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Vibrational Spectroscopy of Water at Interfaces

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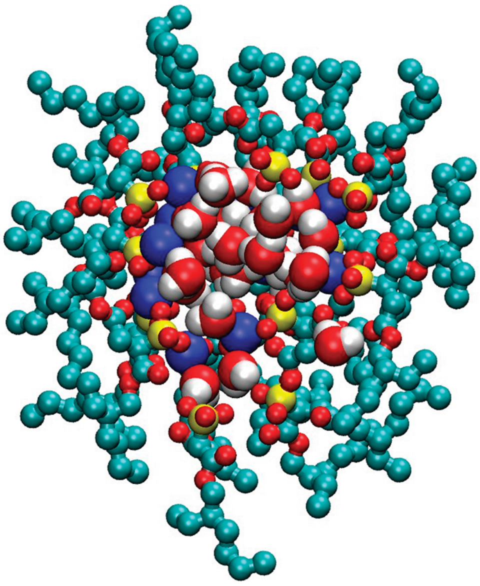

Understanding liquid water's behavior at the molecular level is essential to progress in fields as disparate as biology and atmospheric sciences. Moreover, the properties of water in bulk and water at interfaces can be very different, making the study of the hydrogen-bonding networks therein very important. With recent experimental advances in vibrational spectroscopy, such as ultrafast pulses and heterodyne detection, it is now possible to probe the structure and dynamics of bulk and interfacial water in unprecedented detail.

We consider here three aqueous interfaces: the water liquid–vapor interface, the interface between water and the surfactant headgroups of reverse micelles, and the interface between water and the lipid headgroups of aligned multi-bilayers. In the first case, sum-frequency spectroscopy is used to probe the interface. In the second and third cases, the confined water pools are sufficiently small that techniques of bulk spectroscopy (such as FTIR, pump-probe, two-dimensional IR, and the like) can be used to probe the interfacial water. In this Account, we discuss our attempts to model these three systems and interpret the existing experiments.

For the water liquid–vapor interface, we find that three-body interactions are essential for reproducing the experimental sum-frequency spectrum, and presumably for the structure of the interface as well. The observed spectrum is interpreted as arising from overlapping and canceling positive and negative contributions from molecules in different hydrogen-bonding environments. For the reverse micelles, our theoretical models confirm that the experimentally observed blue shift of the water OD stretch (for dilute HOD in H_2O) arises from weaker hydrogen bonding to sulfonate oxygens. We interpret the observed slow-down in water rotational dynamics as arising from curvature-induced frustration. For the water confined between lipid bilayers, our theoretical models confirm that the experimentally observed red shift of the water OD stretch arises from stronger hydrogen bonding to phosphate oxygens. We develop a model for heterogeneous vibrational lifetime distributions, and we implement the model to calculate isotropic and anisotropic pump-probe decays. We then compare these results with experimental data.

Clearly, recent experimental advances in vibrational spectroscopy have led to beautiful new results, providing information about the structure and dynamics of water at interfaces. These experimental and concomitant theoretical advances (particularly the unified theoretical framework of non-linear response functions) have greatly contributed to our understanding of this unique and important substance.

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I. Introduction

Liquid water is a unique and important substance, characterized by its molecular structure, dynamics, and thermodynamics. It is convenient for chemists to discuss these properties in terms of hydrogen bonding, for example, the average number of hydrogen bonds per molecule, the time scale for making and breaking hydrogen bonds, and so forth.[1] As important as the properties of bulk water are, it is perhaps even more important to understand the analogous properties of water at interfaces. In atmospheric sciences, an important interface is the surface of a water droplet, where adsorption, reaction, and evaporation occur. In biology, important interfaces are at the surfaces of, for example, proteins and membranes. The structure of water at protein surfaces controls the thermodynamics of solvation and folding. Water at membrane surfaces affects membrane stability, permeability, and other properties. The properties of water at these and other important interfaces can be very different from those of water in the bulk.

One powerful approach for understanding water stucture and dynamics involves infrared (IR) spectroscopy, particularly of the OH stretch.[2] This is an effective technique because the frequency of a local OH stretch is very sensitive to its molecular environment, and hence, at every instant in time, it is a good reporter of local structure. As the environment rearranges in time due to molecular dynamics, the OH stretch frequency changes accordingly, and so it is also a good reporter of local dynamics. One complication of OH stretch spectroscopy in water arises from intra- and intermolecular vibrational coupling, which means that the instantaneous vibrational eigenstates are not actually localized on one OH bond, or even one molecule, and that time-domain observables have strong contributions from vibrational energy transfer.[3−5] One can alleviate this complication by studying dilute HOD in H_2O or D_2O, focusing on the OD or OH stretch of the HOD molecule, respectively. In these cases, the effects of vibrational coupling are minimized, since the OD and OH stretch frequencies are so far off resonance.[2]

In this paper, we will consider water at three different interfaces, the first of which is the water liquid/vapor interface. In order to study water only at the interface (and not in the bulk), one requires a surface-sensitive technique such as sum-frequency generation.[6,7] Seminal experiments were first performed by Shen and co-workers on H_2O.[8] The first experiments using isotope dilution were performed by Richmond and co-workers.[9,10] The first phase-sensitive experiments, which determine the all-important imaginary part of the signal directly, were very recently performed by Shen and co-workers.[11,12] They discovered a low-frequency peak that is positive in sign, indicating that the OH dipoles are pointing out toward the vapor phase. This feature has resisted theoretical description (but see refs 13 and 14). Herein, we show that, with a new water simulation model,[15,16] involving explicit three-body interactions, we reproduce the positive low-frequency peak and also provide a molecular interpretation of its origin.[17,18] Some very recent and very high resolution heterodyned sum-frequency measurements[19] have shown that the free-OD peak of dilute HOD in H_2O is red-shifted from the free OD peak in neat D_2O by 17 cm^{-1}. We also qualitatively reproduce this result with our calculations.[19] The blue-shift in the neat liquid relative to the dilute case is interpreted as arising from intramolecular vibrational coupling. Using a theoretical estimate of the size of this coupling, we can infer the frequency of the "other" (hydrogen-bonded) OD on the same molecule, which absorbs close to the average frequency for bulk water. We take this to be evidence for a very sharp interface.[19]

The second interfacial system we consider is water confined inside AOT (bis(2-ethylhexyl)sulfosuccinate) reverse micelles. These are made from ternary mixtures of a nonpolar liquid (like iso-octane), a surfactant (like AOT), and water. The nonpolar liquid is in excess, and the size of the self-assembled reverse micelles is determined by the ratio of the water to surfactant concentrations, called w_0. In this way, the number of water molecules confined by the surfactant headgroups ranges from about 25 to tens of thousands, providing controlled model systems for studying confined water. Ultrafast IR spectroscopy experiments on water (actually dilute HOD in H_2O) in AOT (an anionic surfactant) reverse micelles have been performed by Fayer and co-workers[20−23] and others,[24,25] as a function of micelle size. Fourier transform infrared (FTIR) spectra blue-shift (compared to that of bulk water) as the micelle size decreases, as a result of weaker hydrogen bonds with sulfonate oxygens. Spectral diffusion (the dynamics of frequency fluctuations) and rotational dynamics, as measured by echo peak shift and pump−probe experiments, respectively, are both markedly slower than those in bulk water, and the time scales increase with decreasing micelle size. In this Account, we summarize our efforts to model this system and these experiments and to provide a molecular-level interpretation.

The third interfacial system we consider is water confined between lipid bilayers. This binary system is characterized by the ratio of water to lipid concentrations, *X*. Similar to the case of reverse micelles, these systems allow one to study water very close to the lipid headgroups. Fayer and co-workers[26] performed ultrafast IR spectroscopy experiments on a system with aligned zwitterionic dilauroylphosphatidylcholine (DLPC) lipid multibilayers, with X ranging from 2 to 16. In contrast to the situation with water in reverse micelles, FTIR spectra (for dilute HOD in H_2O) are red-shifted compared to those in bulk water, due to stronger hydrogen bonding to charged phosphate groups.[26] Like in reverse micelles, rotational dynamics is slowed down considerably as the hydration level decreases.[26,27] In this Account, we also summarize our efforts to model this system and these experiments.

II. General Theoretical Considerations

To model each of these systems, we use a mixed quantum/classical approach, where the OD or OH stretch of interest is treated quantum mechanically, and all other nuclear degrees of freedom are either frozen (as is the case for other high-frequency stretches) or treated classically with a molecular dynamics simulation. To model the vibrational spectroscopy, at each time step in the simulation, we need to determine the (anharmonic) frequency for the transition between the ground and first excited quantum states of the OD or OH stretch, and the magnitude of the transition dipole moment. For the sum-frequency spectroscopy, we also need the transition polarizability. For these we use "maps", determined from electronic structure and nuclear quantum mechanical calculations on clusters of water molecules, with or without anions and cations present.[3,18,28−34] The molecular dynamics simulation produces trajectories for these fluctuating quantities, which are then used within the mixed quantum/classical framework to calculate the spectroscopic observables.[35]

For example, the FTIR line shape for an OD or OH stretch chromophore is given approximately by[36]

$$I(\omega) \sim \mathrm{Re} \int_0^\infty \mathrm{d}t\, e^{i\omega t} \left\langle m_x(t)\, m_x(0)\, e^{-i\int_0^t \mathrm{d}\tau \{\omega(\tau) - \frac{i}{2T_1(\tau)}\}} \right\rangle \qquad (1)$$

where $m_x(t)$ is the (lab-fixed) x component of the fluctuating (in time) transition dipole moment, $\omega(t)$ is the fluctuating transition frequency, $T_1(t)$ is the fluctuating vibrational lifetime of the first excited state (in some cases the lifetime depends on the molecular environment), and the brackets denote a classical ensemble average (obtained in practice by averaging over all possible locations for the H or D atom, and from a time-average over the trajectories). For an isotropic system, the choice of lab-fixed component is arbitrary, while for the aligned bilayer system, if the $\hat{z}$ axis is normal to the bilayers and the k vector of the light is along $\hat{z}$,[26] then one would want to consider the x (or y) component, as above.

For the *ssp* sum-frequency experiment, the resonant susceptibility is given by[37]

$$\chi_{ssp}(\omega) \sim i \int_0^\infty \mathrm{d}t\, e^{i\omega t} \left\langle a_{xx}(t)\, m_z(0)\, e^{-i\int_0^t \mathrm{d}\tau\, \omega(\tau)} \right\rangle e^{-t/2T_1} \qquad (2)$$

where $\hat{z}$ is now the surface normal and a_{xx} is the transverse diagonal component of the transition polarizability tensor. In this case, we have assumed a constant lifetime.

Other observables can be calculated with similar but more complicated expressions. Details of the molecular dynamics simulations and the spectroscopic maps are provided in the original papers.[18,38,39]

III. The Water Liquid/Vapor Interface

Our previous efforts[37] to calculate the imaginary part of the *ssp* susceptibility for dilute HOD in H_2O or D_2O used the SPC/E water simulation model,[40] and failed to produce the positive low-frequency peak observed experimentally very recently.[11,12] The SPC/E model is an example of a rigid (nonvibrating) two-body (the potential is a sum of pairwise interactions) model. On the other hand, it is known that three-body interactions contribute considerably to the binding energy for water clusters and liquid water.[41,42] Thus, the SPC/E model must be considered an *effective* two-body model, wherein the three-body interactions are included in some average or mean-field way. Such a treatment of these three-body interactions evidently works reasonably well for bulk water, where the molecules are in centro-symmetric environments (on the average). But at the surface of liquid water, where the symmetry is broken, it is not clear that such a model will still work well.

The usual treatment of three-body interactions involves a polarizable potential. We, however, wanted to develop a potential model where the three-body interactions are treated explicitly. We used electronic structure calculations to determine the form of the three-body interactions,[15] which was later confirmed by Bowman and co-workers,[43] and experiment to parametrize them.[16] Our new three-body model, called E3B (for explicit three-body), is quite robust, providing reasonably accurate properties for the liquid, the liquid/vapor interface, the second and third virial coefficients, and the melting point.[16]

We then used this model to calculate the sum-frequency spectrum, from a simulation of the liquid/vapor interface.[18] The imaginary part of the *ssp* susceptibility, for dilute HOD in

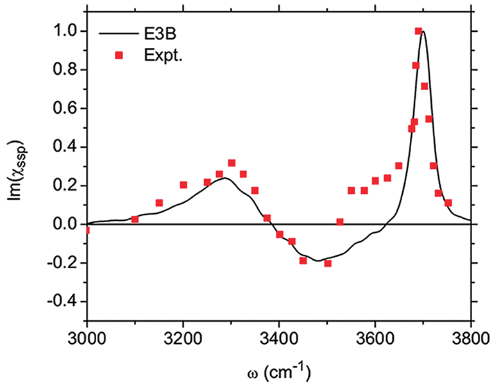

FIGURE 1. Imaginary part of the *ssp* susceptibility for dilute HOD in D_2O. The red squares are the experimental points,[12] and the solid curve is from theory using the E3B potential.[17]

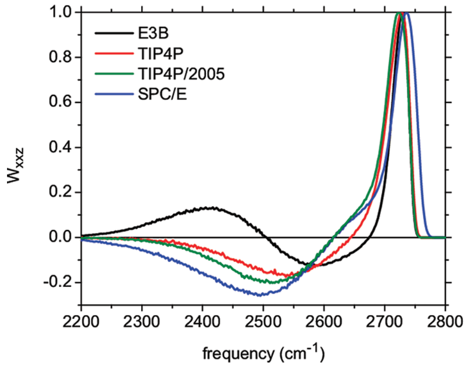

FIGURE 2. *ssp* spectral densities for dilute HOD in H_2O from several different simulation models, as labeled.[17]

D_2O, is shown in Figure 1. Also shown are the experimental results (deduced from finite HOD concentrations) by Tian and Shen.[12] The correspondence between theory and experiment for all three positive and negative features is quite good (except the theory does not produce the shoulder to the red side of the free−OH peak at 3700 cm^{-1}). The positive "free-OH" feature at about 3700 cm^{-1} has not been difficult to reproduce theoretically;[37,44−46] most importantly, here the theory reproduces the positive low-frequency peak.

First let us ascertain that the positive low-frequency peak results from the three-body interactions. In Figure 2, we show the spectral density (which is closely related to the imaginary part of the susceptibility[46]) for dilute HOD in H_2O, for the E3B model, and for the SPC/E model and two other two-body models (TIP4P[47] and TIP4P/2005[48]). None of the two-body models produce the positive low-frequency peak (while the E3B model does). The E3B model is similar to the TIP4P model (in that it uses that model as a reference), and so the methods used to calculate the spectroscopic signal are identical, implying that any difference in the spectral density must be due to different molecular configurations, as sampled during the course of the molecular dynamics simulation. This leads us to believe that three-body interactions are essential for a proper description of the sum-frequency spectroscopy, and presumably for the structure of the interface as well.

We can then go on to develop a molecular understanding of the sum-frequency spectrum. We decompose the spectral density into additive contributions from molecules in different hydrogen-bonding environments.[37,46] The major contributions come from single-donor molecules with a total of two hydrogen bonds (called 2_S molecules), single-donor molecules with a total of three hydrogen bonds (3_S), and double-donor molecules with a total of four hydrogen bonds (4_D).[18] The 2_S and 3_S molecules contribute to all frequencies of the spectral density, while the 4_D molecules contribute only in the lower-frequency hydrogen-bonding region. In this region, the (net) spectral densities for the 2_S and 3_S molecules are negative, while that for the 4_D molecules is positive, and, interestingly, all three spectral densities have contributions over the entire frequency range. Thus, the positive feature at low frequency arises from a delicate cancellation of these spectral densities. This interpretation is not consistent with the idea of icelike ordering at the liquid surface.[12,49]

Recent heterodyne-detected sum-frequency experiments are able to resolve a small blue-shift of 17 cm^{-1} from the free OD peak of dilute HOD in H_2O to that of neat D_2O, in the imaginary parts of the susceptibilities.[19] This shift is attributed to the effects of intramolecular vibrational coupling between the two stretch local modes, which are noticeable for D_2O, but not for HOD (because of the frequency mismatch). Our sum-frequency theory for coupled chromophores[37] is able to reproduce qualitatively this effect.[19] A knowledge of the coupling constant for a D_2O molecule stradling the interface,[18] together with the measured blue-shift, gives us an estimate of the frequency of the "other" OD bond (the one pointing in toward the liquid) of this surface molecule, which is near that of the bulk liquid, indicating that the interfacial width is very short indeed.[19]

IV. Water in Reverse Micelles

We simulate[38] these systems with an all-atom model of isooctane, AOT surfactant, and water,[50] for $w_0 = 2$, 4, and 7.5, corresponding to 52, 140, and 525 molecules confined in the interior, respectively. A snapshot of the smallest ($w_0 = 2$) micelle is shown in Figure 3. Note the irregularlity of the water nanopool shape. For these nanopools of water, nearly

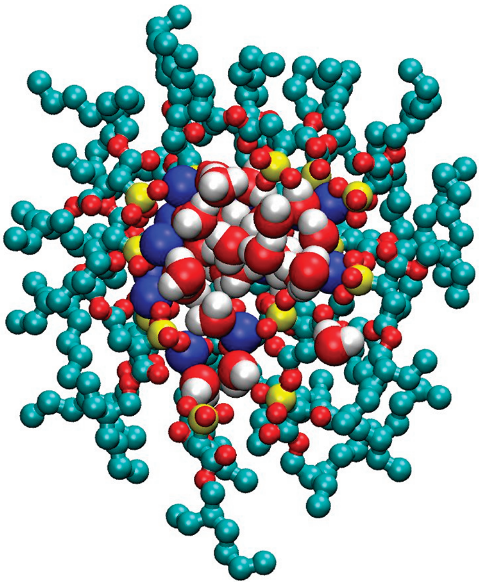

FIGURE 3. Snapshot cross section for the $w_0 = 2$ reverse micelle.[38] The nonpolar iso-octane phase is omitted for clarity. Atoms are as follows: oxygen (red), hydrogen (white), sodium (blue), sulfur (yellow), and carbon (cyan).

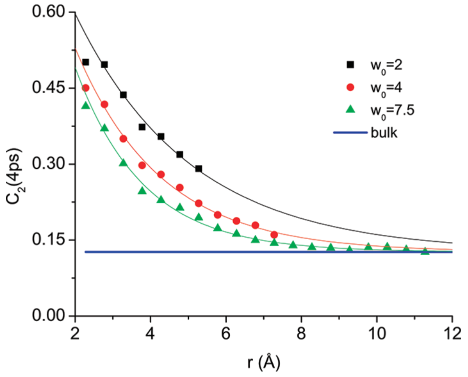

FIGURE 4. Rotational "P_2" time-correlation function at 4 ps for water in the reverse micelles for different distances from the headgroups.[38] The distance is defined as that between the water oxygen and the nearest sulfonate oxygen. The blue line shows the value for bulk water. For each reverse micelle, the solid lines are exponential fits, which show that the smaller the micelle, the farther from the interface the water molecules must be to attain bulklike dynamics.

all molecules feel the effect of the surfactant headgroups, and so one can study these interfacial perturbations with conventional FTIR and nonlinear vibrational spectroscopy.

As mentioned earlier, the FTIR line shape of dilute HOD in H_2O (in the nanopools) shifts to the blue as w_0 decreases,[20] corresponding to weaker hydrogen bonding with the sulfonate headgroups (than with other waters). Our spectroscopic model captures these shifting line shapes quite well.[38] We also calculate the frequency time-correlation function and the "P_2" rotational time-correlation function for the different micelle sizes and compare to results deduced from echo peak shift and pump−probe experiments,[20] respectively. Agreement with experiment is qualitative, but the trends are correctly reproduced; both spectral diffusion and reorientation dynamics slow down considerably as the nanopools decrease in size.

What is the physical origin of this slow-down? Is it a confinement effect, resulting from a spherical nanopool of finite size? Or is it due to specific interactions with the surfactant headgroups, more of which occur for smaller micelles? Experiments on surfactants with neutral headgroups, and headgroups of different sign, give quite similar results, suggesting that it is a confinement effect.[51] To consider these issues, we calculated the P_2 time-correlation function for HOD molecules at different distances from the nearest surfactant headgroup, for different micelles sizes. Specifically, we compared the value of this time-correlation function at one (arbitrary) time, 4 ps, and plotted this as a function of distance. The results[38] are shown in Figure 4. A striking feature is that, at every distance from the interface, rotational relaxation is slower as the micelle gets smaller. We interpret this as resulting from "curvature-induced frustration". This is consistent with the idea that the slow-down is more a confinement effect than one resulting from specific headgroup interactions. Note, however, that specific interactions necessarily play a role in this frustration. Also note that the surfactant/water interface in these reverse micelles is quite rough, and the nanopools are not spherical, making it difficult to isolate any effect as being due to confinement alone.[38]

V. Water in Hydrated Lipid Multi-Bilayers

The system studied in this section is aligned and stacked DLPC lipid bilayers, hydrated with variable amounts of water. Closely following the recent study of this system by Zhang and Berkowitz,[27] we[39] have performed simulations of this zwitterionic lipid in water. Snapshots at two different hydration levels are shown in Figure 5. For $X = 2$, note that each water molecule is in close proximity to lipid atoms.

One interesting feature of the FTIR spectra for this system (with dilute HOD in H_2O) is that the line shapes shift to the red with decreasing hydration[26] (rather than to the blue, as above). Zhao et al. suggested that this is due to stronger hydrogen bonding to the phosphate moieties of the zwitterionic headgroup.[26] We calculated the FTIR spectra with our spectroscopic model and found qualitative agreement with experiment, in terms of the sign and magnitude of the spectral shift.[39] We analyzed the red shift by considering

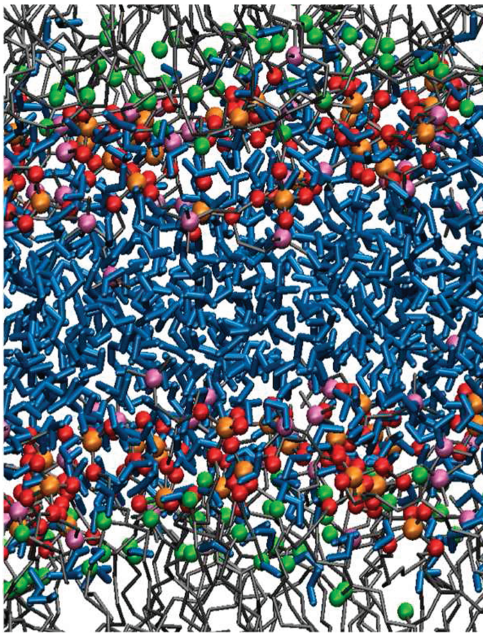

FIGURE 5. Snapshots of equilibrated lipid bilayers for two different hydration levels, $X = 2$ and 16.[39] The water molecules are blue, and other atoms are as follows: phosphate oxygen (red), carbonyl oxygen (green), nitrogen (pink), phosphorus (orange), and (united) carbon (gray).

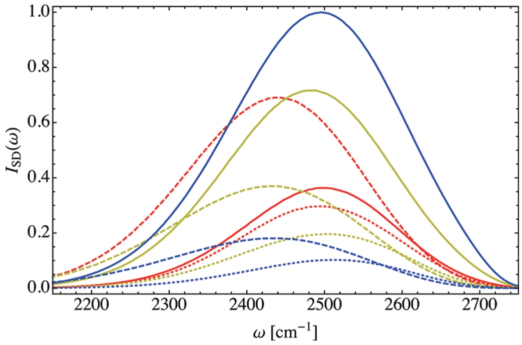

FIGURE 6. Spectral densities for HOD in H_2O in the hydrated multibilayers, with $X = 2$ (red), 6 (yellow), and 16 (blue).[39] The contributions are from water-associated (solid lines), phosphate-associated (dashed lines), and carbonyl-associated (dotted lines) water molecules. Note that the shapes and positions of each contribution are roughly independent of hydration level.

the spectral densities for HOD molecules in different molecular environments: phosphate-associated, carbonyl-associated, and water-associated. This decomposition, for different hydration levels, is shown in Figure 6. One sees that, roughly speaking, the observed red-shift simply comes from an increasing fraction of phosphate-associated molecules, as the hydration level decreases.

We also calculate the experimentally measured isotropic and anisotropic pump−probe signals.[26] These calculations are tricky because the vibrational lifetime of the OD stretch appears to be sensitive to the molecular environment. One can include this effect of a fluctuating lifetime, for example as in eq 1 for the line shape, as long as one has a molecular model for the lifetime distribution. Following ideas of Zhao et al.,[26] we develop such a model where the lifetime can have two values, depending on whether the OD is water-associated or lipid-associated. We then use this model to calculate the isotropic pump−probe signal. Comparison with experiment allows us to determine the lifetimes of these two populations as a function of hydration level. We can then use this information to calculate the anisotropic pump−probe signal and compare to experiment. In this case, agreement with experiment is quite good, especially at low and high hydration, showing a dramatic slow-down of rotational dynamics as the hydration level decreases.[39]

VI. Conclusions

Recent experimental advances in vibrational spectroscopy (ultrafast pulses, heterodyne detection, etc.) have led to beautiful new results, providing information about the structure and dynamics of water at interfaces. In this Account, we have considered some very recent experiments on water at three different interfaces. For the free water surface, current experiments provide information more about interface structure than dynamics, but 2DSFG spectral diffusion experiments are on the horizon.[52,53] We have provided what we believe is a convincing interpretation of new phase-sensitive measurements on isotopically diluted samples, in terms of hydrogen-bonding structure at the interface. The reverse micelle experiments are more focused on dynamics. We interpret the slow-down in rotational dynamics in terms of curvature-induced frustration. The lipid multi-bilayer system presents an example of a particular theoretical challenge, that of a heterogeneous and fluctuating lifetime distribution. We have discussed a possible scenario for dealing with this challenge.

How *is* water at interfaces different from that in the bulk? At the liquid/vapor interface, there appears to be no "icelike" reconstruction. In other words, distributions of the different kinds of hydrogen-bonded molecules seem to be similar to those in the bulk liquid, although of course the populations of the molecules with more hydrogen bonds decrease rapidly as one moves through the interface.[18] The interface is surprisingly sharp,[19] meaning, for example, there are double-donor four-hydrogen-bonded molecules within a few Ångstroms of the surface.[18] The interface of water in the reverse micelle nanopools with the surfactant headgroups is quite rough. The dynamics of water in the smallest micelles is much (several hundred times) slower than that in the bulk. A tentative conclusion is that this is a confinement effect, only weakly dependent on the details of the interactions with surfactant headgroups.[51] But because confinement always involves a confining potential, which, experimentally anyway, is not smooth or spherical, it will always be difficult to disentangle these two effects. Like with the reverse micelles, the dynamics of water in hydrated lipid multibilayers is much slower than that in bulk water (especially at low hydration levels). At low hydration levels, nearly all water molecules are associated with lipids. Water penetrates deeply into the headgroup region, which at first glance is perhaps surprising. But for phosphatidylcholine lipids, water can interact favorably with phosphate and carbonyl groups, which are, in fact, 5−10 Å from the headgroup surface.

Along with experimental advances have come theoretical advances, particularly the unified theoretical framework of nonlinear response functions.[35] Within a mixed quantum/classical approach, the framework allows one to calculate different experimental observables for very complex systems, by including non-Gaussian frequency fluctuations, non-Condon effects,[54] rotational dynamics, and heterogeneous fluctuating lifetime effects. Clouding this otherwise sunny picture are lingering doubts about force field validity, spectroscopic map accuracy, the neglect of nuclear quantum effects, and the phenomenological treatment of vibrational relaxation. Clarifying these issues are all research problems for the future.

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BIOGRAPHICAL INFORMATION

James L. Skinner attended the University of California at Santa Cruz, where he was a double major in physics and chemistry. He then entered Harvard University, where he studied with Professor Peter Wolynes, receiving his Ph.D. in chemical physics in 1979. He did his postdoctoral work at Stanford under the direction of Hans Andersen. In 1981, Skinner joined the faculty of Columbia University, and in 1990 he moved to the University of Wisconsin, as the Joseph O. Hirschfelder Professor of Chemistry and Director of the Theoretical Chemistry Institute. He served as Department Chair during 2004−2007. Skinner's research interests are in the theoretical chemistry of condensed phases.

Piotr A. Pieniazek received his M.S. degree from the Gdansk University of Technology in 2003 with Prof. Janusz Stangret, investigating hydrophobic hydration using infrared spectroscopy. He then moved to the University of Southern California to obtain his Ph.D. in 2008 with Prof. Anna I. Krylov and Prof. Stephen E. Bradforth. His research was focused on the development of electronic structure methods for the description of open-shell systems. He did his postdoctoral work with Prof. James L. Skinner at the University of Wisconsin—Madison working on theoretical spectroscopy and molecular modeling of confined and interfacial water. His research interests include collective dynamics in heterogeneous environments and its impact on nonlinear spectroscopy.

Scott M. Gruenbaum graduated from Miami University in 2005 with a B.S. in chemistry and mathematics. He received his Ph.D. in chemistry in 2010 from Cornell University, working with Professor Roger F. Loring on the semiclassical calculation of nonlinear vibrational response functions. In 2010, he joined the group of Professor James L. Skinner at the University of Wisconsin—Madison as a postdoctoral researcher, where he currently studies the vibrational spectroscopy of hydration water in complex environments such as in lipid bilayers. His other research interests include quantum dynamics and vibrational energy flow in molecules.

FOOTNOTES

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