ROTATION-TUNNELING ANALYSIS OF EXCITED-STATE PROTON TRANSFER IN DEUTERATED TROPOLONE

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The origin band of the $\tilde{A}^1\mathrm{B}_2 - \tilde{X}^1\mathrm{A}_1$ ($\pi^* \leftarrow \pi$) absorption system in monodeuterated tropolone (TrOD) has been probed with rotational resolution by applying polarization-resolved degenerate four-wave mixing (DFWM) spectroscopy under ambient, bulk-gas conditions. Judicious selection of polarization geometries for incident and detected electromagnetic waves alleviated intrinsic spectral congestion and facilitated dissection of overlapping transitions, thereby enabling refined rotational-tunneling parameters to be extracted for the $\tilde{A}^1\mathrm{B}_2$ ($\pi^*\pi$) manifold. A pronounced 2.14(5) cm^{-1} bifurcation of rovibronic features is measured for the zero-point level of electronically excited TrOD, reflecting the presence of a substantial potential barrier along the $\mathrm{O{-}D \cdots O} \longleftrightarrow \mathrm{O \cdots D{-}O}$ reaction coordinate[a] and representing nearly a ten-fold decrease in magnitude over the analogous tunneling-induced splitting for the parent (TrOH) isotopolog. The dependence of hydron-migration dynamics on internal degrees of freedom will be discussed in light of donor-acceptor displacements incurred by $\pi^* \leftarrow \pi$ electron promotion and structural effects accompanying selective isotopic modification of the tropolone molecular framework.

[a]Estimated to be of 1270.6 cm^{-1} height at the fully-optimized EOM-CCSD/aug-cc-pVDZ level of theory; L. A. Burns, D. Murdock, and P. H. Vaccaro, $J.Chem.Phys.$ **130**, 144304 (2009).