AN INVESTIGATION OF SUBSTITUENT EFFECTS ON LOW-BARRIER HYDROGEN BONDING

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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. Recent studies performed on acetylacetone (AA), one of the simplest members of this class, have implicated a low-barrier hydrogen bond (LBHB) in the electronically-excited $\tilde{B}\,^1\mathrm{B}_2(\pi^*\pi)$ manifold, with the shuttling proton "locked" midway between two oxygen atom centers. Quantum chemical calculations[a] and photodissociation experiments[b] have indicated that replacement of the methyl groups in AA by electron-withdrawing fluoromethyl moieties adversely affects hydrogen-bond strength. In order to explore the influence of substituents upon LBHB phenomena, Resonance Raman (RR) spectroscopy has been enlisted to interrogate the excited-state structure and dynamics of hexafluoroacetylacetone (HFAA), where steric and electronic factors conspire to yield an unsymmetrical (C_1) equilibrium geometry for the $\tilde{X}\,^1\mathrm{A}_1$ ground state. Vapor-phase RR data acquired at excitation wavelengths chosen to span the $\pi^* \leftarrow \pi$ absorption system ($\lambda_{max} = 266$nm), as well as pre-resonant portions of the spectrum, display significant differences in intensity patterns for vibrations involving distortion of the chelate ring. Of special note is the $1700 - 3300$ cm^{-1} region, which is not expected to contain any fundamentals, yet exhibits rich structure that has been attributed to overtones and combination bands. While prior investigations of AA in our laboratory have shown marked enhancement of RR features involving displacement of the O$\cdots$O distance and wagging of the hydroxylic proton, such behavior is less prominent in the fluorinated analog. These observations suggest that HFAA undergoes smaller structural changes upon electronic excitation, in keeping with assertions of a weaker hydrogen bond and a higher proton-transfer barrier. Ongoing spectroscopic measurements and *ab initio* analyses of HFAA will be discussed, as will concurrent efforts designed to model RR scattering profiles quantitatively.

[a] S. F. Tayyari, F. Milani-Hejad, and H. Rahemi, *Spectrochimica Acta*, **58A**, 1669 (2002).
[b] M. Yoon, Y. S. Choi, and S. K. Kim, *J. Phys. Chem. A*, **104**, 4352 (2000).