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Spectral signatures of large amplitude vibrations in solvated ions. What do the intensities tell us about structure, bonding and dynamics?

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In this talk, I will discuss recent work in our group in which we made connections between proton transfer processes and hydrogen bonding and vibrational frequencies and intensities. Due to the large amplitude motions associated with proton transfer along a hydrogen bond, the vibrational spectra of these systems contain features that cannot be understood by the usual harmonic description of molecular vibrations. The breakdown reflects both the anharmonicity along this coordinate and coupling between this mode and other low frequency modes in these systems. It also reflects changes in the electronic structure as molecules vibrate. The presentation will draw from reported vibrational spectra for systems either containing intra- or intermolecular hydrogen bonds. Both the theoretical approaches used to study these systems and the insights gained from the studies will be described. The theoretical approaches range from the introduction of higher order terms to the harmonic analysis to adiabatic treatments in which the high- and low-frequency modes are treated at different levels of approximation and diffusion Monte Carlo studies in the full dimensionality of the system of interest.