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, \( J_{N_{1}, N_{2}} = 101 - 000, 200 - 101, 303 - 202, \) and \( 404 - 303 \), 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 rotational 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)