

THEORETICAL DESCRIPTIONS OF THE FUNDAMENTALS OF CH, NH AND OH STRETCH VIBRATIONS WITH SIMPLE MODELS THAT INCLUDE ANHARMONIC EFFECTS

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In this talk I review our work on theoretically modeling of spectra in the frequency range of the fundamentals of high-frequency XH vibrations (where X = C, N, or O) of medium size molecules. These vibrations are often coupled to nearly degenerate overtone and combination bands, and this coupling complicates the interpretation of many spectral features. When a molecule contains multiple XH groups, assigning the spectrum is more difficult, especially when multiple conformers are present. I will present experimental/theoretical collaborative approaches appropriate for addressing these challenges. Our work focuses on molecules for which the densities of states is sufficiently high at the energies of the fundamentals that calculating eigenstate-resolved spectra is not useful due to long time state-mixing effects. Nonetheless, using ideas based on perturbation theory, local modes, effective Hamiltonians, the transferability of anharmonic couplings, and empirical scalings of vibrational frequencies we have developed approaches for modeling complex spectra with Hamiltonians that approach the simplicity of Hückel Hamiltonians. Several molecular systems will be presented to illustrate these ideas as well as one for which it fails entirely.