THE EFFECT OF INTERMOLECULAR MODES ON THE XH-STRETCHING VIBRATIONS IN HYDROGEN BONDED COMPLEXES

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Vibrational spectra of hydrogen bonded bimolecular complexes (XH$\cdots$Y, where X is the hydrogen bond donor atom, and Y is the acceptor atom) have long been a theoretical challenge. Specifically, the XH-stretching motion is difficult to describe due to the effect of the large amplitude intermolecular modes inherent to complexes. We have developed a vibrational model, the Local Mode Perturbation Theory (LMPT) model, to accurately determine the transition wavenumber and oscillator strength of the XH-stretching transition in hydrogen bonded bimolecular complexes. The model is based on a local mode (LM) model of the XH-stretching transition and the effect of the intermolecular modes is included via Rayleigh-Schrödinger perturbation theory. Our model has significantly improved results obtained using the LM model (see Figure). Additionally, our LMPT model does not require a full-dimensional anharmonic calculation, which enables application to large systems and the usage of higher level *ab initio* theory for the required potential energy surfaces. This work was inspired by our recent efforts to accurately determine equilibrium constants of complex formation, which rely on an accurate determination of the oscillator strength of the XH-stretching transition.