INTENSITIES OF FUNDAMENTAL AND OVERTONE VIBRATIONAL TRANSITIONS

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We have measured and calculated vibrational XH-stretching overtone spectra (where X is C,N,O,S,..) for a range of molecules and hydrated complexes (e.g. water dimer). Spectroscopic studies of such systems are difficult because: vibrational overtone transitions have low intensities, species that exhibit intramolecular hydrogen bonding typically have low vapor pressures and hydrated complexes have small equilibrium constants. The use of coupled cluster theory including perturbative triples, CCSD(T) or CCSD(T)-F12, as well as a large augmented basis, aug-cc-pVTZ or VDZ-F12, is necessary to obtain calculated vibrational spectra of near experimental accuracy. We explain the interesting intensity patterns in terms of an anharmonic oscillator local mode model. The intensity ratio of the fundamental to first XH-stretching overtone covers a wide range. In the past decade, we have used this local mode model to explain observed spectra of both molecules and complexes. I will show recent results for amines and complexes with amines and will illustrate how the ratio of calculated to measured intensity can provide the room temperature equilibrium constant for formation of the binary complex, a quantity that is difficult to calculate accurately.