MILLIMETER WAVE SPECTROSCOPY OF THE VINYL-D (H_2CCD) RADICAL GENERATED BY UV LASER PHOTOLYSIS IN A PULSED SUPERSONIC JET EXPANSION. DETERMINATION OF THE PROTON TUNNELING SPLITTING

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The rotational and proton tunneling spectra of the vinyl-d (H_2CCD) radical have been observed by millimeter wave spectroscopy combined with a pulsed supersonic jet technique. H_2CCD was generated by the 193 nm excimer laser photolysis of vinyl chloride-d(H_2CCDCl). The pure rotational transitions (*a*-type transitions), $N_{K_aK_c}$=$1_{01}-0_{00}$, $2_{02}-1_{01}$, $3_{03}-2_{02}$, $2_{11}-1_{10}$, $2_{12}-1_{11}$ in the 0^+ and 0^- states, were observed in the frequency region of 52.9−158.7 GHz. The $0^+ \leftarrow 0^-$ and $0^- \leftarrow 0^+$ proton tunneling transitions (*b*-type transitions), $N_{K_aK_c}$=$1_{11}-0_{00}$, $1_{10}-1_{01}$, $2_{11}-2_{02}$, $2_{12}-2_{01}$, were observed in the frequency region of 184.7−236.8 GHz. The observed rotational lines were split into fine and hyperfine components due to the spin-rotation interaction and the spin- nuclear spin interaction of the acetylenic (CD) deuteron (α-deuteron) and the methylenic (CH_2) protons (β- protons). The moleculer constants such as rotational constants, spin- rotation interaction constants, and hyperfine interection constants, were determined by a least squares fitting of the observed spectrum, together with the proton tunneling splitting $\Delta E_0 = 1164.861(20)$ MHz. The barrier height of the double minimum potential was estimated to be 1520 cm^{-1} from the observed tunneling splitting assuming a one dimensional model. This potential barrier height is consistent with that of the normal species(H_2CCH), 1580 cm^{-1}, derived from the tunneling splitting reported to be 16271.8429(59) MHz [a], if the zero point energy is taken into consideration.

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