NONLINEAR SPECTROSCOPIC PROBES OF UNIMOLECULAR DYNAMICS: VIBRATIONALLY-MEDIATED TUNNELING IN $\tilde{X}\,^1\mathrm{A}_1$ TROPOLONE

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The mode specificity of proton-transfer dynamics in the ground state ($\tilde{X}\,^1\mathrm{A}_1$) of tropolone has been explored at near-rotational resolution by implementing a fully coherent variant of stimulated emission pumping within the framework of two-color resonant four-wave mixing spectroscopy (TC-RFWM). Ongoing studies have exploited rovibronically-resolved features of the $\tilde{A} - \tilde{X}$ origin band as a "doorway" for selectively interrogating vibrationally-excited levels of the ground electronic manifold, with judicious selection of incident/detected polarization characteristics affording a means for discriminating rotational branches and alleviating spectral congestion.[a] Several mid-range vibrational transitions ($E_{vib} \leq 1700\ cm^{-1}$) have been interrogated under ambient, bulk-gas conditions, with term energies determined for the symmetric and antisymmetric (tunneling) components enabling the attendant tunneling-induced bifurcations to be extracted.[b] The dependence of tunneling rate (or hydron migration efficiency) on vibrational motion is discussed in terms of corresponding atomic displacements and permutation-inversion symmetries for the tropolone skeleton.

[a] A. E. Bracamonte and P. H. Vaccaro, *J. Chem. Phys.* **119**(2), 887 (2003); **120**(10), 4638 (2004).
[b] D. Murdock, L. A. Burns and P. H. Vaccaro, *J. Chem. Phys.* **127**, 081101 (2007).