

## Integration or Segregation: How Do Molecules Behave at Oil/Water Interfaces?

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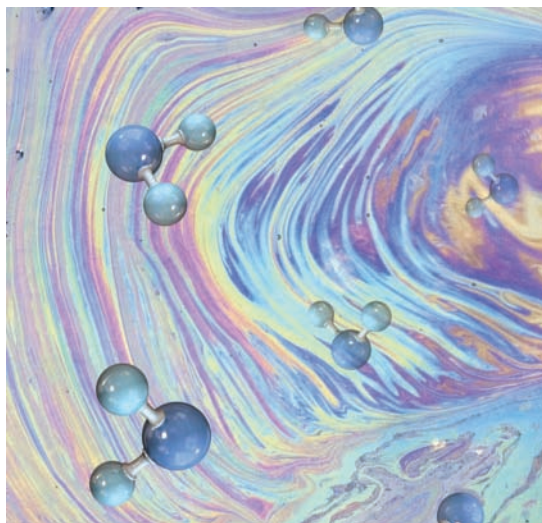
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### CONSPECTUS

It has been over 250 years since Benjamin Franklin, fascinated with the wave-stilling effect of oil on water, performed his famous oil-drop experiments; nevertheless, the behavior of water molecules adjacent to hydrophobic surfaces continues to fascinate today. In the 18th century, the calming of the seas seemed the most pertinent application of such knowledge; today, we understand that oil-on-water phenomena underlie a range of important chemical, physical, and biological processes, including micelle and membrane formation, protein folding, chemical separation, oil extraction, nanoparticle formation, and interfacial polymerization. Beyond classical experiments of the oil–water interface, recent interest has focused on deriving a molecular-level picture of this interface or, more generally, of water molecules positioned next to any hydrophobic surface. This Account summarizes more than a decade's work from our laboratories aimed at understanding the nature of the hydrogen bonding occurring between water and a series of organic liquids in contact. Although the common perception is that water molecules and oil molecules positioned at the interface between the immiscible liquids want nothing to do with one another, we have found that weak interactions between these hydrophilic and hydrophobic molecules lead to interesting interfacial behavior, including highly oriented water molecules and layering of the organic medium that extends several molecular layers deep into the bulk organic liquid. For some organic liquids, penetration of oriented water into the organic layer is also apparent, facilitated by molecular interactions established at the molecularly thin region of first contact between the two liquids. The studies involve a combined experimental and computational approach. The primary experimental tool that we have used is vibrational sum frequency spectroscopy (VSFS), a powerful surface-specific vibrational spectroscopic method for measuring the molecular structures of aqueous surfaces. We have compared the results of these spectroscopic studies with our calculated VSF spectra derived from population densities and orientational distributions determined through molecular dynamics (MD) simulations. This combination of experiment and theory provides a powerful opportunity to advance our understanding of molecular processes at aqueous interfaces while also allowing us to test the validity of various molecular models commonly used to describe molecular structure and interactions at such interfaces.



### Introduction

We are all familiar with the adage that “oil and water don’t mix”. Likely too, we are all familiar with the practical consequences of this reality from oil slicks to prismatic layers on rain puddles. So

inured to these occurrences have we become that it is difficult to realize even these most basic oil-on-water behaviors mesmerized accomplished naturalists 200 years ago. Indeed, Benjamin Franklin found these effects so intriguing that he vowed to carry oil with him “in the hollow joint of

my bamboo cane" whenever he went into the country so as to be able to repeat his experiment: the creation of acre-wide oil slicks on ponds using mere teaspoons of oil.

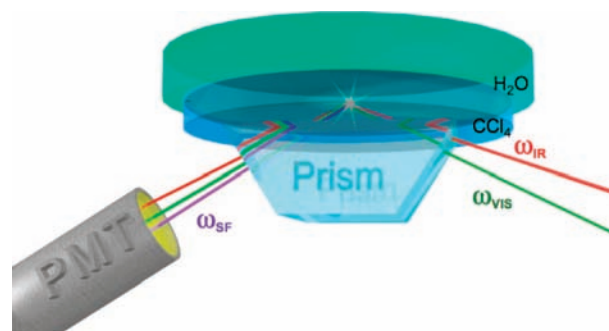
The questions he may well have puzzled over while observing those slicks are still very relevant to us today. What interactions exist between oil and water as the oil spreads on a water surface? Do these interactions result in a very abrupt interface between the two substances or is it more gradual? Are there different kinds of oil (or other substances) that exhibit these behaviors to a greater or lesser degree? How do ions approach and transport across this interface? What might be learned from this interface that will help us understand water at other insoluble fluid surfaces or membranes?

In more modern eras, understanding these issues has implications well beyond mere curiosity. Ion transport across membranes, protein folding, chemical separation strategies, and nanoparticle formation are only a few of the multitude of processes that involve the interaction of a polar water phase with a hydrophobic oil/organic phase.

In this paper, we provide a summary of the insights gained in recent years in our laboratory about how interfacial molecules structure and bond at oil–water interfaces. The picture that has evolved is the result of a closely coupled experimental and computational effort. Experimentally, surface vibrational sum frequency spectroscopy (VSFS) is employed to measure the vibrational spectrum of interfacial water molecules, and from this we derive an initial picture of how the organic and water molecules structure, orient, and bond at the interface. Concurrently, molecular dynamic calculations are used to provide additional details about the bonding, population density, and orientation of interfacial species and their VSF response. Knowing the individual VSF response from each of the contributing species, we then calculate an overall VSF spectrum that, by comparison with experiment, provides a check on the models used in the simulations. This combined approach provides a richer picture of the molecular behavior at these complex interfaces.

## Experimental Considerations

VSFS is a nonlinear optical method that allows the measurement of the vibrational spectrum of molecules at surfaces.<sup>1,2</sup> Because it is a second-order process, it is only allowed in regions of the medium where symmetry is broken, such as at an interface.<sup>3</sup> Figure 1 shows a cartoon diagram for a typical experimental cell configuration. In the experiment, a visible laser beam ( $\omega_{\text{vis}}$ ) and a tunable infrared (IR) laser beam ( $\omega_{\text{IR}}$ ) are coincident at the interface. By scanning the energy of the IR laser over the vibrational mode energies of the surface mol-



**FIGURE 1.** Experimental geometry for VSFS spectra of a liquid/liquid system studied in TIR geometry.

ecules and monitoring the generated sum frequency signal at  $\omega_{\text{SF}} = \omega_{\text{IR}} + \omega_{\text{vis}}$ , a vibrational spectrum of the interfacial molecules is obtained. The intensity of the sum-frequency radiation is proportional to the intensity of each incident beam and to the square of the effective second-order susceptibility,  $\chi_{\text{eff}}^{(2)}$ :

$$I(\omega_{\text{SF}}) \propto |\chi_{\text{eff}}^{(2)}|^2 I(\omega_{\text{vis}}) I(\omega_{\text{IR}}) \quad (1)$$

$\chi_{\text{eff}}^{(2)}$  can be expressed as the sum of resonant and nonresonant components,  $\chi_{\text{R}}^{(2)}$  and  $\chi_{\text{NR}}^{(2)}$ . Where  $\chi_{\text{NR}}^{(2)}$  is usually treated as a constant to be determined in the experiment. The resonant component is frequency dependent and proportional to the number density of molecules,  $\mathbf{N}$ , and the orientationally averaged molecular hyperpolarizability,  $\beta_{\mathbf{v}}$ , as follows

$$\chi_{\text{R}\mathbf{v}}^{(2)} = \frac{\mathbf{N}}{\epsilon_0} \langle \beta_{\mathbf{v}} \rangle \quad (2)$$

The molecular hyperpolarizability,  $\beta_{\mathbf{v}}$ , is enhanced when the frequency of the IR field is resonant with a SF-active vibrational mode of a molecule at the surface or interface. This enhancement in  $\beta_{\mathbf{v}}$  leads to an enhancement in the nonlinear susceptibility,  $\chi_{\text{R}\mathbf{v}}^{(2)}$ , which contains the product of the Raman and the IR transition moments.

This spectroscopic approach (VSFS) has advantages over linear spectroscopies, because it is highly specific to the thin layer of molecules within the interfacial region, this region itself being defined by the extent of anisotropic orientation and bonding of its molecules relative to the bulk phase. The disadvantages are more extensive instrumentation and the more complex spectral response. Since VSFS is a coherent spectroscopy, each oscillator's contribution to a response has an associated phase that can interfere constructively or destructively with adjacent modes, making analysis and spectral assignments challenging. This coherence can also be an advantage because, when interpreted appropriately, it can provide information about molecular orientation in the interfacial region.

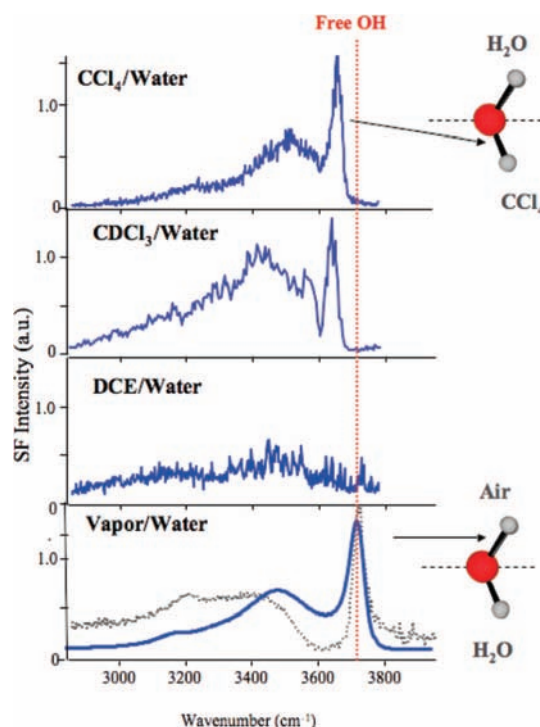
The experimental sum-frequency generation (SFG) response depends on the polarization of each of the two incident beams and the sum-frequency emission generated is itself polarized. By adjusting polarization combinations of incident and outgoing light, the different SFG responses (each related to one or more elements of the  $\chi^{(2)}$  tensor) can be selectively probed. The notation for these sorts of studies requires distinguishing between light polarized parallel to the plane of incidence (*P*) and perpendicular to the plane of incidence (*S*). All polarization notations are given in the order sum-frequency, visible, IR, for example, (*SPS*).

All of the liquid/liquid studies described herein were accomplished on Nd:YAG laser based systems with the IR (from nonlinear optical generation methods) and visible beams incident on the interface through a prism in a total internal reflection (TIR) geometry to maximize the weak VSF signal. The details of the experimental systems used to collect the spectra shown in this Account have been discussed in previous publications.<sup>4–7</sup> The cells are typically made of Kel-F to withstand the requisite aggressive cleaning protocols and contact with the organic liquids used. For our chloroform/water investigations, deuterated chloroform ( $\text{CDCl}_3$ ) was used. This was necessitated by the comparatively strong IR absorption that occurs in  $\text{CHCl}_3$ .

## Insights from Spectroscopic Measurements

Our VSF studies of oil–water interfaces have provided a progressively deeper understanding of the interactions at the interface between water and several hydrophobic organic liquids and films of varying polarity and molecular structure. Figure 2 shows the VSF spectra of interfacial water for three of these systems<sup>6–9</sup> along with the air/water interface<sup>10,11</sup> for comparison. The spectra reveal OH stretch modes of water molecules that are highly sensitive in frequency and intensity to the degree of hydrogen bonding between molecules.<sup>12,13</sup> The polarizations employed here (*SSP*) probe OH modes that have a dipole component perpendicular to the surface plane.

The  $\text{CCl}_4/\text{H}_2\text{O}$ ,  $\text{CDCl}_3/\text{H}_2\text{O}$ , and vapor/ $\text{H}_2\text{O}$  interfaces show similar spectral features, indicative of general similarities in the orientation and hydrogen bonding of water at these interfaces. The often-found peak near  $3700\text{ cm}^{-1}$ , is referred to as the “free OH” mode. This peak arises when one of the OH bonds of a water molecule orients into the hydrophobic phase, whether that be organic liquid or air. Its companion OH bond (referred to commonly as the “donor” mode because it can act as a hydrogen bond donor to nearby water molecules) orients into the aqueous phase and is one of the primary con-

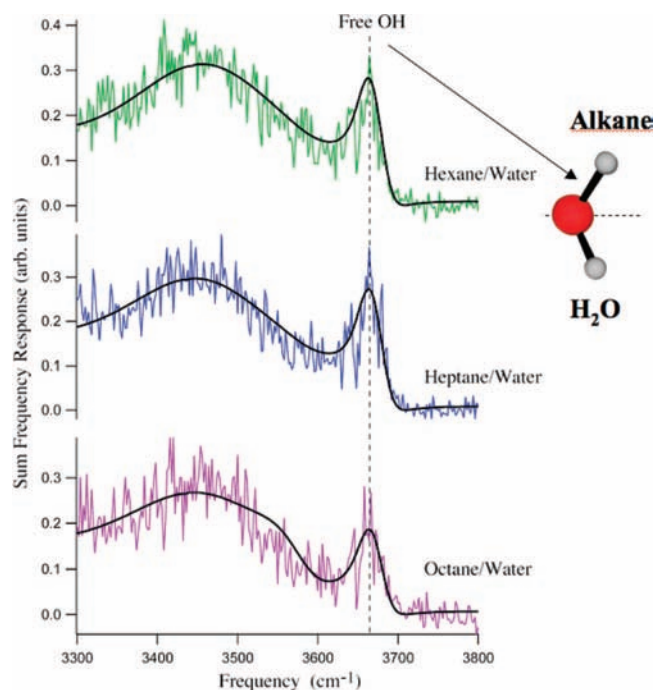


**FIGURE 2.** Resonant VSF spectra of water at three organic/water interfaces and the air/water interface. The dotted line through the cartoon molecules represents the interface, and the associated arrow indicates the free OH bond. The red line is a guide to the eye for the free OH frequency. The air/water spectrum (gray) contains a large nonresonant (NR) background. With its NR background removed (blue) a comparison with organic/water systems (having almost zero NR background) is made possible. Spectra are taken with *SSP* polarization.

tributors to intensity in the  $3200\text{--}3500\text{ cm}^{-1}$  region. Its VSF contribution is red-shifted and broader than the free OH mode because it is bonded to nearby water molecules. There are also contributions in the  $3000\text{--}3500\text{ cm}^{-1}$  region from stronger bonded water species, but these are nearly impossible to characterize based on any spectral fitting routines. We have used two methods for deconvoluting these spectral regions, spectral fitting with isotopic dilution experiments using HOD/ $\text{D}_2\text{O}$  mixtures<sup>6,14</sup> and molecular dynamics simulations that allow extraction of different water bonded species based on their calculated VSF response.<sup>15–17</sup> The former method works well for understanding weakly bonded and vibrationally uncoupled interfacial water species, and the latter assists in further understanding of both weakly and more strongly bonded interfacial water species.

There are a number of important general insights gained from the systems studied thus far. First, the presence of oriented water molecules that have a free OH mode indicates that the interfacial region for most of the systems that we have studied is relatively sharp, certainly within the dimensions of  $5\text{--}10\text{ \AA}$ , consistent with X-ray data of similar liquid/liquid





**FIGURE 3.** Resonant VSF spectra of water at the interface of three alkane/water systems. Taken with SSP polarization. Data from ref. 9.

**TABLE 1.** VSFS Measured Free OH Frequency of Water Measured at Different Interfaces

system	free OH ( $\text{cm}^{-1}$ )
vapor/ $\text{H}_2\text{O}$	$3705 \pm 5$
F-monolayer/ $\text{H}_2\text{O}$	$3694 \pm 3$
H-monolayer/ $\text{H}_2\text{O}$	$3674 \pm 2$
hexane, heptane, octane	$3674 \pm 3$
$\text{CCl}_4/\text{H}_2\text{O}$	$3669 \pm 2$
$\text{CDCl}_3/\text{H}_2\text{O}$	$3650 \pm 3$

interfaces.<sup>18–20</sup> Second, we have found that the free OH frequency is an indicator of the presence of weak water–organic interactions present at these interfaces and the relative strength of this interaction.<sup>21</sup> For example, for  $\text{CCl}_4/\text{H}_2\text{O}$ , the free OH appears at  $3669 \pm 4 \text{ cm}^{-1}$ ,<sup>22</sup> red-shifted from its value at the vapor/water interface at  $3705 \text{ cm}^{-1}$ .<sup>14</sup> The larger red shift for chloroform ( $\sim 3650 \text{ cm}^{-1}$ ) is indicative of a stronger interaction between water and this slightly more polar molecule.<sup>7</sup>

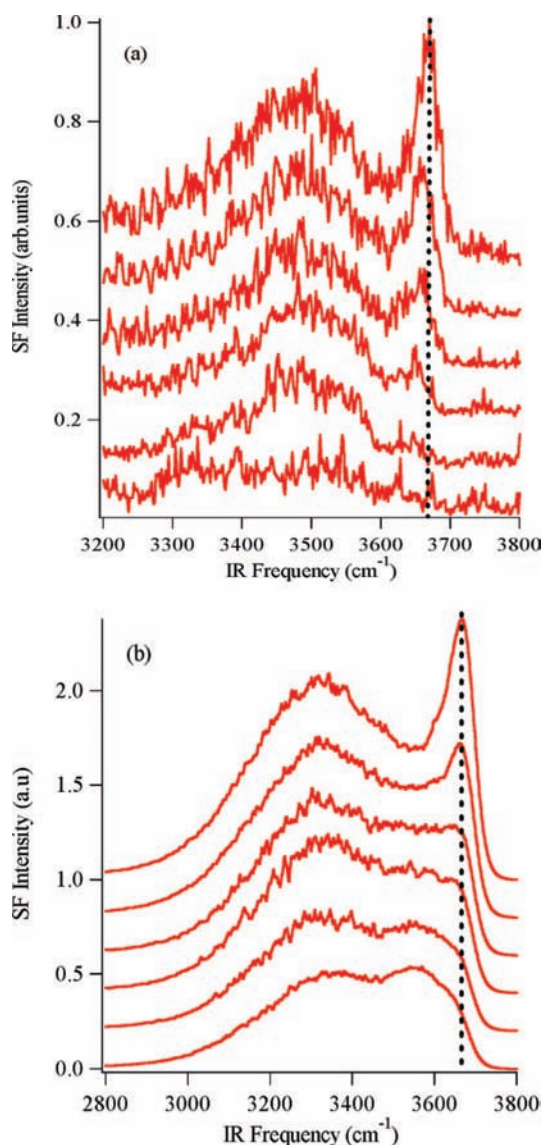
The alkane/water interfaces show spectral responses similar to those found with  $\text{CCl}_4/\text{H}_2\text{O}$  and  $\text{CDCl}_3/\text{H}_2\text{O}$  (Figure 3). However the free OH is at  $3674 \text{ cm}^{-1}$ ,<sup>23</sup> indicative of a weaker alkane–water interaction than that for the chlorinated solvents. We conclude that the broader free OH peak found for all the alkanes represents a more diverse range of water–alkane interfacial interactions. Interestingly, all alkanes studied give the same free OH frequency. Table 1 summarizes the free OH frequency of systems studied in this laboratory. F-monolayer and H-monolayer entries refer to

perfluorinated and hydrogenated monolayers, which are discussed further below.

For several of the organic/water systems, we find spectral intensity near the free OH resonance, which suggests the presence of water molecules that have negligible interaction with other water molecules but that are highly oriented with their dipoles perpendicular to the interface and their hydrogens pointing into the organic phase. These “water monomers” bond weakly to neighboring interfacial organic molecules or as OH bond acceptors to other water molecules, a factor we believe contributes to the overall orientation of the interfacial region.<sup>6</sup> They appeared in our earliest work with  $\text{CCl}_4/\text{H}_2\text{O}$  and our latest work with chloroform. Our ability to see the small number of these weakly bonded water molecules is largely due to the windfall of spectral interferences that come with the VSF technique. These will be discussed in more detail in the molecular dynamics (MD) section.

Interestingly, the neat  $\text{CCl}_4/\text{H}_2\text{O}$  spectrum, which we have studied most extensively, is remarkably similar to the resonant vapor/water interfacial spectrum. The vapor/water spectrum shown in Figure 2 (dotted line) contains a significant nonresonant background, which is not present for the organic/water systems studied. When this nonresonant contribution is removed using isotopic dilution experiments, the resonant vapor/water spectrum (shown in blue) shows even stronger resemblance to the organic/water interfaces.

Of the systems discussed thus far, the spectrum of the 1,2-dichloroethane (DCE)/water interface shown in Figure 2 is strikingly different in displaying no free OH mode. The DCE/ $\text{H}_2\text{O}$  interface has been the subject of considerable attention in the electrochemistry community because of its relatively large polarizable window and the question as to its nature being either sharp or diffuse.<sup>24</sup> Given the observed lack of distinct spectral features found for DCE/ $\text{H}_2\text{O}$ , we opted to explore this system further by “doping” increasing amounts of DCE into the organic phase of the more spectrally distinct  $\text{CCl}_4/\text{H}_2\text{O}$  system.<sup>7,17</sup> As shown in Figure 4a, with increased amounts of DCE added, the free OH from neat  $\text{CCl}_4$  red-shifts and the free OH oscillator intensity decreases significantly. This leads us to conclude, as we initially did, that the interface for the DCE/ $\text{H}_2\text{O}$  system is much more diffuse, with a lack of distinct water orientation found in the other systems. Here, insights from our MD simulations have been invaluable. Our simulations readily reproduced the spectral trends as shown in Figure 4b. When we extract the bonding and orientation information from these simulations, which so well fit the data, a very different and fascinating picture emerges and will be described later.



**FIGURE 4.** Experimental (a) and computed (b) spectra of the (CCl<sub>4</sub> + DCE)/H<sub>2</sub>O interface where the mole fraction of DCE ranges from zero (top) to 1.0. Intermediate concentrations are approximately 8%, 12%, 20%, and 35% DCE. Spectra have been shifted vertically for clarity. A dashed black line has been added to help identify the small red shift in the total free OH peak. Reproduced from ref 17. Copyright 2007 American Chemical Society.

Additional studies have probed how water at hydrophobic monolayer/water interfaces compare with these liquid/liquid interfaces. The results show that water interacts at the terminal end of these organic monolayers in a very similar manner as at the liquid/liquid interfaces.<sup>25</sup> Two types of monolayers have been examined under water, hydrogenated (octadecyltrisilane) and perfluorinated monolayers (1*H*,1*H*,2*H*,2*H*-perfluorodecyl-siloxane, FTDS) bound to Si/SiO<sub>2</sub>.<sup>26</sup> For well-formed monolayers, we find that a free OH is present for water at the terminal portion of both the hydrocarbon and fluorocarbon monolayers. For hydrocarbon monolayers, the OH

spectral profile and the free OH behavior mirrors that of the alkane/water systems.<sup>26</sup> The small red shift in the free OH frequency for the fluorocarbon monolayer system relative to air/water shows that a weak water–fluorocarbon interaction is present at these interfaces.

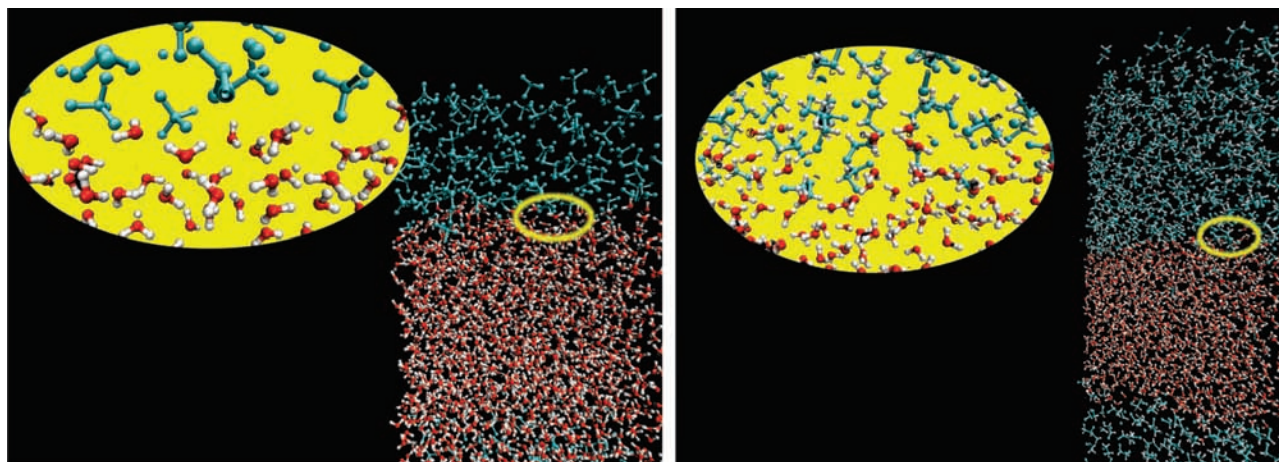
## Insights from Molecular Dynamics Simulations

Our MD work is used to complement and enhance our experimental studies and falls into two broad categories. The first uses and expands upon a formalism introduced by Hirose et al.<sup>27</sup> in which MD simulations are used along with hyperpolarizability calculations to compute the VSF response<sup>28</sup> of interfacial water for the air/water and organic/water systems we have studied.<sup>15,17,29</sup> With good correlation between calculated and experimental spectra, we proceed to extract detailed information from the simulations about the different water bonded species in the interfacial region, their degree of bonding, orientation, and interfacial depth. The second MD effort examines the orientation and ordering of both the water and “oil” species in the interfacial region.<sup>30,31</sup>

The starting point for all of this work is fully atomistic, polarizable descriptions of the molecules under study. These descriptions are combined with initial “boxes” of molecules chosen to accurately reflect the actual bulk experimental densities of the systems being simulated. Volumes of the simulated systems are on the order of 13 000 Å<sup>3</sup>, and they typically contain on the order of 2000 water molecules and between 400 and 500 “oil” molecules in order to get the densities correct. The simulation environment used for this work has changed over the years; most recently the AMBER7 suite of programs has been utilized.<sup>32</sup>

Our MD simulations of the various liquid/liquid interfaces discussed above all display a high degree of water orientation in the interfacial region. For water and carbon tetrachloride, weak bonding interactions play a significant role in establishing interfacial orientation (see below for further examination of this). For the CCl<sub>4</sub>/water, chloroform/water, and alkane/water systems, we find that the interfaces are molecularly sharp with widths of ~5–6 Å, which correlate well with simulations of others on related systems.<sup>33,34</sup> The calculations confirm our experimentally derived conclusions that a small but significant number of water molecules are found to interact weakly with the alkanes and CCl<sub>4</sub> despite their non-polar nature. For the alkanes, two types of weak interactions with water are present and are responsible for the observed broadening of the free OH peak relative to CCl<sub>4</sub>/H<sub>2</sub>O and CDCl<sub>3</sub>/H<sub>2</sub>O.<sup>23</sup> The more polar organics studied in the simula-



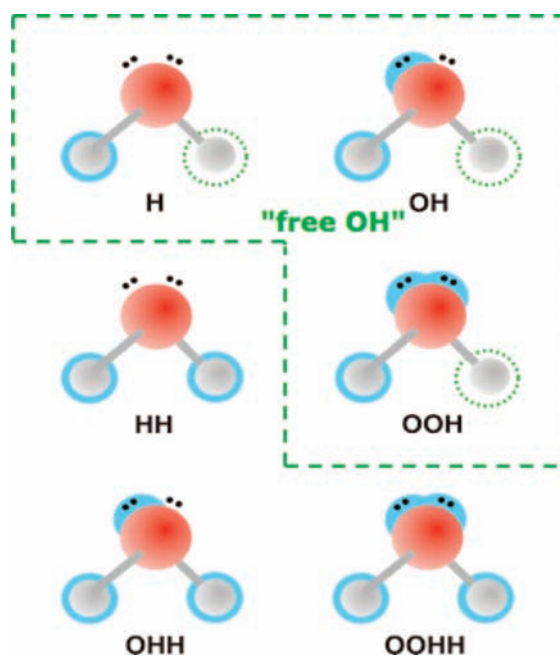


**FIGURE 5.** Picture of the DCE/water (right) and  $\text{CCl}_4$ /water (left) interfaces derived from the MD simulations.

tions, DCE and dichloromethane, also form well-defined interfaces. Figure 5 displays pictures for visual comparison from the simulations of the  $\text{CCl}_4/\text{H}_2\text{O}$  and the slightly more diffuse DCE/ $\text{H}_2\text{O}$  interfaces. Orientational and hydrogen-bonding analysis for all three systems show a large density of water molecules in the interfacial region that orient with their dipoles almost parallel to the interfacial plane and significant bonding with adjacent water molecules. This population of nearly in-plane water molecules is “invisible” to VSF in any polarization combination because of their isotropic in-plane orientation. The simulations for all systems also show to varying degrees a small number of very weakly interacting water molecules that are in the organic-rich interfacial region and are oriented with their hydrogens directed toward the organic bulk phase, as has been suggested by our experiments.

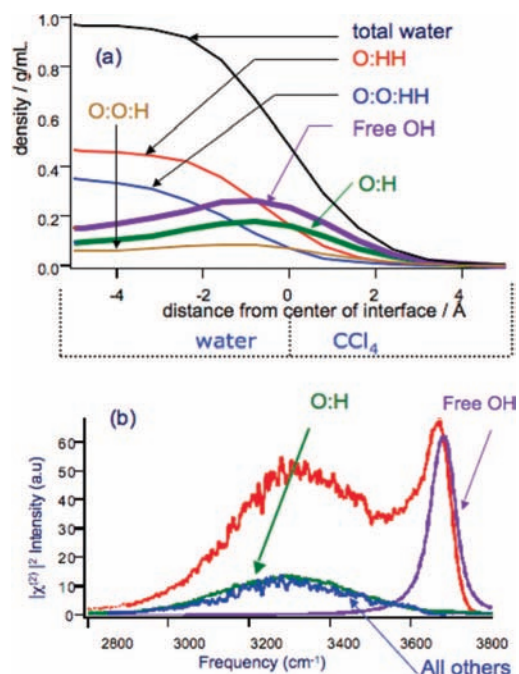
All interfaces are awash with water molecules that exhibit a constellation of different bonding interactions and orientations. Our calculations allow us to probe this further as we determine the number density for the different mono-, di-, tri-, and tetracoordinated water species at the interface, their polar orientation, and the VSF contribution that each type of bonded molecule makes to the overall measured spectrum. In characterizing these interactions, we have used the following naming scheme (depicted in Figure 6):<sup>35</sup> Tetracoordinated molecules are denoted as OOH $\text{H}$ -bonded species, tricoordinated species can be either OOH- or OHH-bonded, dicoordinated are OH-, HH-, or OO-bonded species, and mono-coordinated species are designated as H- or O-bonded. Water molecules that straddle the interface have a free OH bond and a companion donor OH bond that can participate in H, OH, or OOH bonding.

As an example of the information extracted from these simulations, Figure 7a shows the results for the populations of these different water bonded species across the interfacial



**FIGURE 6.** Different contributing water bonded species and the labeling scheme. The blue shading indicates whether the atom is involved in H bonding to nearby water molecules. Dotted green circles indicate which H atom is part of the “free OH” oscillator.

region for the  $\text{CCl}_4$ /water interface. Peaking in the center of the interfacial region are water molecules that straddle the interface as evidenced by the relatively high population of free OH and donor OH (with OH bonding) near the center of the interfacial region. These two modes are also found in related calculations to be highly oriented with each showing a preferred orientation perpendicular to the surface but antiparallel to one another, consistent with the straddling water molecule picture. Tetrahedrally bonded water and water molecules with OHH bonding are also evident but tend to show their presence deeper in the interfacial region and, of course, exist into the bulk aqueous phase. Within the significant population of topmost water molecules that orient with their



**FIGURE 7.** (a) Density profiles across the interface for the dominant water species at the  $\text{CCl}_4/\text{H}_2\text{O}$  interface. Labels refer to the bonded species in Figure 6. (b) Calculated VSF spectrum of the  $\text{CCl}_4/\text{H}_2\text{O}$  interface (red) and the most dominant contributors to the SSP spectrum. Adapted from ref 17.

dipoles largely in the plane of the surface, these tend to be involved in OHH bonding.

The conclusions drawn from these calculations can be validated by incorporating these density profile plots and related orientational plots into a calculation of a VSF spectrum for these systems. Comparison of the calculations with the experimental results (See Figure 4, for example) show that for the  $\text{CCl}_4/\text{H}_2\text{O}$  and  $\text{DCE}/\text{H}_2\text{O}$  interfaces there is remarkable agreement. Although there is still room for improvement, that such agreement can be achieved even with the rather stark differences in polarity and symmetry of the nonaqueous components is a testament to the rigor and robustness of the approach.

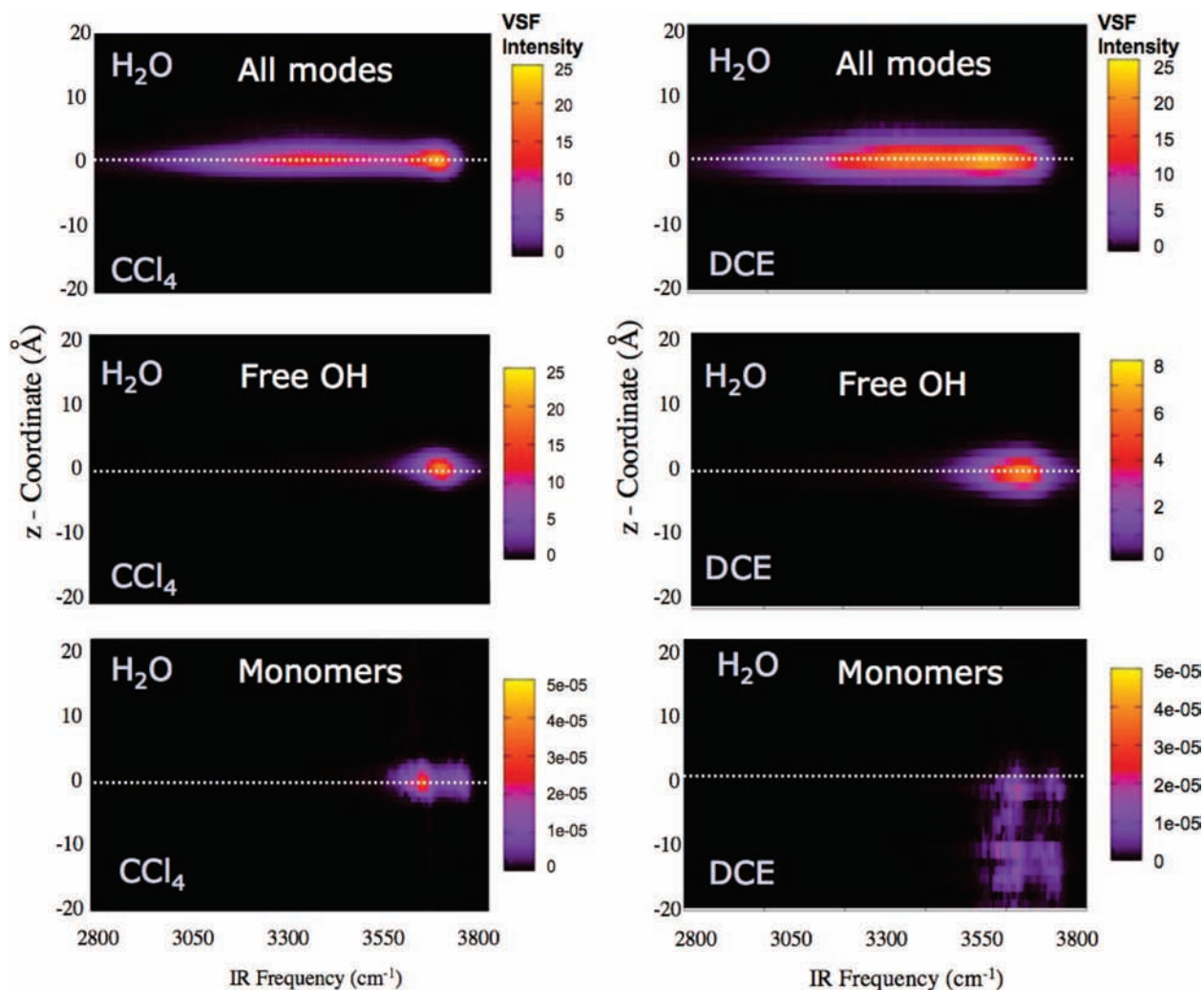
The calculations provide additional information about what species make the largest contribution to the VSF spectrum for the most commonly used SSP polarization.<sup>17</sup> The results for the dominant species for  $\text{CCl}_4/\text{H}_2\text{O}$  are depicted in Figure 7b. As shown, most of the intensity for this polarization comes from those molecules that are highly oriented and that straddle the interface. The greatest number of other contributions come from OOH- and OHH-bonded water molecules. A small number of oriented water monomers (no bonding to water) are present in the more organic-rich interfacial region and orient with their hydrogens directed into the  $\text{CCl}_4$  phase. The contribution from these monomers is negligibly small because

of their low densities and is included in the “all others” category. These results confirm our experimental observations and will be discussed in more detail below.

Along with our liquid/liquid effort, we have conducted similar experimental and computational studies of the vapor/water interface,<sup>15</sup> following computationally on the work of Morita and Hynes.<sup>28</sup> It is important to note that we find that the  $\text{CCl}_4/\text{water}$  interface shows striking similarity to the vapor/water interface except for the free OH frequency and the presence of unbonded and oriented monomers. This is consistent with theoretical studies<sup>36</sup> that suggest weak bonding interactions at a water/hydrophobic surface although our studies do not provide evidence for any significant vacuum-like drying region at this interface.

We now return to the question of why the  $\text{DCE}/\text{H}_2\text{O}$  spectrum is so different from the alkane/water,  $\text{CCl}_4/\text{H}_2\text{O}$ , and the  $\text{CDCl}_3/\text{H}_2\text{O}$  spectra. Is the spectrum telling us that the  $\text{DCE}/\text{H}_2\text{O}$  interface is truly broad and disordered as a cursory examination of the featureless spectra might suggest? The MD simulations provide needed insight.<sup>37</sup> The results show that the interfacial population density and interfacial orientation of water molecules near DCE is quite similar to the other systems except for several notable variations that result in the decidedly different VSF spectrum. These are best demonstrated visually from our depth spectral profiling results shown in Figure 8. In these studies, we have calculated the spectral profile of the different water bonded species as a function of interfacial depth (+z for the water region and -z for the organic).<sup>16,37</sup> Since the generation of VSF intensity comes from water molecules that have an anisotropic distribution in the medium, the z-dimension breadth of the region from which the intensity originates is a good measure of the depth of the interfacial region on both sides of the interface. Figure 8 (top) shows the total SSP VSF response plotted as a function of interfacial depth for  $\text{CCl}_4/\text{H}_2\text{O}$  (left) and  $\text{DCE}/\text{water}$  (right). In contrast to  $\text{CCl}_4$ , with the slightly more polar DCE, the greater width of the spectral profile for the later indicates that this interface is indeed more diffuse than the  $\text{CCl}_4/\text{H}_2\text{O}$  interface, consistent with other MD studies.<sup>34</sup> The free OH is clearly present at the  $\text{DCE}/\text{water}$  interface (Figure 8 center) but covers a broader spatial and spectral region due to stronger and more diverse water–organic interactions. These effects conspire to produce a combination of spectral congestion and interferences that result in a largely featureless spectrum.

Related MD simulations focus specifically on molecular orientation and ordering in the interfacial region. Since the simulations are of equilibrium conditions, the coordinate sets can be analyzed for statistical information about the location and



**FIGURE 8.** Computational VSF spectral profiles as functions of frequency (horizontal axis) and interfacial depth (vertical axis) in SSP for  $\text{CCl}_4$ - $\text{H}_2\text{O}$  (left) and  $\text{DCE}$ - $\text{H}_2\text{O}$  (right) interfaces. Resolution (bin size) for each graph is 1 Å and 1  $\text{cm}^{-1}$ : (top) VSF depth profile for all contributing species; (middle) the free OH modes; (bottom) water monomers. Adapted from ref 37.

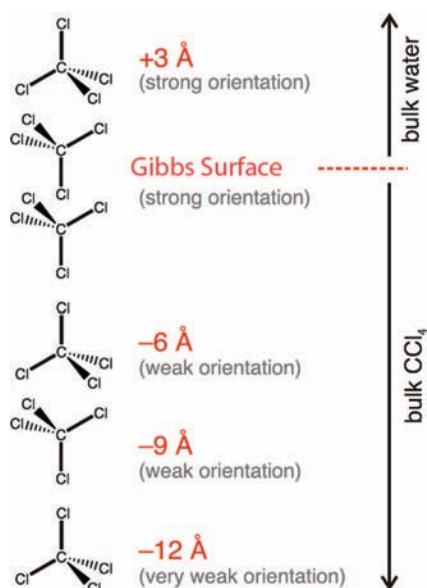
orientation of molecules within the system.<sup>30,31</sup> Typically, the species of interest is the minority species, for example, oil molecules that have crossed the interface into the water region or  $\text{H}_2\text{O}$  molecules that have moved into the oil region. Particularly for polar molecules, statistics of these distributions are useful and can be used to generate order parameters for the molecular configuration. With appropriate visualization techniques, these derived data allow a sophisticated understanding of the interfacial environment.<sup>30,31</sup>

An exceptionally interesting result is the orientational layering of the organic side of the interface found for the  $\text{CCl}_4/\text{H}_2\text{O}$  system.<sup>30</sup> A study of the  $\text{CCl}_4$ -vapor interface has found no preferred orientations of the surface  $\text{CCl}_4$  molecules,<sup>38</sup> alluding to the role that water likely plays in supporting this layered structure. The cartoon in Figure 9 indicates the sort of layering arrangement that can be discerned by an orientational analysis of MD data.<sup>31</sup> That the molecules in the sys-

tem are oriented and interacting in this fashion is certainly taken into account during the calculation of a simulated VSF spectrum, but the ability to visualize the structure of the organic provides for a parallel understanding and appreciation of the microstructure experienced by the constellation of  $\text{H}_2\text{O}$  oscillators present in this region of the interface. We attribute the alignment in part to the presence of polar oriented interfacial water molecules interacting with the polarizable  $\text{CCl}_4$ .

Another oil, chloroform, has a uniquely defined directional aspect (the C-H bond direction), and both the population density statistics and orientation statistics for this system have been studied.<sup>31</sup> The take-home message from this study is that the average chloroform molecule in the interfacial region is oriented such that its C-H bond is directed toward the  $\text{H}_2\text{O}$  phase. This is not the entire story, however, because it is also the case that studies indicate that a layered ordering exists in





**FIGURE 9.** At an aqueous interface, carbon tetrachloride molecules form an alternating layer structure, consisting of corner and face contacts between tetrahedra. The width of most of the layers corresponds to that of a single  $\text{CCl}_4$  molecule. Reproduced from ref 30. Copyright 2007 American Chemical Society.

the C–H bond statistics. While the population of chloroform molecules decreases monotonically with distance into the  $\text{H}_2\text{O}$  phase, there are a series of alternating orientations assumed by the molecules making up this distribution such that their hydrogens are alternately pointing deeper into the water phase or out of the water phase.

The picture is more complicated for  $\text{H}_2\text{O}$  near the chloroform/water interface because its molecular structure is such that it has not one but two orientational angles to be considered. Hence, there are two order parameters associated with water in the chloroform/water system, one for water tilt and one for water twist. Visualization of these statistics is significantly more challenging and is best considered in detail in the original publication.<sup>31</sup> To appreciate a summary of this work, one must understand that ordering in the chloroform/water system occurs in a balance between dipole compensation and the optimization of the hydrogen-bonding network. Portions of the interfacial region may be more favorable to a particular hydrogen-bonding geometry, and in these there may be a net dipole orientation resulting in a net volume charge density on the water side of the interface. We have suggested that such a net orientation could help explain the presence of an enhanced hydroxide ion concentration at hydrophobic/water surfaces.

## Conclusions and Future Directions

It has been more than 200 years since Benjamin Franklin purportedly wandered the environs of the eastern seaboard of

North America with a supply of oil concealed in his walking cane. The industrial revolution has come and gone, and the 21st century has opened with the promise of great technical and scientific advances but also with an ever-increasing awareness and concern as to the environmental impact of global development. The curious behavior of the oil/water interface is no different today than it was in Franklin's time. However, interest in understanding these layers has surely morphed into something far beyond simple curiosity.

In these studies, we have found that at the closest contact point between water and the organic, the interfacial water shows very weak bonding character with other water molecules, similar to what is observed at the vapor/water interface. We have also learned about the important role that weak water–organic interactions have in the structuring of the interface. Across all the oil/water systems that we have studied, these weak interactions drive a molecular ordering behavior that can extend well into the organic phase. The resulting net orientation creates fields that may assist in the incursion of polar species into the organic phase, as well as serving to draw ions into the interfacial region. Both of these topics are currently under further investigation in our laboratory.

Key to our nuanced understanding is the application of an appropriate surface-specific experimental probe of molecular structure and orientation. When combined with molecular dynamics simulations that yield both a calculated nonlinear optical response and molecular orientation, we can achieve a triangulation of sorts that unerringly points toward the actual microstructure at the interface. This combined approach, as well as exciting new advances from other research efforts in the application of X-ray and neutron scattering techniques and other simulation efforts, is surely helping us answer many of the questions that Benjamin Franklin would have wanted to ask about the oil/water interface. There are many frontiers ahead in this area in both experiment and theory. The understanding of these interfaces will continue to evolve with improvements in probe techniques and improved molecular models for simulating complex interactions. As such, this review provides a snapshot of where nonlinear spectroscopic measurements coupled with MD simulations have brought us in recent years.

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**Fred Moore's** research interests relate to understanding inhomogeneous systems by applying spectroscopic and modeling techniques. He received B.A. degrees in mathematics and physics from Lewis & Clark College and a Ph.D. in Applied Physics from the Oregon Graduate Center. After two years as a National Research Council Postdoctoral fellow at the Naval Research Laboratory, he joined the faculty of Whitman College where is now Professor and Chair of Physics.

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## REFERENCES

- Du, Q.; Superfine, R.; Freysz, E.; Shen, Y. R. Vibrational spectroscopy of water at the vapor/water interface. *Phys. Rev. Lett.* **1993**, *70*, 2313–2316.
- Shen, Y. R. Surface properties probed by second harmonic generation and sum-frequency generation. *Nature* **1989**, *337*, 519–525.
- Bloembergen, N.; Pershan, P. S. Light waves at the boundary of nonlinear media. *Phys. Rev.* **1962**, *128*, 606–622.
- Conboy, J. C.; Messmer, M. C.; Richmond, G. L. Dependence of alkyl chain conformation of simple ionic surfactants on head group functionality as studied by vibrational sum-frequency spectroscopy. *J. Phys. Chem. B* **1997**, *101*, 6724–6733.
- Conboy, J. C.; Messmer, M. C.; Richmond, G. L. Investigation of surfactant conformation and order at the liquid-liquid interface by total internal reflection sum-frequency vibrational spectroscopy. *J. Phys. Chem.* **1996**, *100*, 7617–7622.
- Scatena, L. F.; Richmond, G. L. Orientation, hydrogen bonding, and penetration of water at the organic/water interface. *J. Phys. Chem. B* **2001**, *105*, 11240–11250.
- McFearin, C. L.; Richmond, G. L. Understanding how organic solvent polarity affects water structure and bonding at halocarbon-water interfaces. *J. Mol. Liq.* **2007**, *136*, 221–226.
- Richmond, G. L. Structure and bonding of molecules at aqueous surfaces. *Annu. Rev. Phys. Chem.* **2001**, *52*, 357–389.
- Walker, D. S.; Brown, M. G.; McFearin, C. L.; Richmond, G. L. Evidence for a diffuse interfacial region at the dichloroethane/water interface. *J. Phys. Chem. B* **2004**, *108*, 2111–2114.
- Raymond, E. A.; Tarbuck, T. R.; Brown, M. G.; Richmond, G. L. Hydrogen bonding interactions at the vapor/water interface as investigated by vibrational sum frequency spectroscopy of HOD/H<sub>2</sub>O/D<sub>2</sub>O mixtures and molecular dynamics simulations. *J. Phys. Chem. B* **2003**, *107*, 546–556.
- Richmond, G. L. Molecular bonding and interactions at aqueous surfaces as probed by vibrational sum frequency spectroscopy. *Chem. Rev.* **2002**, *102*, 2963–2724.
- Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: Oxford, U.K., 1997.
- Scherer, J. R. The vibrational spectroscopy of water. In *Advances in Infrared and Raman Spectroscopy*; Clark, R. J. H., Hester, R. E., Eds.; Heyden: Philadelphia, PA, 1978; Vol. 5, pp 149–216.
- Raymond, E. A.; Tarbuck, T. R.; Richmond, G. L. Isotopic dilution studies of the vapor/water interface as investigated by vibrational sum-frequency spectroscopy. *J. Phys. Chem. B* **2002**, *106*, 2817–2820.
- Walker, D. S.; Richmond, G. L. Understanding hydrogen bonding effects at the vapor/water interface through molecular dynamics calculations of the vibrational sum frequency spectra of H<sub>2</sub>O/D<sub>2</sub>O/HOD Mixtures. *J. Phys. Chem. C* **2007**, *111*, 8321–8330.
- Walker, D. S.; Richmond, G. L. Depth profiling of water molecules at the liquid-liquid interface using a combined surface vibrational spectroscopy and molecular dynamics approach. *J. Am. Chem. Soc.* **2007**, *129*, 9446–9451.
- Walker, D. S.; Moore, F. G.; Richmond, G. L. Vibrational sum frequency spectroscopy and molecular dynamics simulations of the carbon tetrachloride–water and 1,2-dichloroethane–water interfaces. *J. Phys. Chem. C* **2007**, *111* (16), 6103–6112.
- Luo, G. M.; Malkova, S.; Pingali, S. V.; Schultz, D. G.; Lin, B. H.; Meron, M.; Graber, T. J.; Gebhardt, R.; Vanysek, P.; Schlossman, M. L. X-Ray studies of the interface between two polar liquids: neat and with electrolytes. *Faraday Discuss.* **2005**, *129*, 23–34.
- Schlossman, M. L. Liquid-liquid interfaces: Studied by X-ray and neutron scattering. *Curr. Opin. Colloids Surf.* **2002**, *7* (3–4), 235–243.
- Mitrinovic, D. M.; Tikhonov, A. M.; Li, M.; Huang, Z. Q.; Schlossman, M. L. Noncapillary-wave structure at the water-alkane interface. *Phys. Rev. Lett.* **2000**, *85* (3), 582–585.
- Richmond, G. L. Molecules at aqueous surfaces. *Annu. Rev. Phys. Chem.* **2001**, *292*, 257–285.
- Scatena, L. F.; Richmond, G. L. Water at hydrophobic surfaces: Weak hydrogen bonding and strong orientation effects. *Science* **2001**, *292*, 908–911.
- Brown, M. G.; Walker, D. S.; Raymond, E. A.; Richmond, G. L. Vibrational sum-frequency spectroscopy of alkane/water interfaces: Experiment and theoretical simulation. *J. Phys. Chem. B* **2003**, *107* (1), 237–244.
- Girault, H. H.; Schiffrin, D. J. Thermodynamic surface excess of water and ionic solvation at the interface between immiscible liquids. *J. Electroanal. Chem.* **1983**, *150*, 43–49.
- Becraft, K. A.; Richmond, G. L. Surfactant adsorption at the salt/water interface: Comparing the conformation and interfacial water structure for selected surfactants. *J. Phys. Chem. B* **2005**, *109*, 5108–5117.
- Hopkins, A. J.; McFearin, C. L.; Richmond, G. L. Investigations of the solid-aqueous interface with vibrational sum frequency spectroscopy. *Curr. Opin. Solid State Mater. Sci.* **2005**, *9*, 19–27.
- Hirose, C.; Akamatsu, N.; Domen, K. Formulas for the analysis of surface sum-frequency generation spectrum by CH modes of methyl and methylene groups. *J. Chem. Phys.* **1992**, *96*, 997–1004.
- Morita, A.; Hynes, J. T. A theoretical analysis of the sum frequency generation spectrum of the water surface. *Chem. Phys.* **2000**, *258*, 371.
- Walker, D. S.; Hore, D. K.; Richmond, G. L. Understanding the population, coordination, and orientation of water species contributing to the nonlinear optical spectroscopy of the vapor-water interface through molecular dynamics simulations. *J. Phys. Chem. B* **2006**, *110*, 20451–2059.
- Hore, D. K.; Walker, D. S.; Richmond, G. L. Layered organic structure at the carbon tetrachloride–water interface. *J. Am. Chem. Soc.* **2007**, *129* (4), 752–753.
- Hore, D.; Walker, D. S.; MacKinnon, L.; Richmond, G. L. Molecular structure of the chloroform–water and dichloromethane–water interfaces. *J. Phys. Chem. C* **2007**, *111*, 8832–8842.
- Case, D. A.; et al. *AMBER 7* University of California: San Francisco, 2002.
- Chang, T.-M.; Dang, L. X. Molecular dynamics simulations of CCl<sub>4</sub>-H<sub>2</sub>O liquid-liquid interface with polarizable potential models. *J. Chem. Phys.* **1996**, *104*, 6772–6783.
- Benjamin, I. Molecular structure and dynamics at liquid-liquid interfaces. *Annu. Rev. Phys. Chem.* **1997**, (48), 407–451.
- Buch, V. Molecular structure and OH-stretch spectra of a liquid water surface. *J. Phys. Chem. B* **2005**, *109*, 17771–17774.
- Chandler, D. Interfaces and the driving force of hydrophobic assembly. *Nature* **2005**, *437*, 640–647.
- Walker, D. S.; Richmond, G. L. Interfacial depth profiling of the orientation and bonding of water molecules across different organic–water interfaces. *J. Phys. Chem. C* **2008**, *112*, 201–209.
- Chang, T.-M.; Peterson, K. A.; Dang, L. X. Molecular dynamics simulations of liquid, interface, and ionic solvation of polarizable carbon tetrachloride. *J. Chem. Phys.* **1995**, *103*, 7502–7513.