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

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The origin band of the $\tilde{A}^1B_2 - \tilde{X}^1A_1 (\pi^* \leftarrow \pi)$ 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 $\tilde{A}^1B_2 (\pi^* \pi)$ 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 O···D···O $\leftrightarrow$ O···D O reaction coordinate 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).