

A PATH FROM GAS TO LIQUID: DEVELOPMENT OF MODEL HAMILTONIANS FOR CONDENSED PHASE
LOCAL MODE IR SPECTRA VIA BENZENE (Bz) AND Bz₂

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Condensed-phase systems represent a vast swath of chemical problems that are of biological and atmospheric interest. Force fields for simulations of these liquid phases need to be able to model intermolecular interactions accurately. Moreover, reliable potentials for spectroscopic calculations need to reproduce site energies and molecular properties, as well as predict fluctuations in molecular coupling appropriately. A local mode approach to the calculation of IR spectra of condensed phase systems of CH stretches will be taken. This is justified because solutions of only CH stretches tend to exhibit less correlated network behavior than solutions of mixed CH/XH (X=O,N) stretch solvents due to weaker intermolecular forces. In an effort to understand solvent effects in the condensed phase, previously developed model gas-phase Hamiltonians will be extended to describe liquid CH stretch systems. As a first step, benzene will be investigated due to its high degree of symmetry and availability of force fields that describe its intermolecular interactions. Benzene represents a technical challenge for vibrational spectroscopy due to the presence of a Fermi triad in its CH stretch IR spectrum. By incorporating these couplings into the model Hamiltonian, it will be possible to consider solvent effects on the IR spectrum of the noncovalently bound benzene dimer. Extension of the dimer model to the condensed phase will allow for discussion of other relevant spectra of benzene, especially its vibrational sum-frequency generation (VSFG) spectrum.