

Surface of Liquid Water: Three-Body Interactions and Vibrational Sum-Frequency Spectroscopy

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ABSTRACT: Phase-sensitive vibrational sum-frequency experiments on the water surface, using isotopic mixtures of water and heavy water, have recently been performed. The experiments show a positive feature at low frequency in the imaginary part of the susceptibility, which has been difficult to interpret, and impossible to reproduce using two-body (pairwise-additive) water simulation models. We have reparameterized a new three-body simulation model for liquid water, and with this model we calculate the imaginary part of the sum-frequency susceptibility, finding good agreement with experiment for dilute HOD in D₂O. Theoretical analysis provides a molecular-level structural interpretation of these new and exciting experiments. In particular, we do not find evidence of any special ice-like ordering at the surface of liquid water.

Vibrational sum-frequency (VSF) spectroscopy is one of the most powerful experimental techniques for probing the structure of the water liquid/vapor interface.^{1,2} In these experiments, visible and infrared light beams impinge upon the sample, and the intensity of the scattered light at the sum of the two input frequencies is measured, as a function of the infrared frequency. Contributions to the signal come only from molecules that are not centrosymmetric on the average, and hence the technique is surface sensitive. Vibrational resonances, in this case for the OH stretch, appear as peaks in the spectrum. Such VSF spectra have two interesting features:³ a sharp peak at about 3700 cm⁻¹, corresponding to "free" OH groups protruding out from the liquid phase, and a broad peak from 3000 to 3600 cm⁻¹, corresponding to hydrogen-bonded OH groups. The interpretation of this broad peak has been controversial.^{2,4–11}

Two recent experimental developments have dramatically clarified the situation. First, VSF experiments with deuterium isotopes have been very helpful in the interpretation of spectra.⁶ In pure water, intramolecular and intermolecular vibrational coupling causes the vibrational eigenstates for one quantum of OH stretch excitation to spread over a number of molecules, each in a different hydrogen-bonding environment,^{11–13} which makes interpretation of spectra very difficult. But, for example, if one considers dilute HOD in D₂O, the OH stretch is, to an excellent approximation, an isolated chromophore, and so its spectroscopy reflects the environments of individual molecules, and thus can report directly on the structure and dynamics of the D₂O surface.⁶ Second, while the VSF intensity is proportional to the squared magnitude of the relevant complex susceptibility, phase-sensitive detection has now allowed for direct measurement of its imaginary part.^{14–16} The real part has resonant and nonresonant

contributions, while the imaginary part has only resonant contributions. In fact, it is the absorptive imaginary part that is most interesting from a theoretical point of view, and provides the most molecular-level information about the system. Attempts have been made to extract the imaginary part from the VSF intensity,⁶ although in general it is difficult to obtain reliable results with this approach. Therefore, this new technique^{14–16} represents a significant advance.

Thus, new phase-sensitive VSF experiments on H₂O/HOD/D₂O mixtures, extrapolated to dilute H₂O, have provided new data for the imaginary part of the susceptibility for dilute HOD in D₂O.¹⁷ The imaginary part can be positive or negative, depending on the sign of the projection of the OH transition dipole on the surface normal. The data for one particular (*ssp*) polarization show three peaks: the positive free-OH peak at about 3700 cm⁻¹, a negative peak at about 3500 cm⁻¹, and a positive peak at about 3300 cm⁻¹, as shown in Figure 1. The latter two peaks are interpreted¹⁷ as arising from "water-like" three- and four-hydrogen-bonded molecules, whose OH bonds are pointing into the liquid (on average), and from "ice-like" four-hydrogen-bonded molecules, whose OH bonds are pointing toward the vapor (on average), respectively.

As Tian and Shen suggest at the close of their paper,¹⁷ the imaginary part of the VSF spectrum for dilute HOD in D₂O provides important experimental data for comparison with theory. In fact, we have recently calculated¹¹ the imaginary part of the susceptibility for this system, using the SPC/E simulation model,¹⁸ and spectroscopic maps that we have developed.¹⁹ Our spectra do not show the positive feature at low frequency. However, a recent theoretical study of neat H₂O does show this positive feature²⁰ (although its amplitude is smaller than in experiment). The theoretical model and calculations are quite complex,²⁰ and the molecular mechanism suggested to be responsible for the low-frequency peak, anisotropic induced polarization arising from orientational correlations, is very different from that suggested by Tian and Shen.¹⁷

As mentioned above, our calculation¹¹ of the imaginary part of the susceptibility involved simulations of the SPC/E water model,¹⁸ whose potential energy is a sum of pairwise interactions between molecules. This and other pairwise models have been very successful in reproducing structural and dynamical properties of bulk water,²¹ and even a qualitative description of the ice phase diagram.²² Still, it is known from quantum chemistry calculations that the binding energy of liquid water has contributions from three-body interactions accounting for nearly 20% of the energy.^{23–25} Thus, the SPC/E model must be considered an

Received: April 5, 2011

Published: June 15, 2011

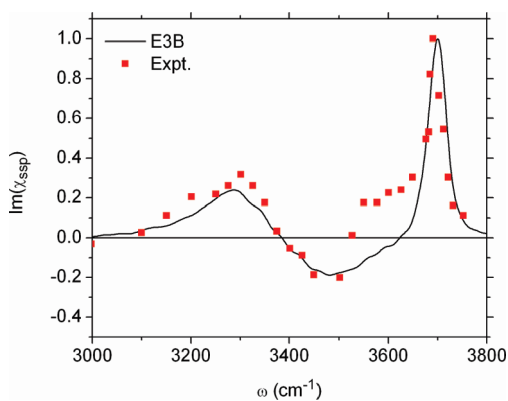


Figure 1. Imaginary part of the *ssp* susceptibility for dilute HOD in D₂O. Red squares are experimental points,¹⁷ deduced from a sample with concentrations of H₂O/HOD/D₂O in the ratio 1/8/16. The solid curve is from theory using the E3B potential.

effective two-body model, wherein three-body interactions are included in some average way.

This suggests the possibility that in a heterogeneous situation such as the water liquid/vapor interface, an effective two-body model is not adequate, and that for this problem one must take three-body interactions into account explicitly.^{26,27} We recently developed a three-body model,²⁸ the form of which was determined from quantum chemistry calculations on water trimers extracted from a liquid-state simulation, and some of the parameters in the model were determined by fitting to experimental data. More extensive and accurate quantum chemistry calculations for the water trimer confirm the correctness of our form of the three-body interactions.²⁹ We have now reparameterized this explicit three-body (E3B) model, fitting to a wide range of experimental data, for the diffusion constant, rotational correlation time, density of the liquid, liquid/vapor surface tension, melting point, and the ice Ih density.³⁰ The robustness of the model was then evaluated by comparing to experiment for a number of other quantities (enthalpy of vaporization, dielectric constant, Debye relaxation time, temperature of maximum density, and the temperature-dependent second and third virial coefficients), with generally good agreement.³⁰ The third virial coefficient is, of course, an excellent test of the potential for three molecules.

We now recalculate the imaginary part of the VSF spectrum using the E3B simulation model, and newly developed spectroscopic maps³¹ (which can be used without modification for any simulation model with the TIP4P geometry and charges, such as this one). Besides the change in the potential, there are some subtle differences between this and our previous calculation,¹¹ namely, that the contribution from different OH chromophores is switched off gradually as the distance from the surface increases, and the position of the OH chromophore is given by the position of its transition dipole (which is intermediate between the O and H atoms).³² Our theoretical E3B results for dilute HOD in D₂O are also shown in Figure 1. One sees good quantitative agreement with experiment, with the three features, two positive and one negative, having about the right intensity and peak frequencies. One also sees a discrepancy between theory and experiment around 3600 cm⁻¹, where experiment shows a positive shoulder and theory does not. At this point we do not understand the origin of this discrepancy, but we intend to consider this issue in the future.

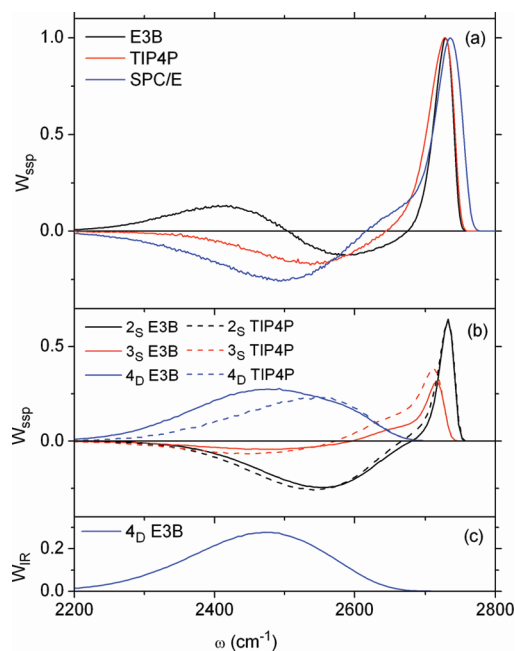


Figure 2. (a) VSF spectral densities for dilute HOD in H₂O obtained using E3B, TIP4P, and SPC/E water models. (b) Main contributions to the total VSF spectral density for different hydrogen-bonding classes, for the E3B and TIP4P models. See text for explanation of notation. (c) 4_D contributions to the bulk liquid IR spectral density for the E3B model.

To ascertain that the appearance of the positive low-frequency feature is due to the three-body interactions in the E3B potential, we need to compare to results from two-body potentials. For simplicity we consider the VSF spectral density instead of the imaginary part of the spectrum (the former is a good approximation to the latter),¹¹ and since we are actually more interested in the properties of H₂O than of D₂O, we consider the OD stretch of dilute HOD in H₂O. The results for the (two-body) TIP4P and E3B models are shown in Figure 2a. One sees that the E3B model shows the positive feature at low frequency, while the TIP4P model does not. Note that the calculation for the TIP4P model used the exact same procedure and spectroscopic maps, showing that the difference must come only from the different interface structure produced by the different model potential. We also show results for the SPC/E model, in this case using the same procedure but with the appropriate spectroscopic maps.^{11,19} Again, the two-body SPC/E model fails to reproduce the positive low-frequency feature. From this we conclude that three-body interactions are crucial for a proper description of the VSF spectrum, and presumably for the structure of the interface as well.

To provide a molecular interpretation of these results, for the E3B and TIP4P models we decompose the VSF spectral density into additive contributions from HOD molecules in different hydrogen-bonding environments. We label the hydrogen-bonding classes by the total number of hydrogen bonds (according to an electronic-structure based definition³³), and a letter (S or D) corresponding to whether the molecule is a single or double donor, respectively.³⁴ Thus, a 2_S molecule is one with two hydrogen bonds, with either the H or D atom donating a hydrogen bond. The main contributions to the total spectral density, which are shown in Figure 2b, arise from 2_S, 3_S, and 4_D molecules. Note that for the 2_S and 3_S molecules, if the single

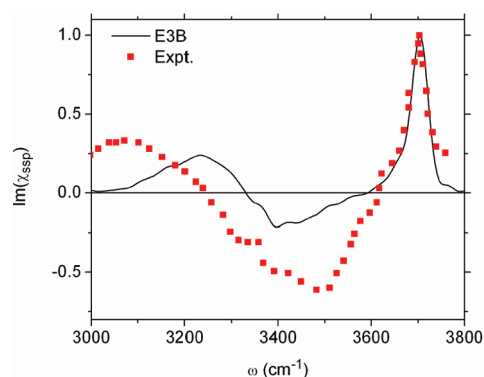


Figure 3. Imaginary part of the *ssp* susceptibility for H₂O. Red squares are experimental points,¹⁷ and the solid curve is from theory using the E3B potential.

donor is the H atom, the D atom is not hydrogen bonded, leading to the (net) positive free-OD peak above 2700 cm⁻¹. On the other hand, if the single donor is the D atom, this produces a (net) negative contribution in the lower-frequency hydrogen-bonding region. The 4_D molecules make a (net) positive contribution, only in the hydrogen-bonding region.

It is important to make several observations about Figure 2b. First, the spectral density from each of the three classes is very broad (in the hydrogen-bonding region), extending from 2200 to 2700 cm⁻¹. Thus, as we have seen before, for the surface and the bulk,³⁵ molecules in a given hydrogen-bonding environment do not generally absorb over a narrow frequency range. Second, the positive and negative features in the total spectral density, and thus the imaginary part of the susceptibility, arise from a delicate cancellation of these broad positive and negative contributions. In particular, the positive low-frequency feature arises from the larger positive contribution of the 4_D molecules at low frequency. Third, the decomposed spectral densities for the TIP4P and E3B models are qualitatively similar (even though their sum is very different), and the positive low-frequency feature for the E3B model can be traced to a slightly larger fraction of 4_D molecules, whose spectral density tail extends to slightly lower frequencies, as shown in the figure. Both of these are due to the extra stabilization of donor–acceptor–donor–acceptor cooperative hydrogen-bonding three-body interactions in the E3B model.²⁸

Our resulting interpretation of the VSF spectrum differs dramatically from that of Ishiyama and Morita,²⁰ in that we do not have anisotropic induced dipoles in our model. Our interpretation also differs from that of Tian and Shen,¹⁷ in that we do not see evidence of ice-like 4_D molecules absorbing over a narrow frequency range. Indeed, the E3B VSF spectral density for 4_D molecules shown in Figure 2b is very similar to the IR spectral density (which can only be positive¹³) for bulk liquid 4_D molecules shown in Figure 2c. Thus, the 4_D molecules at the surface are similar to those in the bulk, implying that there is no particular ice-like ordering at the surface of liquid water.

We conclude by summarizing the three main points of this paper. First, three-body interactions appear to be essential for describing the VSF spectrum of the water surface, and presumably for the structure of the interface as well. Second, the positive and negative features in the imaginary part of the susceptibility arise from delicate cancellations of broad (in frequency) contributions from molecules in different hydrogen-bonding environments (and hence these features are not due to relatively

narrow positive or negative resonances). Third, our description of the VSF spectrum does not reflect any ice-like ordering at the surface of liquid water.

For completeness, in Figure 3 we show the experimental¹⁷ and theoretical VSF results for pure H₂O. There are significant differences between these results and those shown in Figure 1, due to intramolecular and intermolecular vibrational coupling, as discussed above. This coupling makes the experiments more difficult to interpret, and the theory more difficult to calculate. Agreement between theory and experiment is clearly not as good for this case as it is for HOD/D₂O, although the features of the experiment are still described qualitatively by the theory. A more thorough discussion of results for both pure liquids (H₂O and D₂O) and both dilute isotope mixtures will appear elsewhere.

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ACKNOWLEDGMENT

We thank NSF and DOE for support of this research, from CHE-1058752 and DE-FG02-09ER16110, respectively.

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