

HIGH-RESOLUTION INFRARED SPECTROSCOPY OF GAS-PHASE CYCLOBUTYL RADICAL IN THE α -CH STRETCH REGION: STRUCTURAL AND DYNAMICAL INSIGHTS

YA-CHU CHAN, *JILA and the Department of Chemistry, University of Colorado Boulder, Boulder, CO, USA*; DAVID NESBITT, *JILA, Department of Chemistry, and Department of Physics, University of Colorado Boulder, Boulder, CO, USA*.

Gas-phase cyclobutyl radical ($\cdot\text{C}_4\text{H}_7$) is generated at a rotational temperature of 15 K in a slit-jet discharge mixture of 70% Ne/30% He and 0.5-0.6% cyclobutyl bromide ($\text{C}_4\text{H}_7\text{Br}$). The fully rovibrationally resolved absorption spectra of the α -CH stretch fundamental band are observed and analyzed, yielding the first precision structural information for this radical species. The band origin is determined to be $3068.7801(25) \text{ cm}^{-1}$, which from previous infrared spectroscopic studies of cyclobutyl radicals in droplets^a implies a 0.8 cm^{-1} blue shift due to the presence of liquid helium. This value is also in good agreement with high-level *ab initio* calculations at CCSD(T) level of theory with a PVnZ ($n = 2,3$) and ANOn ($n = 0,1$) basis set, which predicts an anharmonic frequency of 3076.4 cm^{-1} from second-order vibrational perturbation theory (VPT2).^b A complete rovibrational analysis is underway, progress toward which will be reported. Of particular dynamical interest in such results will be the large amplitude nature of the ring puckering motion, specifically whether this radical possesses a planar (C_{2v}) or puckered (C_s) geometry. While CCSD(T) theoretical calculations predict a C_s electronic minimum and a C_{2v} first-order saddle point, the ratio of out-of-plane puckering frequency to interconversion barrier constitutes the dominant influence on the vibrationally averaged molecular geometry and dynamics of large amplitude motion for cyclobutyl radical.

^aA. R. Brown, P. R. Franke and G. E. Douberly, "Helium nanodroplet isolation of the cyclobutyl, 1-methylallyl, and allylcarbinyl radicals: Infrared spectroscopy and *ab initio* computations," *J. Phys. Chem. A* 121, 7576-7587 (2017).

^bD. A. Matthews, L. Cheng, M. E. Harding, F. Lipparini, S. Stopkowitz, T.-C. Jagau, P. G. Szalay, J. Gauss and J. F. Stanton, "Coupled-cluster techniques for computational chemistry: The CFOUR program package," *J. Chem. Phys.* 152, 214108 (2020).