

RING OPENING AND TUNNELING INVERSION IN THE CYCLOPROPYL RADICAL AND CATION

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We report spectroscopic and theoretical studies of the cyclopropyl radical and cation ($c\text{-C}_3\text{H}_5$)¹. Through synchrotron VUV photoionization spectroscopy and novel spectral simulations, we establish the transition state nature of the cation, which is unstable towards ring-opening to the allyl cation. Additionally, we report preliminary results of the rotational spectroscopy of the radical, which exhibits inversion tunneling of the α -H atom through the C-C-C ring plane.

The large energy difference between the allylic equilibrium geometry and the unstable cyclic configuration on the cation potential energy surface (PES) required the development of propagator-based methods that avoid the construction of cationic vibronic eigenstates to simulate the ionization spectrum². The results of our simulations, combined with high accuracy single-point *ab initio* calculations, compare well with new mass-selected threshold photoelectron measurements performed at the SOLEIL synchrotron, and attest to the transition state nature of the cation. Our results shed light on the most basic properties of the fundamental pericyclic reactions between allyl and cyclopropyl radicals and cations, which were among the very first systems to be studied from the perspectives of Woodward-Hoffmann rules and correlation diagrams. Additionally, we provide a qualitative explanation for the quantum mechanical effects that make the ionization transition favorable to a portion of a PES with negative curvature.

[1] Genossar *et al.*, *J. Am. Chem. Soc.*, 144 (40), 18518-18525, 2022. [2] Changala *et al.*, *J. Chem. Phys.*, 157, 124102, 2022.