

## EFFECTS OF VIBRATIONAL EXCITATION ON THE TUNNELING DYNAMICS OF $\tilde{X}^1A_1$ TROPOLONE

D. MURDOCK, L. A. BURNS, and P. H. VACCARO, *Department of Chemistry, Yale University, P.O. Box 208107, New Haven, CT 06520-8107.*

High resolution spectroscopy can provide valuable insights regarding the ubiquitous processes of proton transfer and hydrogen bonding, particularly when concomitant occurrence of quantum mechanical tunneling leads to the observable bifurcation of rovibrational features. This especially is true in the case of tropolone (2-hydroxy-2,4,6-cycloheptatriene-1-one), where a potential barrier of finite height hinders the symmetric transfer of a hydron between hydroxylic (proton-donating) and ketonic (proton-accepting) oxygen centers that are attached to adjacent positions on a conjugated seven-membered ring. A variety of experimental and theoretical endeavors have attempted to unravel the influence that vibrational and electronic degrees of freedom exert upon the unimolecular dynamics exhibited by this prototypical species. While studies of the first excited singlet state ( $\tilde{A}^1B_2$ ) have shown attendant proton-transfer processes to be highly mode specific (*e.g.*, out-of-plane O–H ··· O motion readily quenches the hydron transfer), information of similar scope and refinement has not been available for the ground electronic state ( $\tilde{X}^1A_1$ ). To remedy this situation, a folded variant of the nonlinear Two-Color Resonant Four-Wave Mixing (TC-RFWM) technique has been enlisted to probe  $\tilde{X}^1A_1$  tropolone under ambient (bulk-gas) conditions. In particular, our work has exploited rovibronically-resolved features of the  $\tilde{A} - \tilde{X}$  absorption spectrum as a “doorway” for selectively interrogating vibrationally-excited levels of the ground electronic manifold, with judicious selection of incident/detected polarization characteristics affording a facile means for discriminating rotational transitions and alleviating spectral congestion.<sup>a</sup> Investigations performed on the low-lying ( $E_{vib} \leq 1000\text{ cm}^{-1}$ ) portions of the  $\tilde{X}^1A_1$  potential energy surface will be highlighted and efforts designed to elucidate vibrational-specificity of the proton-transfer reaction in tropolone will be discussed.

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<sup>a</sup>A. E. Bracamonte and P. H. Vaccaro, *J. Chem. Phys.* **119**(2), 887 (2003); **120**(10), 4638 (2004).