

VIBRATIONAL SPECIFICITY AND ISOTOPIC DEPENDENCE OF PROTON-TRANSFER DYNAMICS IN ELECTRONICALLY EXCITED 6-HYDROXY-2-FORMYLFULVENE

LIDOR FOGUEL, ZACHARY VEALEY, PATRICK VACCARO, *Department of Chemistry, Yale University, New Haven, CT, USA.*

The vibrational specificity and isotopic dependence of hindered proton-transfer dynamics have been explored in the lowest-lying singlet excited state, \tilde{A}^1B_2 ($\pi^*\pi$), of 6-hydroxy-2-formylfulvene (HFF) and its monodeuterated isotopolog (HFF-*d*). Both systems have been probed under bulk-gas conditions by employing polarization-resolved degenerate four-wave mixing (DFWM) spectroscopy, where judicious selection of incident and detected polarization geometries served to alleviate spectral complexity and to allow for the quantitative extraction of rotation-tunneling information. The observed >1000 -fold decrease in tunneling rate that accompanies the $\pi^* \leftarrow \pi$ electron promotion (transitioning from ultrafast ground-state dynamics^a to near-complete quenching of analogous excited-state behavior) makes HFF a compelling model system for investigating the nuanced nature of low-barrier hydrogen bonding and its ability to regulate attendant hydron-migration events. A thorough analysis of low-energy vibronic bands in the \tilde{A}^1B_2 manifold will be presented, with the dependence of unimolecular reactivity on heavy atom motion and isotopic modification being discussed in the context of structural predictions emerging from high-level quantum-chemical calculations.

^aZ. N. Vealey, L. Foguel and P. H. Vaccaro, *J. Phys. Chem. Lett.* **9**, 4949 (2018)