MILLIMETER-WAVE SPECTROSCOPY OF THE VINYL 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 radical have been observed by millimeter-wave spectroscopy combined with a pulsed supersonic jet technique. The vinyl radical was generated by the 193 nm excimer laser photolysis of vinyl bromide. The pure rotational transitions, $N_{K_a K_c} = 1_{01} - 0_{00}$, $2_{02} - 1_{01}$, $3_{03} - 2_{02}$, and $4_{04} - 3_{03}$, observed in the frequency region of $60 - 250$ GHz, consisted of two components, 0^+ and 0^-, confirming the proton tunneling motion of the vinyl radical. 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 (CH) as well as methylenic (CH_2) protons. The pure rotational spectra for $K_a = 1$ were also observed both for the 0^+ and 0^- components. The rotatinal constants, spin-rotation coupling constants, and hyperfine coupling constants for each tunneling components obtained were consistent with the results of the ESR spectroscopy in the Ar matrix[a] and the infrared diode laser spectroscopy[b]. The *b*-type *Q*-branch lines for the $0^+ \leftarrow 0^-$ proton tunneling transition were observed around 200 GHz. The proton tunneling splitting was determined to be about 0.54 cm^{-1}, and the barrier height of the double minimum potential to be about 1250 cm^{-1}.

[a] P. H. Kasai, *J. Am. Chem. Soc.* **94**, 5950 (1972)
[b] H. Kanamori, Y. Endo, and E. Hirota, *J. Chem. Phys.* **92**, 197 (1990)