

ROTATION-TUNNELING ANALYSIS OF PROTON-TRANSFER DYNAMICS IN ELECTRONICALLY EXCITED 6-HYDROXY-2-FORMYLFULVENE USING DEGENERATE FOUR-WAVE MIXING

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The multidimensional nature of classically hindered proton transfer is demonstrated clearly by the pronounced effects engendered by attendant electronic and vibrational degrees of freedom, the selective excitation of which can enhance or diminish the rate of hydron migration greatly. To explore the provenance of such phenomena, the origin band (0_0^0) of the $\tilde{A}^1B_2-\tilde{X}^1A_1$ absorption system in 6-hydroxy-2-formylfulvene (HFF) has been probed under ambient bulk-gas conditions by using polarization-resolved degenerate four-wave mixing (DFWM) spectroscopy. The alleviation of rovibronic congestion and suppression of rotational-branch structure afforded by judicious selection of incident/detected polarizations for the DFWM interaction has enabled refined rotation-tunneling information to be extracted for the lowest-lying singlet excited manifold, \tilde{A}^1B_2 ($\pi^*\pi$). In contrast to the ultrafast dynamics ($\tau_{pt} \leq 120$ fs) that characterize the \tilde{X}^1A_1 ground electronic state of HFF, the $\pi^* \leftarrow \pi$ electron promotion is found to impede intramolecular proton transfer markedly, leading to the near complete quenching of tunneling-induced spectral signatures. The intrinsic dependence of reaction coordinate and proton-transfer efficacy on the nuances of potential-surface topology and transition-state geometry will be discussed in light of these experimental results, with complementary quantum-chemical calculations serving to elucidate the dramatic impact that subtle changes in energy landscape can exert upon unimolecular dynamics.