_3$ linelists to find direct application in modeling of the spectra of extrasolar planets and brown dwarfs.

Quantum number assignments in the experimental linelists are difficult because of extensive perturbations and the poor convergence of traditional Hamiltonians based on perturbation theory. A new theoretical linelist, known as BYTe, was computed variationally to assign and model spectra with ammonia temperatures up to 1500 K. It was computed using the NH3-2010 spectroscopically-determined potential energy surface and the TROVE rovibrational computer program. Intensities were calculated using an ab initio dipole moment surface. BYTe comprises more than 1.1 billion transitions in the wavenumber range from 0 to 12000 cm$^{-1}$, constructed from 1.3 million energy levels lying below 18000 cm$^{-1}$. Given an accurate potential energy surface, variational calculations are able to account automatically for perturbations.
DIRECT EXCITATION OF THE REACTION COORDINATE: OVERTONE-INDUCED PREDISSOCIATION OF THE HYDROXYMETHYL RADICAL

HANNA REISLER, MIKHAIL RYAZANOV and CHIRANTHA P. RODRIGO, Department of Chemistry, University of Southern California, Los Angeles, CA, 90089-0482.

The overtone-induced vibrational predissociation of the hydroxymethyl radical is achieved following excitation of the radical to the third O-H stretch overtone. The excited O-H stretch is also the bond that breaks; i.e. overtone excitation is in the reaction coordinate. The production of H atoms takes place via tunneling through the barrier to the H + formaldehyde channel. H-atom photofragment yield spectra in the region of the third overtone reveal two mixed bands with contributions from the third OH overtone and a combination band comprised of two quanta of OH stretch and one quantum of CH asymmetric stretch. Using velocity map imaging, sliced images of H-atom products are obtained with kinetic energy resolution sufficient to reveal the vibrational structure in the formaldehyde co-fragment. As expected, most of the formaldehyde molecules are born without vibrational excitation but some exhibit excitation in other modes, such as wagging and CO stretch. The rotational contours of the vibrational bands are well described by temperatures in the range 100-150 K. Slice imaging allows scanning the pump laser while monitoring H fragments in selected kinetic energy ranges, and in this way it is demonstrated that all the observed vibrational levels of formaldehyde have their parentage in the hydroxymethyl radical. The barrier to isomerization to methoxy is comparable to the barrier to direct dissociation and the role of isomerization is investigated by using partially deuterated radicals.

AUTOIONIZATION BRANCHING RATIOS FOR METAL HALIDE MOLECULES

JEFFREY J. KAY, Lawrence Livermore National Laboratory, Livermore, CA 94550; ROBERT W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

There is currently much interest in the production metal halide ions that are both translationally and internally cold. One potential route to the production of rotationally and vibrationally cold ions is excitation of a vibrationally autoionizing state of the neutral molecule. However, the autoionization dynamics of most molecules are difficult to predict since the key parameters that describe the process, the quantum defect derivatives with respect to internuclear distance, are only known for a very small number of molecules. We recently developed a complete quantum defect model for calcium monofluoride (CaF), a prototypical metal halide molecule, that is fully capable of describing all vibrational autoionization processes. Here, we use this model to calculate the distribution of ionic rovibrational states that result from autoionization of Rydberg states of CaF, and discuss the general prospects for the selective preparation of rotationally and vibrationally cold metal halide ions.
RE. DYNAMICS
THURSDAY, JUNE 23, 2011 – 8:30 am
Room: 2015 McPHERSON LAB
Chair: MARILYNN JACOX, NIST, Gaithersburg, Maryland

RE01 15 min 8:30
INTER-RING AND HEXYL CHAIN TORSIONAL POTENTIALS IN POLY (3-HEXYLTHIOPHENE) OLIGOMERS: SCALING WITH THE LENGTH OF THE CONJUGATED POLYMER BACKBONE

RAM S. BHATTA, DAVID S. PERRY, Department of Chemistry, The University of Akron, OH 44325-3601; YENENEH YIMER AND MESFIN TSIGE, Department of Polymer Science, The University of Akron, OH 44325-3909.

Density functional theory calculations are presented for the equilibrium structures and torsional potentials for isolated Poly (3-Hexylthiophene) (P3HT) oligomers up to 12 monomer units (up to 302 atoms). Calculations were performed at B3LYP/6-31++G(d,p) treating both the backbone of thiophene rings and the hexyl chains explicitly. One-dimensional inter-ring torsional potentials were calculated by rotating backbone around the central inter-ring bond and hexyl torsional potentials were calculated rotating n-hexyl group adjacent to the central inter-ring bond for each oligomer. The torsional and electronic properties change significantly for oligomers with 2 to 8 units but reach asymptotic values for a 10 unit P3HT chain, thereby suggesting the 10 unit long oligomer as a molecular model for the extended polymer. For P3HT oligomers having 10 or more units, all the rings and the hexyl groups are approximately coplanar except for one hexyl group at head end. The principal interaction that promotes the coplanarity of the hexyl groups is the attraction of the proximal methylene hydrogens to the sulfur on the adjacent thiophene ring. The cis conformation of the backbone is about 2kT higher than the trans minimum at room temperature. The gauche conformation of the hexyl group is within about half kT of the planar minimum. Therefore conformational polymorphisms of both types will likely be significant in the heterogeneous environment of photovoltaic devices.

RE02 15 min 8:47
VIBRATIONAL STATE DEPENDENT LARGE AMPLITUDE TUNNELING DYNAMICS IN MALONALDEHYDE

GRANT BUCKINGHAM AND DAVID J. NESBITT, JILA, National Institute of Standards and Technology and University of Colorado, and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309.

The quantum dynamics of intramolecular proton transfer in malonaldehyde has represented a major challenge for first principles theoretical calculation, in large measure due to the highly concerted motion of all 9 nuclei throughout the tunneling event. This talk describes efforts to predict quantum state dependent tunneling rates from high level ab initio calculations, exploiting the large amplitude motion (LAM) Hamiltonian methods of Hougen, Bunker and Johns. An effective adiabatic potential surface for the tunneling path is constructed from CCSD(T)/AVnZ-F12 calculations using explicitly correlated basis set methods and extrapolated to the complete basis set (CBS) limit. This potential is adiabatically corrected by zero point excitation in the remaining 3N-7 = 20 vibrational modes, with the multidimensional tunneling dependence of the effective mass explicitly taken into account and numerically solved with Numerov methods. Of special importance, this method permits calculation of mode dependent tunneling splittings as a function of vibrational quantum state, which offers interesting prospects for comparison with recent FTIR slit jet cooled data of Suhm and coworkers.

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RE03 15 min 9:04
VIBRATIONAL RELAXATION AND CONTROL OF SALICYLIDENE ANILINE

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

We have shown that vibrational excitation prior to reaction can control the course of certain photoreactions in isolated molecules. We seek to extend vibrational control to the liquid phase. To this end, we have previously shown that the excited-state reaction dynamics of trans-stilbene are insensitive to vibrational excitation prior to electronic excitation. This insensitivity is likely due to poor coupling of the vibrational modes we excite to modes which correspond to the reaction coordinate, as well as rapid vibrational relaxation relative to the timescale of the reaction. In this work, we focus our attention on salicylidene aniline, a model system for excited-state intramolecular proton transfer (ESIPT) reactions. The proton transfer in salicylidene aniline occurs on the same timescale as vibrational relaxation in solution, suggesting that vibrational control may be viable. Here we present the results of experiments measuring the rate of vibrational relaxation in salicylidene aniline. We also present preliminary results of experiments exploring the influence of vibrational excitation on the ESIPT dynamics of salicylidene aniline.

RE04 15 min 9:21
DEVELOPMENT OF FEMTOSECOND STIMULATED RAMAN SPECTROSCOPY AS A PROBE OF VIBRATIONAL DYNAMICS

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

Femtosecond stimulated Raman spectroscopy (FSRS) has proven to be a reliable probe of condensed phase dynamics by simultaneously achieving both exceptional temporal and frequency resolution. We report on preliminary attempts to utilize FSRS as a probe of vibrational relaxation on the ground electronic state of cyclohexane. We implement a 400 nm Raman pump/probe process following an IR actinic pump pulse which excites the C-H stretch overtone. Progress toward the use of FSRS as a tool alongside transient absorption measurements in vibrationally mediated photoisomerization experiments will also be discussed.

RE05 15 min 9:38
VIBRATIONAL DYNAMICS OF TRICYANOMETHANIDE

DANIEL WEIDINGER, CASSIDY HOUCHINS, and JEFFREY C. OWRUTSKY, Code 6111, Naval Research Laboratory, 4555 Overlook Ave SW, Washington, D.C. 20375.

Time-resolved and steady-state IR spectroscopy have been used to characterize vibrational spectra and energy relaxation dynamics of the CN stretching band of the tricyanomethanide (TCM, C(CN)₃⁻) anion near 2170 cm⁻¹ in solutions of water, heavy water, methanol, formamide, dimethyl sulfoxide (DMSO) and the ionic liquid 1-butyl methyl imidazolium tetrafluoroborate ([BMIM][BF₄]). The band intensity is strong (~1500 M⁻¹cm⁻¹) and the vibrational energy relaxation times are relatively long (~5 ps in water, 12 ps in heavy water, and ~30 ps in DMSO and [BMIM][BF₄]). They are longer than those previously reported for dicyanamide in the same solvents. Although the static TCM frequency generally shifts to higher frequency with more strongly interacting solvents, the shift does not follow the same trend as the vibrational dynamics. The results for the experimental frequencies and intensities agree well with results from ab initio calculations. Proton and electron affinities for TCM are also calculated because they are relevant to potential applications of this anion in low viscosity ionic liquids.

Intermission
PHOTOCHEMISTRY OF HALOGENATED TRANSITION METAL DIANIONS

ALEXANDER N. TARNOVSKY, IGOR L. ZHIELDAKOV, EVGENIIA V. BUTAEVA, and ANDREY S. MERESHCHENKO, Department of Chemistry, Bowling Green State University, Bowling Green, OH, 43402.

Separation of two negative charges in aqueous PtBr$_6^{2-}$ is investigated by means of femtosecond broadband pump-probe spectroscopy using several excitation wavelengths, in concert with time-resolved x-ray absorption spectroscopy and DFT/TDDFT calculations.

PHOTOCHEMISTRY OF BROMOFORM AND TRIBROMIDES OF OTHER ELEMENTS IN SOLUTION

ANDREY S. MERESHCHENKO, KANYKEY E. KARABAEVA, ALEXANDER N. TARNOVSKY, Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403; PATRICK Z. EL-KHOURY, Institute for Surface and Interface Science, University of California Irvine, Irvine, CA 92697; AND SUMAN K. PAL, School of Basic Sciences IIT Mandi, Vallabh Degree College Campus, Mandi 175001, India.

Photochemistry of bromoform in solution was studied by means of ultrafast time-resolved transient absorption spectroscopy. After 255 nm excitation, bromoform dissociates to the CHBr$_2$ radical and bromine atom, which recombine to form iso-bromoform CHBr$_2$-Br. In nonpolar solvents, such as methylcyclohexane, this isomer has a lifetime significantly greater than time window (1.2 ns), while in polar solvents, such as acetonitrile and methanol, iso-bromoform relaxes to the parent molecule in about 200 ps. This behavior is consistent with DFT intrinsic reaction coordinate calculations of the ground state potential energy surfaces in these solvents. Also, we showed photochemical formation of isomers with Br-Br bond in tribromides of other elements.

ISOMERIZATION BETWEEN CH$_2$ClI AND CH$_2$Cl-I IN CRYOGENIC MATRICES STUDIED ON ULTRAFAST TIMESCALE

THOMAS J. PRESTON, MAITREYA DUTTA, BRIAN J. ESSELMAN, MICHAEL A. SHALOSKI, ROBERT J. MCMAHON, and F. FLEMING CRIM, The University of Wisconsin-Madison Department of Chemistry, 1101 University Avenue, Madison, WI, 53705; AMIABLE KALUME, LISA GEORGE, and SCOTT A. REID, Department of Chemistry, Marquette University, Milwaukee, WI, 53233.

Photodissociation of species entrained in solid matrices potentially leads to reassociation of the newly formed fragments. After fixing CH$_2$ClI in various atomic and molecular matrices, we measure ultrafast transient absorptions to monitor the photolysis of the precursor and isomerization to form iso-CH$_2$ClI. We probe the two lowest energy electronic absorption features of CH$_2$Cl-I near 435 nm and 800 nm. Probing the low energy side of the 435-nm band interrogates the formation and subsequent cooling of the hot, newly formed products. We find that the recoiling fragments, CH$_2$Cl and I, lose large amounts of energy to the environment in the initial collision with the matrix cage, which leads to formation of the isomer.

ISOMERIZATION OF CH$_2$Cl-I TO CH$_2$Cl-I IN CRYOGENIC MATRICES: A STUDY ON ULTRAFAST TIMESCALE

THOMAS J. PRESTON, MAITREYA DUTTA, BRIAN J. ESSELMAN, MICHAEL A. SHALOSKI, ROBERT J. MCMAHON and F. FLEMING CRIM, The University of Wisconsin-Madison Department of Chemistry, 1101 University Avenue, Madison, WI, 53706; AMIABLE KALUME, LISA GEORGE and SCOTT A. REID, Department of Chemistry, Marquette University, Milwaukee, WI, 53233.

We follow up on the previous talk on ultrafast timescale studies of the isomerization between CH$_2$ClI and CH$_2$Cl-I in cryogenic matrices. We establish a population of CH$_2$Cl-I in cryogenic matrices and then pump the two lowest electronic absorption features of CH$_2$Cl-I near 435 nm and 800 nm. Then we study the formation of CH$_2$Cl and CH$_2$Cl-I by probing electronic absorption features of both isomers.
PHOTODISSOCIATION DYNAMICS OF A TRIATOMIC PSEUDO-DIHALIDE: ABSORPTION CROSS SECTION AND DYNAMICS OF SOLVATED ICN\textsuperscript{−}

JOSHUA P. MARTIN, QUANLI GU\textsuperscript{a}, JOSHUA P. DARR\textsuperscript{b}, JILA, Department of Chemistry and Biochemistry
University of Colorado at Boulder, Boulder, CO 80309; ANNE B. McCOY, Department of Chemistry, The Ohio State University, Columbus, OH 43210; and W. CARL LINEBERGER, JILA, Department of Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, CO 80309.

We report the photoabsorption cross section and photoproduct branching ratios of mass-selected bare ICN\textsuperscript{−} and ICN\textsuperscript{−}(CO\textsubscript{2}) following excitation to the \( A^\prime \ 2\Pi_1/2 \) electronic excited state. Previous studies of CO\textsubscript{2} solvated-heteronuclear dihalides, IX\textsuperscript{−}(CO\textsubscript{2})\textsubscript{n} (X=Cl, Br), reported three excited state selective classes of photoproducts: I\textsuperscript{−}, X\textsuperscript{−}, and IX\textsuperscript{−} based clusters. Photoabsorption of bare ICl\textsuperscript{−} and IBr\textsuperscript{−} that leads to population in the \( A^\prime \ 2\Pi_1/2 \) state have maxima near 680 nm and 740 nm, respectively, and result in I\textsuperscript{−} photoproducts exclusively over the entire band corresponding to \( A^\prime \ 2\Pi_1/2 \leftarrow X \ 2\Sigma_1/2 \) excitation. Interestingly, following excitation of bare ICN\textsuperscript{−} to the comparable state (430-650 nm, maximum at 490 nm), I\textsuperscript{−} is the dominant ionic photoproduct, but CN\textsuperscript{−} photoproducts are observed as well. When a single CO\textsubscript{2} solvent molecule is added to ICN\textsuperscript{−}, the same \( A^\prime \ 2\Pi_1/2 \leftarrow X \ 2\Sigma_1/2 \) excitation results in apparent charge transfer within the complex. Therefore, the observed ionic photoproducts are not just the expected I\textsuperscript{−} and I\textsuperscript{−}(CO\textsubscript{2}), but CN\textsuperscript{−} and solvated CN\textsuperscript{−}(CO\textsubscript{2}) photoproducts are also significant products. Analysis of the experimental results using calculated potential energy curves of ICN\textsuperscript{−} reveals intriguing dynamics of the photoexcited triatomic pseudo-dihalide. Supported by NSF and AFOSR.

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\textsuperscript{b}Present address: Department of Chemistry, University of Nebraska, Omaha, NE 68182

EXCITED-STATE DYNAMICS IN 6-THIOGUANOSINE FROM FEMTOSECOND TO MICROSECOND TIME SCALE

CAO GUO, CHRISTIAN REICHARDT AND CARLOS E. CRESCO-HERNÁNDEZ, Department of Chemistry and the Center for Chemical Dynamics, Case Western Reserve University, 10900 Euclid Avenue, Cleveland, Ohio 44106.

6-thioguanine is a widely used pro-drug in which the oxygen atom in the carbonyl group of guanine is replaced by a sulfur atom. Previous studies have shown that patients treated with 6-thioguanine can metabolize and incorporate it in DNA as 6-thioguanosine (6tGuo). These patients show a high incidence of skin cancer when they are exposed to extended periods of sunlight irradiation. In this work, the photodynamics of 6tGuo is investigated by broad band time resolved transient spectroscopy. Similar to previously studied 4-thiothymidine, our results show that excitation of 6tGuo with UVA light at 340 nm results in efficient and ultrafast intersystem crossing to the triplet manifold (\( \tau = 0.31 \pm 0.05 \) ps) and a high triplet quantum yield (\( \phi = 0.8 \pm 0.2 \)). The triplet state has a lifetime of 720 ± 10 ns in \( N_2 \)-saturated vs. 460 ± 10 ns in air-saturated aqueous solution. In addition, a minor picosecond deactivation channel (80 ± 15 ps) is observed, which is tentatively assigned to internal conversion from the lowest-energy excited singlet state to the ground state. Quantum chemical calculations support the proposed kinetic model. Based on the high triplet quantum yield measured, it is proposed that the phototoxicity of 6tGuo is due to its ability to photosensitized singlet oxygen, which can result in oxidative damage to DNA.

RF. MINI-SYMPHOSIUM: THE THz COSMOS
THURSDAY, JUNE 23, 2011 – 1:30 pm
Room: 160 MATH ANNEX

Chair: ERIC HERBST, The Ohio State University, Columbus, Ohio

RF01

INTERSTELLAR HYDRIDE SPECTROSCOPY WITH HERSCHEL

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The Herschel satellite is now giving access with unprecedented sensitivity to the THz spectral range. In particular ground state lines of simple neutral and ionized hydrides have been detected in a wide range of interstellar environments, leading to a renewed understanding of the formation processes of interstellar molecules in the diffuse interstellar medium.

In this talk, I will present recent results obtained with the Herschel HIFI and PACS instruments on the carbon, oxygen and nitrogen hydrides. I will discuss how CH and HF can be used as tracers of molecular hydrogen in the diffuse interstellar matter, the new diagnostic capabilities of the cosmic ray ionization rate opened by the OH\(^+\) and H\(_2\)O\(^+\) molecular ions, and the role of the dissipation of turbulence in the production of the CH\(^+\) and SH\(^+\) reactive ions.

Figure 1: Example of Herschel/HIFI spectra towards the massive star forming region G10.6–0.4. The diffuse interstellar matter along the line of sight towards this massive object is producing multiple absorption features from ~ 6 to ~ 50 km/s while the emission or absorption signals between -20 to 5 km/s are caused by the massive source itself.
CHEMICAL HERSCHEL SURVEYS OF STAR FORMING REGIONS (CHESS)

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CHESS is an unbiased line survey of low-, intermediate-, and high-mass star forming regions at different stages of their evolution. The eight sources in the CHESS program are observed with the HIFI instrument on board of the Herschel Space Telescope, which provides a high spectral resolution ($R \sim 10^6$) and covers a frequency range from 480 to 1910 GHz. The objective of CHESS is to study the chemical composition and physical conditions in star forming regions and their variation with mass and evolutionary stage. To date about 50% of the program have been completed.

One of the eight objects in the CHESS program is the hot core NGC 6334 I. With an envelope mass of 200 $M_\odot$ and temperatures 100 K, NGC 6334 I is very line rich. In this object emission lines of more than 40 species have been identified, including first detections of $H_2Cl^+$ (Lis et al. 2010) and $H_2O^+$ (Ossenkopf et al. 2010). Furthermore, several lines of ortho and para water and ammonia have been detected, allowing to determine the ortho/para ratio of these crucial species. In addition many hydrides (HF, CH) and hydride ions (SH+, OH+, CH+) have been found.

In the low mass protostar IRAS 16293-2422, another source of our sample, several deuterated species, including the first detection of ND (Bacmann et al. 2010), were found. The data allowed also the first determination of the ortho/para ratio of $D_2H^+$ ($> 2.6$) (Vastel et al. 2010).

In this talk I will give a summary of the conducted observation and highlight the most important results.

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OBSERVATIONS OF INTERSTELLAR HYDROGEN FLUORIDE AND HYDROGEN CHLORIDE IN THE GALAXY

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We present Herschel/HIFI observations of interstellar hydrogen chloride (HCl) and hydrogen fluoride (HF) along the line-of-sight towards Galactic sources with strong submillimeter continuum emission from the PRISMAS and HEXOS GT KP. The halogen-containing molecules are of special interest because of their unique thermochemistry and their important role as tracers of the neutral ISM. The detection of foreground absorption by HF $J = 1–0$ transition line in each source probes the distribution of HF throughout the Milky Way, in diffuse clouds with varying values of the visual extinction, as a potential valuable surrogate for molecular hydrogen. For the optically thin absorption components we calculate the column densities of HF. We find that, in many of the background clouds, the abundances of HF with respect to $H_2$ is consistent with the theoretical prediction that HF is the main reservoir of gas-phase fluorine for these clouds. Observations of hydrogen chloride isotopologues, $^{35}$HCl and $^{37}$HCl $J = 1–0$ transition line at different galactocentric distances provide insights of how elemental abundances change with location in the Galaxy. We model the HCl observations with a non-LTE radiative transfer model to derive gas densities and HCl column densities for sources with HCl emission. Interstellar HCl abundances and isotopic ratios [$C^{35}/C^{37}$] are essential for improving our understanding of stellar nucleosynthesis and global chemical enrichment and evolution in the Galaxy.
THE STRATOSPHERIC OBSERVATORY FOR INFRARED ASTRONOMY (SOFIA)

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The joint U.S. and German Stratospheric Observatory for Infrared Astronomy (SOFIA) is a 2.5-meter infrared airborne telescope in a Boeing 747-SP that began science flights in 2010. Flying in the stratosphere at altitudes as high as 45,000 feet, SOFIA can conduct photometric, spectroscopic, and imaging observations at wavelengths from 0.3 microns to 1.6 millimeters with an average transmission of greater than 80 percent. SOFIA is staged out of the NASA Dryden Flight Research Center aircraft operations facility at Palmdale, CA and the SOFIA Science Mission Operations Center (SSMOC) is located at NASA Ames Research Center, Moffett Field, CA. SOFIA’s first-generation instrument complement includes high speed photometers, 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. About 100 eight to ten hour flights per year are expected by 2014, and the observatory will operate until the mid 2030’s. We will review the status of the SOFIA facility, its initial complement of science instruments, and the opportunities for advanced instrumentation.

INFRARED SPECTROSCOPIC STUDIES WITH THE STRATOSPHERIC OBSERVATORY FOR INFRARED ASTRONOMY (SOFIA)

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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 interstellar medium and 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. First light images and early science results related to these topics will be presented.

ROTATIONAL SPECTROSCOPY FOR ASTROPHYSICAL APPLICATIONS: THE THZ FREQUENCY REGION

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Recent missions, such as the Herschel Space Observatory and the Stratospheric Observatory for Infrared Astronomy (SOFIA), have pointed out the need for precise and accurate frequency measurements and spectroscopic parameters in the THz range. In the present contribution, the THz spectrometer working at the University of Bologna and its applications are presented. The focus is here on the accuracy of the retrieved transition frequencies of neutral as well as ionic species and on line-broadening investigations.

Intermission
UNRAVELING THE MYSTERIES OF COMPLEX INTERSTELLAR ORGANIC CHEMISTRY USING HIFI LINE SURVEYS

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We are undertaking a Herschel Space Observatory OT1 program to conduct HIFI spectral line surveys of interstellar clouds to probe the influence of physical environment on molecular complexity. We will observe a large sample of sources, cover a range of physical environments, and target selected frequency windows containing transitions from several known complex organic molecules. We have an ongoing complementary program in ground-based astronomy using the Caltech Submillimeter Observatory to collect spectral line surveys at lower frequencies, and plan to undertake additional interferometric observations using the CARMA and ALMA arrays to further examine the spatial distributions of the molecules detected toward our target sources. The goal of these observations is to correlate the relative abundances of organic molecules with the physical properties of the source (i.e. temperature, density, age, dynamics, etc.). Our broader research goal is to improve astrochemical models to the point where accurate predictions of complex molecular inventory can be based on the physical and chemical environment of a given source. The information gained from these observations will serve as a benchmark for these astrochemical models and holds the promise of significantly advancing our understanding of interstellar chemical processes. In this talk, we will overview the major goals of this observational program, and report on any preliminary results from these ongoing observations.

PROGRESS TOWARDS THE ROTATIONAL SPECTRUM OF H$_5^+$ AND ITS ISOTOPOLOGUES

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The reaction of H$_5^+$ with H$_2$, arguably the most common bimolecular reaction in the universe, proceeds through the H$_5^+$ collisional complex. This reaction, and consequently H$_5^+$, greatly influence the chemical and physical processes in the interstellar medium, playing crucial roles in such varied processes as isotopic fractionation and the formation of complex organic molecules. A thorough understanding of the role of H$_5^+$ in interstellar chemistry is contingent upon its definitive astronomical detection, necessitating the acquisition of a laboratory rotational spectrum. Rotationally-resolved spectra of H$_5^+$ in the terahertz region have not yet been observed experimentally. The prediction of this spectrum based on a high-level theoretical study is therefore an important first step to guide experiment. The highly fluxional nature of H$_5^+$ presents major challenges for theory, especially for the pure rotational spectrum due to the difficulties in determining an accurate dipole moment from a correct description of the highly delocalized zero-point wavefunction. We have now completed this work using the most recent potential energy and dipole moment surfaces for H$_5^+$ and its isotopologues DH$_4^+$, D$_2$H$_3^+$, D$_3$H$_2^+$, D$_4$H$^+$, and D$_5^+$. Pure rotational spectra have been predicted for these species based on the optimized minimum-energy geometries and the zero-point averaged dipole moments calculated from our potential energy surface. We will discuss the implications of these results for the detection of each ion’s rotational spectrum, show preliminary predictions of the rotational spectrum for those species possessing permanent dipole moments, and comment on the degree of expected spectral splitting arising from internal motion. Finally, we will report on progress toward the laboratory spectroscopic investigation of these species in the terahertz region.
Although water is just a simple triatomic molecule, its spectroscopy still remains a challenge due to the ever increasing amount of available data. Two types of data have been recently obtained for water:

- Accurate frequencies have been measured for transitions in the sub millimeter and terahertz domains involving high-lying rovibrational levels up to the first triad. 149 transitions have been measured between 300 GHz and 2 THz and 26 from 2.5 to 2.7 THz. These $b$-type transitions take place within one of the five first vibrational states.

- Far infrared transitions involving high-lying rovibrational levels have been recorded recently in the 50 to 600 cm$^{-1}$ region using the emission spectrum of a continuous flow of water vapor rovibrationally excited by an electroless radio-frequency discharge.\textsuperscript{a} 3793 transitions with $\Delta K_a = 1$ within one of the five first vibrational states of the molecule have been assigned so far and involve $J$-values up to 25 and $K_a$-values up to 15. There remains a large number of unassigned transitions involving either higher lying vibrational states, larger values of $\Delta K_a$, or taking place between different vibrational states.

The paper will focus on the results of the analysis of a large data set consisting of already published data\textsuperscript{b} and of the two new data sets. The number of data is equal to 20491 and the bending-rotation theoretical approach\textsuperscript{c} will be used for the energy level calculation.


HCN has historically been used as a tracer of the dense gas in the interstellar medium. The envelopes of carbon rich asymptotic giant branch stars are generally rich in HCN; however, the large and generally variable infrared flux emitted by the star enormously complicates the interpretation. HCN in IRC+10216 shows an enormous number of masers and lasers pumped by the central star and often enhanced by line overlaps with other abundant molecules such as acetylene in the infrared. A total of seven laser transitions including two previously unreported transitions associated with the 040 – 011 interacting bands have been observed. To understand the astronomical observations a study of the radio frequency discharge plasma of CH$_4$ and N$_2$ was performed. Rotational transitions of HCN in vibrational states up to 15,000 cm$^{-1}$ have been observed including inverted levels and a number of previously undetected states. The spectra from IRC+10216 and the laboratory are presented.

\textsuperscript{a}A part of this work was performed at the Jet Propulsion Laboratory, California Institute of Technology under contract with the National Aeronautics and Space Administration. Copyright 2010© California Institute of Technology. All rights reserved.
RF11

SHOCK-INDUCED MOLECULAR ASTROCHEMISTRY IN DENSE CLOUDS


Supernovae have a formidable impact on the dynamics, chemistry and evolution of their local environments. Shocks carve into dense molecular clouds, radiatively cooling the remnant through strong molecular hydrogen and atomic lines. One of important postshock reaction is to convert atomic oxygen to molecular form such as CO, OH and water and these lines fall into THz. I will present observations of a dozen interacting remnants with prominent infrared lines detected by Spitzer, ISO, and ground-based IR telescopes, and show motivation of our granted Herschel and SOFIA observations. Supernovae provide simpler cases of impact of shock than other systems such as protoplanetary disks or protostellar jets where photoionization takes place. In the supernova remnants, the excitation of IR lines of molecular hydrogen requires both a slow shock through dense clumps, and a fast shock through interclump gas. The ortho-to-para ratio is typically much less than LTE, indicating shocks propagating into cold quiescent cloud cores. Evidence of dust grain heating and shattering by the shock is derived from black-body fits to the dust continuum. While radiative cooling and dust processing is beginning to be well understood, the observed oxygen chemistry deviates from equilibrium. We observe enhanced ionization in the shocked gas, which may be by cosmic rays as several of these interacting remnants are prominent GeV gamma-ray sources. The CO, OH and water have been detected from remnants by ISO and water is more than OH, but OH has still elevated abundance compared to theoretical predictions. Finally with Herschel and SOFIA provide opportunity to resolve complicated cooling and astrochemical networks of oxygen-bearing molecules and oxygen chemistry.

RF12

THE LABORATORY AND OBSERVATIONAL STUDY OF 2-BUTANONE AS A TEST FOR ORGANIC CHEMICAL COMPLEXITY IN VARIOUS INTERSTELLAR PHYSICAL ENVIRONMENTS

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We have undertaken a combined laboratory, observational, and modeling research program in an attempt to more fully understand the effects that physical environment has on the chemical composition of astronomical sources. To this end, deep millimeter and submillimeter spectral line surveys of multiple interstellar sources with varied physical conditions have been collected. These sources cover a range of physical environments, including hot cores, shocked regions, low-mass star forming regions, and stellar outflows. We have conducted broadband spectral line surveys at $\lambda =1.3$ mm of 10 sources at the Caltech Submillimeter Observatory (CSO). These are forerunner observations to our Herschel OT1 program to continue these line surveys at higher frequencies. Only a fraction of the lines observed in the CSO spectra can be assigned to known molecules. Laboratory spectra of many additional candidates for interstellar detection must therefore be collected before these spectral line surveys can be fully-analyzed. One such molecular target is 2-butaneone [also known as methyl ethyl ketone (MEK), CH$_3$COCH$_2$CH$_3$], which contains similar functional groups to other known interstellar molecules and is therefore a likely product of interstellar organic chemistry. The microwave spectrum for MEK was collected with the chirped-pulse waveguide Fourier Transform Microwave (FTMW) spectrometer at New College Florida, and the millimeter and submillimeter spectrum was collected using the direct absorption flow cell spectrometer at Emory University. We will report here both on the laboratory characterization of MEK and the analysis of the observational line surveys in the context of the identification of new, complex organic molecules in the ISM.
HIGH RESOLUTION FAR INFRARED FOURIER TRANSFORM SPECTROSCOPY OF THE NH$_2$ RADICAL.

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First identified toward Sgr B2$^a$, the NH$_2$ radical has recently been detected in the interstellar medium by the HIFI instrument on board of Herschel$^b$. Despite the fact that this radical has not been detected in brown dwarfs and exoplanets yet, it is already included in physical and chemical models of those environments$^c$ (temperature higher than 2000 K expected in several objects). Its detection in those objects will depend on the existence of a reliable high temperature and high resolution spectroscopic database on the NH$_2$ radical.

The absorption spectrum of NH$_2$ has been recorded between 15 and 700 cm$^{-1}$ at the highest resolution available using the Bruker IFS125HR Fourier transform interferometer connected to the far infrared AILES beamline at SOLEIL (R=0.001 cm$^{-1}$). The radical was produced by an electrical discharge (DC) through a continuous flow of NH$_3$ and He using the White-type discharge cell developped on the beamline (optical path: 24m). Thanks to the brilliance of the synchrotron radiation, more than 700 pure rotational transitions of NH$_2$ have been identified with high N values ($N_{max}=25$) in its fundamental and first excited vibrational modes. By comparison to the previous FT spectroscopic study on that radical in the FIR spectral range$^d$, asymmetric splitting as well as fine and hyperfine structure have been resolved for several transitions.


THE PURE ROTATIONAL SPECTRA OF ACETALDEHYDE AND GLYCOLALDEHYDE ISOTOPOLOGUES MEASURED IN NATURAL ABUNDANCE BY CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTROSCOPY

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Complex organic molecules (COMs) such as glycolaldehyde (HOCH$_2$CHO) and acetaldehyde (CH$_3$CHO) have now been detected in numerous interstellar sources. Glycolaldehyde has been detected in two hot cores, Sgr B2(N) and G31.41+0.31. Acetaldehyde has been observed in various sources, including the translucent clouds CB 17 and CB 24, cold molecular clouds such as TMC-1 and L134N, and hot cores such as Sgr B2(N), NGC 6334F, and the Orion Compact Ridge. Such COMs are known to have rich and complex spectra that add to the line confusion problem faced in observations of molecule-rich sources. Laboratory studies of excited vibrational states and isotopologues for known COMs therefore provide important guidance for sorting out the interstellar line confusion problem. Detection of isotopologues and determination of their abundance relative to the main isotopic species would also provide important constraints on interstellar chemical models, as these isotopic ratios are dependent on the formation mechanism for each species. The isotopic ratios for $^{13}$C/$^{12}$C, $^{18}$O/$^{16}$O, and D/H are known in various interstellar environments for simple molecules, but remain relatively unexplored for more complex species such as glycolaldehyde and acetaldehyde. The rotational spectra of the main isotopologues for glycolaldehyde and acetaldehyde have been well-characterized through microwave, millimeter, and submillimeter laboratory spectroscopy. Here we present the laboratory characterization of the isotopologues of acetaldehyde and glycolaldehyde in natural abundance by chirped pulse Fourier transform microwave spectroscopy (CP-FTMW). This spectroscopic information lays the groundwork for additional higher-frequency studies that can be directly applied to the interpretation of millimeter and submillimeter observations.
The vibration-rotation spectrum of the $\nu_1$-0, $\nu_2$-0 and $\nu_3$-0 bands of glycolaldehyde was recorded up to 12 THz, using the far-infrared beamline AILES at the synchrotron SOLEIL and a Fourier transform spectrometer coupled to a multipass cell. More than eight thousands lines were assigned, revealing the rotation structure up to $J=80$, $K_a=38$ for the ground state. The THz data were fitted simultaneously with pure rotational transitions of better accuracy observed in the microwave (1), in the millimeter-wave (2) and in the sub-millimeter-wave (3) range. In addition new data were recorded at Lille in the 150-300 GHz and 750-950 GHz range. The THz lines and the microwave - (sub)-millimeterwave lines are reproduced with a standard deviation of $2 \times 10^{-4}$ cm$^{-1}$ and 40 KHz, respectively.

Glycolaldehyde has been identified toward the galactic center (4). The vibrational state partition function can be re-evaluated according to the bands origins associated with $\nu_1$, $\nu_2$, and $\nu_3$, which are observed experimentally for the first time.

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VIBRATIONAL SPECTRA OF CRYOGENIC PEPTIDE IONS USING H₂ PREDISSOCIATION SPECTROSCOPY

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H₂ predissociation spectroscopy was used to collect the vibrational spectra of the model protonated peptides, GlyGly, GlySar, SarGly and SarSar (Gly=glycine and Sar=sarcosine). H₂ molecules were condensed onto protonated peptide ions in a quadrupole ion trap cooled to approximately 10 K. The resulting spectra yielded clearly resolved vibrational transitions throughout the mid IR region, 600-4200 cm⁻¹, with linewidths of approximately 6 cm⁻¹. Protonation nominally occurred on the amino terminus giving rise to an intramolecular H-bond between the protonated amine and the neighboring amide oxygen. The sarcosine containing peptides incorporate a methyl group onto either the amino group or the amide nitrogen causing the peptide backbone to adopt a different structure, resulting in the shifts in the amide I and II bands and the N-H stretches.

VIBRATIONAL CHARACTERIZATION OF SIMPLE PEPTIDES USING CRYOGENIC INFRARED PHOTODISSOCIATION OF H₂-TAGGED, MASS-SELECTED IONS

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We present infrared photodissociation spectra of two protonated peptides that are cooled in a 10 K quadrupole ion trap and tagged with weakly bound H₂ molecules. Spectra are recorded over the range 600 - 4300 cm⁻¹ using a table-top laser source, and are shown to result from one-photon absorption events. This arrangement is demonstrated to recover sharp ($\Delta \nu = 6$ cm⁻¹) transitions throughout the fingerprint region, despite the very high density of vibrational states in this energy range. The fundamentals associated with all of the signature N-H and C=O stretching bands are completely resolved. To address the site-specificity of the C=O stretches near 1800 cm⁻¹, we incorporated one $^{13}$C into the tripeptide. The labeling affects only one line in the complex spectrum, indicating that each C=O oscillator contributes a single distinct band, effectively reporting its local chemical environment. For both peptides, analysis of the resulting band patterns indicates that only one isomeric form is generated upon cooling the ions initially at room temperature into the H₂ tagging regime.
RG03

USING AN ORGANIC SCAFFOLD TO MODULATE THE QUANTUM STRUCTURE OF AN INTRAMOLECULAR PROTON BOND: CRYOGENIC VIBRATIONAL PREDISSOCIATION SPECTROSCOPY OF H₂ ON PROTONATED 8-NAPHTHALENE-1-AMINE

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The quantum structure of the intermolecular proton bond is a key aspect in understanding proton transfer events that govern the efficiency of fuel cells and various biological membranes. Previously, we have constructed a soft binding motif, that consists of a point contact between the lone pairs of two small molecules (combinations of ethers, alcohols, ammonia, and water) that are linked by a shared proton [Science 2007, 613, 249]. Although the frequency of the shared proton vibration has been correlated with effects of acid and base structure, such as proton affinities and dipole moments, the spatial arrangement of the proton donor and acceptor remains unexplored. Towards this aim, we have obtained a molecule of rigid topology that contains a proton donor and acceptor capable of intramolecular proton-bonding (protonated 8-flouronaphthalene-1-amine). Using electrospray ionization coupled with a novel cryogenic mass spectrometry scheme, we employ vibrational predissociation spectroscopy of H₂ tagged ions to elucidate how a forced spatial configuration of the acid and base perturbs the energetics of the proton bond.

RG04

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

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Serine is an amino acid which has long been known to form the magic-number serine octamer [Ser₈ + H]⁺. It has been showna that the serine octamer exhibits strong preference for homochirality. Although a few possible structures for the homochiral serine octamer have been proposed, no definite conclusion has so far been drawn. Last year at this conference, we reported on the study of the protonated serine octamer and dimer as well as the chiral recognition in these clusters using infrared multiphoton dissociation (IRMPD) spectroscopic technique coupled with a Fourier transform ion cyclotron (FTICR) mass spectrometer. Here we present our latest results on the search for the infrared signatures of chiral recognition in the serine octamer and the dimer using a mixture of the deuterated 2,3,3-d₃-L-serine and normal D-serine solution. Using the isotopic labeled species, we could isolate the heterochiral species and obtain their IRMPD spectra which can be directly compared with those of the homochiral species. As an aid to interpret the observed spectra, molecular structures and vibrational frequencies of both homochiral and heterochiral octamer and dimer have been predicted by ab initio calculations. New insights into the hitherto undetermined structure of the serine octamer will be discussed.

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Malonaldehyde is an open 5-membered ring molecule which exhibits interesting quantum-mechanical effects due to tunnelling of one of its protons. This results in a 21 cm\(^{-1}\) tunnelling-splitting in the ground vibrational state, which has been well-studied by microwave spectroscopy\(^a\). We have taken far-infrared Fourier transform spectra of malonaldehyde at the Canadian Light Source synchrotron, and have recorded a number of rotation-vibration fundamental bands between 100-1000 cm\(^{-1}\) at 0.00096 cm\(^{-1}\) resolution. The data permit us to determine with high precision the changes in the tunnelling-splitting induced by vibrational excitation. We have also observed spectra at 240 and 219 cm\(^{-1}\) that appear to be transitions from the two components of the ground vibrational state to a common upper state that is not mentioned in conventional vibrational analyses of malonaldehyde\(^b\). We will offer suggestions as to the nature of the newly-observed state.


VIBRATIONAL ANALYSIS AND VALENCE FORCE FIELD FOR NITROTOLUENES, DIMETHYLANILINES AND SOME SUBSTITUTED METHYLBENZENES

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The Fourier transform infrared (FTIR) and Raman spectra of 2-amino-4-nitro-toluene; 2-amino-5-nitrotoluene; 2,4-dimethylaniline; 2,5-dimethylaniline; 2,6-dimethylaniline; 1,2,4-trimethylbenzene; 1,3,5-trimethylbenzene and pentamethylbenzene have been recorded in the range 4000-400 cm$^{-1}$ and 4000-30 cm$^{-1}$, respectively. A normal coordinate analysis was carried out for both in-plane and out-of-plane vibrations of these molecules using an 81-parameter modified valence force field. The force constants were refined using 251 frequencies of eight molecules in the Overlay least-square technique. The reliability of force constants was tested by making zero-order calculations for both in-plane and out-of-plane vibrations for five related molecules. The potential energy distribution (PED) and eigen vectors calculated in the process were used to make unambiguous vibrational assignment of all the fundamentals.

THE HIGH RESOLUTION SPECTRUM OF JET-COOLED METHYL ACETATE IN THE C=O STRETCH REGION

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Methyl acetate (MA) has two inequivalent methyl tops, i.e., the acetyl CH$_3$ and methoxy CH$_3$ groups, which have significantly different internal rotation barrier.$^a$ One previous study$^b$ has reported that coupling of the carbonyl stretching mode with the methyl rotor modes in MA plays significant roles in internal vibrational redistribution (IVR), whose effect has been observed in the FT-IR spectrum of carbonyl band of MA. Surprisingly, the jet-cooled high resolution ro-vibrational spectrum of MA in the C=O stretch region we recorded does not show strong IVR effect. The spectrum was measured by a rapid scan infrared laser spectrometer equipped with an astigmatic multipass cell. Using the ground state combination differences calculated from the rotational constants of the vibrational ground state determined by a global fit of the microwave and millimeterwave lines,$^c$ the spectral assignment of the C=O stretching band has been made. The spectroscopic constants of the vibrationally excited state have been determined. The spectrum of deuterated MA has been also recorded in high resolution, and the difference in the degree of IVR in the isotopically substituted MA will be discussed.

$^c$M. Tudorie and I. Kleiner, private communication.
INFRARED FLUORESCENCE MEASUREMENTS OF GASEOUS BENZENE WITH A NEW HOME-MADE SPECTROMETER

G. FÉRAUD, Y. CARPENTIER*, T. PINO, P. PARNEIX, T. CHAMAILLÉ, Institut des Sciences Moléculaires d’Orsay, Université Paris-Sud 11, Orsay, France; E. DARTOIS, Y. LONGVAL, Institut d’Astrophysique Spatiale, Université Paris-Sud 11, Orsay, France; R. VASQUEZ and Ph. BRÉCHIGNAC, Institut des Sciences Moléculaires d’Orsay, Université Paris-Sud 11, Orsay, France.

Production and characterization of organic molecules such as gas phase Polycyclic Aromatic Hydrocarbons (PAHs) are one of the major challenges in laboratory astrophysics. Infrared spectral signatures are emitted by molecules in interstellar clouds submitted to UV radiations from surrounding stars. These infrared bands, the so-called Aromatic Infrared Bands (AIBs), have been attributed to PAHs since now 27 years. However, experimental works on infrared emission are quite rare. That is why we are developing an unique infrared spectrometer which collects and detects the infrared emission light from gas phase UV-excited PAHs. We are currently testing the spectrometer with benzene and its derivatives. Their infrared fluorescence decays will be presented, with an attempt to understand the competitive relaxation pathways.

This work was in part supported by the French INSU-CNRS national program ‘Physique et Chimie du Milieu Interstellaire (PCMI)’.

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INFRARED ION-GAIN SPECTROSCOPY AND FRACTIONAL ABUNDANCE MEASUREMENTS OF CONFORMER POPULATIONS

EVAN G. BUCHANAN, JACOB C. DEAN, BRETT M. MARSH, and TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN 47907-2804.

Studies of the single-conformation spectroscopy of large, flexible molecules has as one of its goals providing incisive tests of the predictions of calculations on the isolated molecules, whether ab initio or semi-empirical in nature. An important aspect of this comparison that is often lacking is quantitative data on the fractional abundances of the conformations. Previous studies from our group have provided such data using mass-resolved infrared population transfer (IRPT) spectroscopy. In this talk, we present an alternative method that in certain circumstances has advantages over IRPT, especially in ease of implementation. The method, infrared ion-gain (IRIG) spectroscopy, was first introduced by Fujii and co-workers on molecules without conformational isomers. Here we extend the method to conformationally flexible molecules, and test whether it can be used to provide fractional abundances by comparing with IRPT results on jet-cooled Ac-γ2-hPhe-NHMe, using thermal methods for vaporization of the molecule. The comparison provides some confidence that IRIG can be used for this purpose, but also points out conditions where it must be used with care. Analogous fractional abundance measurements on a prototypical lignin monomer will also be described, this time brought into the gas phase by laser desorption. Details of the laser desorption scheme used will also be provided.


SINGLE-CONFORMATION SPECTROSCOPY OF A DIASTEREOMERIC LIGNIN MONOMER: EXPLORING THE HYDROGEN BONDING ARCHITECTURES OF A TRIOL CHAIN

JACOB C. DEAN, EVAN G. BUCHANAN, ANNA GUTBERLET, WILLIAM H. JAMES III, BIDYUT BISWAS, P. V. RAMACHANDRAN, and TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN 47907.

The double-resonance methods of UV-UV holeburning and resonant ion-dip infrared (RIDIR) spectroscopy were implemented in this study to obtain conformer-specific UV and IR spectra on the two diastereomers (R,R)/(R,S) 1-(4-hydroxy-3-methoxyphenyl)propane-1,2,3-triol (R,R/R,S-HMPPT). HMPPT is a monomeric unit common to the lignin biopolymer in most plant types, and its spectroscopic signatures as well as conformational preferences yield valuable insight into its structuring in the polymer network. By probing the isolated molecule in the supersonic expansion, the infrared signatures of each OH allow the assessment of unique patterns in the IR spectrum associated with the different types of hydrogen bonded networks sampled in the jet. These observed conformational families are compared between diastereomers to understand the effect of chirality on the conformational minima available to the molecule. A total of nine conformational isomers have been characterized. Examples of three types of H-bonded chains and two H-bonded cycles are observed. Relative populations of the isomers in each diastereomer have also been obtained using a newly developed method, infrared ion gain spectroscopy. Striking differences are observed between the diastereomers, which configure the OH groups in unique positions relative to one another.

THE TORSIONAL FUNDAMENTAL BAND OF METHYLFORMATE

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Methylformate (HCOOCH₃) is one of the most important molecules in astrophysics, first observed in 1975. The rotational structure of its ground and first excited torsional states are well known from millimeter wave measurements. However, some of the torsional parameters are still not precisely determined because information on the torsional vibrational frequency νₜ = 1 − 0 is missing.

To overcome that problem, the far infrared spectrum of HCOOCH₃ was recorded with a 150 m optical path in a White cell and a Bruker IFS 125 HR Fourier transform spectrometer at the AILES beamline of the synchrotron SOLEIL facility. The analysis of the very weak fundamental torsional band νₜ = 1 − 0 observed around 130 cm⁻¹ was carried out. It led to the first precise determination of the torsional barrier height and the dipole moment induced by the torsional motion.

This work is partly supported by the "Programme National de Physico-Chimie du Milieu Interstellaire" (PCMI-CNRS) and by the contract ANR-BLAN-08-0054.

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A FAR INFRARED SYNCHROTRON-BASED INVESTIGATION OF 3-OXETANONE

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The four membered ester ring 3-oxetanone is a precursor for adding oxetane subunits into pharmaceuticals which then block metabolically exposed sites in the bioactive molecule without increasing its lipophilicity. The high resolution (0.00096 cm\(^{-1}\)) rovibrational spectrum of 3-oxetanone was recorded for the first time using far infrared radiation from the Canadian Light Source (CLS) synchrotron facility coupled to a Bruker IFS125HR FTIR spectrometer. A total of six rotationally-resolved vibrational bands were observed between 360 and 1150 cm\(^{-1}\) at room temperature. The assignment of the dense spectrum is currently underway and the progress will be discussed in this talk.

FAR-INFRARED SYNCHROTRON-BASED SPECTROSCOPY OF FURAN: ANALYSIS OF THE \(\nu_{14} - \nu_{11}\) PERTURBATION AND THE \(\nu_{18}\) AND \(\nu_{19}\) LEVELS

D. W. TOKARYK, S. D. CULLIGAN\(^a\), Department of Physics and Centre for Laser, Atomic and Molecular Sciences, University of New Brunswick, Fredericton, NB, Canada E3B 5A3; B. E. BILLINGHURST, Canadian Light Source, Inc., 101 Perimeter Road, University of Saskatchewan, Saskatoon, SK, Canada S7N 0X4; and J. A. van WIJNGAARDEN, Department of Chemistry, University of Manitoba, Winnipeg, MB, Canada R3T 2N2.

The \(\nu_{14}\) vibrational level of furan lies 603 cm\(^{-1}\) above the ground vibrational state. It is the lowest lying vibrational level for which a transition from the ground state is allowed. Other groups have conducted rotational analyses on fundamental bands of furan at 745 cm\(^{-1}\) (\(\nu_{13}\))\(^b\), 995 cm\(^{-1}\) (\(\nu_{7}\))\(^c\) and at 1067 cm\(^{-1}\) (\(\nu_{6}\))\(^d\). We have taken the rotationally resolved spectrum of the \(c\)-type \(\nu_{14}\) band at the Canadian Light Source synchrotron with a Bruker IFS125HR Fourier transform spectrometer operating at 0.00096 cm\(^{-1}\) resolution, and have found it to be perturbed by the \(\nu_{11}\) band at 600 cm\(^{-1}\), for which transitions from the ground vibrational state are forbidden. By taking the spectra of the \(b\)-type \(\nu_{18}\) fundamental band and of the very weak \(c\)-type \(\nu_{18} - \nu_{11}\) band we have been able to analyze the \(\nu_{14} - \nu_{11}\) perturbation. We have also analyzed the spectrum of the \(b\)-type \(\nu_{19}\) fundamental band.

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WAVEGUIDE CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE (CP-FTMW) SPECTRUM OF ALLYL CHLORIDE

ERIN B. KENT, MORGAN N. McCABE, MARIA A. PHILLIPS, BRITTANY P. GORDON and STEVEN T. SHIPMAN, Division of Natural Sciences, New College of Florida, Sarasota, FL 34243.

The microwave spectrum of allyl chloride at 0 °C was measured from 8.7–18.3 GHz with waveguide chirped-pulse Fourier transform microwave spectroscopy (CP-FTMW). The spectrum consists of contributions from $^{35}$Cl and $^{37}$Cl isotopomers of the cis and skew isomers. As the vibrational partition function for each of these conformers is approximately 4, the microwave spectrum contains a few thousand transitions with intensities above a 3:1 S/N ratio after a few hours of averaging. We will discuss our progress on the analysis of this spectrum, which has been aided with an automated strategy to find candidate assignments.

WAVEGUIDE CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE (CP-FTMW) SPECTRUM OF ORTHO-FLUOROTOLUENE

IAN A. FINNERAN and STEVEN T. SHIPMAN, Division of Natural Sciences, New College of Florida, Sarasota, FL 34243.

The microwave spectrum of o-fluorotoluene has been measured at 0 °C from 8.7–18.3 GHz with waveguide chirped-pulse Fourier transform microwave spectroscopy (CP-FTMW). We have extended previous assignments of the lowest energy A- and E-states by Susskind and Mäder and report on preliminary assignments of vibrationally excited states. This molecule also serves as a proof-of-principle for “coarse” microwave-microwave double resonance (MW-MW DR) measurements, in which we pump all transitions within a relatively broad frequency range (> 50 MHz) simultaneously. Transitions connected to peaks within the bandwidth of the coarse pulse are intensity modulated, revealing approximate connectivities that can be refined by performing “fine” MW-MW DR measurements. Prospects for using this method to perform automated, time-efficient MW-MW DR on samples with dense spectra and unknown assignments will be discussed.

A LOOK AT A SERIES OF ALKYL AND PERFLUORALKYL BROMIDES AND CHLORIDES

BRITTANY E. LONG, STEPHEN A. COOKE, Department of Chemistry, The University of North Texas, 1155 Union Circle, #305070, Denton, TX 76203-5017, U.S.A.; GARRY S. GRUBBS II, Department of Chemistry, Wesleyan University, Hall-Atwater Laboratories, 52 Lawn Ave., Middletown, CT 06459-0180, U.S.A.

The pure rotational spectrum for bromoperfluoroethane between 8.0 and 14.0 GHz and chloroperfluoroethane between 8.0 and 16.0 GHz has been measured on a chirped pulse Fourier transform microwave spectrometer for the first time. A total of 839 transitions for the bromoperfluoroethane, which includes the $^{79}$Br, $^{81}$Br parent isotopologues and the four $^{13}$C’s, have been assigned quantum numbers. 496 transitions were observed for chloroperfluoroethane, which includes the $^{35}$Cl and $^{37}$Cl species. Only the trans conformers were observed for which the rotational constants are reported. Nuclear electric quadrupole coupling constants have been determined and reported. Also, two dipole forbidden/quadrapole allowed $\Delta J = 2$ transitions were observed in only the bromoperfluoroethane spectra. No forbidden transitions were observed in the chloroperfluoroethane.
METHYL GROUP INTERNAL ROTATION IN THE PURE ROTATIONAL SPECTRUM OF 1,1-DIFLUOROACETONE

G. S. GRUBBS II, S. A. COOKE, Department of Chemistry, The University of North Texas, 1155 Union Circle, # 305070 Denton, TX 76203-5017, USA; P. GRONER, Department of Chemistry, University of Missouri-Kansas City, 5100 Rockhill Road, Kansas City, MO 64110.

We have used chirped pulse Fourier transform microwave spectroscopy to record the pure rotational spectrum of the title molecule. The spectrum was doubled owing to the internal rotation of the methyl group. The spectrum has been assigned and two approaches to the spectral analysis have been performed. In the first case, the A and E components were fit separately using a principal axis method with the SPFIT code of Pickett. In the second case, the A and E states were fit simultaneously using the ERHAM code. For a satisfactory analysis of the spectral data it has been found that the choice of Hamiltonian reduction, i.e. Watson A or S, is very important. The barrier to the internal rotation has been determined to be 261.1(8) cm$^{-1}$ and it will be compared to that of acetone and other halogenated acetone species recently studied in our laboratory.

FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF ALKALI METAL ACETYLIDES


Fourier transform microwave spectroscopy has been used to record pure rotational transitions of lithium, sodium and potassium acetylides and their deuterium isotopologues in their ground electronic state. The metal acetylides were produced by discharge assisted laser ablation of solid lithium, sodium and potassium in the presence of acetylene and deuterated acetylene. Rotational transitions in the 5 - 40 GHz range were measured and hyperfine splittings due to the alkali metals and deuterium were resolved. Alkali metal quadrupole coupling constants were determined for each species and deuterium quadrupole coupling constants were determined for the deuterated species. An interpretation of the hyperfine parameters in terms of metal-ligand bonding character will be discussed.

ANALYSIS OF ROTATIONAL STRUCTURE IN THE HIGH-RESOLUTION INFRARED SPECTRA OF THE TRANS-HEXATRIENE-1,1-D$_2$ AND -CIS-1-D$_1$ SPECIES

NORMAN C. CRAIG, HANNAH A. FUSON, and HENGFENG TIAN, Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH 44074; THOMAS A. BLAKE, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352.

Hexatriene-1,1-$d_2$ with some admixture of the cis-1-$d_1$ and trans-1-$d_1$ species was synthesized by reaction of 2,4-pentadienal and (methyl-$d_3$)-triphenylphosphonium iodide (Wittig reagent). The trans isomer was isolated by preparative gas chromatography, and the high-resolution (0.0015 cm$^{-1}$) infrared spectrum was recorded on a Bruker IFS 125HR instrument. The rotational structure in two C-type bands for the 1,1-$d_2$ species was analyzed. For this species the bands at 902.043 and 721.864 cm$^{-1}$ yielded composite ground state rotational constants of $A_0 = 0.801882(1)$, $B_0 = 0.041850(2)$, and $C_0 = 0.039804(1)$ cm$^{-1}$. For the cis-1-$d_1$ species the C-type band at 803.018 cm$^{-1}$ gave $A_0 = 0.809384(2)$, $B_0 = 0.043530(3)$, and $C_0 = 0.041321(2)$ cm$^{-1}$. By iodine-catalyzed isomerization, we have obtained some of the much less favored cis isomer and hope to obtain microwave spectra for its three deuterium-substituted species. The rotational constants reported here contribute to data needed for determining a semi-experimental structure for trans-hexatriene, which should show that the structural consequences of pi-electron delocalization increase with the chain length of polyenes.
ANALYSIS OF THE ROTATIONAL STRUCTURE IN THE HIGH-RESOLUTION INFRARED SPECTRUM OF TRANS-HEXATRIENE-1-13C1

NORMAN C. CRAIG and HENGFENG TIAN, Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH 44074; THOMAS A. BLAKE, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352.

Hexatriene-1-13C1 was synthesized by reaction of 2,4-pentadienal and (methyl-13C)-triphenylphosphonium iodide (Wittig reagent). The trans isomer was isolated by preparative gas chromatography, and the high-resolution (0.0015 cm⁻¹) infrared spectrum was recorded on a Bruker IFS 125HR instrument. The rotational structure in two C-type bands was analyzed. For this species the bands at 1010.7 and 893.740 cm⁻¹ yielded composite ground state rotational constants of $A_0 = 0.872820(1)$, $B_0 = 0.0435868(4)$, and $C_0 = 0.0415314(2)$ cm⁻¹. The ground state rotational constants for the 1-13C species were also predicted with Gaussian 03 software and the B3LYP/cc-pVTZ model. After scaling by the ratio of the observed and predicted ground state rotational constants for the normal species, the predicted ground state rotational constants for the 1-13C species agreed within 0.005 % with the observed values. Similar good agreement between observed and calculated values (0.016 %) was found for the three 13C species of the cis isomer. We conclude that ground state rotational constants for single heavy atom substitution can be calculated with adequate accuracy for use in determining semi-experimental equilibrium structures of small molecules. It will be unnecessary to synthesize the other two 13C species of trans-hexatriene.

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Intermission

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ROTATIONAL SPECTRUM SPECTRUM AND COUPLED-CLUSTER CALCULATIONS OF SILICON OXYSULFIDE, O=Si=S

S. THORWIRTH, I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany; L. A. MÜCK, J. GAUSS, Institut für Physikalische Chemie, Universität Mainz, 55099 Mainz, Germany; F. TAMASSIA, Dipartimento di Chimica Fisica e Inorganica, Università di Bologna, I-40136 Bologna, Italy; V. LATTANZI, M. 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.

Silicon oxysulfide, OSiS, and seven of its minor isotopic species have been characterized for the first time in the gas phase at high spectral resolution by means of Fourier-transform microwave spectroscopy. The equilibrium structure of OSiS has been determined from a combination of experimental ground state rotational constants and calculated vibrational corrections to those. The structural parameters are in good agreement with values from high-level quantum-chemical calculations using coupled-cluster techniques together with sophisticated additivity and extrapolation schemes.

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STRUCTRURAL DETERMINATION OF SILACYCLOBUTANE AND SILACYCLOPENTANE USING FOURIER TRANSFORM MICROWAVE (FTMW) AND CHIRPED PULSE FOURIER TRANSFORM MICROWAVE (cp-FTMW) SPECTROSCOPY

ZIQIU CHEN, CODY VAN DIJK AND JENNIFER VAN WIJNGAARDEN, Department of Chemistry, University of Manitoba, Winnipeg MB R3T 2N2 Canada.

The pure rotational spectra of the ground states of silacyclobutane (SCB) and silacyclopentane (SCP) were measured in a supersonic jet in the 6-24 GHz range using Fourier transform microwave spectroscopy and the chirped-pulse variant of this technique. Heavy atom isotopic substitution for the silicon and each of the carbon atoms within the rings enabled the accurate determination of the $r_s$ and $r_0$ structural parameters of the ring backbones of both SCB and SCP. For SCB, splitting due to ring inversion in the ground state has been observed and analyzed.
ROOM-TEMPERATURE CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE (CP-FTMW) SPECTRUM OF 2-METHYLFURAN

IAN A. FINNERAN and STEVEN T. SHIPMAN, Division of Natural Sciences, New College of Florida, Sarasota, FL 34243.

The microwave spectrum of 2-methylfuran has been measured at temperatures between 0 °C and 50 °C from 8.7–18.3 GHz with waveguide chirped-pulse Fourier transform microwave spectroscopy (CP-FTMW). Using the enhanced sensitivity of this technique relative to that of prior measurements from Stark-modulated instruments, we have been able to extend the assignments of the lowest energy A- and E-states from Norris and Krisher\(^a\) to include transitions up to \(J = 60\) and \(K_a = 35\). We will also report on our progress towards assigning higher-lying states and compare the fit results to those from \textit{ab initio} calculations.


THE MICROWAVE SPECTRUM OF METHYL VINYL KETONE REVISITED

DAVID S. WILCOX, AMANDA J. SHIRAR, OWEN L. WILLIAMS, BRIAN C. DIAN, Department of Chemistry, Purdue University, West Lafayette, IN, 47907.

A chirped-pulse Fourier transform microwave spectrometer was used to record the rotational spectrum of methyl vinyl ketone (MVK, 3-butene-2-one) from 6 to 18.9 GHz. Two stable conformations were identified: the previously documented antiperiplanar (\textit{ap}) conformer and synperiplanar (\textit{sp}), which is reported for the first time in this microwave study. Methyl torsional analysis with XIAM resulted in \(V_3\) barrier heights of 433.8(1) and 376.6(2) \text{cm}^{-1} for \textit{ap}- and \textit{sp}-MVK, respectively. Heavy atom isotopic species were detected in natural abundance allowing bond lengths and angles of the molecular frames to be calculated through Kraitchman analysis. A comparison with \textit{ab initio} calculations is included.

HIGH RESOLUTION ROTATIONAL SPECTROSCOPY OF A FLEXIBLE CYCLIC ETHER


Crown ethers stand as one cornerstone molecular class in host-guest Supramolecular Chemistry and constitute building blocks for a broad range of modern materials. We report here the first high resolution rotational study of a crown ether: 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5 ether,15c5). Molecular beam Fourier transform microwave spectroscopy\(^a\) has been employed. The liquid sample of 15c5 has been vaporized using heating methods\(^b\). The considerable size of 15c5 and the broad range of conformations allowed by the flexibility of its backbone pose important challenges to spectroscopy approaches. In fact, the ab-initio computational study for isolated 15c5\(^c\), yields at least six stable conformers with relative free energies within 2 \text{kJ mol}^{-1} (167 \text{cm}^{-1}). Nevertheless, in this investigation it has been possible to identify and characterize in detail one stable rotamer of the 15c5 molecule and to challenge different quantum methods for the accurate description of this system. The results pave the ground for an extensive description of the conformational landscape of 15c5 and related cyclic ethers in the near term.

An experimental study has been performed shedding light on the conformational energies of \( n \)-butyl ethyl ether. Rotational spectroscopy between 7.8 GHz and 16.2 GHz has identified two conformers of \( n \)-butyl ethyl ether, \( \text{C}_4\text{H}_9\text{OC}_2\text{H}_5 \). In these experiments spectra were observed as the target compound participated in an argon expansion from high to low pressure causing molecular rotational temperatures to be below 4 K. For one conformer, 95 pure rotational transitions have been recorded, for the second conformer, 20 pure rotational transitions were recorded. Rotational constants and centrifugal distortion constants are presented for both butyl ethyl conformers. The structures of both conformers have been identified by exploring the multi-dimensional, molecular potential energy surface using ab initio calculations. From the numerous low energy conformers identified using ab initio methods, the three lowest conformers were pursued at increasingly higher levels of theory, i.e. complete basis set extrapolations and also coupled cluster methods. The two conformers observed experimentally are only revealed to be the two lowest energy conformers when high levels of quantum chemical methodologies are employed.
RI THEOREY
THURSDAY, JUNE 23, 2011 – 1:30 pm
Room: 1015 McPherson Lab

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

RI01  INVITED TALK  30 min 1:30
COMPOSITE APPROACHES FOR AB INITIO SPECTROSCOPY: THE CCN, CCSb, AND HNNO RADICALS

KIRK A. PETERSON, J. GRANT HILL, JAMES SHEAROUSE, Department of Chemistry, Washington State University, Pullman, WA 99164; ALEXANDER MITRUSHCHENKOV, Laboratoire de Modélisation et Simulation Multi Echelle, Université Paris-Est Marne-la-Vallée, 77454 Marne la Vallée, Cedex 2, France; and JOSEPH S. FRANCISCO, Department of Chemistry, Purdue University, West Lafayette, IN 47907.

Over the last several years, composite methods have found great utility in the area of accurate ab initio thermochemistry. Utilizing highly correlated wavefunction-based methods such as CCSD(T) in conjunction with basis set extrapolations and corrections due to relativistic effects, core electron correlation, etc., accuracies approaching 1 kJ/mol have been possible in some cases. In the present work a similar methodology, including the use of explicitly correlated F12 methods and the inclusion of spin-orbit coupling, has been employed for the near-equilibrium potential energy surfaces of the $^2\Pi$ ground states of CCN and CCSb. A detailed analysis of the anharmonic vibrational spectra calculated from these surfaces and the Renner-Teller effect in these molecules will be discussed. The vibrational spectrum of the HNNO radical is found to be a challenging case for ab initio methods due to strong higher level electron correlation effects.\textsuperscript{a}


RI02  15 min  2:05
EMPLOYING DIFFUSION MONTE CARLO IN THE CALCULATION OF MINIMIZED ENERGY PATHS OF THE CH$_3^+$ + H$_2$ ↔ CH$_5^+$ ↔ CH$_5^+$ + H$_2$ REACTION AND ITS ISOTOPIC VARIANTS

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

Protonated methane is presumed by astrochemists to be an important intermediate in the reaction CH$_3^+$ + HD → CDH$_4^+$ → CH$_3$D$_4^+$ + H$_2$ within the interstellar medium. Understanding this reaction can also help shed light on the observed nonstatistical H/D isotopic abundance in the isotopologues of CH$_3^+$ within the interstellar medium. Interestingly, based on kinetic studies, Gerlich and co-workers showed that all of the reactions in the series CH$_3^+$−$n$D$_n$ + HD → CH$_4$−$n$D$_{n+1}$ → CH$_2$−$n$D$_{n+1}$ + H$_2$ have identical net rate constants.\textsuperscript{a} This result is independent of the value of n.

In previous studies of CH$_5^+$, we have employed Diffusion Monte Carlo (DMC)\textsuperscript{b} to study ground,\textsuperscript{c} and excited states.\textsuperscript{d,e,f} By performing the simulation in Jacobi coordinates, we can use Adiabatic DMC\textsuperscript{g} to study the properties of the minimized energy paths of CH$_5^+$ and isotopologues. To determine the minimized energy path, we calculate the quantum zero-point energy and ground state wave function as a function of the distance between the center of mass of the H$_2$ group and the center of mass of the CH$_5^+$ group over a range from 0 to 6 Å. Over this range, we find 5 distinct regions of interaction, short-range repulsion region, CH$_3^+$ complexation, short-range fragment interaction, long-range fragment interaction, and a region of no interaction between the two fragments. Interestingly, the range of H$_2$/CH$_5^+$ distances spanned by each of the regions is roughly independent of the number or location of the deuteron atoms. Interestingly, the range of H$_2$/CH$_5^+$ distances spanned by each of the regions is roughly independent of the number or location of the deuteron atoms.

\textsuperscript{f}C. E. Hinkle, A. S. Petit, A. B. McCoy, in preparation.
POTENTIAL ENERGY SURFACES OF M+NG, M = K, RB, CS AND NG = HE, NE, AR

J. Blank, David E. Weeks, Engineering Physics Department, Air Force Institute of Technology, 2950 Hobson Way, WPAFB, OH 45433-7765; Gary S. Kedzoria, High Performance Technologies, Inc. 2435 5th St., WPAFB, OH USA 45433-7765.

Pressure broadening (PB) plays an important role in the operation of optically pumped alkali lasers (OPAL) by broadening the absorption features of the alkali metal via a perturbing noble gas. While sophisticated PB models exist, they require a knowledge of the interaction potentials involved to become predictive. As a first step toward studying the PB at work in OPAL systems, ab initio potential energy surfaces have been generated for a series of combinations of alkali metals (K, Rb, and Cs) and noble gas atoms (He, Ne, and Ar) which potentially may comprise such systems. These surfaces include the ground state $X^2\Sigma^+_1/2$, as well as the excited states $A^2\Pi_{1/2}$, $A^2\Pi_{3/2}$, and $B^2\Sigma^+_1$. They are calculated using the multiconfigurational singles and doubles configuration interaction method, including the spin-orbit interaction through the use of two-component pseudopotentials, implemented in the COLUMBUS suite of molecular structure programs. Where possible, results are compared to both experimentally measured and previous theoretical predictions of spectroscopic constants as well as experimentally determined vibrational energy levels.

A QUANTUM CHEMICAL STUDY OF XH AND XH$_2$ (X=Be,C,N,O): 2s$^2$ RECOUPLED PAIR BONDING

Lu Xu, D. E. Woon, and T. H. Dunning, Jr., Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

High level MRCI and RCCSD(T) calculations using large correlation consistent basis sets were used to study the low-lying states of the XH and XH$_2$ hydrides of the first row p block elements. Recoupled pair bonding is found in states such as the BeH $X^2\Sigma^+$ ground state, the BH $a^3\Pi$ excited state, the CH $a^4\Sigma^-$ excited state, the NH $A^3\Pi$ excited state, and OH $^2\Delta$ and $^2\Sigma^+$ excited states. The 2s$^2$ recoupled bonding exhibited by these elements is similar to, but quantitatively different from, the 3p$^2$/3s$^2$ recoupled pair bonding of the second row late p block elements (P, S, Cl). The differences arise from the well-understood distinction between the orbitals involved in recoupling. One of the dissimilarities between the two groups of elements is how favorable it is to form the second bond via covalent or recoupled pair bonding. In SF$_2$ and CHF$_2$, forming two recoupled pair bonds from the 3p$^2$ pair is more stable than forming one recoupled bond and one covalent bond due to the antibonding character of the singly occupied orbital containing the electron left over from recoupling; using this orbital to form a second bond reduces the antibonding character and stabilizes the molecule. In B and C, the recoupled 2s$^2$ pair is a set of lobe orbitals, and there is less driving force to bond to the second lobe than to the singly occupied 2p orbital that is also present. The $X^2\Sigma^+_1$ ground state of BH$_2$ and the $X^3\Delta$ ground state of CH$_2$ are both therefore bent at about 130° with bonding that represents a linear combination of one recoupled bond and one covalent bond (the $X^1\Sigma^+_g$ ground state of BeH$_2$ is linear with two recoupled bonds because there is only one electron available in BeH($X^2\Sigma^+$)).

COMPUTATIONAL AND SPECTROSCOPIC STUDY OF THE B-N DATIVE BOND IN AMMONIA BORANE

Ashley M. Wright, Gregory S. Tschumper, and Nathan I. Hammer, University of Mississippi, Department of Chemistry & Biochemistry, Oxford, MS 38677.

Ammonia borane is the archetypal small molecule employed to study dative bonds (also known as coordinate covalent or dipolar bonds) theoretically. We analyze the sensitivity of the B-N dative bond to method and basis set by computing the B-N bond length and the B-N stretching frequency. Our goal is to find the least computationally demanding method and basis set combination that yields trustworthy results. Previous researchers have demonstrated the inaccuracy of the B3LYP method for describing this type of bond. Here, we compare results using the M06-2X hybrid density functional with ab initio methods including MP2, CCSD, and CCSD(T) with different sized basis sets. We compare these results to experimental solid state and gas phase Raman spectra. Monomer calculations overestimate the B-N bond length and underestimate the B-N stretch in ammonia borane when compared to experimental values. However, calculations performed on clusters of ammonia borane molecules do a better job of reproducing the solid state experimental results. This agreement could be due to dihydrogen bonding between the ammonia borane molecules.
EXCITED STATES IN SOLUTION AT EOM-CCSD LEVEL WITH THE POLARIZABLE CONTINUUM MODEL OF SOLVATION

M. CARICATO, Gaussian, Inc., 340 Quinnipiac St., Bldg 40, Wallingford, CT 06492.

Electronic excited states are at the center of many research areas, and theoretical simulations are increasingly important. Although approximate methods based on time dependent density functional theory represent a useful tool, accurate wave function methods are still the most reliable approach. These methods, however, suffer from high computational cost that limits their range of applicability. This is particularly so when the system under study is in solution. In fact, the treatment of a large number of solvent molecules, even when modeled at a low level of theory (like molecular mechanics), is cumbersome due to the large number of conformations that needs to be considered. When the solvent is not directly involved in the process, its effect can be properly accounted for by using polarizable continuum models (PCMs) where the conformational average is implicit in the solvent dielectric constant. In this contribution, the treatment of electronic excited state energy and structure of molecules in solution at the EOM-CCSD/PCM level of theory is presented. This approach represents an effective compromise between computational cost and accurate treatment of the central part of the system while taking into account the non-negligible effect of the solvent.

Intermission

EXPLORING TRANSITION METAL CATALYZED REACTIONS VIA AB INITIO REACTION PATHWAYS

HRACTHIAN, Gaussian, Inc., 340 Quinnipiac St., Bldg 40, Wallingford, CT 06492.

The study and prediction of chemical reactivity is one of the most influential contributions of quantum chemistry. A central concept in the theoretical treatment of chemical reactions is the reaction pathway, which can be quite difficult to integrate accurately and efficiently. This talk will outline our developments in the integration of these pathways on ab initio potential energy surfaces. We will also describe results from recent studies on the kinetics of transition metal catalyzed reactions, including the importance of vibrational coupling to the reaction coordinate and the role of this coupling in catalytic rate enhancement.

NON-PRODUCT SMOLYAK GRIDS FOR COMPUTING SPECTRA: HOW AND WHY?

GUSTAVO AVILA and TUCKER CARRINGTON JR., Chemistry Department, Queen’s University, Kingston, Ontario K7L 3N6, Canada.

Spectra are computed by solving the time-independent Schrödinger equation. If the number of atoms in a molecule is greater than about 4 the dimensionality of the Schrödinger equation makes solution very difficult. Standard discretization strategies for large dimensional systems \( D \geq 9 \) yield matrices and vectors that are too large for modern computers. This is the so-called "curse of dimensionality". Both the basis size and quadrature grid size are problems. Several ingenious schemes have been developed in the last decades to reduce the basis size. We have focused on reducing the size of the quadrature grid. The Smolyak algorithm allows one to create non-product quadrature grids with structure. Because of the structure they can be used with pruned product basis sets and the Lanczos algorithm to compute spectra. In this talk we shall explain the nature of these grids and why they are useful for computing spectra.
RI09 15 min 4:19

USING A NON-PRODUCT QUADRATURE GRID TO COMPUTE THE VIBRATIONAL SPECTRUM OF C$_2$H$_4$

GUSTAVO AVILA and TUCKER CARRINGTON JR., Chemistry Department, Queen's University, Kingston, Ontario K7L 3N6, Canada.

We present an accurate 12-D basis set calculation of the lowest 100 energy levels of the C$_2$H$_4$ molecule. A Smolyak non-product quadrature grid, a pruned product basis set, and the Lanczos algorithm are used. This scheme allows one to reduce the size of the basis set by almost 7 orders of magnitude (from $9 \times 10^{12}$ to $1.3 \times 10^6$) and the size of the quadrature grid by almost 6 orders of magnitude (from $5.6 \times 10^{13}$ to $1.52 \times 10^9$). Basis pruning and the nonproduct quadrature grid therefore enable us to solve a problem, numerically exactly, that would be impossible without these tools.

RI10 15 min 4:36

PROGRESS TOWARDS THE ACCURATE CALCULATION OF ANHARMONIC VIBRATIONAL STATES OF FLUXIONAL MOLECULES AND CLUSTERS WITHOUT A POTENTIAL ENERGY SURFACE

ANDREW S. PETIT and ANNE B. McCOY, Department of Chemistry, The Ohio State University, Columbus, OH 43210.

The accurate calculation of anharmonic vibrational states of highly fluxional systems is complicated by the need to first obtain the full-dimensional potential energy surface (PES). Although commonly exploited as a way around this problem, grid-based methodologies scale exponentially with system size while reduced dimensional approaches are highly system dependent, both in terms of the details of their application and in terms of their suitability. Moreover, the achievement of converged variational calculations of highly anharmonic systems is complicated by the necessity of using a very large basis and hence the construction and diagonalization of enormous Hamiltonian matrices.

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 and using only a handful of basis functions per degree of freedom. More specifically, the potential energy and G-matrix elements are calculated on a set of points obtained from a Monte Carlo sampling of the most important regions of configuration space, allowing for a significant reduction in the number of required sampling points. The Hamiltonian matrix is then constructed using an evolving basis which, with each iteration, captures the effect of building H from an ever-expanding 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, including ion water complexes, will be reported along with its observed convergence properties.

RI11 15 min 4:53

HOW LIGAND PROPERTIES AFFECT THE FORMATION AND CHARACTERISTICS OF RECOUPLED PAIR BONDS

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

Our group has developed a theoretical framework for understanding hypervalency called recoupled pair bonding. In a recoupled pair bond, a singly occupied orbital of an incoming ligand is able to decouple a pair of electrons on a central atom and form a bond with one of the electrons. The other electron is then free to bond with a second ligand. However, not every ligand is able to induce recoupling and lead to the formation of hypervalent compounds; SF$_4$ exists, but SH$_4$ is not stable, for example. We have investigated a large variety of monovalent ligands (including H, F, Cl, OH, NH$_2$, CH$_3$, and other radicals) to discover which ligands are capable of recoupling the 3p$^2$ electron pair of sulfur and to quantify the strength of these bonds relative to covalent bonds formed with the same ligand. Also of interest is which properties of the various ligands correlate with their ability to recouple a pair of electrons. We have also benchmarked the accuracy of density functional theory in the description of recoupled pair bonds compared to high level MRCI and RCCSD(T) calculations as a possible way to test the recoupling ability of larger ligands such as the phenyl radical (C$_6$H$_5$).
RI12  

A QUANTUM CHEMICAL STUDY OF THE STRUCTURE AND CHEMISTRY OF HZnCH$_3$, A TRANSITION METAL COMPOUND WITH 4s$^2$ RECOUPLED PAIR BONDING  

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

A structure was recently reported by Flory et al.$^a$ for methyl zinc hydride, HZnCH$_3$, a molecule that may be formed via the direct insertion of Zn into one of the CH bonds of methane. The experiments were not able to demonstrate the formation pathway conclusively. The structures, bond energies, and other properties of HZnCH$_3$, ZnH, and ZnCH$_3$ were determined with high level coupled-cluster theory and multireference configuration interaction calculations in order to better understand the nature of the chemistry of HZnCH$_3$. The Zn–H and Zn–C bonds in HZnCH$_3$(X$^1A_1$) were found to be formed through recoupling the 4s$^2$ pair of Zn($^3S$) in a manner that is very similar to the bonding in HBeCH$_3$ and other compounds where the 2s$^2$ pair of Be is recoupled. Various formation pathways were characterized, such as the analogous family of exchange reactions H + CH$_4$ → CH$_4$ + H, Zn + CH$_4$ → ZnCH$_3$ + H, and Be + CH$_4$ → BeCH$_3$ + H. Direct insertion may involve an intersystem crossing from the Zn($^3$P) + CH$_4$ triplet surface to the singlet surface, which has been explored.


RI13  

THE SEARCH FOR AN OBSERVABLE HELIUM COMPLEX  

ADRIAN M. GARDNER, TIMOTHY G. WRIGHT, School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom; COREY J. EVANS, Department of Chemistry, University of Leicester, University Road, Leicester, LE1 7RH, United Kingdom.  

Calculations on the He···MX, Ne···MX, and Ar···MX (M = Cu, Ag, Au; X = F, Cl) complexes at the CCSD and CCSD(T) levels of theory have been conducted.$^a$ The RG···MX (RG = He, Ne, and Ar) dissociation energies for these complexes have been evaluated by extrapolation to the complete basis set limit. The dissociation energies determined for the He···CuF and He···AuF complexes have been found to be significant, at $\approx$26 kJ mol$^{-1}$. The nature of the interactions present in these species have been investigated employing atoms-in-molecules (AIM) analysis, natural bond order analysis, and through evaluation of the dipole/induced dipole and ion/induced dipole interactions. This analysis has shown that the bonding in the strongly bound He···CuF and He···AuF complexes is slightly covalent in nature.

DEHYDROGENATION AND IONS
THURSDAY, JUNE 23, 2011 – 1:30 pm
Room: 2015 McPherson Lab

Chair: LAURA McCUNN, Marshall University, Huntington, West Virginia

RJ01 15 min 1:30
DEHYDROGENATION OF ETHYLENE: SPECTROSCOPY AND STRUCTURES OF La(C2H2) AND La(C4H6) COMPLEXES

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

Hydrogen elimination is observed in the reaction of laser-ablated La atoms and ethylene (C2H4) in a pulsed molecular beam source. Dehydrogenated products, La(C2H2) and La(C4H6), are identified by time-of-flight mass spectrometry and studied by pulsed-field-ionization zero-electron kinetic energy spectroscopy and density functional theory calculations. La(C2H2) is determined as a triangle (C2v) in the 2A1 ground electronic state, where La binds with C2H2 in a two-fold mode (η6). La(C4H6) is identified as a diligand species with La being sandwiched between C2H2 and C2H2, each in a two-fold binding mode, and the complex is in the 2A1 ground electronic state. The adiabatic ionization energies of La(η2-C2H2) and La(η2-C4H6)(η5-C2H4) are measured to be 41174(5) and 39405(5) cm−1, respectively. La+-C2H2 and La+-C4H6 stretching and C-H bending frequencies of the corresponding ions are also determined, and the vibrational assignments are confirmed with deuterated ethylene measurements.

RJ02 15 min 1:47
DEHYDROGENATION AND C-H BOND INSERTION OF PROPENE: La(η2-C3H4) AND HLa(η3-C3H5)

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

Dehydrogenation and C-H bond insertion are observed in the reaction of laser-ablated La atoms and propene (C3H6) in a pulsed molecular beam source. Several dehydrogenated and inserted products are identified by the time-of-flight mass spectrometry. La(C3H2) formed from H2 elimination and HLa(C3H5) formed by C-H bond insertion are characterized by pulsed-field-ionization electron and ion spectroscopy, in combination with density functional theory calculations. Two isomers of La(C3H4) are identified from 1,2- and 1,3-dehydrogenation. The adiabatic ionization energies of 1,2- and 1,3-dehydrogenated isomers are measured to be 40506(5) and 40941(5) cm−1, respectively. For the inserted product HLa(C3H5), La atom is bound to the allyl radical in a three-fold binding mode (η5). It is observed that the ionization energy of the HLa(η2-C3H5) insertion complex (41130(5) cm−1) is close to that of the 1,3-dehydrogenated La(η2-C3H4) species.

RJ03 15 min 2:04
OBSERVATION OF TWO La(C3H2) ISOMERS FORMED BY DEHYDROGENATION OF PROPYLENE

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

C-H bond activation of small hydrocarbons is of importance in chemistry and industrial applications. La(C3H2) was formed by the reaction of laser-ablated La atoms and propyne (C3D4) in supersonic molecular beams. Two isomers of La(C3H2) were detected for the first time by mass-analyzed threshold ionization (MATI) spectroscopy. From the MATI spectra, the two isomers exhibit origin bands at 42953(5) and 43609(5) cm−1 and vibrational intervals of 425 and 535 cm−1, respectively. They were identified as La(CCCH2) formed from 1,3-dehydrogantion and La(HCCCH) formed by 3,3-dehydrogenation and were confirmed by measurements with deuterium substituted propyne (C3D4) as the precursor. The 1,3-dehydrogenated complex shows a higher ionization energy and larger metal-ligand stretching frequencies than the 3,3-dehydrogenated species. Based on DFT/B3LYP calculations, the electronic transitions responsible for the observed MATI spectrum of La(HCCCH) isomer is 1A′ ← 2A, and that of La(CCCH2) isomer is 1A ← 2A′.
VIBRONIC SPECTROSCOPY OF THE PHENYLCYANOMETHYL RADICAL

DEEPALEI N. MEHTA, NATHANAEL M. KIDWELL, and TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN 47907.

Resonance stabilized radicals (RSRs) are thought to be key intermediates in the formation of larger molecules in planetary atmospheres. Given the nitrogen-rich atmosphere of Titan, and the prevalence of nitriles there, it is likely that nitrile and isonitrile RSRs could be especially important in pathways leading to the formation of more complex nitrogen-containing compounds and the aerosols (StoholinsT) that are ultimately produced. In this talk, the results of a gas phase, jet-cooled vibronic spectroscopy study of the phenylcyanomethyl radical (C_6H_5˙CHCN), the nitrogen-containing analog of the 1-phenylpropargyl radical, will be presented. A resonant two color photon ionization spectrum over the range 21,350-22,200 cm^{-1} (450.0-468.0 nm) has been recorded, and the D_0-D_1 origin band has been tentatively identified at 21,400 cm^{-1}. Studies identifying the ionization threshold, and characterizing the vibronic structure will also be presented. An analogous study of the phenylisocyanomethyl radical, C_6H_5˙CHNC, is currently being pursued for comparison with that of phenylcyanomethyl radical.

SPECTROSCOPIC IDENTIFICATION OF ISOMERIC TRIMETHYLBENZYL RADICALS GENERATED IN CORONA DISCHARGE OF TETRAMETHYLBENZENE

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

The visible vibronic emission spectra were recorded from the corona discharge of precursor tetramethylbenzene with a large amount of inert carrier gas helium using a pinhole-type glass nozzle coupled with corona excited supersonic expansion (CESE) well developed in this laboratory. The spectra showed a series of vibronic bands in the D_1 → D_0 electronic transition of jet-cooled benzyl-type radicals formed from the precursor in a corona excitation. The analysis confirmed that two isomeric radicals, 2,3,4- and 2,3,6-trimethylbenzyl radicals and three isomeric radicals, 3,4,5-, 2,3,5- and 2,4,6-trimethylbenzyl radicals were produced, respectively, from 1,2,3,4- and 1,2,3,5-tetramethylbenzenes as a result of removal of a hydrogen atom from the methyl group at different substitution position. For each isomeric trimethylbenzyl radical generated in the corona discharge of precursor, the electronic transition and a few vibrational mode frequencies were determined in the ground electronic state by comparing with those from both ab initio calculations and the known vibrational data of the precursor. The substitution effect that states the shift of electronic transition depends on the nature, the number, and the position of substituents on the ring has been qualitatively proved for the case of benzyl-type radicals.

INFRARED SPECTRA OF PRODUCTS OF THE ULTRAVIOLET AND VACUUM ULTRAVIOLET IRRADIATION OF BENZENE TRAPPED IN SOLID NEON

Marilyn E. Jacox and Warren E. Thompson, Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441.

When a solid solution of benzene in a large excess of neon is exposed to the 254-nm output of a medium-pressure mercury arc, prominent infrared absorptions of fulvene and of o-benzyne appear. On prolonged photolysis, propyne absorptions grow substantially. Analogous experiments using benzene-d_6 yield the first infrared spectral data for fulvene-d_6, for which the positions of the most prominent absorptions agree well with those predicted by density functional calculations. Studies in which the benzene is exposed to 10.2 eV or to 16.6 to 16.85 eV radiation during deposition have also been conducted. At these energies, ionization may occur. In addition to absorptions of the same products as those obtained on 254-nm photolysis, new absorptions appear. Possible carriers of these new peaks will be considered.

Intermission
INFRARED SPECTROSCOPY OF PROTONATED MIXED BENZENE-WATER CLUSTERS

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

Mixed clusters of protonated benzene and water are created via arc discharge in a molecular beam cluster source. Infrared spectroscopy (1000 cm$^{-1}$ to 4500 cm$^{-1}$) of these mixed clusters H$^+$(H$_2$O)$_x$(Bz)$_y$ (x=1-4, y=1-4) tagged with argon is employed to investigate the structures of these clusters, particularly with regards to the location of the proton. Studies as a function of cluster size investigate solvation effects within the mixed clusters.

MASS-ANALYZED THRESHOLD IONIZATION AND STRUCTURES OF M$_3$C$_2$(M=Sc, La)

LU WU, ROUDJANE MOURAD and D. S. YANG, Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.

M$_3$C$_2$ (M=Sc, La) clusters are produced by laser vaporization in a pulsed metal-cluster source and identified by photoionization mass spectrometry. Vibrationally resolved ion spectra are obtained with mass-analyzed threshold ionization (MATI) spectroscopy. The MATI spectra of M$_3$C$_2$ (M=Sc, La) exhibit a weak 0-0 transition, indicating a significant geometry difference between the neutral and ionized clusters. The ionization energies of Sc$_2$C$_2$ and La$_3$C$_2$ are measured to be 36398(5) and 30051(5) cm$^{-1}$, respectively. In addition, the spectra of the two clusters display a number of vibrational intervals that are associated with M$_3$ deformations. Preliminary data analysis shows that both clusters have a C$_{2v}$ bi-pyramid structure in the neutral state and a D$_{3h}$ bi-pyramid structure in the ion state, and the spectra may be assigned to the $^1$A$_1$ $^1$B$_2$ transitions.

VIBRATIONAL AND GEOMETRIC STRUCTURES OF La$_3$C$_2$O AND La$_3$C$_2$O$^+$ FROM MASSE-ANALYZED THRESHOLD IONIZATION

ROUDJANE MOURAD, LU WU and D. S. YANG, Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.

La$_3$C$_2$O is produced for the first time by laser vaporization in a pulsed cluster source and identified by photoionization time-of-flight mass spectrometry. Vibrationally-resolved ion spectra are obtained with mass-analyzed threshold ionization (MATI) spectroscopy. The adiabatic ionization energy of La$_3$C$_2$O is measured to be 30891(5) cm$^{-1}$. The spectra display several short vibrational progressions, and these progressions are associated mainly with La-La, La-C and La$_3$C$_2$O stretching excitations. The electron-spin multiplicities and molecular symmetries of La$_3$C$_2$O and La$_3$C$_2$O$^+$ are determined by combining the experimental measurements with ab initio calculations at MP2 level. Preliminary data analysis shows that the $^1$A$_1$ $^1$B$_2$ transition is responsible for the observed MATI spectra. The cluster has C$_{2v}$ symmetry with La$_3$C$_2$O in a bi-pyramid structure and oxygen being attached to the La$_3$ plane.
AN UNEXPECTED GAS-PHASE BINDING MOTIF FOR METAL DICATION COMPLEXATION WITH PEPTIDES: IRMPD SPECTROSCOPIC STRUCTURE DETERMINATION

ROBERT C. DUNBAR, Chemistry Department, Case Western Reserve Univ., Cleveland, OH 44106; JEFFREY STEILL, Sandia National Laboratory, Livermore, CA; NICOLAS POLFER, Chemistry Department, University of Florida, Gainesville, FL; GIEL BERDEN, FOM Institute for Plasma Physics, Nieuwegein, Netherlands; JOS OOMENS, FOM Institute for Plasma Physics, Nieuwegein, and University of Amsterdam, Netherlands.

The favorable orientation of the amide linkage and the aromatic side chain of N-terminal Phe or Trp leads to several favorable motifs for metal ion binding to dipeptides, having distinct characteristics in the IR spectrum. Infrared multiple photon photodissociation spectroscopy using the FELIX free electron laser has enabled clear resolution of these isomeric forms. The spectral patterns of complexes of small dications (Mg$^{2+}$, Ni$^{2+}$ and Co$^{2+}$) reveal an unexpected new isomeric form, in which the metal ion displaces the amide hydrogen, forming a metal-nitrogen bond with covalent character which is unprecedented in such gas-phase complexes. 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 laser at wavelengths in the approximate range 500 to 1900 cm$^{-1}$.

SPECTROSCOPIC INVESTIGATION OF ELECTRON-INDUCED PROTON TRANSFER IN THE FORMIC ACID DIMER, (HCOOH)$_2$

HELEN K. GERARDI, CHRIS M. LEAVITT, ANDREW F. DEBLASE, AND MARK A. JOHNSON, Yale University, Department of Chemistry, New Haven, CT.

We have isolated the stable form of the formic acid dimer anion (HCOOH)$_2^-$, a model for electron-induced proton transfer between nucleic acid base-pairs, in the gas phase. The vibrational signatures of this species and its various isotopomers were investigated using Ar predissociation and photodetachment spectroscopies in the 600-3800 cm$^{-1}$ range. We relate the experimental infrared transitions of the anion to those predicted for its calculated lowest energy structure in order to determine if a proton transfer event does in fact occur upon excess electron attachment to this simple hydrogen-bonded dimer. Additionally, we determined its vertical detachment energy (VDE), 1.8 eV, using velocity-map photoelectron imaging.

VIBRATIONALLY MEDIATED ELECTRON CAPTURE IN THE CO$_2$(H$_2$O)$_6$ ANION

KRISTIN J. BREEN, Sterling Chemistry Laboratory, Yale University, P.O. Box 208107, New Haven, CT 06520; ANDREW F. DEBLASE, Sterling Chemistry Laboratory, Yale University, P.O. Box 208107, New Haven, CT 06520; and MARK A. JOHNSON, Sterling Chemistry Laboratory, Yale University, P.O. Box 208107, New Haven, CT 06520.

We report the vibrational predissociation spectrum of the CO$_2$(H$_2$O)$_6$ anion and show how we can force an electron capture event by exciting transitions in the Mid-IR. We demonstrate that the argon-tagged species (CO$_2$(H$_2$O)$_6$ -Ar) is almost completely composed of a reactive isomer, where the CO$_2$ molecule is attached on the backside of the anionic water hexamer network. Detailed investigation of the vibrational predissociation spectrum of this species reveal two different loss channels, each dominant in different regions of the IR. The loss of 2 water molecules and 1 argon atom is the main loss channel in the higher energy range and shows transitions associated with OH-stretching of water hexamer anion. The loss of 1 water and 1 argon, on the other hand, dominates our lower energy range in the Mid-IR, not only confirming the anionic nature of the water hexamer, but also revealing neutral character to the CO$_2$. By exciting transitions throughout the Mid-IR, we are able to trigger electron capture from the water hexamer anion onto the CO$_2$ molecule. This releases the reaction exothermicity via the loss of water and argon, and pushing the reaction forward from the reactive entrance channel complex to the valence ion form, where the CO$_2$ anion is solvated by the remaining water molecules.
Singly charged dicarboxylic acid anions, studied in depth by Wang et al.\textsuperscript{a}, offer insight into the role of ring strain and conformation on the formation of intramolecular hydrogen bonds. These shared proton bonds, common in proteins and polymer systems, can be crucial in secondary and tertiary structure formation. By tracking the infrared spectra of dicarboxylic acid anions as charge and aliphatic chain length are varied, the tendency of these anions to form ring-like structures with an internally shared proton can be assessed. To adapt the time-of-flight mass spectrometry/infrared predissociation experiment to larger systems with significant latent vibrational energy and negligible vapor pressure, an electrospray ionization (ESI)/cryogenic quadrupole trap ion source has been interfaced to the Yale time of flight mass spectrometer. Infrared predissociation spectroscopy is carried out on a series of carboxylate anions cooled to 10K and H\textsubscript{2}-tagged in a cryogenic ion trap, underscoring the power of this technique to vibrationally quench and structurally characterize large (> 20 atoms) gaseous ions. This technique recovers sharp transitions (6 cm\textsuperscript{-1} FWHM) in the linear single photon absorption regime which greatly facilitates comparison with ab initio calculations. The methodology used to condense H\textsubscript{2} on these ions is described, revealing the benefits of a pulsed trapping gas paired with a time delay before ion extraction. The sensitivity of the perturbed H\textsubscript{2} transition to charge center exposure is probed by varying the charge and aliphatic chain length of carboxylate anions. Finally, the structure of four carboxylate anions are characterized using their predissociation spectra.

FA01  INVITED TALK  30 min  8:30
EXPLORING NEW SPECTRAL WINDOWS WITH THE HERSCHEL SPACE OBSERVATORY

EDWIN A. BERGIN AND THE HEXOS TEAM, Department of Astronomy, University of Michigan (email to: ebergin@umich.edu).

The Herschel Space Observatory, an ESA cornerstone mission with NASA participation, has been in operation for over a year. I will briefly outline the overall capabilities of Herschel which has both photometric and spectroscopic coverage from 63 to 610 microns. Herschel offers unprecedented sensitivity as well as continuous spectral coverage across the gaps imposed by the atmosphere, opening up a largely unexplored wavelength regime to high resolution spectroscopy. In particular, I will present results from the guaranteed time key program: Herschel observations of Extra-Ordinary Sources (HEXOS). Our program is nearing completion of data acquisition and I will discuss the most complete molecular spectrum of star-forming gas ever obtained in the spectrum of Orion KL and the galactic center molecular cloud Sagittarius B2. These spectra have over 1.4 THz of bandwidth and a resolution of 1 MHz. We estimate that there are over 100,000 spectral lines alone in the Orion KL spectrum with numerous lines of water vapor, ammonia, sulfur-bearing molecules, and numerous organics. I will demonstrate the power of molecular spectroscopy in characterizing the physical state of dense gas near massive stars through the perspective offered by observations of hundreds of lines of a single molecule and are revealing a new tracer of active galactic nuclei. I will show how the spectra provide a near complete chemical assay and cooling census of star-forming gas. Ultimately the gains from Herschel have tremendous potential to extend our understanding of the physics of star birth and feedback while informing on the origin of water and organics in space.

FA02  15 min  9:05
HERSCHEL OBSERVATIONS OF EXTRA-ORDINARY SOURCES (HEXOS): ANALYSIS OF THE HIFI 1.2 THZ WIDE SPECTRAL SURVEY TOWARD ORION KL

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We present a full spectral survey of the Kleiman-Low nebula within the Orion Molecular Cloud (Orion KL), one of the most chemically rich regions in the galaxy, using the HIFI instrument on board the Herschel Space Observatory. These observations span a frequency range of 490 – 1240 GHz and 1430 – 1900 GHz at a spectral resolution of 1.1 MHz (corresponding to 0.7-0.2 km/s). These observations encompass the largest spectral coverage ever obtained of a star-forming region in the sub-mm with high spectral resolution. As a result, we are sensitive to lines with excitation energies over an unprecedented range observed with the same instrument and near uniform efficiency. Reliable multi-transitional studies using hundreds to thousands of lines emitted by the same molecule can therefore be carried out. We will present the results of a full band analysis of this survey exploring the spectral emissions of over 20 molecules within this range. Initial results hint at the presence of excitation gradients. In addition, some species exhibit emissions at very high energies (> few hundred K) and temperatures, while others only probe warm (∼100 K) regions along the line of sight. These facets will be combined with an exploration of molecular origins in hot gas.
DETECTION OF OH$^+$ AND H$_2$O$^+$ TOWARD ORION KL

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The reactive molecular ions, OH$^+$, H$_2$O$^+$, and H$_3$O$^+$, key probes of the oxygen chemistry of the interstellar gas, have been observed toward Orion KL with the Heterodyne Instrument for Far Infrared on board the Herschel Space Observatory. All three $N = 1$–$0$ fine-structure transitions of OH$^+$ at 909, 971, and 1033 GHz and both fine-structure components of the doublet $ortho$-H$_2$O$^+$, 1$\Sigma$ $\rightarrow$ 0$\Sigma$ transition at 1115 and 1139 GHz were detected, and an upper limit was obtained for H$_3$O$^+$. OH$^+$ and H$_3$O$^+$ are observed purely in absorption, showing a narrow component at the source velocity of 9 km s$^{-1}$, and a broad blue shifted absorption similar to that reported recently for HF and $para$-H$_2$O$^+$. We estimate column densities of OH$^+$ and H$_2$O$^+$ for the 9 km s$^{-1}$ component of $9 \pm 3 \times 10^{12}$ cm$^{-2}$ and $7 \pm 2 \times 10^{12}$ cm$^{-2}$, and those in the outflow of $1.9 \pm 0.7 \times 10^{13}$ cm$^{-2}$ and $1.0 \pm 0.3 \times 10^{13}$ cm$^{-2}$. Upper limits of $2.4 \times 10^{12}$ cm$^{-2}$ and $8.7 \times 10^{12}$ cm$^{-2}$ were derived for the column densities of $ortho$ and $para$-H$_3$O$^+$ from transitions near 985 and 1657 GHz. The column densities of the three ions are up to an order of magnitude lower than those obtained from recent observations of W31C and W49N. A higher gas density, despite the assumption of a large ionization rate, may explain the comparatively low column densities of OH$^+$ and H$_2$O$^+$.

$^a$A part of this work was performed at the Jet Propulsion Laboratory, California Institute of Technology under contract with the National Aeronautics and Space Administration. Copyright 2010 © California Institute of Technology. All rights reserved.

IS WATER ICE THE PRECURSOR TO OH$^+$ AND H$_2$O$^+$ IN ORION KL?

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The reactive ions OH$^+$ and H$_2$O$^+$ have been observed in an outflow in front of the Orion KL region at significant column densities of $\sim 10^{13}$ cm$^{-2}$ with the Heterodyne Instrument for the Far Infrared (HIFI) on the Herschel Space Observatory. No H$_3$O$^+$ was observed, establishing an upper limit of $\approx 10^{12}$ cm$^{-2}$. This is unexpected, because both OH$^+$ and H$_2$O$^+$ react with molecular hydrogen to form H$_3$O$^+$. The primary destruction of H$_3$O$^+$ is by recombination with electrons.

We explore the low velocity Orion KL outflow with a gas-grain PDR model where UV radiation, cosmic rays, X-rays, and temperature depend on both depth into the cloud and time. The model starts with cold core conditions and a radiation field of $\chi = 1$ and $\zeta_{H_2} = 5 \times 10^{-17}$ s$^{-1}$ at the edge. Water ice collects on the grains at this time, and then as stars form, $\chi$ increases to $10^4$ and $\zeta_{H_2}$ becomes $5 \times 10^{-15}$ s$^{-1}$ at the edge. At all times, temperature is calculated via thermal balance using the Meudon PDR code. At $A_V < 4$ into the cloud the water desorbs off grains and becomes ionized by cosmic rays and X-rays, and dissociated by UV photons, increasing the rates of OH$^+$ and H$_2$O$^+$ formation. On the other hand, the increased electron fraction depletes the H$_3$O$^+$. The results of this model agree to within a factor of 5 with observation, and place the H$_2$O$^+$ column at $\approx 5 \times 10^{11}$ cm$^{-2}$. We will discuss the model and its results for the OH$^+$ and H$_2$O$^+$ ions as well as predicted abundances for other species.

Intermission
With the advent of extremely sensitive, broadband THz observational instruments such as the heterodyne receivers on ALMA, The Herschel Space Observatory, and SOFIA, astronomers are now facing the reality of extracting their observational results from extremely dense spectra containing thousands of unidentified lines. Observation and analysis of the line confusion limited spectra of well-characterized sources will help us better understand the extent of this challenge. We have previously reported on the observation and analysis of a line confusion limited spectral line survey from 223 – 251 GHz of the Orion-KL source using the the Caltech Submillimeter Observatory. Spectral analysis has now been completed for all previously-identified molecules in this source using the information from publicly-available catalogs, including the JPL Spectral Line Catalog, the Cologne Database for Molecular Spectroscopy, and the NRAO Splatalogue database. A new spectral analysis program was written to automate the line identification process through a least-squares comparison between the catalog information and the observational spectra, which yields best-fit values for the column density and temperature based on the assumption of local thermal equilibrium (LTE). A co-added spectral simulation including all known lines for all known molecules can then be compared to the observed spectrum. While this analysis revealed little new information regarding the molecular inventory of this source, it did reveal useful information that gives a glimpse into the future challenges for interpreting line confusion limited spectra in astronomy. Only \( \sim 1200 \) lines were assigned to known molecules, which accounts for slightly less than half of those observed. We will present on the results of our analysis, and the implications of this study for future line confusion limited observations using the next generation of telescopes in the THz frequency range.

\[ ^{15}\text{N}/^{14}\text{N} \] RATIO DETERMINATION IN THE ISM WITH HERSCHEL WITH HIGH RESOLUTION SPECTROSCOPY OF NITROGEN RADICALS

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The very high resolution of the HIFI instrument (134 kHz-1MHz) on board of Herschel needs very accurate laboratory measurements to detect unambiguously the signature of stable and unstable molecular species. Concerning the pure rotation spectra of new species, and particularly of open shell molecules, the first prediction could be far away and up to few hundred MHz. The \(^{15}\text{N}/^{14}\text{N} \) ratio is not well measured in the ISM. However, the \(^{15}\text{N}/^{14}\text{N} \) in the isotopomers is a potential tracer of the formation processes and the possible link with cometary molecules. Recent measurements include the detection of \(^{15}\text{NH}_2\text{D}^4\), \(^{15}\text{N}\text{H}^4\text{H}^6\) and \(^{15}\text{NH}_3^c\). The NH and \(^{15}\text{NH}_2 \) species are the simplest nitrogen radicals and are intermediate products in the \(^{15}\text{NH}_3 \) synthesis. They have been easily detected by Herschel and it therefore is interesting to now search for \(^{15}\text{NH} \) and \(^{15}\text{NH}_2 . \) No spectroscopic data have been reported for these two radicals up to now.

We present here the studies with high resolution spectroscopy in the THz range. The high sensitivity and the wide range of Sychrotron (0.6-6 THz) was essential to improve the prediction of the spectra of these two species in order to measure them in Lille (0.6-1 THz) with both a higher accuracy and resolution. The combined studies now give the most accurate predictions. ISM searches on these radicals are in progress in the Herschel spectra.

This work is supported by the Programme National de Physico-Chimie du Milieu Intergalactique (PCMI-CNRS)

FA07 15 min 10:44

THZ SPECTROSCOPY OF $^{13}$C ISOTOPIC SPECIES OF A “WEED”: ACETALDEHYDE

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Our studies of the isotopic species of $^{13}$C and D isotopologues of methyl formate (HCOOCH$_3$), have allowed the detection of more than 600 lines in Orion$^{a,b}$. This confirms that many observed U-lines are coming from isotopic species of one of the most abundant molecules in space. Since its first detection in 1976 in SgrB2 and in Orion A, acetaldehyde (CH$_3$CHO) was detected in many other numerous objects$^c$. If its deuterated species (CD$_3$CHO$^d$ and CH$_3$CDO$^e$) have been previously studied in the millimeterwave range, the data concerning the $^{13}$C species are limited to few lines measured in 1957 up to 40 GHz$^f$. In this context we decided to study the $^{13}$C species of acetaldehyde.

Acetaldehyde molecule displays a large amplitude motion: the hindered rotation of the methyl group with respect to the rest of the molecule. The analysis is performed with the Rho Axis Method$^{g}$. Recent versions of the codes include high orders term in order to reproduce the observed frequencies for large quantum numbers values as $J$-values as high as 70$^{a,b,h}$. Measurements and analysis of the rotational spectra of $^{13}$C isotopic species are in progress in Lille with a solid-state submillimetre-wave spectrometer (50-950 GHz), the first results will be presented. This work is supported by the contract ANR-08-BLAN-0054 and by the Programme National de Physico-Chimie du Milieu Interstellaire (PCMI-CNRS).

$^g$Kleiner, I. J. Mol. Spectrosc. 260, (2010) 1
$^h$Ilyushin, V.V.; Kryvda, A; and Alekseev, E.J. Mol. Spectrosc. 255, (2009) 32

FA08 15 min 11:01

THE ROTATIONAL SPECTRUM OF $^{13}$CH$_3$NH$_2$ UP TO 1 THz

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Methyamine (CH$_3$NH$_2$) is a molecule of astrophysical importance detected in interstellar medium for the first time in 1974$^a$. Also it has been discovered in the atmosphere of Jupiter$^b$. It is suggested that methyamine can be a precursor of the simplest amino acid glycine. In this context we present a new study of rotational spectrum of the ground vibrational state of $^{13}$C isotopic species of methyamine in the frequency range up to 1 THz. The spectrum of $^{13}$CH$_3$NH$_2$ was recorded and analyzed for the first time. All the spectra were obtained using the Lille spectrometer based on the solid state sources.

The analysis of the rotational spectrum of methyamine is complicated by two large-amplitude motions: CH$_3$ torsion and NH$_2$ wagging. The Hamiltonian used in the present study is based on the group-theoretical high-barrier tunneling formalism developed by Ohashi and Hougen$^c$. This model proved to be efficient in the previous studies of the parent species of methyamine$^d$ since it allowed fitting within experimental accuracy all the rotational transitions of the ground vibrational state with $J \leq 30$. In view of extended frequency range of the present study the fitting program will be modified in order to take into account the rotational transitions with $J > 30$. For the parent isotopic species, measurements and analysis using the same approach are in progress. The latest results will be discussed. This work is supported by the Programme National de Physico-Chimie du Milieu Interstellaire (PCMI-CNRS) and by the contract ANR-08-BLAN-0054.

THE EXTENDED SPECTROSCOPIC DATABASE ON FORMAMIDE: PARENT, $^{13}$C AND DEUTERATED SPECIES UP TO 1 THz

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Formamide (NH$_2$CHO) is the simplest interstellar molecule containing a peptide bond that provides polymerization of amino acids. It is also considered as a precursor of acetamide if another molecule containing a peptide bond that has been recently discovered in interstellar medium. While the rotational spectra of the parent isotoipc species of formamide were extensively studied up to 500 GHz only few data are available on its deuterated species. We present the new study of the rotational spectra of all singly deuterated isotopologues of formamide as well as new analysis of the rotational spectra of the parent and $^{13}$C isotopic species of formamide in the frequency range up to 1 THz. All the measurements have been performed using the Lille spectrometer based on the solid state sources. In total, about 2500 newly measured transition frequencies have been added to existing dataset on the rotational spectra of formamide and its isotopologues. This work is supported by ANR-08-BLAN-0225, the french Programme National de Physique Chimie du Milieu Interstellaire. A.K. would like to acknowledge the support of the Embassy of France in Ukraine.

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MONTE CARLO MODELING OF GAS-GRAIN CHEMISTRY IN STAR-FORMING REGIONS

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An understanding of the complex grain-surface chemistry responsible for the formation of organic molecules in regions of star and planet formation requires the details of the structure of icy grain mantles to be included into astrochemical models. Here, we present a new macroscopic gas-grain Monte Carlo model with an icy grain mantle treated as a chemically reactive surface and a chemically inert bulk consisting of multiple molecular layers. The model allows us to track the chemical history of ice during its build-up in cold protostellar cores. Desorption processes important in the transition to the hot core stage of star formation are also included. The model is computationally efficient, which allows us to simulate a realistically complex chemistry based on the OSU.2008 network of gas-phase reactions and an extended set of grain-surface reactions, including the chemistry of complex organic species. The model is applied to simulate the chemistry that occurs during the evolution of protostellar matter from a cold core to a hot core phase. The results of modeling and their key differences from results obtained with traditional two-phase (gas-surface) astrochemical models will be presented.
We present Herschel/HIFI observations of interstellar hydrogen chloride (HCl) and hydrogen fluoride (HF) along the line-of-sight towards Galactic sources with strong submillimeter continuum emission from the PRISMAS and HEXOS GT KP. The halogen-containing molecules are of special interest because of their unique thermochemistry and their important role as tracers of the neutral ISM. The detection of foreground absorption by HF J = 1–0 transition line in each source probes the distribution of HF throughout the Milky Way, in diffuse clouds with varying values of the visual extinction, as a potential valuable surrogate for molecular hydrogen. For the optically thin absorption components we calculate the column densities of HF. We find that, in many of the background clouds, the abundances of HF with respect to H$_2$ is consistent with the theoretical prediction that HF is the main reservoir of gas-phase fluorine for these clouds. Observations of hydrogen chloride isotopologues, H$^{35}$Cl and H$^{37}$Cl J = 1–0 transition line at different galactocentric distances provide insights of how elemental abundances change with location in the Galaxy. We model the HCl observations with a non-LTE radiative transfer model to derive gas densities and HCl column densities for sources with HCl emission. Interstellar HCl abundances and isotopic ratios [$Cl^{35}/Cl^{37}$] are essential for improving our understanding of stellar nucleosynthesis and global chemical enrichment and evolution in the Galaxy.
FB01 15 min  8:30
AUGER ELECTRONS VIA Kα X-RAY LINES OF PLATINUM COMPOUNDS FOR NANOTECHNOLOGICAL APPLICATIONS

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We will report study on the Kα X-ray lines of platinum. Pt compounds, such as cisplatin, are common in biomedical applications. The active element Pt can emit or absorb hard X-rays. We have obtained the photoionization cross sections from the oscillator strengths of 1s-2p (Kα) transitions in Pt ions. We find that these transitions appear as resonances in photoionization in the hard X-ray energy range of 64 - 71 keV (0.18 - 0.17 Å below the K-shell ionization and with a strength orders of magnitude higher compared to that at the K-shell ionization. This is the focus of our study for possible initiation of an emission cascade of Auger electrons at the resonant energy. We will present the oscillator strengths and attenuation coefficients per unit mass for all the Kα transitions in the event platinum cascades through various, namely from fluorine-like to hydrogen like, ionic states. The study is motivated by our proposed method, Resonant Theranosticsb,c (RT) for biomedical applications, which aims to find narrow band X-ray energy that corresponds to resonant photo-absorption and leads to emission of Auger electrons. As the next step of the RT method we will also report on experimental results on producing monochromatic X-rays, targeted to the resonant energy, from the wide band Bremsstrahlung radiation of a conventional X-ray source.

a Partially support: DOE, Computational Facility: Ohio Supercomputer Center, Columbus, Ohio.

FB02 15 min  8:47
A QUANTUM CHEMICAL EXPLORATION OF THE SFnO SERIES (n = 1 – 5): AN ATOM-BY-ATOM APPROACH

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The recoupled pair bonding model and high level ab initio calculations (MRCI, RCCSD(T)) with correlation consistent basis sets were used to examine the optimized structures, transition states, bonding and bond energies of the SFnO series (n = 1 – 5). Oxygen is capable of participating in covalent, recoupled pair, and dative bonding and, unlike monovalent ligands, forms both σ and π bonds. This study explores the effect of oxygen in order to anticipate its impact on trends in bond energy and other properties similar to those observed in previous SFn (n = 1 – 6) recoupled pair bonding studies. 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.
A COMPUTATIONAL INVESTIGATION OF c-C$_3$H$_2...HX(X = F, Cl, Br) H-BONDED COMPLEXES

PRADEEP R. VARADWAJ, ARPITA VARADWAJ, GILLES H. PESLHERBE, Centre for Research in Molecular Modeling & Department of Chemistry and Biochemistry, Concordia University, Montreal, QC, Canada.

Cyclopropenylidene (c-C$_3$H$_2$) is of significant importance in interstellar chemistry and synthetic chemistry (e.g., transition metal and organic catalysis). Because of its peculiar structure, c-C$_3$H$_2$ can act as a hydrogen-bond donor or acceptor. In order to gain insight into this feature, the ground-state potential energy surfaces of singlet c-C$_3$H$_2$ complexed with hydrogen halides HX (X = F, Cl, Br) have been explored extensively by density-functional theory (B3LYP) and \textit{ab initio} quantum chemistry (MP2) with a variety of basis sets, cc-pVxZ and aug-cc-pVxZ (x = D, T). The complexes characterized have the carbenic end of c-C$_3$H$_2$ H-bonded to HX, with some proton transfer occurring, the extent of which follows the order HF < HCl < HBr. Accompanying the complex formation are the dipole moment enhancement, the charge transfer, red shifts of the HX vibrational stretching frequencies together with the significant enhancement of band intensity and concomitant HX bond elongation. The nature of H-bonding in these complexes has been explored, based on energy decomposition schemes and the Bader’s quantum theory of atoms-in-molecules, with the conclusion that c-C$_3$H$_2$ is a strong H-bond acceptor with respect to the hydrogen halides.

ELECTRONIC STRUCTURE OF ETHYNYL SUBSTITUTED CYCLOBUTADIENES

FRANK LEE EMMERT III, STEPHANIE J. THOMPSON, and LYUDMILA V. SLIPCHENKO, Department of Chemistry, Purdue University, West Lafayette, IN 47907.

We investigated the effects of ethynyl substitution on the electronic structure of 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 electronic energy of cyclobutadiene is challenging for single-reference \textit{ab initio} methods such as HF, MP2 or DFT because of Jahn-Teller distortions and the diradical character of the singlet state. We determined the vertical and adiabatic singlet-triplet energy splittings, the natural charges and spin densities 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.$^c$ The adiabatic singlet-triplet gaps decrease upon substituent addition, but the singlet state is always lower in energy. However, we found that the results are affected by spin-contamination of the reference state and deteriorate when an unrestricted HF reference is employed.


APPLICATIONS OF PATH INTEGRAL LANGEVIN DYNAMICS TO WEAKLY BOUND CLUSTERS AND BIOLOGICAL MOLECULES

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We present the use of path integral molecular dynamics (PIMD) in conjunction with the path integral Langevin equation thermostat for sampling systems that exhibit nuclear quantum effects, notably those at low temperatures or those consisting mainly of hydrogen or helium. To test this approach, the internal energy of doped helium clusters are compared with white-noise Langevin thermostatting and high precision path integral monte carlo (PIMC) simulations. We comment on the structural evolution of these clusters in the absence of rotation and exchange as a function of cluster size. To quantify the importance of both rotation and exchange in our PIMD simulation, we compute band origin shifts for (He)$_N$-CO$_2$ as a function of cluster size and compare to previously published experimental and theoretical shifts. A convergence study is presented to confirm the systematic error reduction introduced by increasing path integral beads for our implementation in the Molecular Modelling Toolkit (MMTK) software package. Applications to carbohydrates are explored at biological temperatures by calculating both equilibrium and dynamical properties using the methods presented.

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FB06 15 min 9:50

INTERPRETATION OF THE IR/UV SPECTRA OF Ac-Trp-Tyr-NH$_2$ and Ac-Trp-Tyr-Ser-NH$_2$ USING MOLECULAR DYNAMICS AND AB INITIO METHODS.

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The peptides Ac-Trp-Tyr-NH$_2$ and Ac-Trp-Tyr-Ser-NH$_2$, which form the N-terminal region of a folding nucleus in β-lactoglobulin, were studied in the gas phase using IR/UV double resonance spectroscopy and initial results were presented at a previous symposium. Molecular dynamics (AMBER 99/99SB, CHARMM 27) and ab initio calculations (RI-B97-D/TZVPP, pbe GGA/cc-PVDZ) resulted in an improved interpretation of the spectra and assignments for the observed conformers. Results are compared to similar molecules such as Ac-Trp-NH$_2$ and Ac-Phe-Phe-NH$_2$.

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Intermission
Most living bodies are exposed to sunlight, essential life sustaining processes are using this natural radiation. Sunlight has, however, several components (has a broad spectrum) and in particular the invisible component (UV, ultraviolet) is harmful for living organisms. Scientists around the word are busy to understand what happens in the cell when it is exposed to light: it seems that the building blocks of cells and in particular those carrying the genetic information (DNA and RNA) are highly protected against this exposition. Our research focuses on the spectral properties of the building blocks of DNA and RNA, the so called nucleobases and nucleosides, in order to understand this mechanism.

Due to improvement in computer technology both at hardware and software side we are now able to use the most accurate methods of *ab initio* quantum chemistry to investigate the spectroscopic properties of these building blocks. These calculations provide direct information on the properties of these molecules but also provide important benchmarks for cheaper methods which can be used for even larger systems.

We have calculated the excited state properties for the nucleobases (cytosine, guanine and adenine), their complexes with water and with each other (Watson-Crick base pairs and stacks) as well as corresponding nucleosides at the EOM-CCSD(T)/aug-cc-pVDZ level of theory and try to answer the following questions: (1) how the order of excited states varies in different nucleobases; (2) how hydration influences the excitation energy and order of excited states; (3) is there any effect of the sugar substituent; (4) how do close lying other bases change the spectrum. The calculations involve over hundred correlated electrons and up to thousand basis functions. Such calculations are now routinely available with the recently developed ACESIII code\(^a\) and can make use of hundreds or even several thousand of processors.

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FB09 15 min 11:04

VIBRONIC COUPLING IN ASYMMETRIC DIMERS: GENERALIZATION OF THE FULTON-GOUTERMAN APPROACH

B. NEBGEN and L. V. SLIPCHENKO, Department of Chemistry, Purdue University, West Lafayette, IN 47907.

Fulton and Gouterman proposed a theory for the modeling of vibronic spectra of bichromophores with a symmetry operation exchanging the individual monomers. This model has proven useful for computing absorption and emission spectra for the $S_1 \leftrightarrow S_0$ and $S_2 \leftrightarrow S_0$ electronic transitions of the dimer when there is coupling to the vibrational levels. We have extended the FG model to cases where the bichromophore lacks a symmetry operation. This new model will cover systems with asymmetries arising from the environment, conformation, or composition of the dimer. Application of this theory to the spectra of the asymmetric bichromophore $d_5$-diphenylmethane (diphenylmethane with all of the aromatic hydrogens on one phenyl group replaced by deuterium atoms) will be presented and compared to high resolution laser-induced fluorescence (LIF) and single vibronic level fluorescence (SVLF) experimental spectra.

Zwier, private communication

FB10 15 min 11:21

Post-deadline Abstract

PREDICTION OF FUNDAMENTAL VIBRATIONAL FREQUENCIES AND INFRARED INTENSITIES: A BENCHMARK STUDY

JUANA VÁZQUEZ, MICHAEL E. HARDING, JOHN F. STANTON, Institute for Theoretical Chemistry, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712.

In this work we investigate the performance of second-order vibrational perturbation theory (VPT2) using force fields computed at the fc-CCSD(T) level in conjunction with different double-, triple-, and quadruple-ζ basis sets for the prediction of fundamental vibrational frequencies and infrared intensities. A benchmark study comprising more than thirty small and medium sized molecules illustrates the accuracy and limitations of the presented scheme.


FB11 10 min 11:38

Post-deadline Abstract

VIBRATIONAL CORRECTIONS TO MOLECULAR PROPERTIES: SECOND-ORDER VIBRATIONAL PERTURBATION THEORY VS VARIATIONAL COMPUTATIONS

MICHAEL E. HARDING, JUANA VÁZQUEZ, JOHN F. STANTON, Institute for Theoretical Chemistry, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712, USA; GREGOR DIEZEMANN, and JÜRGEN GAUSS, Institut für Physikalische Chemie, Universität Mainz, Jakob-Welder-Weg 11, D-55128 Mainz, Germany.

For a small set of linear and non-linear molecules, a detailed comparison of two different procedures for predicting vibrationally averaged molecular properties, i.e., second-order vibrational perturbation theory (VPT2) and a variational approach, is carried out. Results for vibrational corrections to dipole and quadrupole moments, nuclear quadrupole moments, static electric-dipole polarizabilities, NMR chemical shielding tensors, nuclear spin-rotation tensors, magnetizabilities, and rotational g-tensors are reported.
Establishment of ultraviolet radiation’s role in DNA mutation has led to an increasing interest in understanding the electronic excited state dynamics of DNA. It is known that upon excitation of the ground state, the DNA bases are excited to an optically bright $\pi\pi^*$ state that then quickly decays back to the ground state; however, further investigations have shown that there are long-lived states within the excited state manifolds, which may be able to influence the excited state dynamics. The goal of our study is to calculate, with the aid of time-dependent density functional theory, several transient infrared spectra of double stranded and single stranded DNA in both gas phase and in solution, in order to help sort out the exact role of these states in the relaxation processes of DNA by comparison to available experimental data.
FC. INFRARED/RAMAN
FRIDAY, JUNE 24, 2011 – 8:30 am
Room: 1000 McPHERSON LAB

Chair: MANFRED WINNEWISSE, The Ohio State University, Columbus, OH

FC01 15 min 8:30
NEW METHOD OF FITTING EXPERIMENTAL RO-VIBRATIONAL INTENSITIES TO THE DIPOLE MOMENT FUNCTION: APPLICATION TO HCl

G. LI, P. F. BERNATH, Department of Chemistry, University of York, Heslington, York YO10 5DD; I. E. GORDON, L. S. ROTHMAN, Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge MA 02138, USA.

A dipole moment function (DMF) for hydrogen chloride (HCl) has been obtained using a direct fit approach that fits the best available and appropriately weighted experimental data for individual ro-vibrational transitions. Combining wavefunctions derived from an empirical potential and a semi-empirical DMF, line intensities were calculated numerically for bands with Δν=0, 1, 2, 3, 4, 5, 6, 7 up to ν′=7. The results have demonstrated the effectiveness of inclusion of rotational dipole moment matrix elements and appropriate weighting of the experimental data in the DMF fitting. The new method is shown to be superior to the common method of fitting only the rotationless dipole moment elements, especially when the experimental data are scarce. While the new approach is more sophisticated it is easy to implement in particular with the use of modern spectroscopic numerical programs, such as Levela. We also show that in case the exact potential energy function is not available, the use of wavefunctions derived from the Rydberg-Klein-Rees (RKR) numerical method can be very efficient. Finally, the previously reported dipole moment functions of HCl are critically reviewed.


FC02 15 min 8:47
EXTENSIVE AND HIGHLY ACCURATE LINE LISTS FOR HYDROGEN HALIDES

G. LI and P.F. BERNATH, Department of Chemistry, University of York, Heslington, York YO10 5DD, UK; I.E. GORDON, L.S. ROTHMAN, C. RICHARD, Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge MA 02138, USA; R.J. LE ROY, Department of Chemistry, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada; J.A. COXON, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada; P. HAJIGEORGIOU, Department of Life and Health Sciences, University of Nicosia, 46 Makedonitissas Ave., P.O. Box 24005, Nicosia 1700, Cyprus.

New dipole moment functions (DMF) for the ground X 1Σ+ electronic states of the hydrogen halides (HF, HCl, HBr, HI) have been obtained using a direct fit approach that fits the best available and appropriately weighted experimental line intensity data for individual ro-vibrational transitions. Combining the newly developed (taking into account the most recent experiments) empirical potential energy functions and the DMFs, line positions and line intensities of the hydrogen halides and their isotopologues have been calculated numerically using program LEVELb. In addition, new semi-empirical algorithms for assigning line-shape parameters for these species have been developed. Using these improvements, new line lists for hydrogen halides were created to update the HITRAN spectroscopic database. These new lists are more accurate and significantly more extensive than those included in the current version of the database (HITRAN2008)b.

ARE AB INITIO QUANTUM CHEMISTRY METHODS ABLE TO PREDICT VIBRATIONAL STATES UP TO THE DISSOCIATION LIMIT FOR MULTI-ELECTRON MOLECULES CLOSE TO SPECTROSCOPIC ACCURACY?

PÉTER G. SZALAY, Eötvös Loránd University, Budapest, Hungary; FILIP HOLKA, Slovak University of Technology, Trnava, Slovak Republic; JULIEN FREMONT, MICHAEL REY, VLADIMIR G. TYUTEREV, Reims University, Reims, France.

The aim of the study was to explore the limits of initio methods towards the description of excited vibrational levels up to the dissociation limit for molecules having more than two electrons. To this end a high level ab initio potential energy function was constructed for the four-electron LiH molecule in order to accurately predict a complete set of bound vibrational levels corresponding to the electronic ground state. It was composed from: a) an ab initio non-relativistic potential obtained at the MR-CISD level including size-extensivity corrections and quintuple-sextuple ζ extrapolation of the basis, b) MVD (Mass-velocity-Darwin) relativistic corrections obtained at icMR-CISD/cc-pwCV5Z level, and c) DBOC (Diagonal Born-Oppenheimer correction) obtained at the MR-CISD/cc-pwCVTZ level. Finally, the importance of non-adiabatic effects was also tested by using atomic masses in the vibrational kinetic energy operator and by calculation of non-adiabatic coupling by ab initio methods.

The calculated vibrational levels were compared with those obtained from experimental data [J.A. Coxon and C.S. Dickinson, J. Chem. Phys., 2004, 121, 9378]. Our best estimate of the potential curve results in vibrational energies with a RMS deviation of only ∼1 cm⁻¹ for the entire set of all empirically determined vibrational levels known so far. These results represent a drastic improvement over previous theoretical predictions of vibrational levels of ⁷LiH up to dissociation, D₀, which was predicted to be 19594 cm⁻¹.

In addition, rotational levels have also been calculated. The RMS deviation between our ab initio calculations and empirical results by Coxon and Dickinson for rotational spacings ΔE = E(v, J = 1) − E(v, J = 0) over all available vibrational states of ⁷LiH from v = 0 to v = 20 is 0.010 cm⁻¹ (with nuclear masses) and 0.006 cm⁻¹ (with atomic masses). Note that for high vibrational states with v > 6 this falls within the uncertainty of the measurements.

ANALYSIS OF THE VIBRATIONAL SPECTRA OF P₃N₃(OCH₂CF₃)₆ AND P₄N₄(OCH₂CF₃)₈

ADRIAN K. KING, DAVID F. PLANT, PETER GOLDING, Atomic Weapons Establishment, Aldermaston, Berkshire, RG7 4PR, United Kingdom; MICHAEL A. LAWSON and PAUL B. DAVIES, University of Cambridge, Department of Chemistry, Lensfield Road, Cambridge, CB2 1EW, United Kingdom.

The cyclic phosphazene trimer P₃N₃(OCH₂CF₃)₆ and the related cyclic tetramer P₄N₄(OCH₂CF₃)₈ have been proposed as the major low-to-medium temperature pyrolysis products of the parent polyphosphazene (PN(OCH₂CF₃)₂)n. Recently, both molecules have been synthesized, isolated and their vapour-phase vibrational spectra recorded using a high-resolution FTIR instrument.

The interpretation of these spectra is achieved primarily by comparison with the results of high-quality density functional calculations, which enable the principal absorption features to be assigned and conclusions to be drawn regarding the geometries and conformations adopted by both molecules. These in turn allow interesting comparisons to be made with analogous cyclic halo-phosphazenes such as P₃N₃Cl₆ and P₄N₄Cl₈.

Work to record in situ the spectra of the vapour-phase pyrolysis products of (PN(OCH₂CF₃)₂)n and to analyse these results in terms of the tetramer and trimer spectra will also be presented.

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This study concerns the gas phase rovibrational spectroscopy of organosulfide and organophosphorous which are considered as non toxic model compounds in the analysis of chemical weapon materials, high pathogenic and mutagenic agents, and other environmentally interesting air-borne species. The coupling of the synchrotron radiation with multipass cells and the FTIR spectrometer allowed to obtain very conclusive results in term of sensitivity and resolution and improved the previous results obtained with classical sources.\(^a\) For DMSO, using an optical path of 150 m the spectra have been recorded at the ultimate resolution of 0.001 cm\(^{-1}\) allowing to fully resolve the rotational structure of the lowest vibrational modes observed in the THz region. In the 290 – 420 cm\(^{-1}\) region, the rovibrational spectrum of the perpendicular and parallel vibrational bands associated with, respectively, the asymmetric \(\nu_23\) and symmetric \(\nu_11\) bending modes of DMSO have been recorded with a resolution of \(1.5 \times 10^{-2}\) cm\(^{-1}\).\(^b\) The gas phase vibrational spectra of organophosphorous compounds were measured by FTIR spectroscopy using the vapor pressure of the compounds. Except for TBP, the room temperature vapor pressure was sufficient to detect all active vibrational modes from THz to NIR domain. Contrary to DMSO, the rotational patterns of alkyl phosphates and alkyl phosphonates could not be resolved; only a vibrational analysis may be performed. Nevertheless, the spectral fingerprints observed in the THz region allowed a clear discrimination between the molecules and between the different molecular conformations.\(^c\)


Intermission

**FC06**

**HIGH RESOLUTION INFRARED SPECTRA OF SPIROPENTANE, \((C_3H_8)\)**


Infrared spectra of spiropentane have been recorded at a resolution (0.002 cm\(^{-1}\)) sufficient to resolve for the first time individual rovibrational lines. This initial report presents the ground state constants for this molecule determined from the detailed analysis of the \(\nu_{16}(b_2)\) parallel band at 993 cm\(^{-1}\). In addition, the determination included more than 2000 ground state combination-differences deduced from partial analyses of four other infrared-allowed bands, the \(\nu_{24}(e)\) perpendicular band at 780 cm\(^{-1}\), and three \((b_2)\) parallel bands at 1540 cm\(^{-1}\)(\(\nu_{14}\)), 1568 cm\(^{-1}\)(\(\nu_{5}+\nu_{16}\)), and 2098 cm\(^{-1}\)(\(\nu_{5}+\nu_{14}\)). In each of the latter four cases, the spectra show complications; in the case of \(\nu_{24}\) due to rotational \(l\)-type doublings and in the case of the parallel bands, perturbations due to Fermi resonance and Coriolis interactions of the upper states with nearby levels. The unraveling of these is underway but the assignment of many of these transitions permits the confident use of ground state combination-differences in determining the following constants for the ground state (in units of cm\(^{-1}\)) \(B_0 = 0.13947360(2)\), \(D_J = 2.458(1) \times 10^{-5}\), and \(D_{JK} = 8.30(3) \times 10^{-8}\). For the unperturbed \(\nu_{16}\) fundamental, more than 3000 transitions were fit and the band origin was found to be at 992.53792(3) cm\(^{-1}\). The numbers in parentheses are the uncertainties (two standard deviations) in the values of the constants. The results are compared with those computed at the ab initio anharmonic level using the B3LYP density functional method with a cc-pTVZ basis set.
COLLISION-INDUCED INFRARED ABSORPTION BY COLLISIONAL COMPLEXES IN DENSE HYDROGEN-HELIUM GAS MIXTURES AT THOUSANDS OF KELVIN

MARTIN ABEL, LOTHAR FROMMHOLD, Department of Physics, The University of Texas at Austin, Austin, TX 78712; XIAOPING LI, KATHARINE L. C. HUNT, Department of Chemistry, Michigan State University, East Lansing, MI 48824.

The interaction-induced absorption by collisional pairs of H₂ molecules is an important opacity source in the atmospheres of the outer planets and cool stars. The emission spectra of cool white dwarf stars differ significantly in the infrared from the expected blackbody spectra of their cores, which is largely due to absorption by collisional H₂–H₂, H₂–He, and H₂–H complexes in the stellar atmospheres. Using quantum-chemical methods we compute the atmospheric absorption from hundreds to thousands of kelvin. Laboratory measurements of interaction-induced absorption spectra by H₂ pairs exist only at room temperature and below. We show that our results reproduce these measurements closely, so that our computational data permit reliable modeling of stellar atmosphere opacities even for the higher temperatures.

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ROTATIONALLY-RESOLVED INFRARED SPECTROSCOPY OF THE POLYCYCLIC AROMATIC HYDROCARBON PYRENE (C₁₆H₁₀) IN THE MID-INFRARED 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; BENJAMIN J. McCALL, Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

We have constructed a high-resolution infrared spectrometer based on a quantum cascade laser (QCL) which operates near 8.4 μm. The ultimate purpose of this spectrometer is to obtain a rotationally-resolved gas phase spectrum of buckminsterfullerene (C₆₀). We performed initial testing of the spectrometer with methylene bromide (CH₂Br₂), but to test the high-temperature capabilities of our instrument, we have observed a C-H bending mode of pyrene (C₁₆H₁₀) near 1184 cm⁻¹ (near the expected band center of the C₆₀ vibrational band). The observed spectra were rotationally resolved, and individual features had a linewidth (FWHM) of ~10 MHz. To our knowledge, pyrene is the largest molecule to be observed with rotational resolution by infrared absorption spectroscopy. Gas-phase pyrene was generated in a high-temperature (420 - 440 K) oven and cooled by a continuous supersonic expansion from a 150 μm × 1.6 cm slit using argon as a carrier gas. The cooled pyrene was observed by continuous-wave cavity ringdown spectroscopy (cw-CRDS). We have collected 2 cm⁻¹ of the band, which is observed to be a b-type band. The observed spectra were fit to an effective asymmetric top Hamiltonian using PGOPHER. Using this fit and knowledge of the vibrational band strength, we estimate the vibrational temperature of the cooled pyrene to be ~70 K, while the rotational temperature was as low as 13 K.

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Post-deadline Abstract

289

15 min 10:32

Post-deadline Abstract

15 min 10:49

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FC07

Post-deadline Abstract

15 min 10:32

COLLISION-INDUCED INFRARED ABSORPTION BY COLLISIONAL COMPLEXES IN DENSE HYDROGEN-HELIUM GAS MIXTURES AT THOUSANDS OF KELVIN

MARTIN ABEL, LOTHAR FROMMHOLD, Department of Physics, The University of Texas at Austin, Austin, TX 78712; XIAOPING LI, KATHARINE L. C. HUNT, Department of Chemistry, Michigan State University, East Lansing, MI 48824.

The interaction-induced absorption by collisional pairs of H₂ molecules is an important opacity source in the atmospheres of the outer planets and cool stars. The emission spectra of cool white dwarf stars differ significantly in the infrared from the expected blackbody spectra of their cores, which is largely due to absorption by collisional H₂–H₂, H₂–He, and H₂–H complexes in the stellar atmospheres. Using quantum-chemical methods we compute the atmospheric absorption from hundreds to thousands of kelvin. Laboratory measurements of interaction-induced absorption spectra by H₂ pairs exist only at room temperature and below. We show that our results reproduce these measurements closely, so that our computational data permit reliable modeling of stellar atmosphere opacities even for the higher temperatures.

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FC08

Post-deadline Abstract

15 min 10:49

ROTATIONALLY-RESOLVED INFRARED SPECTROSCOPY OF THE POLYCYCLIC AROMATIC HYDROCARBON PYRENE (C₁₆H₁₀) IN THE MID-INFRARED 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; BENJAMIN J. McCALL, Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

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Post-deadline Abstract

289

15 min 10:32
VIBRATIONAL SPECTROSCOPIC STUDY ON SOME HOFMANN TYPE CLATHRATES: M(2-(1-CYCLOHEXENYL)ETHYLAMINE)$_2$Ni(CN)$_4$.2BENZENE (M = Ni AND Cd)

TEKİN İZG, DEPARTMENT OF PHYSICS, ARTS AND SCIENCE FACULTY, İNÃOŬ UNIVERSITY, MALATYA, 44069, TURKEY; CEMAL PARLAK, DEPARTMENT OF PHYSICS, ARTS AND SCIENCE FACULTY, DUMLUPINAR UNIVERSITY, KÜTAHYA, 43100, TURKEY; MUSTAFA SENYEL, DEPARTMENT OF PHYSICS, SCIENCE FACULTY, ANADOLU UNIVERSITY, ESKİŞEHİR, 26470, TURKEY.

New Hofmann type benzene clathrates in the form of M(CyHEA)$_2$Ni(CN)$_4$.2Benzene (where CyHEA = 2-(1-Cyclohexenyl)ethylamine and M = Ni or Cd) have been prepared in powder form and FT-IR and Raman spectra have been reported. The results suggest that title compounds are similar in structure to Hofmann type clathrates and their structures consist of polymeric layers of $\text{M-Ni(CN)}_4\infty$ with the CyHEA molecule bounded to the metal atoms (M).

DETERMINATION OF THE BOND LENGTHS IN MgCCH, CaCCH and SrCCH

D. FORTHOMME, D. W. TOKARYK, C. LINTON, 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, 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.

To determine the three bond lengths in a linear four atom molecule, one requires spectral data from three isotopologues of that molecule. By combining information from previously published analyses with new high resolution isotopically substituted spectra, we have determined the bond lengths for MgCCH, CaCCH and SrCCH. In each case, the $\tilde{A}^2\Pi - \tilde{X}^2\Sigma^+$ spectra of the $\text{M-}^{12}\text{C}_{12}\text{CH}$, $\text{M-}^{12}\text{C}_{12}\text{CD}$ and $\text{M-}^{13}\text{C}_{13}\text{CH}$ isotopologues, where M refers to Mg, Ca and Sr, were considered. This study is of particular interest since it shows how the structure of this family of molecules evolves as we change the alkaline earth atom attached to the CCH ligand. In MgCCH, the structure of the CCH ligand is nearly the same as it is in acetylene, HCCH$^a$. Surprisingly, the bonding in the ligand is quite different from that of acetylene for the two heavier acetylide molecules, with the triple bond between the two carbon atoms experiencing the greatest change.

FD. MINI-SYMPOSIUM: FUNDAMENTAL PHYSICS
FRIDAY, JUNE 24, 2011 – 8:30 am
Room: 1015 McPHERSON LAB

Chair: TREVOR SEARS, Brookhaven National Laboratory, Upton, New York

FD01 INVITED TALK 30 min 8:30
TIME-DOMAIN MW SPECTROSCOPY: FUNDAMENTAL PHYSICS FROM MOLECULAR ROTATION

JENS-UWE GRABOW, Gottfried-Wilhelm-Leibniz-Universität, Institut für Physikalische Chemie & Elektrochemie, Callinstraße 3A, 30167 Hannover, Germany.

In the past, it was a great triumph of Dirac’s theory to predict the fine structure in the energy levels of the simplest atom. Nevertheless, even the relativistic Dirac theory did not completely describe the spectrum of the electron in an H-atom. However, at that time, attempts to obtain accurate information through a study of the Balmer lines have been frustrated by the large Doppler width in comparison to the small shifts. Obtaining more accurate information was the key to provide a delicate test of the relativistic wave equation as well as finding confirmation for line shifts due to coupling of the atom with the radiation field and any non-Coulombic interaction. Then, the advances in microwave (MW) techniques resulted in new physical tools, making it possible to observe the small energy difference of terms that were degenerate in Dirac’s theory. This, as well as the small deviation of the electron’s gyromagnetic ratio $g_e$ from the value 2, provided an excellent test for the validity of quantum electrodynamics (QED).

At present, the electron electric dipole moment (e-EDM) is a particularly good place to find, as proposed by Purcell and Ramsey, a new source for P and T violation that may, in fact, be linked to the matter-antimatter asymmetry of our Universe and, in a wider sense, responsible for our existence. Since the Standart Modell’s (SM) prediction is negligible, any observed $d_e \neq 0$ is direct evidence for “New Physics” beyond the SM. Many supersymmetric theories in extension to the SM, indeed, predict an e-EDM within two orders of magnitude from the current limit $|d_e| < 1.6 \times 10^{-27} e \cdot cm$. However, this limit was published already in 2002, nine years ago. Since then, no progress was made. As at the time when Dirac’s equation was put to test, attempts to obtain accurate information through a spectroscopic study are mostly frustrated by the large Doppler width in comparison to the small shifts. Again, obtaining more accurate information will be the key to provide a delicate test to the proposed theories, potentially making the discovery long awaited for: the e-EDM. And again, employment of an MW method to hunt down a tiny effect, obscured by the linewidth inherent to other techniques, can serve as a new tool for the study of the even smaller shifts in an e-EDM sensitive rotational transition, making it possible to observe the tiny energy difference of terms that are degenerate without an e-EDM.

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HIGH PRECISION UV MEASUREMENTS IN CO, TOWARDS A LABORATORY TEST OF THE TIME-INVARIANCE OF $\mu$.

ADRIAN J. DE NIJS, KJELD S.E. EIKEMA, WIM UBACHS and HENDRICK L. BETHLEM, LaserLaB, VU University Amsterdam, the Netherlands.

The metastable $a^3\Pi$ state of CO has favourable properties for testing the time-invariance of physical constants$^a$. Due to an incidental near-degeneracy between the $\Omega=0, J=8$ and the $\Omega=0, J=6$ the 2-photon microwave transition connecting these two states is highly sensitive to a possible time variation of physical constants, with a sensitivity coefficient ranging from $\approx -300$ to $\approx +150$ for different isotopes. We are planning a molecular beam experiment to measure these transitions. As a first step, spectroscopic measurements have been performed on the $X^1\Sigma^+ \rightarrow a^3\Pi$ transition around 206 nm. We have recorded a total of 40 optical transitions in the six most abundant isotopes. For these measurements, we have used the fourth harmonic of an injection-seeded titanium:sapphire pulsed oscillator. A frequency comb laser referenced to a Rb-clock was used for the absolute calibration of the seed laser. An absolute accuracy of a few MHz was reached. The optical data for $^{12}C^{16}O$, together with published RF and MW data, was fitted to an effective Hamiltonian. The precision of a number of molecular parameters was significantly increased. The obtained parameters were isotope scaled to calculate the optical transition frequencies in other isotopes. These frequencies typically agree with the measurements within 10 MHz. These calculations confirm the high sensitivity of the near degeneracies to variations of $\mu$.


PROSPECTS FOR RAPID DECELERATION OF DIATOMIC MOLECULES WITH OPTICAL BICHROMATIC FORCES

E. E. EYLER and M. A. CHIEDA, Department of Physics, University of Connecticut, Storrs, CT 06269, USA.

Direct laser deceleration and cooling of molecules to ultracold temperatures remains an elusive goal, although successful transverse cooling using a near-cycling transition in the polar diatomic molecule SrF has recently been reported.$^a$ The optical bichromatic force, which employs alternating cycles of excitation and stimulated emission from opposing directions, is an attractive prospect for multiplying the number of decelerating momentum transfers that can take place before a molecule is “lost” to radiative decay into a dark state. In metastable helium atoms, forces more than 100 times the normal radiative force have been demonstrated.$^b$ We describe detailed estimates of the laser requirements and the available momentum transfer for transverse deflection and longitudinal slowing of CaF molecules, using the $Q_{11}(0.5)$ branch of the (0,0) band of the $A^2\Pi_{1/2} \rightarrow X^2\Sigma^+$ transition. Deceleration by up to 150 m/s should be possible, sufficient to bring a slow thermal molecular beam to rest. In addition, significant laser-induced cooling is expected due to the non-adiabatic velocity profile of the bichromatic force, significantly enhancing the brightness of a potential ultracold beam source. As a prelude to actual molecular experiments, we are conducting measurements on non-cycling transitions in atomic helium, and preliminary results will be described.


DECELERATION AND TRAPPING OF HEAVY DIATOMIC MOLECULES FOR PRECISION MEASUREMENTS


We are setting up a novel type of Stark-decelerator optimized for the deceleration and trapping of heavy diatomic molecules. Aim of these experiments is to prepare a trapped sample of ultracold molecules for precision studies of fundamental symmetries. The decelerator uses ring-shaped electrodes to create a moving trapping potential, a prototype of which has been shown to work for CO molecules$^a$. Molecules can be decelerated and trapped in the weak-field seeking part of excited rotational states. The alkaline-earth monohalide molecules (currently we focus on the SrF molecule) are prime candidates for next generation parity violation and electron-EDM studies$^b$. We plan to combine the Stark deceleration with molecular laser cooling to create a trapped sample of molecules at a final temperature of $\sim 200\, \mu K$.

INVESTIGATION OF THE USE OF HE – DIATOMIC VAN DER WAALS COMPLEXES AS A PROBE OF TIME-REVERSAL VIOLATION

JACOB STINNETT, ERIC ABRAHAM, NEIL SHAFER-RAY, Homer L. Dodge Department of Physics, University of Oklahoma, 440 W.Brooks, NH 100, Norman, OK 73019.

We examine the dipole-induced dipole interaction between NO and He in a molecular beam. We show that the effect of the He is to dramatically reduce the parity splitting of the NO rotational levels. We further show that the predicted Stark splitting of a model Hamiltonian computation agrees with a simple vector coupling model. This vector model is in turn in agreement with existing experimental data. This suppression of parity splitting should apply to many systems and could reduce the field required for a study of time reversal asymmetry from thousands of volts/cm to volts/cm. This research is supported by the NSF-REU program.

FREQUENCY COMB VELOCITY MODULATION SPECTROSCOPY

KEVIN C. COSSEL, LAURA C. SINCLAIR, TYLER COFFEY, ERIC CORNELL, 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.

We have developed a novel technique for rapid ion-sensitive spectroscopy over a broad spectral bandwidth by combining the high sensitivity of velocity modulation spectroscopy (VMS) with the parallel nature and high frequency accuracy of cavity-enhanced direct frequency comb spectroscopy. Prior to this research, no techniques have been capable of high sensitivity velocity modulation spectroscopy on every parallel detection channel over such a broad spectral range. We have demonstrated the power of this technique by measuring the \(^4\Pi_u \rightarrow X^2\Sigma_g^+(4,2)\) band of N\(_2^+\) at 830 nm with an absorption sensitivity of \(1 \times 10^{-6}\) for each of 1500 simultaneous measurement channels spanning 150 cm\(^{-1}\). A densely sampled spectrum consisting of interleaved measurements to achieve 75 MHz spacing is acquired in under an hour.

This technique is ideally suited for high resolution survey spectroscopy of molecular ions with applications including chemical physics, astrochemistry, and precision measurement. Currently, this system is being used to map the electronic transitions of HIF\(^+\) for the JILA electron electric dipole moment (eEDM) experiment. The JILA eEDM experiment uses trapped molecular ions to significantly increase the coherence time of the measurement in addition to utilizing the strong electric field enhancement available from molecules. Previous theoretical work\(^\text{c}\) has shown that the metastable \(^3\Delta_1\) state in HIF\(^+\) and ThF\(^+\) provides high sensitivity to the eEDM and good cancellation of systematic effects; however, the electronic level structure of these species have not previously been measured, and the theoretical uncertainties are hundreds to thousands of wavenumbers.\(^\text{d}\) This necessitates broad-bandwidth, high-resolution survey spectroscopy provided by frequency comb VMS in the 700-900 nm spectral window.

\(^b\)A. E. Leanhardt, et. al. arXiv:1008.2997v2

OPTICAL PULSE-SHAPING FOR INTERNAL COOLING OF MOLECULAR IONS

CHIEN-YU LIEN, SCOTT R. WILLIAMS, and BRIAN ODOM, Department of Physics and Astronomy, Northwestern University, 2145 Sheridan Road, Evanston IL 60208.

We propose a scheme to use pulse-shaped femtosecond lasers to optically cool the internal degrees of freedom of molecular ions. Since this approach relies on cooling rotational and vibrational quanta by exciting an electronic transition, it is most straightforward for molecular ions with diagonal Frank-Condon-Factors. The scheme has the advantage of requiring only tens of microseconds to reach equilibrium without blackbody radiation to redistribute the population. For AlH\(^+\), a candidate species, a rate equation simulation shows equilibrium is achieved in 15 \(\mu\)s.
The relativistic pseudopotential (RPP) calculations of valence (spectroscopic, chemical etc.) properties of molecules are very efficient because the modern two-component RPP methods allows one to treat very accurately the correlation and relativistic effects for the valence electrons of a molecule and to reduce dramatically the computational cost. The valence molecular spinors are usually smoothed in atomic cores and, as a result, direct calculation of electronic densities near heavy nuclei within such approach directly is impossible. Precise calculations of such properties, as hyperfine constants and other magnetic properties, parity nonconservation effects, which are described by the operators heavily concentrated in atomic cores, usually require very accurate accounting for both relativistic and correlation effects. Electronic structure should be well evaluated in both valence and atomic core regions. However, precise all-electron four-component treatment of molecules with heavy elements is yet rather consuming. In the report, an alternative approach based on the RPP method and one-center core-restoration technique [1] developed by the authors for such studies is discussed. Its efficiency is illustrated in benchmark to-date calculations of magnetic dipole and electric quadrupole hyperfine—structure constants, as well as the space parity (P) and time-reversal symmetry (T) nonconservation effects in polar heavy-atom molecules, including HfF\textsuperscript{+}, PtH\textsuperscript{+}, ThO and WC, which are studied now as promising candidates for the experimental search of the electron electric dipole moment (eEDM).


\*This work is supported by the RFBR Grant No. 09-03-01034

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Theoretical calculations predict that internal electric fields as high as 90 GV/cm can be attained by polarizing the $^3\Delta_1$ state of ThF\textsuperscript{+}. Consequently, this ion is of interest for investigation of the dipole moment of the electron. However, spectroscopic data have not been reported previously for ThF or ThF\textsuperscript{+}. We have used laser induced fluorescence and resonantly enhanced two-photon ionization to examine ThF. Multiple electronic transitions were observed in the 19530-21300 cm$^{-1}$ range. Rotationally resolved data have been obtained, and the ground state is shown to be $X^2\Delta_{3/2}$. Pulsed field ionization - zero electron kinetic energy spectra have been recorded for the ThF\textsuperscript{+} cation. Vibronic progressions of the $X^1\Sigma^+$ and excited $^3\Delta$ states have been identified. The term energy for the $^3\Delta_1$ state was found to be $T_0=330$ cm$^{-1}$. Details of the experiments and spectroscopic constants for ThF and ThF\textsuperscript{+} will be reported.

LASER SPECTROSCOPY OF THE \( ^4\Gamma \) - \( X^4\Phi \) TRANSITION IN TITANIUM HYDRIDE, TiH

COLAN LINTON, Centre for Laser Atomic and Molecular Sciences and Physics Department, University of New Brunswick, Fredericton, NB E3B 5A3, Canada; SARAH FREY and TIMOTHY C. STEIMLE, Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604.

A gas phase study of the \( ^4\Gamma_{2.5} \) - \( A^4\Phi_{1.5} \) (0, 0) band in the astrophysically important titanium hydride molecule, TiH, has recently been undertaken. Low resolution dispersed fluorescence spectra of TiH and TiD have yielded information on the vibrational structure. A high resolution study at a linewidth of \( \approx 40 \text{ MHz} \) has shown doubling due to resolved hydrogen hyperfine structure in the main \( ^{48}\text{TiH} \) (74% abundance) isotopologue, and the much weaker \( ^{46}\text{TiH} \) (8%) and \( ^{50}\text{TiH} \) (5%) species. Titanium hyperfine structure was also resolved in the weak \( ^{47}\text{TiH} \) (8%, \( I = 2.5 \)) and \( ^{49}\text{TiH} \) (5%, \( I = 3.5 \)) isotopologues. The magnetic tuning properties of TiH have been examined by studying the Zeeman effect on the low-J lines. The analysis is presently in progress and the latest results will be presented at the symposium.

OBSERVATION OF FEMTOSECOND, SUB-ANGSTROM MOLECULAR BOND RELAXATION USING LASER-INDUCED ELECTRON DIFFRACTION

COSMIN I. BLAGA, ANTHONY D. DICIARA, KAIKAI ZHANG, EMILY SISTRUNK, PIERRE AGOSTINI, LOUIS F. DIMAURO, Department of Physics, The Ohio State University, Columbus, OH 43210; JUNLIANG XU, CHII-DONG LIN, Department of Physics, Kansas State University, Manhattan, KS 66506; and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, OH 43210.

Imaging, or the determination of the atomic positions in molecules, has always occupied an essential role in physical, chemical and biological sciences. For structural determination, the well established methods of X-ray and electron diffraction easily achieve sub-Angstrom spatial resolution. However, these conventional approaches are not suitable for investigating structural transformations, such as the reaction of molecules or the function of biological systems that occur on the timescales faster than a picosecond. Over the past decade, major efforts directed at developing femtosecond pulsed sources, e.g. X-ray free-electron lasers and electron beams, have resulted in pioneering investigations on imaging large biological molecules and condensed phase dynamics. We report on a different approach, laser-induced electron diffraction (LIED), for achieving sub-femtosecond, sub-Angstrom spatio-temporal resolution for investigating gas-phase molecular dynamics. In contrast to the above mentioned techniques, the LIED method generates bursts of coherent electron wave packets directly from the molecule under interrogation. The study is performed by measuring the diffracted photoelectron momentum distribution produced by strong-field ionization of oxygen and nitrogen molecules at several mid-infrared wavelengths (1.7-2.3 \( \mu \text{m} \)). The bond lengths retrieved from the LIED analysis show sensitivity to a change of 0.05 \( \text{Å} \) in 1 fs. This initial report provides the first direct evidence of bond relaxation following an electronic excitation and establishes the foundation of the LIED method as a general approach for ultrafast imaging of molecular dynamics.
FE01 15 min  8:30
TOWARD A CONTINUOUS-WAVE SOLID HYDROGEN RAMAN LASER FOR MOLECULAR SPECTROSCOPY APPLICATIONS

W. R. EVANS, Department of Physics, University of Illinois at Urbana-Champaign, Urbana, IL 61801; T. MOMOSE, Department of Chemistry, The University of British Columbia, Vancouver, BC Canada V6T 1Z1; B. J. McCALL, Departments of Chemistry, Physics, and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

We will present our recent work toward the construction of a continuous-wave solid para-H₂ Raman laser for operation first in the visible and later in the mid-infrared. Solid para-H₂ promises to be a good choice for the gain medium in a Raman laser due to its exceptionally high Raman gain coefficient. This not only presents a novel use of an interesting molecular system, but it also offers the potential for the first widely tunable laser source for high resolution spectroscopy in the 5-10 μm range. High resolution spectroscopy requires a tunable continuous-wave laser source. However, up until now, most work in using para-H₂ as a Raman laser gain medium has taken place either with high power pulsed lasers or continuous-wave lasers which require ultra-high finesse cavities. We seek to take advantage of solid para-H₂’s high Raman gain coefficient to construct a continuous-wave Raman laser with a much lower finesse cavity (F ≈ 150). In this presentation, we will talk about our recent work in measuring the index of refraction of solid para-H₂ in the wavelength range 430-1100 nm in preparation for building such a laser. Some details regarding the design and planning for this laser will also be discussed. Finally, current progress and anticipated work on the development of a continuous-wave solid para-H₂ Raman laser will be presented.

FE02 15 min  8:47
PHOTODISSOCIATION OF FORMIC ACID ISOLATED IN SOLID PARAHYDROGEN

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

The in situ photochemistry of dopant molecules isolated in solid parahydrogen (pH₂) typically differs from analogous studies in rare gas crystals for two main reasons: (1) solid pH₂ 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 pH₂ matrix. Our group is currently studying the 193 nm photochemistry of a number of precursor molecules isolated in solid pH₂ via high-resolution FTIR spectroscopy. In this talk I will present results for the 193 nm photolysis of formic acid (FA) in solid pH₂. In rare gas matrices, the analogous FA photochemistry proceeds via the CO+H₂O and CO₂+H₂ photodissociation channels. In solid pH₂, in addition to these channels we observe the production of HCO and HOCO. Further, after the UV laser is turned off, the HOCO concentration continues to increase with a slow first-order rate constant for a period of 10 hours. At this point, we still do not have a full explanation of the chemical mechanism leading to the post-photolysis increase in the HOCO concentration.

FE03

RESONANT TWO-STEP IONIZATION OF Rb AND Cs ATOMS ON HELIUM NANODROPLETS

F. LACKNER, M. THEISEN, and W.E. ERNST, Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria.

Rb and Cs atoms on the surface of helium nanodroplets are ionized by applying a monomer selective resonant two-step ionization scheme. We show that in addition to Rb also Cs atoms stay bound on the surface of helium nanodroplets when excited into the $n^2P_{1/2}$ (Rb: $n = 5$, Cs: $n = 6$) state. Rb atoms are selectively excited either to the $5^2P_{1/2}$ or to the $5^2P_{3/2}$ state and ionized with a pulsed laser. The formation of stable Rb$^+$–He$_n$ ($n < 20$) complexes is observed by ionization via the $5^2P_{3/2}$ state. Ions with masses of up to several thousand amu have been monitored, which can be explained by an immersion of the single Rb (Cs) ions into the helium nanodroplet upon ionization via the $5^2P_{1/2}$ ($6^2P_{1/2}$) state.


FE04

INFRARED AND MICROWAVE-INFRARED DOUBLE RESONANCE SPECTROSCOPY OF METHANOL EMBEDDED IN SUPERFLUID HELIUM NANODROPLETS

PAUL L. RASTON AND WOLFGANG JÄGER, Department of Chemistry, University of Alberta, Edmonton, Alberta T6G-2G2, Canada.

Methanol is one of the simplest torsional oscillators, and has been extensively studied in the gas phase by various spectroscopic techniques. At 300 K, a large number of rotational, torsional, and vibrational energy levels are populated, and this makes for a rather complicated infrared spectrum which is still not fully understood. It is expected that in going from 300 K to 0.4 K (the temperature of helium nanodroplets) that the population distribution of methanol will collapse into one of two states; the $J,K = 0,0$ level for the $A$ symmetry species, and the $J,K = 1,-1$ level for the $E$ symmetry species. This results in a simplified spectrum that consists of narrow $a$-type lines and broader $b$-type lines in the OH stretching region. Microwave-infrared double resonance spectroscopy is used to help assign the $a$-type infrared lines.

FE05

LASER SPECTROSCOPY OF HYDROGEN PEROXIDE EMBEDDED IN HELIUM NANODROPLETS

CHRISSY J. KNAPP, PAUL L. RASTON, and WOLFGANG JÄGER, Department of Chemistry, University of Alberta, Edmonton, AB, Canada T6G 2G2.

Helium nanodroplets provide a gentle matrix in which to isolate reactive species for spectroscopic investigations. In our ongoing effort to generate radical species in helium nanodroplets, we have recently focused our attention on the highly reactive hydrogen peroxide (H$_2$O$_2$) molecule, a potential precursor for the hydroxyl radical. The infrared spectrum of hydrogen peroxide was measured in helium nanodroplets using a cw OPO infrared laser in the OH stretching region. Several rovibrational transitions in the $v_5$ band of hydrogen peroxide (and HOOD) were recorded and assigned. Intensities, shapes, and assignments of lines will be discussed, as will prospects for the use of hydrogen peroxide in the production of hydroxyl radicals in helium droplets using laser photolysis.

Intermission
FE06 Post-deadline Abstract 10 min 10:15

PYRIDINE AGGREGATION IN HELIUM NANODROPLETS

PABLO NIETO, MELANIE LETZNER, DANIEL HABIG, TOERSTEN POERSCHKE, SARAH ANGELIQUE GRÜN, KENNY HANKE, GERHARD SCHWAAB and MARTINA HAVENITH, Department of Physical Chemistry II, Ruhr-University Bochum, Germany.

Pyridine crystals show the unusual property of isotopic polymorphism. Experimentally it has been observed that deuterated pyridine crystals exist in two phases while pyridine does not show a phase transition\(^a\). Therefore, although isotopic substitution is the smallest possible modification of a molecule it greatly affects the stability of pyridine crystals. A possible experimental approach in order to understand this striking effect might be the study of pyridine aggregation for small clusters. By embedding the clusters in helium nanodroplets the aggregates can be stabilized and studied by means of Infrared Depletion Spectroscopy. Pyridine small clusters were identified in the C-H asymmetric vibration region (3000-3200 cm\(^{-1}\)) using this method.


FE07 Post-deadline Abstract 15 min 10:27

IR SPECTROSCOPY STUDY ON THE (HCl)_n(H_2O)_m AGGREGATION IN HELIUM NANODROPLETS

PABLO NIETO, MELANIE LETZNER, DANIEL HABIG, TOERSTEN POERSCHKE, SARAH ANGELIQUE GRÜN, KENNY HANKE, GERHARD SCHWAAB and MARTINA HAVENITH, Department of Physical Chemistry II, Ruhr-University Bochum, Germany.

The study of acid-water clusters is an active area of research due to its fundamental importance for chemistry\(^a,b\). In particular the (HCl)_n(H_2O)_m clusters have been extensively investigated both theoretically and experimentally as a benchmark system. Despite of the great effort devoted to its understanding HCl dissociation in water clusters is still not well understood. An IR-Spectroscopy study on (HCl)_n(H_2O)_m embedded in helium nanodroplets will be presented. The H_16O\text{→}H_18O and isotopic substitution was used in the experiments to probe the bands in the 2650-2760 cm\(^{-1}\) spectral range which has been object of some debate recently\(^c,d\). The observed isotopic shifts for the different bands raise some new questions to be addressed.

\(^b\)V. B. Bondybey et al., Int. Rev. Phys. Chem. 21, 277 (2002).
\(^c\)A. Guthberlet et al., Science 324, 1545 (2009).

FE08 Post-deadline Abstract 10 min 10:44

IR-SPECTROSCOPY OF GLYCINE AND ITS COMPLEXES WITH WATER IN HELIUM NANODROPLETS

M. LETZNER, S. A. GRÜN, G. SCHWAAB and M. HAVENITH, Department of Physical Chemistry II, Ruhr-University Bochum, D-44780 Bochum, Germany.

Glycine is the smallest amino acid, and therefore it is of special interest as a model and starting point for theoretical and experimental studies. Whereas the crystalline form of glycine consists of zwitterions NH\(^3\)+\text{−}CH\(_2\)−COO\(^−\), gas phase glycine is known to exist in the nonionized form NH\(_2\)−CH\(_2\)−COOH\(^b\). The interaction between glycine and water has been widely studied using a large variety of theoretical methods. Depending on the theoretical level used, a stabilisation of the zwitterionic form is predicted for complexes containing from 2 to 7 water molecules. In low-temperature Ar matrices a set of characteristic IR absorption bands for the zwitterionic form has been observed. The higher stoichiometry complexes (glycine)\(\cdot\)\((\text{H}_2\text{O})_n\) with \(n\) larger than 3 are demonstrated to be zwitterionic H-bonded complexes\(^c\). The multitude of conformations expected for these glycine-water complexes makes a combination of low temperature and high resolution spectroscopy essential. We want to use the advantages of our experiment to investigate glycine and its complexes with water in helium-nanodroplets at ultracold temperatures in the range from 3000-3800 cm\(^{-1}\). Our measurements were carried out using a high power IR-OPO (cw: 2.7 W) as radiation source and a helium nanodroplet spectrometer. Helium-nanodroplets are formed by expansion of helium at 55 bar through a 5 \(\mu\)m nozzle which is kept at a temperature of 16 K. The status of the project is presented.

\(^b\)G. Junk et al., J. Am. Chem. Soc. 85, 839 (1963)
HIGHLY COOLED NO MOLECULES ARE SCATTERED FROM A LIQUID GALLIUM SURFACE TO PROBE ROTATIONALLY AND ELECTRONICALLY INELASTIC SCATTERING FROM A MOLTEN METAL. AFTER COLLISIONS AT 45 DEGREES WITH RESPECT TO THE SURFACE NORMAL, SPECULARLY SCATTERED POPULATIONS ARE DETECTED BY CONFOCAL LASER INDUCED FLUORESCENCE (LIF), YIELDING ROTATIONAL, SPIN-ORBIT, AND LAMBDA-DOUBLET POPULATION DISTRIBUTIONS. REVERSE SEEDING IS EMPLOYED TO VARY INCIDENT COLLISION ENERGY FROM 1.0(3) TO 20(6) KCAL/MOL. THE LOWEST COLLISION ENERGIES RESULT IN SINGLE-TEMPERATURE DISTRIBUTIONS FOR SCATTERED NO MOLECULES.

INTERESTINGLY, THE RESULTING TEMPERATURE IS CONSIDERABLY LOWER THAN THAT OF THE SURFACE, A LIKELY MANIFESTATION OF ROTATIONAL COOLING ON DESORPTION FROM AN ENERGETIC WELL BINDING THE MOLECULE TO THE LIQUID METAL. INCREASING COLLISION ENERGY RESULTS IN A STRONG EFFECT ON SCATTERED NO ROTATIONAL ENERGY BUT A WEAK EFFECT ON SPIN-ORBIT BRANCHING. THE OPPOSITE TRENDS ARE SEEN FOR CHANGES IN SURFACE TEMPERATURE, NAMELY STRONG DEPENDENCE FOR ELECTRONIC EXCITATION BUT WEAK DEPENDENCE FOR ROTATIONALLY INELASTIC SCATTERING. THIS CLEAR DIFFERENCE BETWEEN ELECTRONIC AND ROTATIONAL DYNAMICS IS DISCUSSED IN TERMS OF THE POSSIBLE INFLUENCE OF ELECTRON HOLE PAIR EXCITATIONS IN THE CONDUCTING METAL.
The study of aryl radicals is of paramount importance for a different number of reasons. These reactive species are critical intermediates in reactions of explosives and combustion processes, in the generation and the deposition of soot and the formation of organic pollutants. Furthermore these species play an important role in the carcinogenesis and the photocyclic tumour therapy. Based on their high reactivity it is not possible to investigate those substances at room temperature. For this reason previous experimental studies were carried out by embedding the radicals in a low temperature argon matrix. In the present experimental study we wanted to investigate phenyl radicals as a prototype for aryl radicals in helium nanodroplets. In contrast to measurements in an argon matrix (10 K) we were able to get temperatures as low as 0.37 K. Using azobenzene as a precursor the phenyl radicals are generated with the help of a home-made pyrolysis oven at temperatures in the 600 - 1100 K range. The optimization of the phenyl source was carried out by observing the efficiency of the pyrolysis according to changes of different experimental parameters. After obtaining formation of the reactive species and their incorporation into the ultracold helium droplets, the radicals were spectroscopically studied in the spectral region of 3045 cm\(^{-1}\) - 3085 cm\(^{-1}\).

\(^{a}\) J. G. Radziszewski et al., J. Am. Chem. Soc., 1996, 118, 7400-7401


\(^{c}\) A. Mardyukov et al., Chem. Eur. J. 2009, 15, 1462 - 1467
AUTHOR INDEX

BARBER, R. J. – MG02, TJ09, RD09
BARKER, B. J. – TD01, TH02, WG06, RA10, FD09
BARTLETT, R. J. – FB07
BAUERECKER, S. – WF15
BAUM, A. – RA06, RA08
BAUMANN, C. A. – MJ01
BAZSÓ, G. – MJ03
BEAMES, J. M. – TI07, WJ06
BECKLIN, E. E. – RF04, RF05
BEJJANI, M. – MJ08
BELL, T. – FA02
BELLOCHE, A. – TF07
BELLOS, M. A. – MF02
BENNER, D. C. – TE01, TE03, WF17, RB01, RB02
BERDEN, G. – RJ10
BERG, J. E. V. D. – FD04
BERGEMAN, T. H. – TH04
BERGIN, E. A. – FA01, FA02, FA03
BERKE, A. E. – TB09
BERNARD, J. – RF11
BERNATH, P. F. – MG04, TD02, TD03, WA01, RD09, FC01, FC02
BESER, B. – RD03
BETHLEM, H. L. – RD04
BETHE, H. – TF08
BÉCZKA, E. – MJ03
BHATT, R. S. – TB10, RE01
BILJIKOWSKA-JAWORSKA, E. – WH11
BILLINGHURST, B. E. – RG14
BILLS, B. J. – WH09
BINNS, M. K. L. – RH05
BIRD, R. G. – TG05, RC09
BISWAS, B. – RG11
BLAAGA, C. I. – FD11
BLAKE, G. – FB02
BLAKE, T. A. – RH06, RH07, FC06
BLAKE, T. F. – TB02, TB03
BLANCO, S. – RH12
BLANK, L. – RI03
BOBON, M. – TA07
BOCQUET, R. – RB06, RC09
BONDYBEY, V. E. – TD01, RA10
BORHO, N. – RG08
BORSOV, Y. B. – RG06
BOTTINELLI, S. – WF11
BOUZÉ, A. – WF11
BOUDON, V. – WF15, RB03
BOURGES, M. – TG05
BOWMAN, J. M. – RF08
BRAND, C. – TG06
BRATHWAITE, A. D. – MJ04
BRAUER, C. S. – MH09
BRECHIGNAC, P. – WF14, WJ05, RD09
BRECKENRIDGE, W. H. – WG08
BREEN, K. J. – RJ12
BRINEY, K. A. – RE04
BROOKS, A. H. – MH05
BROWN, G. G. – MH10
BROWN, K. R. – MJ01
BROWN, L. R. – TE01, TE03, TE04, WF15, WF16, RB01
BRUMFIELD, B. E. – TA03, FC08
BRUNNEN, S. – TC04, RF09
BUCHINO, M. P. – TC10, RH05
BUCHANAN, E. G. – TD11, WJ10, WJ11, RG10, RG11
BUCKINGHAM, G. – RE02
BUDARZ, J. – TB06
BURROWS, J. – TE11
BUTAÉVA, E. V. – RE06
BÜHLER, C. C. – TB07
C

CABEZAS, C. – MH13, MH14, RC05, RC07, RC08
CAMINATI, W. – MH04, WH08
CAMARGUE, A. – TE09
CARICATO, M. – RI06
CARNEGIE, P. D. – MI05
CAROLLO, R. – MF02
CARPENTIER, Y. – RG09
CARRINGTON JR., T. – RI08, RI09
CARRON, P. B. – RF14
CASE, A. S. – TB13
CASTANO, F. – WH08
CASTO, C. – TE12
CAZZOLI, M. – TC03, RF06
CECCARELLI, C. – WF11
CERNICHARO, J. – FA02
CH'NG, L. C. – TB12
CHAKRAVORTY, T. – MG12, TG08
CHAMAILLÉ, T. – RG09
CHANDRA, P. – MF03
CHANG, C. – TD10
CHEN, H. – TA09, TA11
CHEN, Jinhai – RG09
CHENG, L. – TC03
PEARSON, J. C. – MH09, TC04, TC05, TF13, TF14, WI07, RF09, RF10, FA03
PEEBLES, R. A. – WH09, RC12
PEEBLES, S. A. – WH09, RC12
PELTOLA, J. – TA05
PENA, J. – RC05, RC07
PENG, J. – TA11
PERERA, A. – TB10, WI03, WI09, RD06, RD07, RE01
PESLHERBE, G. H. – FB03
PETERSON, K. A. – RI01
PETIT, A. S. – TJ10, R110
PETITPREZ, D. – TA05
PETITPREZ, D. – TA05
PETROV, A. N. – RA05, FD08
PETROV, A. N. – RA05, FD08
PHILLIPS, D. J. – TB05
PHILLIPS, M. A. – MI11
PERRY, D. S. – TB10, WI03, WI09, RD06, RD07, RE01
PIECH, K. M. – WJ09
PIECE, C. – MI10
PINO, T. – WF14, RG09
PIRAL, O. – WJ05
PIRALI, O. – WF08, RF09, RF13, RF15, RG12, FA06, FC05
PITICCO, L. – TH08
PITZER, R. M. – FB01
PIUZZI, F. – FB06
PLANT, D. F. – FC04
PLOWRIGHT, R. J. – WG08
PLUME, R. – FA02
PLUMMER, G. M. – RB05
PLUSQUELLIC, D. F. – TC06, RB08, RC06
POAD, B. L. J. – MA01
POERSCHKE, T. – FE06, FE07, FE11
POLFER, N. – RA05
POLYANSKYI, O. L. – RD09
POMS, J. – WI12
PONOMAREV, Y. N. – RB03
PORAMBO, M. – MG10, MG11
PRADHAN, A. K. – FB01
PRATT, D. W. – MH11, TH08, TG05, TG06, TG09, WI02, RC09, RD06, RE01
PRESCOTT, J. E. – RG05
PRESTON, T. C. – MG13
PRESTON, T. J. – RE08, RE09
PRICE, J. E. – FC06
PRINGLE, W. C. – MH05, WH14
PRINSEN, E. B. – FD04
PULLIAM, R. L. – WF05
PUZZARINI, C. – TC02, TC03, RF06
QUACK, M. – WF15
R
RADHUBER, M. L. – RF07, FA05
RAGAB, A. – TA04
RAHMLOW, D. – MF02
RAM, R. S. – TD02, TD03
RAMACHANDRAN, P. V. – RG11
RAMANATHAN, N. – MG10, MG11
RAMOS, M. – RB04
RAO, G. R. – RG07
RASONT, P. L. – FE04, FE05
REACH, W. – RF11
REDDICK, M. – WG04
REDDY, B. V. – RG07
REED, Z. D. – MI04
REEVE, S. W. – TA07
REGALIA, L. – WF16
REICHARDT, C. – TG12, TG13, RE11
REID, J. P. – WI08
REID, K. L. – TG01
REID, S. A. – MJ04, MJ05, TH12, RE08, RE09
REILLY, N. – WI05
REISLER, H. – TB12, RD10
REMIIJAN, A. J. – WF01, WF05
REY, M. – FC03
REZAEI, M. – TI04, TI10, TI11
RHO, J. – RF11
RICHARD, C. – WG02, FC02
RICHARD, R. M. – FB12
RICKS, A. M. – MI04
RIMMER, P. – FA03
RIMMER, P. B. – FA04
RITTBY, C. M. L. – MJ08
ROBERTS, M. A. – MG03
ROCHER, B. E. – TB12
RODRIGO, C. P. – RD10
ROSS, A. S. – WG02
ROSS, S. C. – RG05
ROTGER, M. – RB03
ROTHGEB, D. W. – WG14
ROTHMAN, L. S. – TE08, FC01, FC02
ROUDIANE, M. – RJO1, RJO3
ROUJEFF, E. – FA06
ROWSSELL, J. – MJ10
ROY, P. – WI05, RF15, RG12, FA06, FC05
ROY, P. N. – TI09, TJ14, TJ15, TJ16, FB05
RUPASINGHE, P. M. – RA06, RA08
RUTHEFF, A. – MG10
RYAN, S. A. – TE05
RYAZANOVA, M. – RD10
S
SADOVSKII, D. A. – FC05
SAKAI, S. – TA01
SALMI, T. – TJ12
SAMANTA, K. A. – MG12
SANDER, S. P. – TD08, TD09
SANDERS, A. J. – WH09, RC12
SATO, A. – MH03
SAUER, B. E. – RA02
SCHILKE, P. – FA02
SCHLEMMER, S. – MG06, MI13, TF07, WF09
SCHLOSS, J. – MJ10
SCHMIDT, M. – TJ08
SCHMIDT, T. – WF14
SCHMIDT, M. – TG06
SCHWAAB, G. – FE06, FE07, FE08, FE11
SCHWENKE, D. W. – TE02, TE04
SCHAFAER, M. – TH03, TH08
SEARS, T. J. – TD10, TE06, TE07, RA06, RA08
SEBBEE, J. A. – TB08, TD11
SELYBY, T. – TB08
SENYEL, M. – FC09
SERYUCHEKO, A. – TE11
SHERAFEN, N. – RA09, FD05
SHERAFEN, N. E. – RA06, RA07, RA08
SHAJI, S. – WF17
SHALOSKI, M. A. – RE08, RE09
SHEARouse, J. – RI10
SHEPS, L. – MF14
SHERIDAN, P. M. – RH05
SHIN, J. – RE03
SHIPMAN, S. T. – RF12, RH01, RH02, RH10
SHIRAR, A. J. – RH11
SHIRIN, S. V. – RD09
SHY, J. – TA09, TA10, TA11
SIBERT III, E. L. – TJ04, TJ05
SIGNORELLI, R. – MG13
SILLER, B. – MI09, MI10, MI11
SILTANEN, M. – TA05
SINCLAIR, L. C. – FD06
SISTRUNK, E. – FD11
SKRIPNIKOV, L. V. – FD08
SLIPCHENKO, L. V. – FB04, FB09
SMALLMAN, L. J. – RA02
SMIRNOV, A. – FC05
SMITH, M. A. H. – TE03, RB01
SOLODOV, A. A. – RB03
SOLODOV, A. M. – RB03
SPICKLER, P. T. – WF17
SPRAGUE, M. K. – TD08, TD09

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The Coblentz Award is presented annually to an outstanding young molecular spectroscopist under the age of 40. The candidate must be under the age of 40 on January 1 of the year of the award. Nominations, which should include a detailed description of the nominee’s accomplishments, a curriculum vitae and as many supporting letters as possible. Annual updates of files of nominated candidates are encouraged. Please submit nominations by July 15 to the award committee chair: Martin Zanni, zanni@chem.wisc.edu

Ellis R. Lippincott Award. The Ellis R. Lippincott Award is presented annually recognition of significant contributions and notable achievements in the field of vibrational spectroscopy. The medal is sponsored jointly by the Coblentz Society, the Optical Society of America and the Society for Applied Spectroscopy. Recipients of the medal must have made significant contributions to vibrational spectroscopy as judged by their influence on other scientists. Because innovation was a hallmark of the work of Ellis R. Lippincott, this quality in the contributions of candidates will be carefully appraised. Nominations should be submitted by October 1 to: Lippincott Award Chairperson, awards@osa.org

Craver Award. The Craver Award is presented annually to an outstanding young molecular spectroscopist whose efforts are in the area of applied analytical vibrational spectroscopy. The candidate must be under the age of 45 on January 1st of the year of the award. The work may include any aspect of (near-, mid-, or far-infrared) IR, THz, or Raman spectroscopy in applied analytical vibrational spectroscopy. Nominees are welcome from academic, government, or industrial research. Nominations must include a detailed description of the nominee’s accomplishments, curriculum vitae or resume, and a minimum of three supporting letters. Please submit nominations by July 31 to the award committee chair: Brandye Smith-Goettler, brandye_michelle_smithgoettler@merck.com

ABB Bomem-Michelson Award. ABB sponsors the Bomem-Michelson Award award to honor scientists who have advanced the technique(s) of vibrational, molecular, Raman, or electronic spectroscopy. Contributions may be theoretical, experimental, or both. The recipient must be actively working and at least 37 years of age. The nomination should include a resume of the candidate’s career as well as the special research achievements that make the candidate an eligible nominee for the ABB sponsored Bomem-Michelson Award. Nominations have been extended until June 30th for this year. Nominations should be submitted to: Prof. Peter R. Griffiths, pgriff@uidaho.edu.

Honorary Membership. The Coblentz Society awards honorary memberships in the Society to people who have made outstanding contributions to the field of vibrational spectroscopy or any other field related to the purposes of the Society. Nominations close on February 1 each year, with awards announced at the Annual Members Meeting at Pittcon and presented at FACSS. Send your nomination for 2012 to Prof. Michael Myrick, Coblentz Society President at myrick@chem.sc.edu.

The 22nd International Conference on High Resolution Molecular Spectroscopy
Prague, Czech Republic, September 4-8, 2012

The subjects covered at this meeting are largely identical to those covered at the 66th International Symposium on Molecular Spectroscopy. The first circular will be distributed by electronic mail in the fall of 2011.

Information is available from the chairman of the local organizing committee

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