LOW-BARRIER HYDROGEN BONDING IN ELECTRONICALLY-EXCITED ACETYLACETONE

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The *cis*-enol forms of β-diketones are stabilized by the action of strong intramolecular hydrogen bonding that mediates attendant proton-transfer processes. One of the simplest members of this class of compounds, acetylacetone (H_3C-CO-CH_2-CO-CH_3), has been demonstrated (both experimentally and theoretically) to possess an asymmetric equilibrium geometry with the two equivalent enol tautomers of the $\tilde{X}^1A_1$ ground electronic state separated by a barrier of finite height. In contrast, recent *ab initio* calculations[a] have suggested that the less-studied $\tilde{B}^1B_2$ ($\pi^* \leftarrow \pi$) manifold supports a symmetric (C_{2v}) minimum energy configuration. This excited-state structure would imply the presence of a low-barrier hydrogen bond (LBHB), in which the hydrogen is dislocated to a position equidistant from the two oxygen atom centers. Resonance Raman spectroscopy has been used to explore the prediction of an LBHB in acetylacetone and to elucidate the structural changes incurred by $\pi^* \leftarrow \pi$ electron promotion. Vapor-phase measurements were performed at five discrete excitation wavelengths, chosen to span the $\pi^* \leftarrow \pi$ absorption band ($\lambda_{max} \approx 262$ nm) as well as pre-resonant and non-resonant portions of the spectrum. The acquired data displayed marked differences in their vibrationally-resolved intensity patterns. As the incident frequency was tuned toward resonance, vibrations involving distortion of the chelate ring were enhanced, whereas modes localized on the methyl groups did not exhibit significant enhancement. In resonant and pre-resonant spectra, numerous overtone and combination bands were observed in the $1620-2800\,\mathrm{cm}^{-1}$ and $>3000\,\mathrm{cm}^{-1}$ regions. These results are indicative of large geometry changes taking place upon $\pi^* \leftarrow \pi$ excitation, with theoretical analysis based on a time-dependent formalism for Raman scattering being utilized to quantify and interpret such structural modifications.

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[a] H. P. Upadhyaya, A. Kumar, and P. D. Naik, *J. Chem. Phys.* **110**, 11850 (2003).