"PROTON SPONGES": A RIGID ORGANIC SCAFFOLD TO REVEAL THE QUANTUM STRUCTURE OF THE INTRAMOLECULAR PROTON BOND

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Spectroscopic analysis of systems containing charged hydrogen bonds (e.g. the Zundel ion, $H_5O_2^+$) in a vibrationally cold regime is useful in decongesting numerous anharmonic features common to room temperature measurements.[Roscioli, J. R.; et. al. Science 2007] This approach has been extended to conjugate acids of the "Proton Sponge" family of organic compounds, which contain strong intramolecular hydrogen bonds between proton donor (D) and acceptor (A) groups at the 1- and 8-positions. By performing H_2/D_2 vibrational predissociation spectroscopy on cryogenically cooled ions, we explore how the proximity and spatial orientation of D and A moieties relates to the spectroscopic signature of the shared proton. In the cases studied ($\mathrm{D = Me_2N - H^+; A = OH, O(C = O)Ph}$), we observe strong anharmonic couplings between the shared proton and dark states that persist at these cryogenic temperatures. This leads to intense NH stretching features throughout the nominal CH stretching region ($2800 - 3000\mathrm{cm}^{-1}$). Isotopic substitution has verified that the oscillator strength of these broad features is driven by NH stretching. Furthermore, the study of A = O(C=O)Ph has provided a spectroscopic snapshot of the shared proton at work as an active catalytic moiety fostering ester hydrolysis by first order acylium fission ($\mathrm{A_{AC}1}$). This is apparent by the high frequency carbonyl stretch at $1792\ \mathrm{cm}^{-1}$, which is a consequence of the strong hydrogen bond to the ether-ester oxygen atom. Thus, these "Proton Sponges" are useful model systems that unearth the quantum structure and reactivity of shared proton interactions in organic compounds.