

Ring opening in the cyclopropyl radical and cation

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We report spectroscopic and theoretical studies of the cyclopropyl radical and cation ($c\text{-C}_3\text{H}_5$). The cation especially is unstable towards ring-opening to allylic geometries, and the radical exhibits inversion tunneling of the $\alpha\text{-H}$ atom through the C-C-C ring plane. These large amplitude motion phenomena complicate the photoionization spectra (among others) as well as the determination of properties that are of interest due to ring strain in this fundamental cyclic radical. Through multiscale reduced- and full-dimensional *ab initio* descriptions of the potential energy surfaces (PES) of both the radical and the cation, the ionization spectrum of the radical is simulated using advanced perturbative and variational rovibrational treatments.

Due to the large energy difference between the allylic equilibrium geometry and the unstable cyclic configuration on the cation PES, propagator-based methods that avoid the construction of cationic vibronic eigenstates were used to simulate the ionization spectrum. The results of our simulations, combined with high accuracy single-point *ab initio* calculations of the energy difference between the cation and the radical, compare well with both experimental photoionization data from the literature and new mass-selected threshold photoelectron measurements performed at the SOLEIL synchrotron. Further computational efforts are underway to improve the simulations.

Our results shed light on the most basic properties of the fundamental pericyclic reactions between allyl and cyclopropyl radical, and also between their respective cations. These were among the very first systems to be studied from the perspectives of Woodward-Hoffmann rules and correlation diagrams, but the predictions of these seminal methods were never directly explored experimentally in these archetypal systems. Additionally, we provide a qualitative explanation for the quantum mechanical effects that make the ionization transition favorable, despite accessing a portion of a potential energy surface with negative curvature.

