

SLIT DISCHARGE SPECTROSCOPY OF JET-COOLED CYCLOPROPYL RADICAL IN THE ANTISYMMETRIC CH₂ STRETCH (ν_7) MANIFOLD: STRUCTURES, TUNNELING BARRIER AND INTRAMOLECULAR DYNAMICS

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High-resolution infrared spectra of jet-cooled cyclopropyl radical are reported for the first time, specifically sampling the in-phase antisymmetric CH₂ stretch (ν_7) vibration. In addition to yielding first precise gas phase structural information for this radical, the spectra reveal doubling due to quantum tunneling of the lone α -CH with respect to the CCC plane, lift the degeneracy and generating lower (+) and upper (-) tunneling states. The bands clearly reveal intensity alternation (6:10 for even:odd K_a+K_c levels in the lower \leftarrow -lower and 10:6 in the upper \leftarrow -upper) due to H atom nuclear spin statistics, confirming that the tunneling transition state for cyclopropyl radical is of C_{2v} symmetry. However, in addition to the two predicted vibrational bands (i.e. lower \leftarrow -lower and upper \leftarrow -upper), a third band is observed due to IVR mixing of the upper tunneling component (ν_7) with a nearly isoenergetic dark state. From fractional populations in the ground and excited state, the tunneling splittings for cyclopropyl radical in the ground and excited (ν_7) state are estimated to be $3.2 \pm 0.3 \text{ cm}^{-1}$ and $4.9 \pm 0.3 \text{ cm}^{-1}$, respectively. This indicates that stereoracemization of the α -CH radical center is a very fast process ($k=2.0 \times 10^{11} \text{ s}^{-1}$), and that the barrier decreases upon vibrational excitation of the CH₂ in-phase antisymmetric stretch. The barrier height for α -CH inversion through the cyclopropyl plane is also extracted from the analysis of the tunneling dynamics with simple 1D potential energy surface.