SLIT DISCHARGE SPECTROSCOPY OF JET-COOLED CYCLOPROPYL RADICAL IN THE ANTISYMMETRIC CH_2 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 CH_2 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 Ka+Kc 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$0.3 cm^{-1} and 4.9$\pm$0.3 cm^{-1}, respectively. This indicates that stereoracemization of the α-CH radical center is a very fast process (k=2.0x10^{11} s^{-1}), and that the barrier decreases upon vibrational excitation of the CH_2 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.