VIBRATIONAL PREDISSOCIATION SPECTRA IN THE SHARED PROTON REGION OF PROTONATED FORMIC ACID WIRES

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Protonated formic acid networks are thought to form long chains where the excess charge is distributed along the embedded H-bonds holding it together. This system therefore effectively captures anhydrous proton transport at an intermediate state, thereby allowing a detailed look at the underlying mechanism. We present vibrational predissociation spectra of the Ar-tagged (HCOOH)$_n$ H$^+$ cluster ions, formed via supersonic expansion of argon gas seeded with formic acid. The resulting data reveal the first well-defined spectral signatures associated with the collective vibrational motions of the H-bonding backbone, and we follow how these features evolve as the number of formic acid molecules is increased from 2 to 5. Bands in the 700-1500 cm$^{-1}$ range are found to strongly depend on cluster size, and the shifts displaying an even-odd alternation before stabilizing in the n=4 and 5 clusters. We interpret these trends in the context of charge delocalization and the resulting effect on the carbonyl stretches.