VIBRATIONAL SPECTRAL SIGNATURES AND DYNAMICS OF STRONG INTRAMOLECULAR H-BONDS INVESTIGATED WITH GAS-PHASE ION AND SOLUTION-PHASE ULTRAFAST INFRARED SPECTROSCOPIES

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Strong H-bonding interactions often manifest in extremely broad shared proton stretch vibrational transitions and exhibit ultrafast relaxation dynamics which have made the study of strongly H-bonded systems challenging both experimentally and computationally. Here, we report on the characterization of vibrational signatures and dynamics of strong, neutral intramolecular O-H H-bonds in several model systems by complementing frequency-resolved cryogenic ion vibrational spectroscopy on isolated gas-phase species with ultrafast solution-phase transient and 2D IR spectroscopies. The gas-phase experiments reveal the complex interplay between stretch-bend Fermi resonance interactions and coupling of the proton stretch to H-bond soft-mode vibrations. The nonlinear ultrafast experiments directly reveal the high degree of anharmonic mode mixing and coupling between the OH stretch, OH bend, fingerprint modes, and soft modes and show rapid intramolecular population relaxation dynamics. Significant isotopic dependence in polarization anisotropy dynamics suggest key differences in proton vs. deuteron transfer dynamics in the vibrationally excited systems. Time permitting, the initial steps towards combining ultrafast IR spectroscopies with cryogenic ion techniques for the acquisition of multidimensional and time-resolved spectra of isolated ion ensembles will be discussed.