

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

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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··O stretching motion within the \tilde{X}^1A_1 potential surface is found to increase the rate of proton transfer substantially.