ON THE QUANTITATIVE ANALYSIS OF RESONANCE RAMAN SPECTRA: A SYSTEMATIC INVESTIGATION OF HYDROGEN BONDING IN ELECTRONICALLY-EXCITED ACETYLACETONE

S. A. BROADBENT, C. CHATTERJEE, and P. H. VACCARO, *Department of Chemistry, Yale University, P.O. Box 208107, New Haven, CT 06520*; B. R. JOHNSON, *Department of Chemistry, Rice University, P.O. Box 1892, Houston, TX 77251*.

The *cis*-enol tautomers of simple β-diketones such as acetylacetone (H_3C-CO-CH_2-CO-CH_3) are ideal target compounds for the investigation of hydrogen bonding and proton transfer, exhibiting a variety of intramolecular processes (*e.g.*, low-barrier hydrogen bonding) that have been predicted to play pivotal roles in the behavior of substantially larger complexes. Resonance Raman (RR) spectroscopy has been used to probe the electronically-excited $\tilde{B}^1\mathrm{B}_2$ $(\pi^*\pi)$ potential energy surface of acetylacetone, thereby elucidating the changes in structure and dynamics that accompany $\pi^* \leftarrow \pi$ electron promotion of the isolated (vapor-phase) species. Data acquired at discrete excitation wavelengths spanning the $\tilde{B} - \tilde{X}$ absorption system ($\lambda_{max} \approx 262$ nm) displayed pronounced differences in intensity patterns. The selective activity of overtone and combination bands involving displacement of the H–chelated ring indicated a low-barrier, hydrogen-bonding motif for the $\tilde{B}^1\mathrm{B}_2$ manifold. The comprehensive interpretation of all experimental findings was facilitated by *ab initio* geometry optimizations and force-field calculations performed for the pertinent electronic states at substantial levels of coupled-cluster theory (CCSD and EOM–CCSD with augmented correlation-consistent basis sets). The Hessian matrix and gradient vector computed for the electroncially-excited surface at the fully-relaxed ground-state ($\tilde{X}^1\mathrm{A}_1$) geometry led to a harmonically-extrapolated $\tilde{B}^1\mathrm{B}_2$ equilibrium structure that bears evidence for the low-barrier hydrogen bonding phenomenon. The vibrational results emerging from this "vertical Hessian" treatment were employed as initial parameters for a least-squares regression procedure designed to simulate observed RR spectra by means of a time-dependent propagator formalism that incorporated effects arising from the Duschinsky rotation of normal coordinates and the non-Condon character of transition moments. Quantitative information extracted from these analyses will be discussed, with particular emphasis directed towards unraveling the unimolecular dynamics of acetylacetone.