THE MILLIMETERWAVE SPECTROSCOPY OF THE VINYL-2-d_1 RADICAL (HDC=CH)

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

The vinyl-2-d_1 radical HDC=CH, mono-deuteride of the methylenic (CH_2) proton, may have two forms, cis- and $trans$-HDCCH; for cis-HDCCH an unpaired electron is located on the same side of deuterium with respect to the C=C double bond, while on the opposite side for $trans$-HDCCH. If the barrier hight h between the cis- and $trans$-form is sufficiently low and the zero point energy differece between the two forms Δ_{tc0} is small enough ($\Delta_{tc0} \ll 1$ cm^{-1}), the proton on the acetylenic side (CH) will easily transfer through the barrier by tunneling effect, giving us a chance to observe the tunneling transitions between the two forms (0^+ and 0^-). If not, the two forms will remain as two toutomers, cis-HDCCH and $trans$-HDCCH, and will give us a chance to observe the b-type rotational transitions within the cis and $trans$ toutomers instead of the tunneling transitions.

In our previous study [a], we have observed the a-type rotational spectra of cis-HDCCH by millimeter wave spectroscopy in a supersonic jet, while no lines for $trans$-HDCCH were observed. In the present study, we have searched for either the tunneling transitions or the b-type rotational transitions of HDCCH generated by 193 nm excimer laser photolysis of HDCCHCl. The b-type rotational transitions ($N_{K_a K_c}$=$1_{11}-0_{00}$, $2_{12}-1_{01}$, $1_{10}-1_{01}$ and $2_{11}-2_{02}$) only for one form of HDCCH were observed in the frequency region of 158−258 GHz, but no the tunneling transitions. The rotational and hyperfine interction constants, [b] indicate that the observed toutomer is not $trans$-HDCCH but cis-HDCCH.

Our *ab initio* calulation performed in the CCSD(T)/cc-pVQZ level supports the present observation. Althogh the calculated barrier hight between the cis- and $trans$-form is as low as h = 1770 cm^{-1}w, the zero point energy gap between the two toutomers Δ_{tc0} = 30.7 cm^{-1} is large, as the result we have two toutomers, cis-HDCCH and $trans$-HDCCH, to observe the b-type rotational transitions instead of the tunneling transitions. The zero point energy gap Δ_{tc0} 30.7 cm^{-1} is large enough to populate only to the vibrational ground state of cis-HDCCH in the ultra low temperature $T = 15K$ in the supersonic jet giving us no $trans$-HDCCH spectra.

[a] M. Hayashi, K. Harada, K. Tanaka, *International Symposium on Molecular Spectroscopy*, TJ14(2006)

[b] K. Tanaka, M. Toshimitsu, K. Harada, T. Tanaka, *J. Chem. Phys.***120**, 3604 (2004)