EVIDENCE FOR HYDROGEN ATOM DISLOCATION IN EXCITED HEXAFLUOROACETYLACETONE

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The cis-enol tautomers of $\beta$-diketones are stabilized by strong intramolecular hydrogen bonds that mediate proton-transfer events. Recent studies of acetylacetone (AA), one of the simplest members of this class, have provided evidence for a low-barrier hydrogen bond (LBHB) in the excited $\tilde{B}\,^1\mathrm{B}_2(\pi^*\pi)$ state, implying that the hydrogen is shifted to a position equidistant between the two oxygen centers. Since the intrinsic strength of such bonding motifs can be influenced greatly by chemical substitution, Resonance Raman (RR) spectroscopy has been used to probe the analogous hexafluoroacetylacetone (HFAA) system. Vapor-phase measurements were performed at discrete excitation wavelengths, chosen to span the $\pi^* \leftarrow \pi$ absorption system ($\lambda_{max} = 266$nm), as well as pre-resonant and non-resonant portions of the spectrum. The acquired data display pronounced differences in intensity patterns for vibrations ascribed to distortion of the chelate ring, reflecting the key structural changes taking place upon electronic excitation. Detailed analyses of RR experimental results have been performed within the time-dependent (correlation-function/propagator) framework of Raman Scattering, as guided by high-level *ab initio* predictions of requisite first (gradient) and second (Hessian) derivatives in the optically-connected electronic manifolds. The emerging picture of structure and dynamics in electronically-excited HFAA will be discussed and compared to that of AA, with special attention being directed towards the manifestation of hydrogen atom dislocation and low-barrier hydrogen bonding.