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 ($\tilde{X}^{1}A_{1}$) 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 ($\tilde{A}^{1}B_{1}$). More specifically, observed $\tilde{A}^{1}B_{1}$ tunneling splittings are consistent with a decrease in proton-transfer efficiency upon $\pi^{*} \leftarrow \pi$ electron promotion while excitation of O⋯O stretching motion within the $\tilde{X}^{1}A_{1}$ potential surface is found to increase the rate of proton transfer substantially.