

## Water: A Responsive Small Molecule

MARY JANE SHULTZ,\* TUAN HOANG VU, BRYCE MEYER, AND  
PATRICK BISSON

*Laboratory for Water and Surface Studies, Chemistry Department, Pearson  
Building, Tufts University, Medford, Massachusetts 02155, United States*

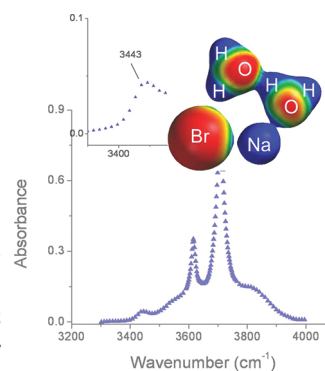
RECEIVED ON FEBRUARY 28, 2011

### CONSPECTUS

Unique among small molecules, water forms a nearly tetrahedral yet flexible hydrogen-bond network. In addition to its flexibility, this network is dynamic: bonds are formed or broken on a picosecond time scale. These unique features make probing the local structure of water challenging. Despite the challenges, there is intense interest in developing a picture of the local water structure due to water's fundamental importance in many fields of chemistry.

Understanding changes in the local network structure of water near solutes likely holds the key to unlock problems from analyzing parameters that determine the three dimensional structure of proteins to modeling the fate of volatile materials released into the atmosphere. Pictures of the local structure of water are heavily influenced by what is known about the structure of ice. In hexagonal  $I_h$  ice, the most stable form of solid water under ordinary conditions, water has an equal number of donor and acceptor bonds; a kind of symmetry. This symmetric tetrahedral coordination is only approximately preserved in the liquid. The most obvious manifestation of this altered tetrahedral bonding is the greater density in the liquid compared with the solid. Formation of an interface or addition of solutes further modifies the local bonding in water.

Because the O–H stretching frequency is sensitive to the environment, vibrational spectroscopy provides an excellent probe for the hydrogen-bond structure in water. In this Account, we examine both local interactions between water and small solutes and longer range interactions at the aqueous surface. Locally, the results suggest that water is not a symmetric donor or acceptor, but rather has a propensity to act as an acceptor. In interactions with hydrocarbons, action is centered at the water oxygen. For soluble inorganic salts, interaction is greater with the cation than the anion. The vibrational spectrum of the surface of salt solutions is altered compared with that of neat water. Studies of local salt-water interactions suggest that the picture of the local water structure and the ion distribution at the surface deduced from the surface vibrational spectrum should encompass both ions of the salt.



### 1. Introduction

Water is the most abundant molecule on Earth, covering 70% of the surface. Interactions with water shape much of the world from large scale molding of the landscape by ice, snow, and rain to molecular scale interactions that determine the macromolecular confirmation of biological molecules. In either environmental or biological systems, water seldom appears in pure form; it nearly always contains solutes, often at high concentrations. The salt content of seawater is 3.5% or approximately 0.6 M; blood is 0.9% saline or approximately 0.16 M. Due to the ion charges, salts influence the structure of water through their electrostatic fields. As shown by Arrhenius

over 100 years ago, at the high concentrations indicated, oppositely charged ions have a mutual electrostatic attraction that is incompletely shielded by their respective hydration spheres.<sup>1–6</sup>

Water, the solvent in a solvent-separated ion pair, is simultaneously affected by the fields of both ions. An interface introduces asymmetry in addition to the electrostatic fields. Surfaces cannot be ignored since in many environmental and biological settings, the action occurs at the interface. It is challenging to probe either the local water–ion interaction or the local water structure at the interface due to the small number densities relative to the surrounding bulk.

This Account describes the results of two experimental approaches for developing a picture of the local water structure. One is termed room temperature matrix isolation spectroscopy, RT-MIS, due to dispersion of water in a near room-temperature liquid in which it is sparingly soluble. The other is a combined infrared and Raman probe of the surface called sum frequency generation, SFG, due to the signal that is produced at the sum of the Raman excitation and dipole vibrational frequencies. The combined results suggest that the hydrogen-bond network of water has both a local and a long-range response to solutes; the surface hydrogen-bond structure is affected by interactions on both length scales.

Vibrational spectroscopy is a particularly effective probe for the hydrogen-bond network since the O–H stretch frequency is sensitive to the local environment; vibrational resonances shift by several hundred wavenumbers upon hydrogen bond formation. Infrared or Raman spectroscopy would thus be a straightforward probe of the local structure but for the dynamic nature of the hydrogen-bond network. Ultrafast spectroscopic studies<sup>7–11</sup> have shown that hydrogen bonds are made and broken on a ps time scale. Thus, the dynamics and the probe have comparable time scales resulting in vibrational features that span hundreds of wavenumbers. Due to the equivalence of numerous bonds throughout the network, there is also a nonlocal contribution influencing frequencies.<sup>12</sup> Many studies thus rely on band profile analysis to separate the local and long-range frequency perturbation.<sup>7</sup> Another approach is to examine dilute HDO in a bath of either H<sub>2</sub>O or D<sub>2</sub>O.<sup>12–15</sup> In this Account, we present an alternative approach, a matrix isolation method. Classic matrix isolation uses a dilute target isolated in a solid matrix often at low temperatures. The approach described here uses a solvent in which water is sparingly soluble to generate isolated water molecules with thermal energies near room temperature; it is a room temperature matrix isolation spectroscopy, RT-MIS.

The aqueous surface plays a particularly large role in atmospheric chemistry. Impinging gas-phase molecules encounter the surface first. An enhanced local surface concentration results from either a barrier to adsorption into the bulk or a thermodynamic partitioning to the surface. Additionally symmetry restrictions for reactions are relaxed at the surface. Arguably, the most famous example of surface enhanced reactions is reactions associated with the ozone hole. Finally, the water structure at the surface is different from that in the bulk. Exactly how it is different is the subject of sometimes heated debate<sup>16</sup> as in the fundamental question of the pH of the aqueous surface.<sup>9</sup> In acidic solutions, the

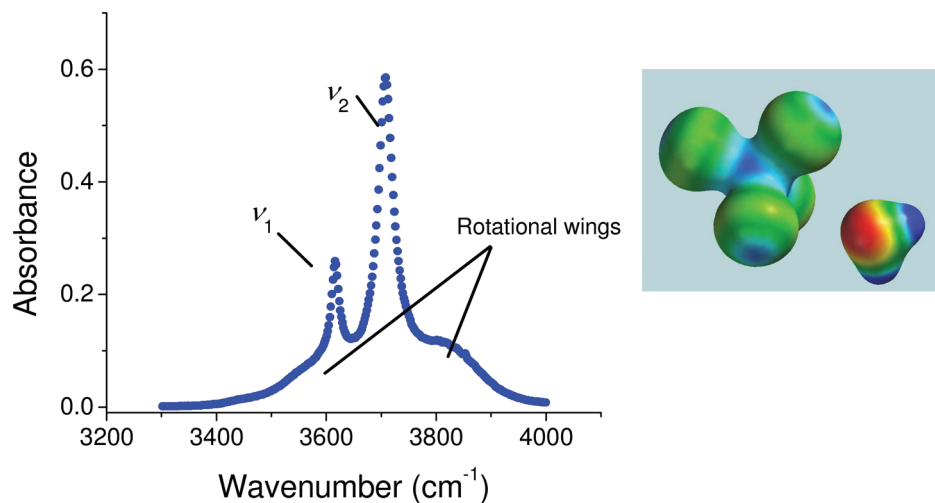
H<sub>3</sub>O<sup>+</sup> surface concentration appears to be enhanced over its bulk concentration leading to the bold statement that the surface of neutral water is acidic.<sup>17,18</sup> Numerous classic measures indicate that the surface of water is negatively charged leading to the equally bold conclusion that the pH of neutral water is very high.<sup>19</sup> We shall not settle this debate here, but make the observation that the surface water structure is altered by both acids<sup>20–23</sup> and bases.<sup>24</sup> How the water structure is altered is still an open question. The work described here sheds some light on changes in the water structure.

The hydrogen bond potential is unusually anharmonic leading to extensive intermolecular coupling and long-range cooperative motion in addition to relatively large oscillator strengths for overtone excitations. Anharmonicity is responsible for photochemical reactions<sup>25,26</sup> in the mainly transparent 2.5  $\mu$  to 700 nm region,<sup>27</sup> as well as water-mediated<sup>28,29</sup> and water-catalyzed reactions.<sup>30,31</sup> The open structure of the water hydrogen-bond network is capable of accommodating guest molecules; an example is clathrate formation. Clathrates are host–guest compounds consisting of a hydrogen-bond water cage surrounding a hydrophobic molecule.<sup>32,33</sup> Unraveling the molecular-level interactions that result in clathrate nucleation is an ongoing activity. This Account discusses application of RT-MIS to probe water–propane interactions. The oxygen lone-pair interaction with the hydrocarbon leads to an unusual blue-shifted hydrogen bond. Consideration of electron flow provides insight into the blue shift.

The current picture of hydrogen bonding in liquid water is heavily influenced by what is known about the structure of ice *I<sub>h</sub>*.<sup>34</sup> Analyzing hydrogen bonding at the surface also starts with ice. The basic view has oscillated from one with collective  $\nu_1$  and  $\nu_3$  vibrations<sup>35</sup> to one of loosely interacting modes<sup>36</sup> back to collective modes.<sup>37</sup> The fundamental shift in the latest view consists of treating ice as a collection of four-coordinate oxygen atoms with a degree of disorder leading to polarization of the tetrahedral unit cell. The result is a central infrared peak accompanied by modes at higher and lower frequencies, called excitonic side bands. At a surface, bands at higher frequency are polarized perpendicular to the interface and labeled as longitudinal bands. Modes at lower frequency are polarized parallel to the interface and are termed transverse bands.

## 2. Water: A Responsive Solvent

**2.1. Local Bonding: Salts.** Due to the very electronegative oxygen atom and two weakly electropositive hydrogen atoms,



**FIGURE 1.** The infrared spectrum of water in carbon tetrachloride shows the symmetric and asymmetric stretches and rotational side bands associated with the asymmetric stretch only. There is no evidence of hydrogen-bond resonances indicating that water molecules are monomers. The rotational structure supports a picture in which electronegative oxygen is attracted to the somewhat positively charged carbon of carbon tetrachloride. The potential surface plot on the right shows negative potential as red, positive as blue, and green as neutral. Note that the carbon of carbon tetrachloride is colored blue indicating that it is slightly positively charged. Pinned at the oxygen, water is free to rotate about the symmetry axis, but rotations about the remaining two axes are highly quenched.

plus the bent geometry, water is polar. Bonding between water and other species reflects the presence of the dipole. Electrons, primarily localized about oxygen, flow in response to the electric field of neighboring species and hence water is also polarizable. The combination of polarity and polarizability makes the O–H stretch vibrational frequency sensitive to the environment. In the isolated molecule, electronegative oxygen withdraws electron density from electropositive hydrogen. In the condensed phase, electron density donation to hydrogen from a neighboring species weakens the covalent OH bond resulting in a red shift of the vibrational resonance. The red shift can be large, up to 20% of the unperturbed frequency. The red shift is thus an excellent probe for interactions with the hydrogen atoms of water.

In addition to weakening the covalent OH bond, the magnitude of the OH dipole is sensitive to the hydrogen atom range of motion. Weakening the covalent OH bond enables the hydrogen to stretch further from the equilibrium position resulting in a significant enhancement of the dynamic dipole, hence an enhanced oscillator strength: up to 2 orders of magnitude.<sup>38</sup> Thus, even a small hydrogen-bond complex concentration is easily detected. This mechanism is sensitive to interactions with the hydrogen atom, to water acting as a donor.

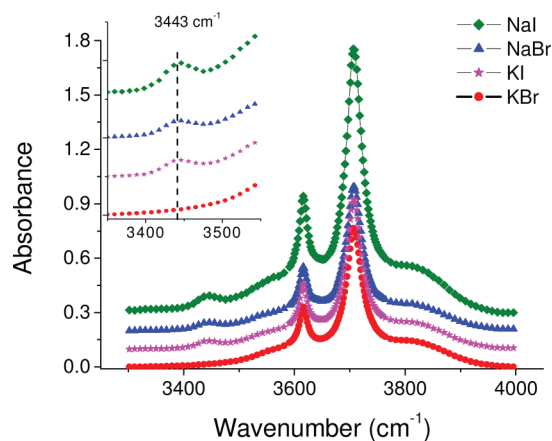
Due to the equal number of donor and acceptor sites in water, the tendency is to view water as a symmetric donor–acceptor. This symmetric picture is likely influenced by the structure of ice, which indeed has a coordination

number of four. Detecting any bias for donating vs accepting is masked by greater numbers in the multiple hydration shells.<sup>41</sup>

Isolating water limits interaction to the local water–solute. Donor and acceptor interactions produce distinct signatures enabling identification of any bias. Carbon tetrachloride is an excellent solvent for this investigation since water is sparingly soluble (saturation concentration 7.5 mM<sup>42</sup>) with only water monomers (Figure 1). This configuration is ideal for detecting interactions with water. Weak interaction with the hydrogen increases the rotational moment of inertia, collapsing the side bands; a strong interaction gives rise to red-shifted bands.

The spectrum of water in carbon tetrachloride with added salts indicates the local water–salt structure (Figure 2). LiCl, KCl, NaCl, and KBr solutions all produce spectra with the same profile as that of water; only the absorbance changes. The immediate conclusion is that for these salts the interaction cannot be between hydrogen and the anion since that would produce hydrogen-bonded resonances; interaction is between the cation and oxygen. Gravimetric analysis<sup>43</sup> indicates that the salt/water ratio is larger than one: on average, one water molecule is associated with an ion cluster. The increased absorbance is due to this additional cluster-bound water.

A few salt solutions, NaBr, NaI, and KI, those with greatest aqueous solubility, produce an additional resonance at 3443 cm<sup>-1</sup> (Figure 2). The red shift indicates that this resonance is due to the OH stretch of water acting as a



**FIGURE 2.** Infrared absorbance for salt water–carbon tetrachloride solutions. Spectra are offset for clarity (by 0.1 absorbance units for subsequent spectra). All aqueous layer salt concentrations are 1 M, and temperature is room temperature. Inset shows an absorbance magnified view (2.5 $\times$ ) of the 3350 to 3550  $\text{cm}^{-1}$  region illustrating the constancy of the feature at 3443  $\text{cm}^{-1}$ ; a feature absent in the spectrum of KBr (also LiCl, NaCl, and KCl not shown).

donor. Significantly, the frequency of this resonance does not shift between the bromide and iodide salts. If water was a hydrogen bond donor to the anion, then the strength of this interaction would vary with the anion charge density. Constancy of the frequency suggests constancy of the acceptor. The only other acceptor in the system is water, so the 3443  $\text{cm}^{-1}$  feature is attributed to a water–water hydrogen bond.<sup>43</sup> Note, three of the four resonances due to a complex such as that shown in the Conspectus are positively identified: (1) the donor OH stretch, 3443  $\text{cm}^{-1}$  and the (2) symmetric and (3) asymmetric stretches of the acceptor contained within the monomer bands at 3615 and 3708  $\text{cm}^{-1}$  respectively. The dangling –OH stretch, expected at  $\sim$ 3660  $\text{cm}^{-1}$  is masked due to a low number density,  $<0.1\%$  (see discussion below).

The water–water hydrogen bond only develops for those salts that are quite soluble in water (Table 1). Ion–water interactions are often analyzed in terms of the ion size complemented by polarizability. The NaBr/KBr and NaBr/NaI pairs illustrate the importance of balancing ion–ion interaction with ion–water interactions: a balance that depends on *both* ions of the pair. Highly soluble salts, also called outer complexes,<sup>1,44</sup> have a relatively weak ion–ion interaction enabling a solvent-separated ion pair. In carbon tetrachloride, the water molecule does not appear to separate the ion pair: if it did there would be a donor interaction with the anion, contrary to observation. Instead, the weaker ion–ion interaction polarizes the water attached at the cation resulting in hydrogen donation to a

**TABLE 1.** Salt and Water Concentration in  $\text{CCl}_4$  in Contact with 1 M Salt Solution, Salt Aqueous Solubility, and Classification as an Inner or Outer Complex

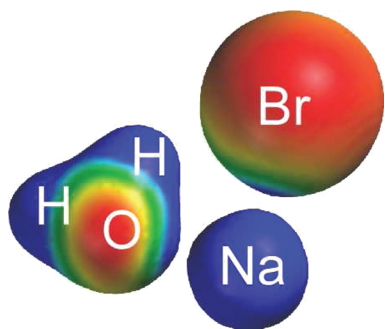
salt	$\text{CCl}_4$ molarity (mM)	water (mM)	aqueous solubility (M)	classification
NaCl	35.2	9.5	6.2	inner
NaBr	25.5	9.5	8.8	outer
NaI	22.2	16.3	11.9	outer
KCl	32.2	9.2	4.8	inner
KBr	24.5	9.2	7.6	inner
KI	19.1	9.4	8.7	outer

second water molecule as shown in the illustration with the Conspectus.

The integrated area of the 3443  $\text{cm}^{-1}$  peak is used to estimate the concentration of these water-dimer, salt complexes. In NaI, the 3443  $\text{cm}^{-1}$  peak is 1.25% of the total area. (KI and NaBr have a similar relative area). Generally, the OH oscillator strength increases by one to two orders of magnitude upon hydrogen bonding.<sup>38</sup> This results in an upper limit for the dimer concentration of 0.1% of the water concentration. It is not surprising that the dimer was not observed in the MD simulation.<sup>45</sup>

For the above-discussed salts, the cation is smaller than the anion. MD simulation<sup>45</sup> confirms that in these cases water is associated with the cation. The simulation also suggests that a combination of a small anion and a larger cation (NaF or KF) would result in water interacting via the hydrogen atom. Several fluoride salts with widely varying aqueous solubility: NaF, KF, and CsF were investigated. No evidence was found for water acting as a hydrogen-bond donor. Instead all fluoride salts serve to dehydrate the carbon tetrachloride layer (water concentration relative to saturated water: 0.68, 0.70, and 0.95, respectively, for NaF, KF, and CsF). The aqueous solubility of these salts varies widely from NaF ( $x = 0.0178$ ,  $x$  is the mole fraction) to KF ( $x = 0.222$ ) to CsF ( $x = 0.304$ ). Interaction in the bulk aqueous solution not only prevents these salts from entering the carbon tetrachloride phase, the interaction dehydrates the carbon tetrachloride layer.

RT-MIS investigation of the local structure of water around salts suggests that experimentally water has a propensity for interaction as an acceptor. This is not surprising from the point of view of electronegativity. The electronegativity difference between oxygen and any cation is larger than that between hydrogen and the anion. Figure 3 shows the result of a density functional B3LYP 6-31G\* calculation of the electrostatic potential for a gas phase water–NaBr complex. There is an electrostatic contact

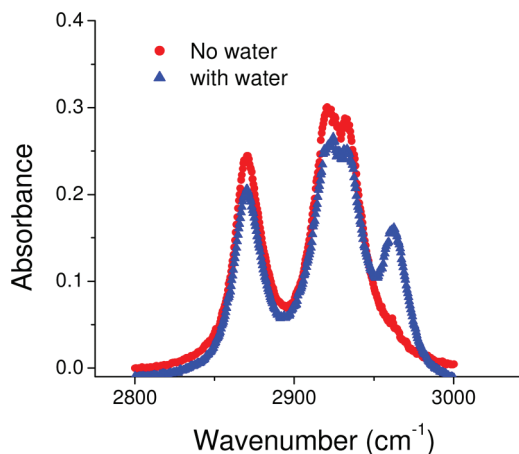


**FIGURE 3.** Density potential surface of the water–NaBr complex showing closer association of water with the cation than with the anion.

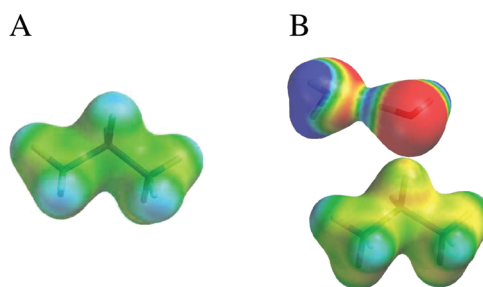
between the smaller sodium cation and the larger bromide ion and between water and the cation. In contrast, there is only a slight polarization toward the bromide anion. The next subsection contains a discussion of the interaction between water and a hydrophobic molecule, propane. The experimental evidence also shows that the interaction is at the oxygen confirming the propensity of water to act as an acceptor.

**2.2. Local Interaction: Hydrocarbons.** As indicated above, water is known to form hydrogen bonds with numerous molecules in the atmosphere. The anharmonicity of the OH covalent bond in the hydrogen-bond complex plays a key role in each of these. Water is also known to form caged or host–guest compounds, called clathrates, with hydrophobic molecules.<sup>32,33</sup> In these compounds, water forms an icosahedral or expanded icosahedral cage with the guest inside. The hydrocarbon concentration in these compounds is very high, on the order of 10% compared with an aqueous solubility of about 0.04%.

The molecular-level interactions that lead to the large concentration increase are largely unexplored due to lack of a suitable probe technique. The limitation for vibrational spectroscopy is that the overwhelming oscillator strength of hydrogen-bonded water renders aqueous solutions opaque. RT-MIS overcomes the opacity by dispersing water in carbon tetrachloride. Since carbon tetrachloride is transparent in the hydrogen-bond region and has open windows in the CH and CD regions, it is an excellent medium for probing these interactions. Propane is a prototypical hydrocarbon containing both methyl and methylene groups. The CH stretch spectrum of propane is complex due to symmetry; six to eight CH oscillators participate in each of the normal modes. To simplify the spectrum and enable identification of the site of interaction between water and propane, the methyl groups were deuterated making  $d_6$ -propane. Figure 4 shows spectra of  $d_6$ -propane and of  $d_6$ -propane with water. The CD



**FIGURE 4.** Spectrum of propane  $d_6$  ( $\text{CD}_3\text{CH}_2\text{CD}_3$ ) in carbon tetrachloride (off set for clarity) compared with propane in the presence of water. Note the emergence of a blue-shifted resonance upon addition of water. Neither the CD stretches nor the water spectrum shows any apparent change indicating that interaction is between the water oxygen and the methylene hydrogen.



**FIGURE 5.** Electrostatic potential surfaces for (A) propane and (B) propane–water complex. The yellow–orange color at the methylene group in the complex illustrates electron density transfer to the LUMO of the methylene carbon. (Density functional calculation at the B3LYP/6-31G\* level.)

stretch region (not shown)<sup>46</sup> does not change upon addition of water; the CH region shows emergence of a new resonance to the blue side of the CH stretches of  $d_6$ -propane. The immediate conclusion is that the site of interaction is the methylene hydrogen atoms. The water spectrum is largely unchanged indicating that the primary interaction is at the oxygen atom as illustrated in Figure 5.

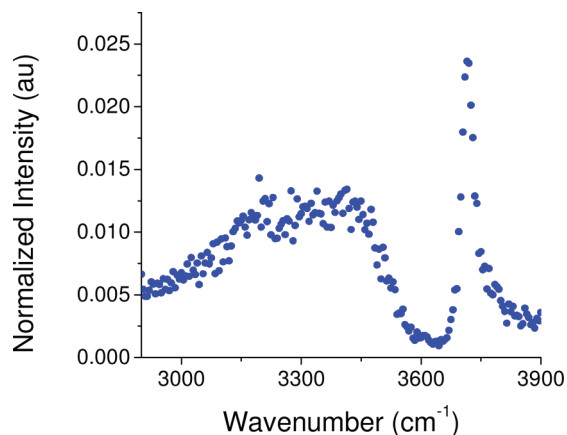
When water acts as a hydrogen bond donor, the covalent OH stretch shifts to the red. How then does the CH oscillator shift to the blue? Carbon is capable of supporting hybridization ranging from  $sp$  through  $sp^3$ . On interaction between propane and water, the water lone pair shifts electron density to the exposed hydrogen into the LUMO of the attached carbon (hence the yellow color of the methylene hydrogen and orange color of the methylene carbon in Figure 5). Some of that electron density is shifted into the

antibonding orbital centered on the carbon atom. Populating the antibonding orbital alters the hybridization toward  $sp^2$  from  $sp^3$ . The greater s character results in a stronger CH bond.<sup>47</sup> Since the LUMO for propane is centered on the methylene carbon, this is the site of interaction. The stronger CH bond gives rise to the blue shift relative to the unperturbed propane. Note that shifting electron density along with proton transfer is also involved in the water catalyzed reactions.

A close inspection of the OH stretch region in water–propane mixtures shows small hydrogen-bond resonances at 3162 and 3338  $\text{cm}^{-1}$  as well as a dangling OH resonance between the symmetric and the asymmetric OH stretches.<sup>46</sup> Together these features indicate a low concentration of water–water complexes. Since water does not form dimers in carbon tetrachloride by itself, the presence of propane has induced this interaction. Shifting electron density from oxygen to carbon unshields the water proton enabling interaction with another water molecule (Figure 5). The small hydrogen-bond resonance intensity indicates that under these moderate conditions ( $-4\text{ }^\circ\text{C}$ ,  $P = 1\text{ atm}$ ) the dimer–propane cluster concentration is small, less than 0.01%. On average, each propane molecule interacts with only one water molecule. Nonetheless, presence of the water–dimer, propane complex demonstrates that interaction with the hydrocarbon polarizes water sufficiently to begin formation of a hydrogen-bond structure around the hydrocarbon.

### 3. Implications for Aqueous Interfaces

Just as with issues concerning the pH of the neutral water interface, consensus has not yet been achieved for the model for hydrogen bonding in aqueous interfaces. Here we summarize observations and suggest a picture based on local structures observed in RT-MIS and global, coordinated dynamics. For nearly a decade and a half, it has been observed that addition of acids,<sup>20,21,23,48</sup> bases,<sup>49</sup> or small inorganic ions<sup>50–52</sup> to water alters the vibrational signature of water at the interface. The first model to rationalize this increased intensity for salts is that of an electric double layer.<sup>20,50,51</sup> Briefly, approaching the aqueous–air interface, there is a differential distribution of anions and cations with the tail of the anion distribution penetrating closer to the interface than that of the cations. This general model is consistent with theoretical<sup>53,54</sup> predictions and surface potential measurements.<sup>55</sup> The double-layer model has subsequently been validated by MD simulations.<sup>56</sup> In general, the larger, more polarizable anion has a local maximum that



**FIGURE 6.** Typical ssp SFG spectrum of the neat water interface at  $0\text{ }^\circ\text{C}$ . The resonance at  $3700\text{ cm}^{-1}$  is due to dangling OH bonds, those that are free of hydrogen bonding. The remaining broad spectrum is due to OH stretches of hydrogen-bond water molecules. One of the challenges in interpreting the spectra of aqueous solutions is lack of assignment of the resonances for the neat aqueous interface.

is nearer to the surface than does the smaller cation. Integrated over the interfacial region, the salt concentration is lower than in the bulk as it must be to be consistent with surface tension results. The location of the anion affects its accessibility for impinging gas-phase reactants, so the precise location of the anions is still the subject of debate. (For example, see remarks about the pH of the aqueous surface.) What is less clear is how the water structure alters in response to the presence of the ions.

SFG spectra of water (Figure 6) or aqueous solutions are very broad. There are at least two features in the hydrogen-bond region: one near  $3200\text{ cm}^{-1}$  and the other near  $3450\text{ cm}^{-1}$ . These features have occasionally been cited as indicating two types of water in the interface; it is far more likely that these features are both heterogeneously and homogeneously broadened due to rapid energy transfer as well as a wide distribution of hydrogen-bond environments. As a broad stroke, the intensity of the  $3200\text{ cm}^{-1}$  peak is greatly enhanced for acidic solutions; the peak near  $3450\text{ cm}^{-1}$  is enhanced for halide salt solutions. Due to the nonlinear nature of SFG, the connection between intensity and the water molecule configuration is not straightforward. Recent phase-sensitive SFG measurements have added data concerning the transition dipole and indicate that increased intensity in the  $3450\text{ cm}^{-1}$  region is associated with an enhanced transition dipole pointing into the solution.<sup>24,57</sup> The source of enhancement in the lower frequency region for acid solutions is still a subject of debate with some experimenters concluding a polarized, 3-coordinate water motif at the surface<sup>58</sup> and others an enhanced polarization

of four-coordinate water.<sup>24</sup> RT-MIS provides insight into the salt solutions.

Thus far, discussion of salt solution spectra has focused on the anions. The RT-MIS results suggest that analysis should encompass both ions. It is helpful to divide water molecules in the interfacial region into three subgroups: (I) those water molecules (if any) above the anion, (II) those water molecules in the double layer region between the anion and the cation, and (III) water molecules in the tail of the double-layer field. If interpretation of the phase-sensitive measurements is correct, then the transition dipole in the 3450 cm<sup>-1</sup> region points into the bulk, parallel to that of the double-layer. Examining the effect of the double layer on OH oscillators in the three regions indicates that all may contribute to the observed increased transition dipole. Region I contains three-coordinate water molecules. If these three-coordinate water molecules reorient with their OH dipole more parallel to the double layer field, they have a larger projection onto the surface normal. Since the SFG amplitude is dependent on the projection of the transition dipole onto the surface normal, reorientation increases the amplitude and thus the observed intensity. Note that this does not suggest that these water molecules are directly bonded to the anion: if they were the frequency would depend on the identity of the anion; contrary to observation. Such reorientation is problematic with the free-OH intensity observed: For concentrations lower than 1 mol %, the free-OH intensity is unaltered indicating that this part of the top monolayer is unperturbed.

Assuming that the double layer field is insufficiently strong to reorient four-coordinate water molecules (those in regions II and III), the contribution to the enhanced SFG amplitude from these water molecules must result from an enhanced transition dipole. There is precedence for such an enhancement: the symmetric stretch of water attached to cations is enhanced due to the water-cation dipole being parallel to the symmetric stretch.<sup>39,59</sup> The conclusion is that water molecules in region II can contribute to the observed increased SFG amplitude by this enhanced transition dipole mechanism. Finally, water molecules in region III, either directly bound to the cation or in the tail of the double layer field will also have an increased oscillator strength parallel to the double layer. Note that water molecules directly bound to the cation are symmetrically arrayed around the cation; however, the complex is embedded in the double-layer field that breaks the inversion symmetry. The conclusion is that the enhanced amplitude in the 3450 cm<sup>-1</sup> region is due to the double layer and includes a contribution from water molecules in regions II and III.

RT-MIS data suggests that water has a propensity to act as an acceptor. With a propensity to bond through the oxygen atom, water molecules in the interfacial region interact strongly with the cation. Water molecules around the cation are caught in the electric field generated by the cation–anion combination oriented with the anions nearer to the surface. These water molecules are more polarized than in the absence of the salt. It is likely that this field alters the oscillator strength for these water molecules and induces hydrogen-bond structures not present without the salts.

*This work was supported in part by the ACS PRF (Grant 46671-AC6) and the United States National Science Foundation (CHE0844986 and CHE0240172). T.H.V. acknowledges support from a GAANN Fellowship.*

#### BIOGRAPHICAL INFORMATION

**Mary Jane Shultz** grew up in Wisconsin, received a B.S. with Honors from the University of Wisconsin and a Ph.D. from MIT. She is a Professor and former Department Chair at Tufts University. She studies all things water.

**Tuan Hoang Vu** grew up in Vietnam, received a B.S. with Honors in chemistry and mathematics from CUNY Brooklyn College and is a Ph.D. student at Tufts University. A Ph.D. student at Tufts University, he studies clathrate hydrate formation.

**Bryce Meyer** grew up in Denver, Colorado. He is an undergraduate majoring in Chemistry at Tufts University.

**Patrick Bisson** grew up in the Connecticut River Valley in Massachusetts, received a B.S. in electrical engineering with Honors from UMASS Amherst, and a B.S. in Chemistry with Honors from UMASS Lowell. A Ph.D. student at Tufts University, he studies ice/water surfaces using sum frequency generation.

#### FOOTNOTES

\*To whom correspondences should be addressed. E-mail: Mary.Shultz@Tufts.edu.

#### REFERENCES

- Fennell, C.; Bizjak, A.; Vlady, V.; Dill, K. Ion Pairing in Molecular Simulations of Aqueous Alkali Halide Solutions. *J. Phys. Chem. B* **2009**, *113*, 6782–6791.
- Heyrovská, R. Dependences of molar volumes in solids, partial molal and hydrated ionic volumes of alkali halides on covalent and ionic radii and the golden ratio. *Chem. Phys. Lett.* **2007**, *436*, 287–293.
- Akhumov, E. I. Hydration of Sulfuric Acid in H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O. *Zh. Prikl. Khim.* **1974**, *47*, 1852.
- Nabivanez, B. I.; Kalabina, L. V. The Dissociation Constants Dependence on H<sub>2</sub>SO<sub>4</sub> Concentration. *Ukr. Chem. Zh.* **1992**, *58*, 997.
- Heyrovská, R. Degrees of dissociation and hydration numbers of twenty six strong electrolytes. *Collect. Czech. Chem. Commun.* **1992**, *57*, 2209.
- Heyrovská, R. Physical Electrochemistry of Solutions of Strong Electrolytes Based on Partial Dissociation and Hydration. *J. Electrochem. Soc.* **1996**, *143*, 1789–1793.
- Bakker, J. H.; Skinner, J. L. Vibrational Spectroscopy as a probe of Structure and Dynamics in Liquid Water. *Chem. Rev.* **2010**, *110*, 1498–1517.
- Schmidt, D. A.; Birer, O.; Funkner, S.; Born, B. P.; Gnanasekaran, R.; Schwaab, G. W.; Leitner, D. M.; Havenith, M. Rattling in the Cage: Ions as Probes of Sub-picosecond Water Network Dynamics. *J. Am. Chem. Soc.* **2009**, *131*, 18512–188517.
- Saykally, R. On the interfacial and dynamical properties of the hydroxide ion. *Chem. Phys. Lett.* **2009**, *481*, 1.

- 10 Fayer, M. D.; Moilanen, D. E.; Wong, D.; Rosenfeld, D. E.; Fenn, E. E.; Park, S. Water Dynamics in Salt Solutions Studied with Ultrafast Two-Dimensional Infrared (2D IR) Vibrational Echo Spectroscopy. *Acc. Chem. Res.* **2009**, *42*, 1210–1219.
- 11 McGuire, J. A.; Shen, Y. R. Ultrafast vibrational dynamics at water interfaces. *Science* **2006**, *313*, 1945–1948.
- 12 Ljungberg, M. P.; Lyubartsev, A. P.; Nilsson, A.; Pettersson, L. G. M. Assessing the electric-field approximation to IR and Raman spectra of dilute HOD in D<sub>2</sub>O. *J. Chem. Phys.* **2009**, *131*, 034501–1–034501–12.
- 13 Li, F.; Skinner, J. L. Infrared and Raman line shapes for ice I<sub>h</sub>. I. Dilute HOD in H<sub>2</sub>O and D<sub>2</sub>O. *J. Chem. Phys.* **2010**, *132*, 204505.
- 14 Sovago, M.; Campen, R. K.; Bakker, H. J.; Bonn, M. Hydrogen bonding strength of interfacial water determined with surface sum-frequency generation. *Chem. Phys. Lett.* **2009**, *470*, 7–12.
- 15 Hyeon-Deuk, K.; Ando, K. Quantum effects of Hydrogen atoms on the dynamical rearrangement of hydrogen-bond networks in liquid water. *J. Chem. Phys.* **2010**, *132*, 164507.
- 16 Wilson, E. Storm in a teacup. *Chem. Eng. News* **2010**, *88*, 35–36.
- 17 Mundy, C. J.; Kuo, I.-F. W.; Tuckerman, M. E.; Lee, H.-S.; Tobias, D. J. Hydroxide anion at the air-water interface. *Chem. Phys. Lett.* **2009**, *481*, 2–8.
- 18 Buch, V.; Millet, A.; Vacha, R.; Jungwirth, P.; Devlin, J. P. Water surface is acidic. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 7342–7347.
- 19 Creux, P.; Lachaise, J.; Graciaa, A.; Beattie, J. K.; Djerdjev, A. M. Strong Specific Hydroxide Ion Binding at the Pristine Oil/Water and Air/Water Interfaces. *J. Phys. Chem. B* **2009**, *113*, 14146–14150.
- 20 Baldelli, S.; Schnitzer, C.; Shultz, M. J.; Campbell, D. Sum Frequency Generation Investigation of Water at the Surface of H<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub> Binary Systems. *J. Phys. Chem. B* **1997**, *101*, 10435–10441.
- 21 Schnitzer, C.; Baldelli, S.; Campbell, D. J.; Shultz, M. J. Sum Frequency Generation of O-H Vibrations on the Surface of H<sub>2</sub>O/HNO<sub>3</sub> Solution and Liquid HNO<sub>3</sub>. *J. Phys. Chem. A* **1999**, *103*, 6383–6386.
- 22 Yang, H.; Finlayson-Pitts, B. J. Infrared Spectroscopic Studies of Binary Solutions of Nitric Acid and Water and Ternary Solutions of Nitric Acid, Sulfuric Acid, and Water at Room Temperature: Evidence for Molecular Nitric Acid at the Surface. *J. Phys. Chem. A* **2001**, *105*, 1890–1896.
- 23 Radüge, C.; Pflumio, V.; Shen, Y. R. Surface vibrational spectroscopy of sulfuric acid-water mixtures at the liquid-vapor interface. *Chem. Phys. Lett.* **1997**, *274*, 140–144.
- 24 Tian, C.; Ji, N.; Waychunas, G. A.; Shen, Y. R. Interfacial Structures of Acidic and Basic Aqueous Solutions. *J. Am. Chem. Soc.* **2008**, *130*, 13033–13039.
- 25 Takahashi, K.; Kramer, Z. C.; Vaida, V.; Skodje, R. T. Vibrational overtone induced elimination reactions within hydrogen-bonded molecular clusters: the dynamics of water catalyzed reactions in CH<sub>2</sub>FOH·(H<sub>2</sub>O)<sub>n</sub>. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3864–3871.
- 26 Vaida, V.; Kjaergaard, H. G.; Hintze, P. E.; Donaldson, D. J. Photolysis of sulfuric acid vapor by visible solar radiation. *Science* **2003**, *299*, 1566–1568.
- 27 Kjaergaard, H. G.; Robinson, T. W.; Howard, D. L.; Daniel, J. S.; Headrick, J. E.; Vaida, V. Complexes of importance to the absorption of solar radiation. *J. Phys. Chem. A* **2003**, *107*, 10680–10686.
- 28 Axson, J. L.; Takahashi, K.; Haan, D. O. D.; Vaida, V. Atmospheric Chemistry Special Feature: Gas-phase water-mediated equilibrium between methylglyoxal and its geminal diol. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 6687–6692.
- 29 Klemperer, W.; Vaida, V. Molecular complexes in close and far away. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 10584–10588.
- 30 Njagic, B.; Raff, J. D.; Finlayson-Pitts, B. J.; Gordon, M. S.; Gerber, R. B. Catalytic role for Water in the Atmospheric Production of ClNO. *J. Phys. Chem. A* **2010**, *114*, 4609–4618.
- 31 Maron, M.; Takahashi, K.; Shoemaker, R.; Vaida, V. Hydration of pyruvic acid to its geminal-diol, 2,2-dihydroxypropanoic acid, in a water-restricted environment. *Chem. Phys. Lett.* **2011**, *513*, 184–190.
- 32 Max, M. D. *Natural Gas Hydrate: In Oceanic and Permafrost Environments*; Kluwer Academic Publishers: Boston, 2000.
- 33 Sloan, E. D.; Koh, C. A. *Clathrate Hydrates of Natural Gases*, 3rd ed.; CRC Press: Boca Raton, FL, 2008.
- 34 Bragg, W. H. The Crystal Structure of Ice. *Proc. R. Soc. London* **1921**, *34*, 98–103.
- 35 Whalley, E. A detailed assignment of the O-H stretching bands of ice I. *Can. J. Chem.* **1977**, *55*, 3429–3434.
- 36 Rice, S.; Bergren, M.; Belch, A.; Nielson, G. A Theoretical analysis of the OH Stretching Spectra of Ice I<sub>h</sub>, Liquid Water, and Amorphous Solid Water. *J. Phys. Chem.* **1983**, *87*, 4295–4308.
- 37 Buch, V.; Devlin, J. P. A new interpretation of the OH-stretch spectrum of ice. *J. Chem. Phys.* **1999**, *110*, 3437–3443.
- 38 Huisken, F.; Kulcke, A.; Laush, C.; Lisy, J. Dissociation of Small Methanol Clusters After Excitation of the O-H Stretch Vibration at 2.7 μm. *J. Chem. Phys.* **1991**, *95*, 3924–3929.
- 39 Vaden, T. D.; Lisy, J. M.; Carnegie, P. D.; Pillai, E. D.; Duncan, M. A. Infrared spectroscopy of the Li<sup>+</sup>(H<sub>2</sub>O)Ar complex: the role of internal energy and its dependence on ion preparation. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3078–3082.
- 40 Vaden, T. D.; Weinheimer, C. J.; Lisy, J. M. Evaporatively cooled M<sup>+</sup>(H<sub>2</sub>O)Ar cluster ions: infrared spectroscopy and internal energy simulations. *J. Chem. Phys.* **2004**, *121*, 3102–3107.
- 41 Krekeler, C.; Site, L. Solvation of positive ions in water: the dominant role of water-water interaction. *J. Phys.: Condens. Matter* **2007**, *19*, 1–7.
- 42 Kuo, M.; Kamelamela, N.; Shultz, M. J. Rotational Structure of Water in a Hydrophobic Environment: Carbon Tetrachloride. *J. Phys. Chem. A* **2008**, *112*, 1214–1218.
- 43 Bisson, P.; Xiao, H.; Kuo, M.; Kamelamela, N.; Shultz, M. J. Ions and Hydrogen Bonding in a Hydrophobic Environment: CCl<sub>4</sub>. *J. Phys. Chem. A* **2010**, *114*, 4051–4057.
- 44 Hribar, B.; Southall, N.; Vlachy, V.; Dill, K. How ions affect the structure of water. *J. Am. Chem. Soc.* **2002**, *124*, 12302–12311.
- 45 Benjamin, I. Structure and Dynamics of Hydrated Ion Pairs in a Hydrophobic Environment. *J. Phys. Chem. B* **2010**, *114*, 13358–13364.
- 46 Vu, T.; Kälin, S.; Shultz, M. J. Spectroscopic Identification of Water-Propane Interaction: Implications for Clathrate Nucleation. *J. Phys. Chem. A* **2010**, *114*, 6356–6360.
- 47 Hobza, P.; Havlas, Z. Blue-shifting hydrogen bonds. *Chem. Rev.* **2000**, *100*, 4253–4264.
- 48 Baldelli, S.; Schnitzer, C.; Shultz, M. J. The Structure of Water at the Surface of HCl Solutions Studied with Sum Frequency Generation. *Chem. Phys. Lett.* **1999**, *302*, 157–163.
- 49 Simonelli, D.; Baldelli, S.; Shultz, M. J. Ammonia-water complexes on the surface of aqueous solutions observed with sum frequency generation. *Chem. Phys. Lett.* **1998**, *298*, 400–404.
- 50 Baldelli, S.; Schnitzer, C.; Shultz, M. J.; Campbell, D. J. Sum Frequency Generation Investigation of Water at the Surface of H<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O/Cs<sub>2</sub>SO<sub>4</sub> Binary Systems. *Chem. Phys. Lett.* **1998**, *287*, 143–147.
- 51 Baldelli, S.; Campbell, D.; Schnitzer, C.; Shultz, M. J. Effect of H<sub>2</sub>SO<sub>4</sub> and Alkali Metal SO<sub>4</sub><sup>2-</sup>/HSO<sub>4</sub><sup>-</sup> Salt Solutions on Surface Water Molecules Using Sum Frequency Generation. *J. Phys. Chem. B* **1999**, *103*, 2789–2795.
- 52 Schnitzer, C.; Baldelli, S.; Shultz, M. J. Sum Frequency Generation of Water on NaCl, NaNO<sub>3</sub>, KHSO<sub>4</sub>, HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> Aqueous Solutions. *J. Phys. Chem. B* **2000**, *104*, 585–590.
- 53 Benjamin, I. Theory and Computer Simulations of the Solvation and Chemical Reactions at Liquid Interfaces. *Acc. Chem. Res.* **1995**, *28*, 233.
- 54 Wilson, M.; Pohorille, A. Interaction of monovalent ion with the water liquid-vapor interface: A molecular dynamics study. *J. Chem. Phys.* **1991**, *95*, 6005–6013.
- 55 Jarvis, N. L.; Scheiman, M. A. Surface Potentials of Aqueous Electrolyte Solutions. *J. Phys. Chem.* **1968**, *72*, 74–78.
- 56 See, for example, thematic issue *Structure and Chemistry at Aqueous Interfaces*; Jungwirth, P., Finlayson-Pitts, B., Tobias, D. J., Guest Eds. *Chem. Rev.* **2006**, *106* and references therein.
- 57 Ji, N.; Ostroverkhov, V.; Tian, C. S.; Shen, Y. R. Characterization of vibrational resonances of water-vapor interfaces by phase-sensitive sum-frequency spectroscopy. *Phys. Rev. Lett.* **2008**, *100*, 096102-1–096102-4.
- 58 Shang, Z.; Piatkowski, L.; Bakker, H.; Bonn, M. Ultrafast vibrational energy transfer at the water/air interface revealed by two-dimensional surface vibrational spectroscopy. *Nat. Chem.* **2011**, *3*, 888–893.
- 59 Vaden, T. D.; Forinash, B.; Lisy, J. M. Rotational structure in the asymmetric OH stretch of Cs<sup>+</sup>(H<sub>2</sub>O)Ar. *J. Chem. Phys.* **2002**, *117*, 4628–4631.