THE $\tilde{A}\,^1B_2 - \tilde{X}\,^1A_1$ ($\pi^* \leftarrow \pi$) ABSORPTION SYSTEM OF TROPOLONE: RE-INVESTIGATION AND ANALYSIS OF EXCITED-STATE VIBRONIC FEATURES HAVING $E_{vib} \leq 800\,\mathrm{cm}^{-1}$

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High-resolution spectroscopy can provide valuable insights regarding the ubiquitous processes of hydrogen bonding and proton transfer, especially when the occurrence of quantum mechanical tunneling leads to the bifurcation of observed rovibrational features. A model compound for investigating these phenomena is tropolone where a potential barrier of finite height hinders the symmetric transfer of a hydron between hydroxylic (proton-donating) and ketonic (proton-accepting) oxygen atoms that are attached to adjacent positions on a conjugated, seven-membered ring. The electronically-excited $\tilde{A}\,^1B_2$ ($\pi^*\pi$) state of tropolone has been explored under ambient (bulk-gas) conditions through use of resonantly-enhanced degenerate four-wave mixing (DFWM) spectroscopy, with judicious selection of polarization characteristics for the incident and detected electromagnetic waves allowing for the discrimination of transitions according to their attendant changes in angular momentum, ΔJ. The resulting ability to suppress $Q-$branch ($\Delta J = 0$) or $P-/R-$branch ($\Delta J = \pm 1$) resonances controllably affords a viable means for alleviating rovibronic congestion and for dissecting complex molecular spectra, as demonstrated previously by detailed analyses performed on the tunneling-split origin band of the tropolone $\tilde{A}\,^1B_2 - \tilde{X}\,^1A_1(\pi^* \leftarrow \pi)$ absorption system.[a] This talk will highlight extensions of these efforts designed to probe low-lying portions of the $\tilde{A}\,^1B_2(\pi^*\pi)$ manifold so as to elucidate the vibrational mode-specificity ascribed to the intramolecular proton-transfer reaction. Excited-state vibronic levels extending up to $800\,\mathrm{cm}^{-1}$ above the $\tilde{A} - \tilde{X}$ origin will be discussed for both the parent tropolone species and its deuterated isotopomers.

[a] A. E. Bracamonte and P. H. Vaccaro, *J. Chem. Phys.* **119**, 887 (2003); **120**, 4638 (2004).