VIBRATIONAL DYNAMICS OF CYCLIC ACID DIMERS: TRIFLUOROACETIC ACID AND FORMIC ACID IN GAS AND DILUTE SOLUTIONS

STEVEN T. SHIPMAN, PAM L. CRUM, ELLEN L. MIERZEJEWSKI, BRIAN C. DIAN, CHARLOTTE E. HINKLE, HYUN S. YOO, BROOKS H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., P.O. Box 400319, Charlottesville, VA 22904*.

Ultrafast time-domain transient absorption spectroscopy has been used to study the vibrational dynamics of hydrogen bonded cyclic dimers of trifluoroacetic acid (TFA) and formic acid (FA) in both the gas- and solution-phase. A tunable 1.4-ps mid-IR pump pulse initially deposits varying amounts of energy into these dimers and a 300-fs mid-IR probe pulse is used to follow the subsequent structural evolution of the system. Preliminary results on these dimers were presented last year at Ohio State; since then, the introduction of a 32-element HgCdTe array detector has allowed us to simultaneously probe broad regions ($\sim$75 cm^{-1}) of the mid-IR spectrum. In particular, the new detector is better suited for studying dynamics in the carbonyl stretching region. In static (non-time-resolved) measurements, there is an isosbestic point between the monomer and dimer acid species, indicating an equilibrium between the two. However, the TFA and FA dimeric species each possess two hydrogen bonds, whereas the monomers possess none and it is reasonable to suppose that there may be short-lived intermediates (such as linear dimers) between the two with only a single hydrogen bond. The transient absorption measurements provide information on the existence, dynamics, and structural properties of these intermediates.