Over the past decades significant progress has been made, which allows spectroscopists to interpret vibrational spectra of molecules that undergo small amplitude displacements from their equilibrium structure. Based on these assignments, one can obtain insights into the structure and bonding of the molecule that is being studied through the use of model Hamiltonians. In this talk, we focus on systems that undergo large amplitude vibrational motions, and where the anharmonicities are manifested in unexpected intensity patterns in the vibrational spectrum. Theoretical and computational approaches used to address such questions will be described, with an emphasis on our group’s work on diffusion Monte Carlo approaches. The ideas will be illustrated through discussions of a variety of protonated and hydrogen bonded systems of current experimental interest including $\text{H}_5^+$, molecules and ions that have intermolecular hydrogen bonds, and ion-water complexes.