EXTENDING THE LOCAL MODE HAMILTONIAN INTO THE CONDENSED PHASE: USING VIBRATIONAL SUM FREQUENCY GENERATION TO STUDY THE BENZENE-AIR INTERFACE

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Surfaces and interfaces play an important role in understanding many chemical process; they also contain molecular configurations and vibrations that are unique compared to those seen in the bulk and gas phases. Sum frequency generated (SFG) vibrational spectroscopy provides an incredibly detailed picture of these interfaces. In particular, the CH stretch region of the spectrum contains an extensive degree of information about the molecular vibrations and arrangements at the surface or interface. The presence of a strong bandwidth SFG signal for the benzene/air interface has generated controversy since it was discovered; since benzene is centrosymmetric, no SFG signal is expected. It has been hypothesized that this signal is primarily a result of bulk contributions that results from electric quadrupole transitions. Our work focuses on testing this conclusion by calculating a theoretical VSF spectrum from pure surface contributions using a mixed quantum/classical local mode Hamiltonian.

We take as a starting point our local mode CH/OH stretch Hamiltonian, that was previously used to study alkylbenzenes, benzene-$(H_2O)_n$, and DPOE-water clusters, and extend it to the condensed phase by including shifts in the intensities and frequencies as a function of the environment. This environment is modeled using a SAPT-based force-field that accurately reproduces the quadrupole for the benzene dimer. A series of independent time-dependent trajectories are used to obtain an ensemble of surface configurations and calculate the appropriate correlation functions. These correlations functions allow us to determine the origins of the VSF signal. Our talk will focus on the challenges of extending our local mode Hamiltonian into the condensed phase.