MILLIMETER-WAVE SPECTROSCOPY OF THE D_2CCD RADICAL

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

The tunneling-rotation transitions of the vinyl-d_3(D_2CCD) radical produced by the 193 nm excimer laser photolysis of vinyl-d_3 chloride(D_2CCDCl) have been observed by millimeter-wave spectroscopy combined with a pulsed supersonic jet technique. The b-type transitions, $N_{K_aK_c}$=1_{11}- 0_{00}, 1_{10}-1_{01}, 2_{12}-1_{01}, for both the $0^- \leftarrow 0^+$ and $0^+ \leftarrow 0^-$ tunneling subbands were observed in the frequency region of 101-183 GHz, split into fine and hyperfine components due to the spin-rotation interaction and the spin-spin interaction of the α(CD)- and the β(CD_2)-deuterons. The molecular constants such as rotational constants, spin-rotation interaction constants, and hyperfine interaction constants were determined by a simultaneous analysis of the observed spectrum and previously reported J=1←0 pure rotational transition[a] together with the tunneling splitting $\Delta E_0 = 771.843(23)$ MHz between the 0^+ and 0^- states.
The tunneling splitting for D_2CCD is less than 1/20 of that for H_2CCH (16 271.842 9(59) MHz)[b] due to the mass effect of the α-H and D, and it is about 2/3 of H_2CCD (1 186.820(26) MHz) indicating the mixing of the vibrational modes for α-H/D and β-H_2/D_2. From the observed tunneling splitting, the barrier height h of the double minimum potential for D_2CCD was estimated to be 1549 cm^{-1} using one dimensional model. The barrier height h for D_2CCD is almost the same as those for H_2CCH and H_2CCD, 1580 and 1520 cm^{-1}, respectively, as expected by B.O. approximation and the isotopic effect due to zero point energies. The off-diagonal Fermi interaction constant, δa_F, which is responsible to the mixing of the wavefunctions of $ortho$(I_β = 0, 2) and $para$(I_β = 1) states, has been determined to be 19.8(30) MHz. The off-diagonal Fermi interaction may cause the nuclear spin conversion between the $ortho$- and $para$-states for D_2CCD.

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[a]E. Kim, S. Yamamoto, *J. Chem. Phys.* **116**, 10713, (2002).
[b]K. Tanaka, M. Toshimitsu, K. Harada, T. Tanaka, *J. Chem. Phys.* **120**, 3604, (2004).