

## MILLIMETER-WAVE SPECTROSCOPY OF TRANSIENT SPECIES IN SUPERSONIC JET

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Submillimeter-wave absorption spectroscopy has been applied to observe transient species produced in the supersonic jet expansion with the UV laser photolysis, such as vinyl <sup>a</sup>, FeCO <sup>b</sup>, CoCO, CoNO, and FeNO.

For vinyl, the proton tunneling-rotation transitions, as well as the pure rotational transitions, have been observed for the H<sub>2</sub>CCH, H<sub>2</sub>CCD and D<sub>2</sub>CCD isotopic species to determine tunneling splitting  $\Delta E_0$  and the potential barrier height  $h$  for the proton (H/D) tunneling motion. Although these isotopic species have very different values for the tunneling splitting  $\Delta E_0$  (16.185, 1.187 and 0.770 GHz), they have almost the same barrier heights  $h$  of 1580, 1520, and 1549 cm<sup>-1</sup>. As for the HDCCH species, the pure rotational transitions (both *a*- and *b*-types) of only one isomer (*cis*-HDCCH:D *cis* to the unpaired electron) were observed in the jet cooled condition, but no lines for the *trans*-form nor *cis-trans* tunneling transitions were detected suggesting HDCCH has *cis*- and *trans*-isomers. The difference in zero point energy between the *cis*- and *trans*-HDCCH isomers is calculated to be 32 cm<sup>-1</sup> with the CCSD(T)/aug-cc-pVTZ level *ab initio* calculation to support the present result. We also observed the large off-diagonal ( $\Delta I = \pm 1$ ) hyperfine interaction constants for H<sub>2</sub>CCD which causes the nuclear spin conversion between the ortho ( $I_\beta=1$ ) and para ( $I_\beta=0$ ) H<sub>2</sub>CCD.

The jet cooled FeCO, CoCO, FeNO, CoNO, and Co(CO)(NO) radicals were produced in a supersonic jet expansion by excimer laser photolysis of Fe(CO)<sub>5</sub>, Co(CO)<sub>3</sub>NO and Fe(CO)<sub>2</sub>(NO)<sub>2</sub> to observe the rotational lines. The molecular structures of FeCO, CoCO, CoNO and FeNO, for example, were confirmed to be linear with their electronic ground states of <sup>3</sup>Σ<sup>-</sup>, <sup>2</sup>Δ<sub>*i*</sub>, <sup>1</sup>Σ<sup>+</sup>, and <sup>2</sup>Δ<sub>*i*</sub> as suggested by high level *ab initio* calculations.

The setup was also used to observe the internal rotation transitions of the He-HCN <sup>c</sup>, H<sub>2</sub>-HCN, Ne-HCN, Ar-HCN, and H<sub>2</sub>-H<sub>2</sub>O complexes in the SMMW range between 60 and 360 GHz. The potential energy surfaces calculated by CCSD(T) *ab initio* calculation were improved to explain the experimental results to the microwave accuracy.

<sup>a</sup>K. Tanaka, M. Toshimitsu, K. Harada, T. Tanaka, *J. Chem. Phys.* **120** 3604, (2004).

<sup>b</sup>K. Tanaka, M. Shirasaka, T. Tanaka, *J. Chem. Phys.* **106** 6820, (1997).

<sup>c</sup>K. Harada, K. Tanaka, T. Tanaka, S. Nanbu, M. Aoyagi, *J. Chem. Phys.* **117** 7041, (2002).