INFRARED PREDISSOCIATION SPECTROSCOPY OF H_2-TAGGED DICARBOXYLIC ACID ANIONS

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Singly charged dicarboxylic acid anions, studied in depth by Wang et al.[a], offer insight into the role of ring strain and conformation on the formation of intramolecular hydrogen bonds. These shared proton bonds, common in proteins and polymer systems, can be crucial in secondary and tertiary structure formation. By tracking the infrared spectra of dicarboxylic acid anions as charge and aliphatic chain length are varied, the tendency of these anions to form ring-like structures with an internally shared proton can be asssesed. To adapt the time-of-flight mass spectrometry/infrared presdissociation experiment to larger systems with significant latent vibrational energy and negligible vapor pressure, an electrospray ionization (ESI)/cryogenic quadrupole trap ion source has been interfaced to the Yale time of flight mass spectrometer. Infrared predissociation spectroscopy is carried out on a series of carboxylate anions cooled to 10K and H_2-tagged in a cryogenic ion trap, underscoring the power of this technique to vibrationally quench and structurally characterize large ($>$ 20 atoms) gaseous ions. This technique recovers sharp transitions (6 cm^{-1} FWHM) in the linear single photon absorption regime which greatly facilitates comparison with ab initio calculations. The methodology used to condense H_2 on these ions is described, revealing the benefits of a pulsed trapping gas paired with a time delay before ion extraction. The sensitivity of the perturbed H_2 transition to charge center exposure is probed by varying the charge and aliphatic chain length of carboxylate anions. Finally, the structure of four carboxylate anions are characterized using their predissociation spectra.

[a] H. K. Woo, X. B. Wang, K. C. Lau and L. S. Wang *J. Chem. Phys. A* **110**, 7801-7805 2006.