PROTON-TRANSFER AND HYDROGEN-BONDING IN THE GROUND AND FIRST EXCITED SINGLET STATES OF MALONALDEHYDE

A. BRACAMONTE, A. A. ARIAS, and P. H. VACCARO , *Department of Chemistry, Yale University, P.O. Box 208107, New Haven, CT 06520-8107 USA*.

As the smallest organic molecule exhibiting a symmetric hydron migration process mediated by an intramolecular hydrogen bond, malonaldehyde (HO–CH=CH–CH=O) provides a model system for probing the influence of nuclear and electronic degrees of freedom upon unimolecular dynamics. The vibrationless level of the ground electronic potential surface ($\tilde{X}^1A_1$) has been the subject of numerous experimental efforts; however, proton transfer and hydrogen bonding in excited vibrational and electronic states have not been explored extensively. By exploiting polarization-selective Degenerate Four-Wave Mixing (DFWM) spectroscopy to extract information that otherwise would be hidden in the congested room temperature spectrum of bulk (gas-phase) malonaldehyde, this presentation will discuss new evidence for the dramatic changes in hydron dynamics that accompany electronic excitation into the lowest-lying singlet manifold ($\tilde{A}^1B_1$). More specifically, observed $\tilde{A}^1B_1$ tunneling splittings are consistent with a decrease in proton-transfer efficiency upon $\pi^* \leftarrow n$ electron promotion while excitation of O$\cdots$O stretching motion within the $\tilde{X}^1A_1$ potential surface is found to increase the rate of proton transfer substantially.