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 [a], FeCO [b], CoCO, CoNO, and FeNO.

For vinyl, the proton tunneling-rotation transitions, as well as the pure rotational transitions, have been observed for the H_2CCH, H_2CCD and D_2CCD isotopic species to determine tunneling splitting ΔE_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 ΔE_0 (16.185, 1.187 and 0.770 GHz), they have almost the same barrier heights h of 1580, 1520, and 1549 cm^{-1}. 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^{-1} 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_2CCD which causes the nuclear spin conversion between the ortho (I_β=1) and para (I_β=0) H_2CCD.

The jet cooled FeCO, CoCO, FeNO, CoNO, and Co(CO)(NO) radicals were produced in a supersonic jet expansion by excimer laser photolysis of $Fe(CO)_5$, $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$ 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 $^3\Sigma^-$, $^2\Delta_i$, $^1\Sigma^+$, and $^2\Delta_i$ as suggested by high level $ab\ initio$ calculations.

The setup was also used to observe the internal rotation transitions of the He-HCN [c], H_2-HCN, Ne-HCN, Ar-HCN, and H_2-H_2O 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.

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