AN INVESTIGATION OF EXCITED-STATE STRUCTURE AND DYNAMICS IN ACETYLACETONE THROUGH USE OF RESONANCE RAMAN SPECTROSCOPY

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Acetylacetone (AA), one of the simplest β-diketones, exhibits a strong intramolecular hydrogen bond that stabilizes the enol tautomer of the isolated (gas-phase) species and mediates the attendant proton- transfer process. Both experiment[a] and theory[b] have demonstrated conclusively that the $\tilde{X}^1\mathrm{A}_1$ ground electronic state exhibits an asymmetrical equilibrium geometry with a potential barrier of finite height separating two equivalent conformers of C_s symmetry. In contrast, *ab initio* calculations[c] have suggested that the electronically excited $\tilde{B}^1\mathrm{B}_2$ $(\pi^*\pi)$ manifold supports a symmetric (C_{2v}) minimum energy configuration which has the shuttling hydron located midway between the oxygen atom centers. This assertion, with its prediction of a low-barrier hydrogen-bonding motif, has been investigated experimentally by means of Resonance Raman Spectroscopy. Excitation at 266 nm, essentially coincident with the peak of the $\pi^* \leftarrow \pi$ transition, results in Raman profiles dominated by intense spectral features that stem from vibrational modes involving substantial distortion of the chelate ring, including marked displacement of the O$\cdots$O distance. Of special note is the $1620 - 2800\,\mathrm{cm}^{-1}$ region, which is not expected to contain any fundamental transitions, yet exhibits rich structure that has been assigned to overtone and combination bands. All of these data are consistent with a large change in molecular geometry upon electronic excitation. Resonance Raman spectra of deuterated derivatives and structural analogues of AA afford an additional means for unraveling the observed excited-state behavior. Ongoing extensions of these studies will be discussed, as well as efforts toward theoretical analysis based on the time-dependent formalism for Raman scattering.

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[b] V. V. Sliznev, S. B. Lapshina, and G. V. Girichev, *J. Struct. Chem.* **43**, 47 (2002).
[c] H. P. Upadhyaya, A. Kumar, and P. D. Naik, *J. Chem. Phys.* **110**, 11850 (2003).