

## ULTRAFAST VIBRATIONAL DYNAMICS OF THE INTRAMOLECULAR H-BOND IN ACETYLACETONE INVESTIGATED WITH 2D IR SPECTROSCOPY

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We report ultrafast transient absorption and 2D IR spectra of the light and deuterated isotopologues of acetylacetone to study the vibrational coupling and dynamics of the strong intramolecular hydrogen bond. Strong 2D IR cross-peaks in the fingerprint region reveal a high level of OH bend character throughout this region. This mode mixing gives rise to a large manifold of OH bend overtone and combination bands in the OH stretch region as evidenced by a highly elongated OH bend excited state absorption transition. As a consequence, strong OH stretch/bend Fermi resonance interactions contribute to a broad OH stretch absorption band that exhibits ultrafast population dynamics on a time scale less than 100 fs. The deuterated species displays similarly strong anharmonic coupling and relaxation dynamics, in addition to coherent oscillations corresponding to the O-O hydrogen bond stretch motion which are absent in the light isotopologue. Polarization anisotropy measurements shows a fast 200 fs reorientation relaxation of the OH stretch while the OD stretch displays a slow 1 ps component. The large isotopic dependence of the anisotropy dynamics is attributed to a combination of differences in anharmonic couplings and proton/deuteron transfer dynamics in the vibrationally hot molecules.