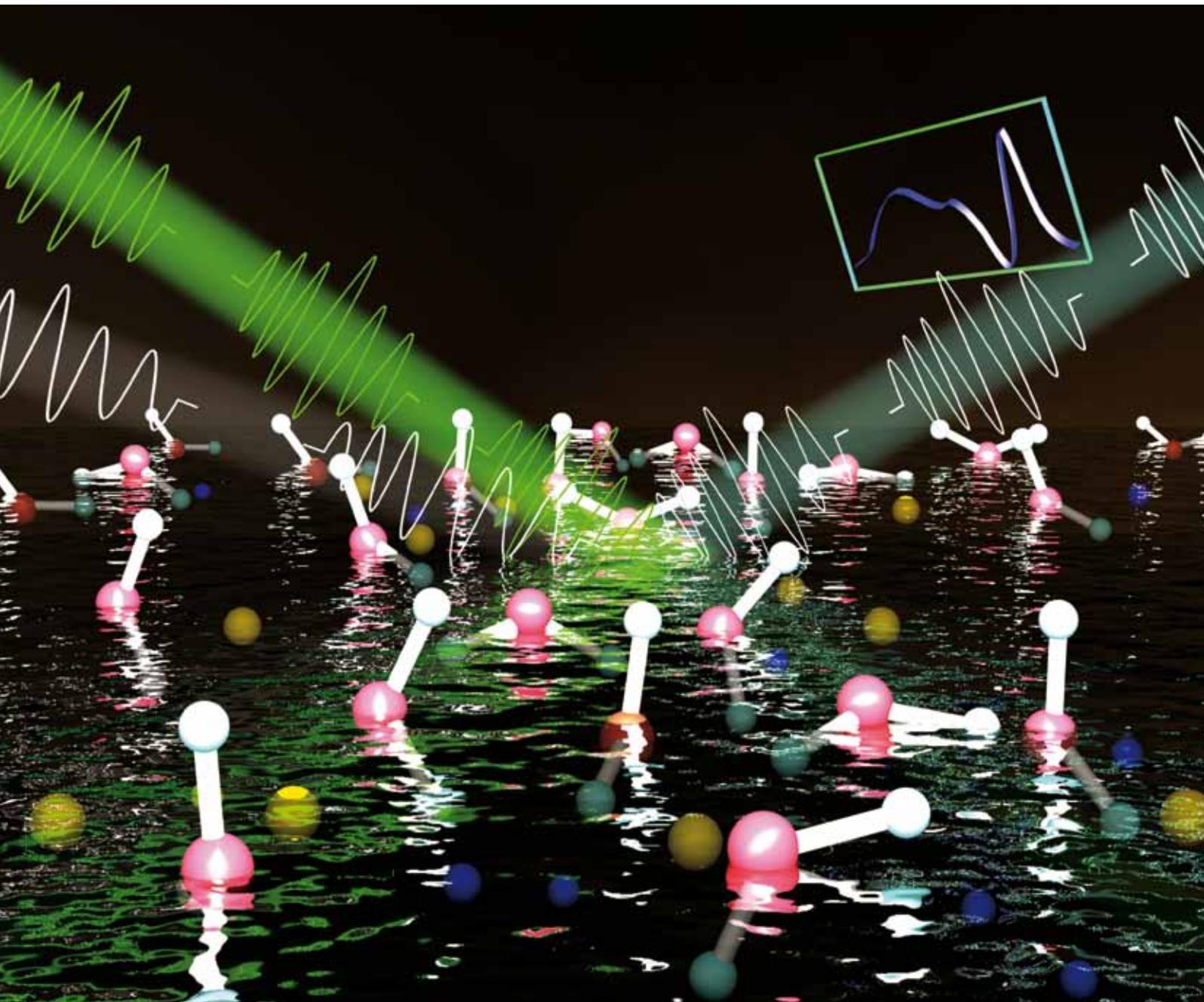


PCCP

Physical Chemistry Chemical Physics

www.rsc.org/pccp

Volume 11 | Number 27 | 21 July 2009 | Pages 5521–5852



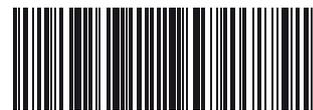
ISSN 1463-9076

COVER ARTICLE

Allen *et al.*
Shedding light on water structure
at air–aqueous interfaces: ions, lipids,
and hydration

HOT ARTICLE

Knight and DeVries
Ice growth in supercooled solutions of a
biological “antifreeze”, AFGP 1–5



1463-9076(2009)11:27;1-U

Shedding light on water structure at air–aqueous interfaces: ions, lipids, and hydration

Heather C. Allen,* Nadia N. Casillas-Ituarte, M. Roxana Sierra-Hernández, Xiangke Chen and Cheng Y. Tang

Received 20th January 2009, Accepted 24th March 2009

First published as an Advance Article on the web 15th May 2009

DOI: 10.1039/b901209e

An account is given of the current state of understanding of aqueous salt, acid, and lipid/water surfaces, interfacial depth, and molecular organization within the air–solution interfacial region. Water structure, hydration, surface propensity of solutes, and surface organization are discussed. In this perspective, vibrational sum frequency generation spectroscopic studies of aqueous surfaces are interpreted. Comment on future directions within the field of aqueous surface structure is provided.

Introduction

The amazing properties of water and the ability of water to solvate molecules and ions, in addition to the intricate details of how this solvation occurs and is maintained, drive scientific discovery in this area. Water and many inorganic ions are necessary for life, and this provides motivation beyond sheer fascination for continued research. Thus, understanding water and its inherently important hydrogen bonding character continues to be of prime focus for many experimentalists and theoreticians.^{1–15} There has been a resurgence in this field due to the ability to now probe the surface of aqueous solutions using vibrational spectroscopy that is interface-selective.^{16–20}

For water, moving from a three-dimensional environment of the bulk to the asymmetric two-dimensional interface has particularly interesting consequences. This environment, the

aqueous surface, has implications for hydration of solutes relative to the bulk. As we learn more about surface structure, we also shed light on the bulk environment. Yet in revealing the intricate nature of solvation, more questions arise. Even so we now know more about both the bulk solvation and interfacial solvation environments. In most cases, the interface, not just the very surface, is different structurally relative to the bulk solution.

We present relatively recent work and unpublished work on aqueous surfaces to better understand the structure of these air–aqueous interfaces. Advances in nonlinear optical technology have propelled a new era of surface spectroscopy. Furthermore, advances in theoretical chemistry and computational technology, and thus predictions from theoreticians,^{21–26} have driven some of the questions that are now being answered with experimentation.^{25,27} The predictions are being tested with surface-selective experiments. Here we focus on our research, but also comment on other research in the field. Hence, a partial summary of our work at air–condensed phase interfaces and in the condensed phase,

Department of Chemistry, The Ohio State University,
100 West 18th Ave, Columbus, OH 43210, USA.
E-mail: allen@chemistry.ohio-state.edu



Heather C. Allen

Heather C. Allen is a Professor of Chemistry at the Ohio State University. She received her BS, MS, and PhD degrees in chemistry at the University of California, Irvine. Currently, she is an Alfred Sloan Fellow and a Camille Dreyfus Teacher-Scholar. Her research interests are focused on aqueous surface structure and molecular interactions. Atmospheric aerosol chemistry, geochemical interfaces, and the biophysics of monolayer lipid and fatty acid

films are of great interest. Water is a central theme, as is the use and development of vibrational nonlinear optical spectroscopic technologies.



Nadia N. Casillas-Ituarte

Nadia N. Casillas-Ituarte received her Bachelors degree from the Autonomous University of Chihuahua, Mexico, as a chemist bacteriologist parasitologist in 2000. In 2005, she obtained a Masters degree in Environmental Sciences (partially funded by the National Council of Science and Technology of Mexico, CONACYT) and is continuing with her PhD degree under the direction of Professor Heather C. Allen at the Ohio State University. She

is currently working on organic films deposited on amorphous silica and water.

and an updated view of our data interpretation are discussed. The majority of our research has been conducted on aqueous surfaces and therefore we focus on all of the aqueous components, water inclusive of the solute. Change in interfacial depth is a recurring theme throughout these presented results, and this is discussed further with respect to the solutes considered.

The motivation behind our research arises from the lack of understanding of atmospheric particulate matter (aerosol) surfaces, both liquid, inclusive of water, and solid phase particles, and the chemistry of such surfaces. We strive for a fundamental understanding of liquid surfaces, and how this then relates to aerosols and ocean surfaces, and in some cases to biological surfaces and membrane biophysics. Water and ions at environmental interfaces, but also at biological interfaces, are of interest, for example, at the lung lining surface, the lung surfactant and its aqueous subphase environment.

Gas phase atmospheric molecules nucleate to form atmospheric nuclei. These nuclei grow in size due to collision and adsorption of other gas phase molecules. The process is far from simple. The surface of a particle, its molecular make-up and its surface structure, has implications for atmospheric chemistry. Atmospheric particles exist everywhere in the lower and upper atmosphere, and have been of interest for many

decades. Since the 1990's, the scientific community has focused on the surface effects of particulate matter.^{28–32} Emphasis is placed on lower atmospheric aerosol in this research including clean and polluted (urban) tropospheric aerosol. The aerosol size fraction below 2.5 micrometres in diameter in the lower atmosphere has implications for health, including respiratory and cardiovascular diseases, and the associated mortality rates.³³ Focus in our work is on the most basic aspects of the relevant surfaces from the perspective of the aerosol surface to the perspective of inhalation by way of the lung.

The primary spectroscopic tool used in our laboratory is vibrational sum frequency generation (VSFG) spectroscopy. Since the 1960's when Bloembergen and Pershan first postulated nonlinear optical phenomena,³⁴ and when Franken and Ward first demonstrated its power experimentally,³⁵ the field has significantly expanded. In 1987, Hunt *et al.* first published VSFG spectra from a monolayer of coumarin dye on water,^{36,37} although the first published account of VSFG from Zhu *et al.* was in 1986.³⁸ Later, in 1993, Du *et al.* published the first paper showing the vibrational spectrum from the surface of water at room temperature that revealed the existence of a dangling bond, the free OH of surface water molecules.¹⁶ Infrared studies on ice, in particular nanoparticle ice, had shown the existence of a small peak that was indeed the free OH of water molecules in their frozen state.³⁹ But the surface spectrum of room temperature water, where the free OH peak was glaringly large relative to the hydrogen bonding region, was a discovery that was unmatched at the time in surface science. Not only were the spectra obtained at room temperature, but also under ambient atmospheric pressure conditions. There were also many VSFG studies on metal surfaces in the 1990's and this area continues to flourish.^{17,40–48} Since the 1993 water surface spectrum, VSFG research (and second harmonic)⁴⁹ in the area of surface water structure of aqueous systems was confined to a few groups^{50–52} and a few researchers focused on VSFG of the air–aqueous interface more generally.^{53,54} Others focusing on VSFG of surface water structure followed shortly thereafter.^{55–63} Since that time, VSFG theory has been furthered,^{20,53,64–73} mostly motivated by a need to improve the interpretation of the VSFG spectral response with special attention paid to the allowed polarization responses, or for modeling the VSFG spectra.



M. Roxana Sierra-Hernández

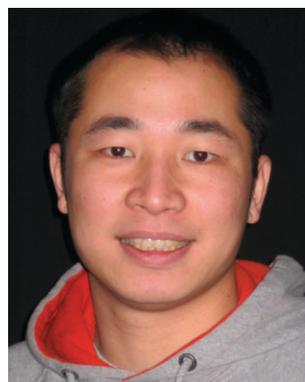
C. Allen. Her current work focuses on the study of aqueous surfaces relevant to atmospheric aerosol chemistry.

M. Roxana Sierra-Hernández received a BS degree in Pharmaceutical Chemistry (2000) from Instituto Politécnico Nacional (Mexico), and a MS degree in Environmental Science (2005) from the Ohio State University. Her Masters work consisted of the online analysis of volatile organic compounds in aqueous solutions by using membrane introduction mass spectrometry. Roxana is currently a PhD candidate under the direction of Professor Heather



Xiangke Chen

Xiangke Chen received his Bachelors degree in chemistry in 2002 and Masters degree in physical chemistry in 2005 from Nanjing University, China. Since 2005 he has been pursuing his PhD degree under the direction of Professor Heather C. Allen at the Ohio State University. His current project is to study biological interfaces such as lipid monolayers on water.



Cheng Y. Tang

Cheng Y. Tang obtained his BSc in Chemical Engineering from the University of Pittsburgh in 2002. At present, he is a graduate student under the supervision of Professor Heather C. Allen. His main interest is focused on the head-group hydration and ionic binding of biologically relevant monolayer systems in the air–aqueous interface using vibrational spectroscopic techniques.

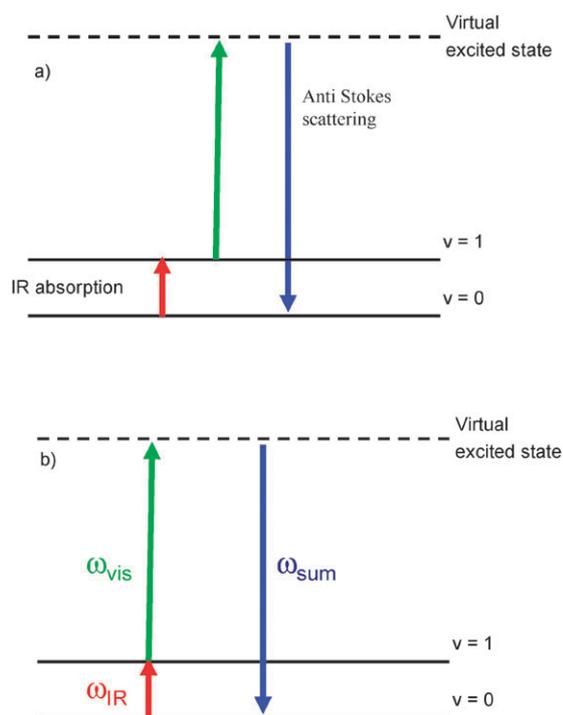


Fig. 1 Energy diagrams of (a) infrared absorption and anti-Stokes Raman scattering, and (b) vibrational sum frequency generation.

In this perspective, in addition to VSFG spectroscopy, other spectroscopic tools are briefly mentioned in the context of understanding bulk *versus* surface structure and interactions. As shown in Fig. 1, Raman and infrared spectroscopies are related to VSFG spectroscopy, and the SFG excitation and emission processes are illustrated. VSFG is the coherent process of exciting surface molecules using infrared photons, and simultaneously exciting an anti-Stokes Raman scattering process from this infrared excited surface. In understanding the basics of VSFG and the polarization combinations that are allowed, ssp and ppp, for example, one can simplistically view the first two polarization states as coming from a coherent anti-Stokes Raman process, the coherent and highly directional scattered beam, and the incident visible beam, respectively. The s and p polarizations are light polarized with the electric field vector perpendicular and parallel, respectively, to the plane of incidence. The last polarization state arises from the incident IR, that is, the infrared excitation beam. Thus, the vibrational modes of the molecular moieties being probed must be both Raman and infrared active to be SFG active. Eqn (1) shows that the hyperpolarizability, β , the molecular response, is proportional to the Raman polarizability, α , and infrared transition dipole moment, μ . The indices l, m, n refer to the molecular axes; g and ν are the ground and excited states.

$$\beta_{lmn,\nu} \propto \langle g | \alpha_{lm} | \nu \rangle \langle \nu | \mu_n | g \rangle \quad (1)$$

In addition to the relationship of VSFG to Raman and infrared transitions, it is critically important to note that the SF response is an allowed process only when there is macroscopic and microscopic non-centrosymmetry. The microscopic lack of inversion is taken into account from eqn (1). However,

a macroscopic interface lacks inversion and is SFG active. Both criteria, macroscopic and microscopic lack of inversion, need to be met. Most liquids, including water, possess inversion centers in the bulk and are therefore SFG inactive. At their surface, clearly, the inversion center is removed. This explanation utilizes the dipole approximation. For surfaces such as crystalline ice, it has recently been proposed that the quadrupole moment in addition to the dipole moment may add significantly to the SFG response.⁷³ When molecules exist in the interfacial region of liquids, the two-dimensionality of this environment perturbs the symmetry of the molecule and therefore can change the character of its vibrational modes. Centrosymmetric molecules with vibrational modes that are symmetric tend to distort at surfaces, and thus these modes can become SFG active in many cases.⁷⁴

At a water surface, lack of inversion about the air–water interface gives rise to SFG activity. It is generally agreed that the VSFG spectrum from neat water is from the first and second water layers. However, when solutes are added, centrosymmetry does not necessarily sharply begin at the third layer, that is, the air–aqueous interface becomes more complicated. If there is a concentration gradient or gradients as one approaches the bulk from the surface, this region is now deemed SFG active, and the VSFG spectrum would contain information from this region (*e.g.* many layers). However, if there are centrosymmetric solvation shell structures, the centrosymmetry creates SFG inactive regions, and then the VSFG spectrum would not contain information from these localized regions. The SFG active region can also extend to the probe depth,⁷⁵ yet more often it is far shallower since SFG activity is strictly defined by the lack of inversion symmetry. Probe depth is defined by the shortest wavelength and the coherence length of the incident pulses. The probe depth and the coherence length do not define the SFG active interface; these do, however, limit the depth that can be investigated by SFG. Without additional experimental evidence it is not clear if a concentration gradient is continuous or if the ions induce structure near the surface. What has traditionally been called the surface now must be defined as an SFG active interfacial region. (Bulk aqueous solutions have an inversion center macroscopically.) In the work presented here and in our previous publications, the concept of interfacial depth variation is an overarching discovery.

Polarization VSFG studies provide invaluable information on vibrational mode analysis and assignment, and relative molecular orientation.^{64,65} Polarization combinations used for aqueous surface studies are typically ssp, sps, and ppp combinations. Wang *et al.* have advanced the use and interpretation of polarization including null angle in SFG studies.⁶⁸ Polarization-angle null analysis has been further developed by Shultz *et al.*⁷³ Additional details relating to dynamics,^{60,76,77} effects of molecular motion, and how this motion relates to polarization and bandwidth have been discussed.^{62,71,78} To determine the absolute molecular orientation, a measurement of the phase needs to be completed. Absolute phase measurements have been recently pioneered by Shen *et al.*^{79,80} however, these types of measurements have been slow to be adopted by other laboratories due to the added experimental complexity.

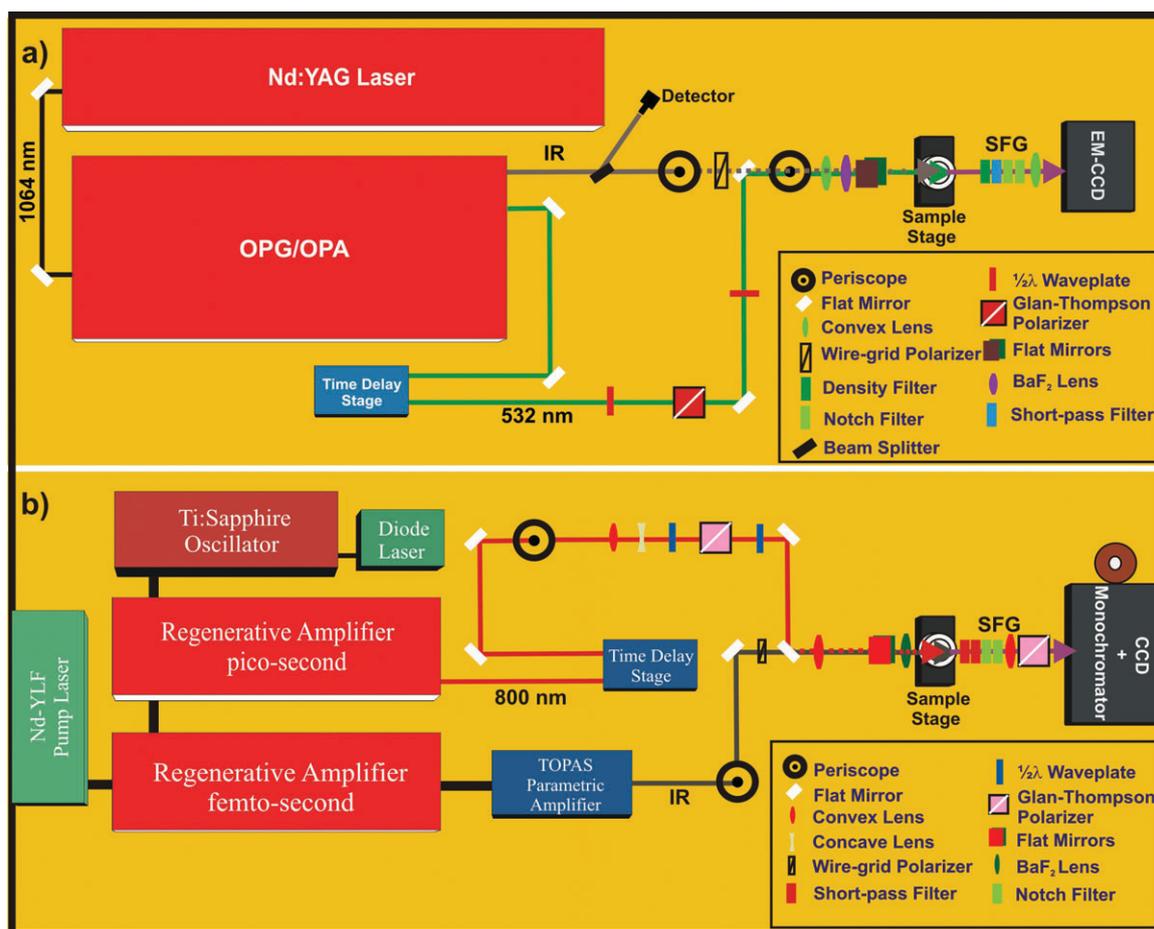


Fig. 2 Schematics of (a) the 10 Hz picosecond scanning VSG system, and (b) the broad bandwidth femtosecond/picosecond VSG system.

When reporting the average orientation, one makes an assumption about the orientation distribution and its parameters. Commonly, the δ function is used for the orientation distribution. More recently, sophisticated methods that include a distribution of orientation, such as a modified Gaussian distribution, have been implemented for simulating SFG response functions for different symmetry groups under three polarization conditions.⁷¹

Details of the VSG instrumentation (scanning and broad bandwidth) used for the spectra shown are presented in the papers referenced herein.^{59,81–84} Most of the spectra exploring the hydrogen-bonded region of aqueous surfaces were obtained from a 10 Hz VSG scanning system (Laser Vision optical parametric amplifier (OPA) system) shown schematically in Fig. 2a. Because of the need to detect small changes in the hydrogen bonding region, we find that a system designed for infrared energy, but moreover, for an evenly distributed infrared energy output in the 2900 to 3700 cm^{-1} region is critically important. Therefore, for our water studies, spectra were obtained with our Laser Vision OPA system, which utilizes KTP nonlinear crystals for optical parametric generation of signal and idler waves, and KTA nonlinear crystals for infrared wave generation. In the 10 Hz scanning system, consistent with other scanning systems in various research laboratories, the incident visible beam is 532 nm (doubled from the 1064 nm fundamental of an Nd:YAG) and has ~ 30 picosecond pulses.

The second VSG system, a broad bandwidth femtosecond/picosecond system, is shown schematically in Fig. 2b. This system, used in some of the studies presented here, is a Ti:sapphire-based ultrafast system (Spectra Physics)^{81,84} that utilizes two amplifiers to produce 2 picosecond and 100 femtosecond 800 nm pulses. The femtosecond pulses are used to drive the infrared generation of the OPA. Again, the infrared energy and profile are taken into consideration for each experiment. The femtosecond pulses produce spectrally broad ($\sim 200 \text{ cm}^{-1}$ FWHM) pulses that then produce stable broad bandwidth infrared pulses in the OPA. We have used this system (modified again in 2008) for a variety of wavelength regions ranging from 1000 cm^{-1} to 3800 cm^{-1} .⁸⁵ Lower wavenumber VSG spectra are more difficult to achieve mainly because of the lower energies produced; however, this spectral region is being accessed more commonly than in past years using picosecond scanning and femtosecond broad bandwidth SFG systems.^{86–91} In the data presented here, we mostly focus on the higher wavenumber region of the water stretching bands.

Results and discussion

Neat water

Before discussing solvation of solutes and ions at the air–aqueous interface, it is important to understand neat water, its

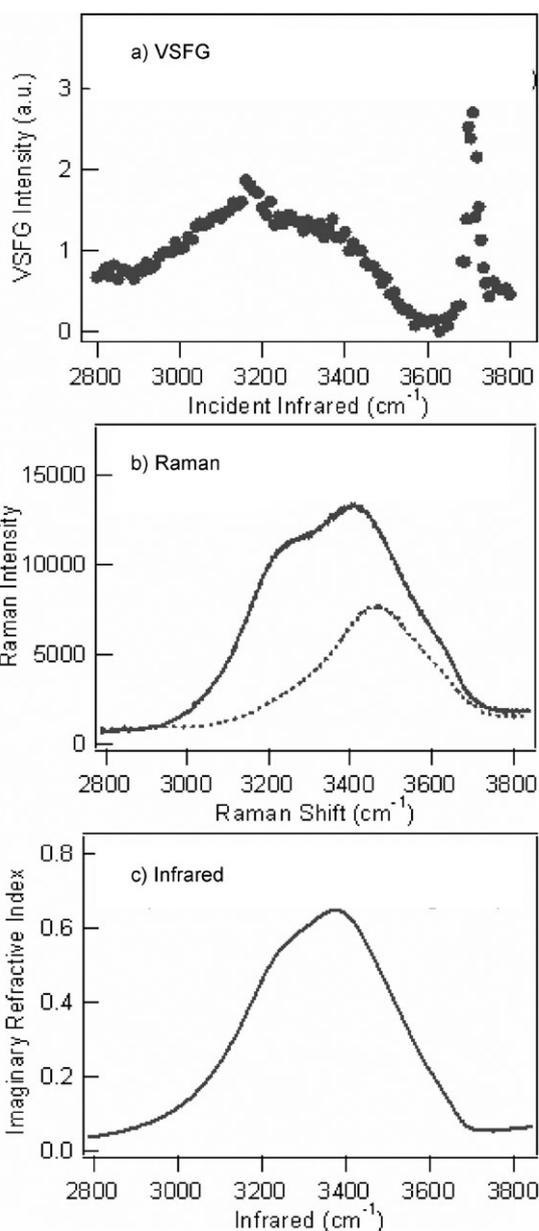


Fig. 3 (a) ssp VSGF spectrum of neat water normalized to IR and Fresnel factors, (b) polarized parallel (continuous line) and polarized perpendicular (discontinuous line) Raman spectra of neat water, and (c) imaginary refractive index of neat water obtained and calculated using infrared reflection absorption spectroscopy (IRRAS) and Kramers–Kronig equations.

surface and bulk structure. In Fig. 3, ssp-polarized VSGF spectra (Fig. 3a) of surface water, the polarized Raman spectra (Fig. 3b), parallel and perpendicular, of bulk water, and the imaginary refractive index component of the infrared reflection spectrum (Fig. 3c) of the surface and bulk water are shown. These selected spectra illustrate the similarities and differences in the spectra from these very different, but related, techniques. Realize that the VSGF data also reveal interference effects since SFG is a coherent spectroscopic technique. The parallel polarized Raman result in Fig. 3b (in addition to IR results) is used for the comparison to the ssp-polarized VSGF spectrum of Fig. 3a.^{82,83}

The broad continuum ranging from 3000 cm⁻¹ to 3650 cm⁻¹ of the VSGF, Raman, and IR spectra is attributed to the OH stretching modes of hydrogen-bonded water molecules, from a more strongly to a more weakly hydrogen bonding network. The precise assignment of the continuum remains somewhat controversial. Some research groups have supported the presence of several hydrogen-bonded water species, whereas other researchers assert the predominance of a broad continuum arising from dynamic fluctuations of water.^{9,11,18–20,92,93} Very recently, the resulting VSGF spectrum of neat water has been assigned to the intramolecular coupling between the stretching and the bending overtone (the Fermi resonance),⁶³ although this is hotly debated.^{94,95}

In the VSGF spectra of Fig. 3, at 3700 cm⁻¹ in the VSGF spectrum, not part of the continuum, a narrow peak is observed and assigned to the dangling OH (free OH) stretch of water molecules that span across the air–water interface

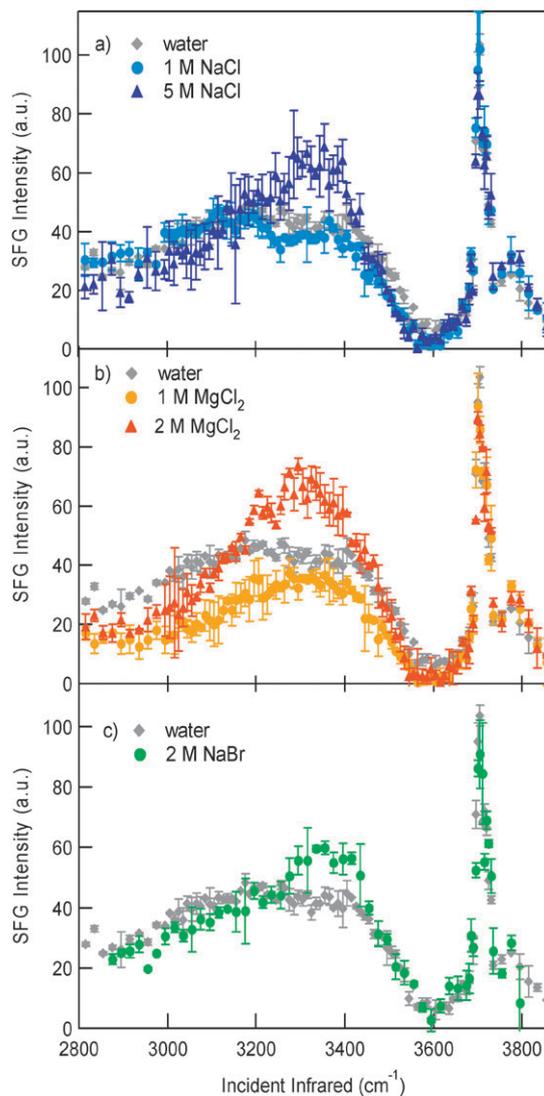


Fig. 4 ssp-polarized VSGF spectra of aqueous solutions of (a) 1 M and 5 M NaCl, (b) 1 M and 2 M MgCl₂, and (c) 2 M NaBr. Neat water VSGF spectra are shown in gray for reference. Error bars are ±1 standard deviation.

with one uncoupled OH bond directed into the gas phase and the other interacting through hydrogen bonding with the liquid phase. Clearly, all of the spectra shown in Fig. 3 are similar with respect to the general appearance of the hydrogen bonding stretch region. Yet, the free OH VSFG peak at 3700 cm^{-1} is not observed in the bulk spectra. The small intensity on the high energy side of the free OH is resonant SFG; however, the appearance of a peak is misleading since its shape appears from incomplete subtraction of the gas phase water above the solution (more evident in Fig. 4). Assignment of this intensity remains controversial.¹⁹

Halides with mono and divalent counter cations

Adding chloride in the 1 M range does not induce large changes to the water ssp VSFG spectra shown in Fig. 4, particularly for sodium chloride.^{19,59} However, for more concentrated aqueous NaCl, the 3400 cm^{-1} and 3200 cm^{-1} regions show a change in their intensity relative to that of water, and the free OH at 3700 cm^{-1} decreases in intensity (Fig. 4a). For aqueous magnesium chloride (Fig. 4b), a slight SFG decrease for 2 M Cl (1 M MgCl_2) in the stretching region is observed. Similar to the 5 M NaCl, the 4 M Cl of MgCl_2 (2 M MgCl_2) shows an enhancement slightly lower in frequency than 3400 cm^{-1} . In addition, a clear decrease in SFG intensity in the 3200 cm^{-1} region is observed, similar to the high concentration Cl spectrum in the NaCl case. In Fig. 4c, the aqueous 2 M NaBr also shows enhancement in the 3400 cm^{-1} region, and a slight decrease in the 3200 cm^{-1} region. These findings suggest that the strength of the hydrogen bonding is somewhat reduced.

At a high salt concentration, for both 5 and 4 M Cl solution surfaces of NaCl and MgCl_2 , respectively, the free OH peak intensity is slightly reduced due to a change in the number density, although there is the possibility of a small orientation change for the 5 M aqueous NaCl surface implied from recent polarization studies.⁹⁶ The lower spectral region intensity around 3200 cm^{-1} consistently shows a small decrease in all three salt spectra; this is more evident in the divalent Mg^{2+} spectrum.

The VSFG spectra in Fig. 4 are shown to demonstrate the changes in interfacial water structure with the introduction of halide salts, both monovalent and divalent cation counterions. Overall, the lower spectral region shows larger decreases in intensity with the divalent cation system. We have shown previously that as the halide increases in size and polarizability ($\text{I}^- > \text{Br}^- > \text{Cl}^-$), the 3400 cm^{-1} region, the solvation shell (hydrating water molecules) of the ion, increases in intensity. This interfacial observation is consistent with the bulk Raman studies, although more enhancement is observed in the interfacial spectra. The VSFG results are indicative of interfacial concentration gradients that also follow $\text{I}^- > \text{Br}^- > \text{Cl}^-$.⁵⁹ In contrast, Raymond and Richmond⁹⁷ concluded that there is a decrease of anion concentration as the surface is approached. In the earlier studies by Shultz and co-workers,^{98–100} a double layer model was used to explain the intensity enhancement in the hydrogen-bonded region. In this model, anions are closer to the surface, in agreement with our findings. Wang and co-workers¹⁰¹ found that the interfacial thickness increases following $\text{Br}^- > \text{Cl}^-$, also

in agreement with our work. Phase data⁷⁹ infer that the direction of the water molecules in aqueous NaCl (up to 1.7 M) does not change relative to the neat water system, although aqueous NaI phase measurements reveal that on average a portion of the water molecules reorient to have their hydrogens pointing toward the interface. What has not been discussed before in our publications is the slight broadening to lower frequency of the 3400 cm^{-1} band by more than 50 cm^{-1} from the aqueous 2 M MgCl_2 surface spectrum, which is still not well understood. For aqueous NH_4Cl , as previously reported,^{19,82} a change in the shape of the spectrum around 3300 cm^{-1} was observed, but to a lesser extent. (The NH stretching modes did not contribute significantly to this observation.) Additional studies of aqueous 1 M $(\text{NH}_4)_2\text{SO}_4$ (and 1 M Na_2SO_4) revealed a 3400 cm^{-1} spectral enhancement similar in frequency to the lower concentration (1 and 2 M)⁵⁹ sodium halide solutions. However, for aqueous 1 M sulfate salts, a 3200 cm^{-1} SFG enhancement was observed, which is contrary to any of the halide salts studied to date. MD simulations explained these findings as an interfacial depth increase due to the divalent sulfate anion being buried about 10 \AA below the surface. The doubly charged sulfate anion orients the water molecules, which is then observed as a 3200 cm^{-1} VSFG enhancement.^{19,82} The 3200 cm^{-1} band intensity is sensitive to the hydrogen bonding strength; water molecules of increased alignment create a strong hydrogen-bonded network. Moreover, the aligned water molecules then contribute additional SFG response relative to the less aligned (less ordered) water molecules, which explains the observed 3200 cm^{-1} enhancement.

The aqueous nitrate systems¹⁰² in Fig. 5 show similar behavior to the halides. Yet, depletion of VSFG intensity in the low frequency region is more evident, and is consistent when comparing the Raman spectra of these different salts. However, not consistent with the Raman spectra are the significant enhancements in the solvation shell region of 3400 cm^{-1} . The smaller polarizability changes in the cations of the nitrate systems also do not explain the increasing enhancement as one goes down the periodic table of the divalent cations. Clearly, the counter cation does matter, but the arrangement of the interfacial water molecules in one or multiple concentration gradients is not easily predicted. The solvation shells of the divalent cations are very different to those of the halide and/or nitrate anions. The water dipoles point in the opposite direction in the solvation shells of cations *versus* those of anions.

The maximum intensity of the low frequency band (sharper peak) in the neat water spectrum actually appears to be at 3180 cm^{-1} . Yet in the presence of divalent cations, an apparent blue shift of this band to about 3200 cm^{-1} and 3280 cm^{-1} is observed as shown in Fig. 4 and 5, respectively. Possible explanations of this phenomenon are still under investigation, although one may attribute this blue shift to a weakening of the hydrogen bonding.

The free OH peak intensity has significantly decreased for the aqueous high concentration nitrate salts in Fig. 5. At 3 M, there are just enough water molecules to form 1 solvation shell per ion on average. Therefore, the drop in free OH intensity is consistent with a drop in number density of water molecules at the surface. Polarization studies, however, also indicate a

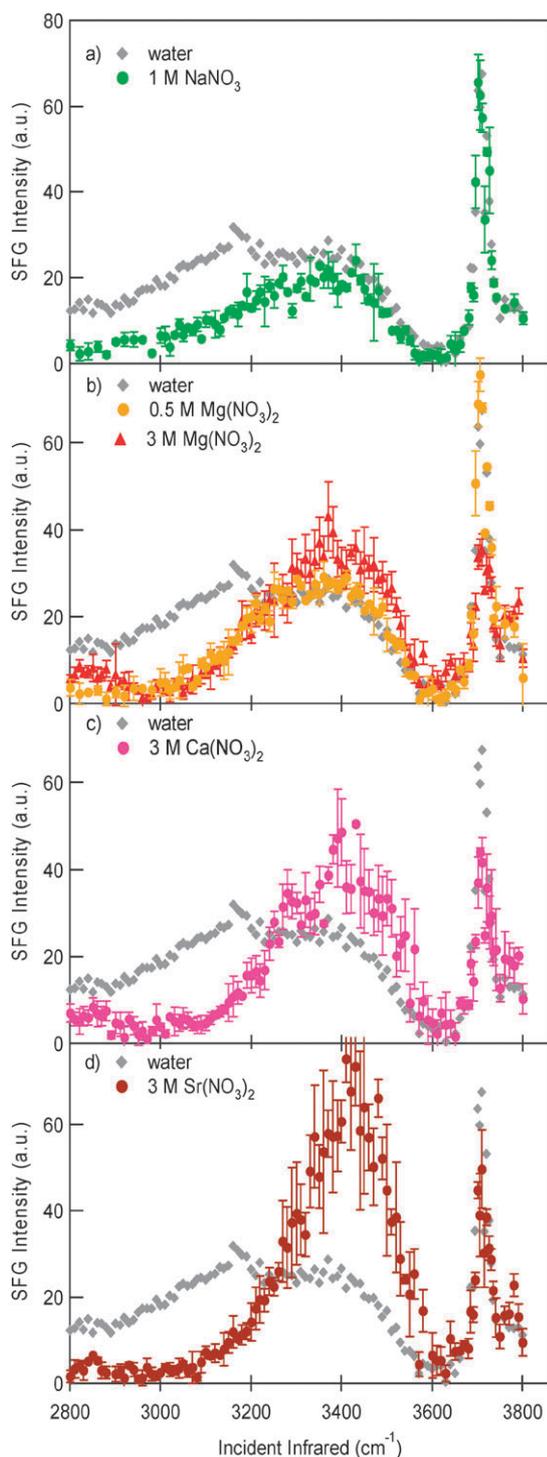


Fig. 5 ssp-polarized VSG spectra of aqueous nitrate solutions of (a) 1 M NaNO_3 , (b) 0.5 M and 3 M $\text{Mg}(\text{NO}_3)_2$, (c) 3 M $\text{Ca}(\text{NO}_3)_2$ and (d) 3 M $\text{Sr}(\text{NO}_3)_2$. Neat water VSG spectra are shown in gray for reference. Error bars are ± 1 standard deviation.

change in orientation, where the free OH is lying closer to the surface plane.¹⁰²

Acids

We have also investigated several aqueous acid systems^{25,83} in addition to halide^{19,59} and nitrate salts,^{91,102,103} and NaOH .²⁵

The aqueous halogen acid interfaces are significantly different than their monovalent salt analogs. Surface tension measurement of halogen acids *versus* salts clearly points to one fundamental difference. In Fig. 6a, the surface tension of salts is shown to increase, whereas that of the corresponding acid decreases the surface tension of water. Surface depletion of the salt and surface activity of the acids have been inferred in the past solely from these findings. However, many researchers^{22,59,104–106} have clearly shown that many salt anions, particularly the large polarizable halides, are quite surface active. Thus, the discrepancy of clearly opposite surface tension measurements has been perplexing until the resurgence of recent experimental and theoretical advances.

The VSFG spectra of halogen acids, HCl, HBr, and HI, have clearly different interfacial water spectra relative to the corresponding salts.^{25,83} In Fig. 6b, the ssp VSFG spectrum of 1 M HBr is shown relative to neat water. Previously published VSFG spectra,^{25,83} and the HBr spectrum shown as an example here, reveal enhancement across the full OH stretch region, with the exception of the free OH, which decreases in intensity with all acids tested. Previously, we have shown that there is a detectable proton continuum at lower frequencies⁸³ which points to either the H_3O^+ and/or H_5O_2^+ surface species. In this past VSFG work, it is also clear that several factors play a role in the enhancement of the regions at or below 3200 cm^{-1} that is not observed in the corresponding salt

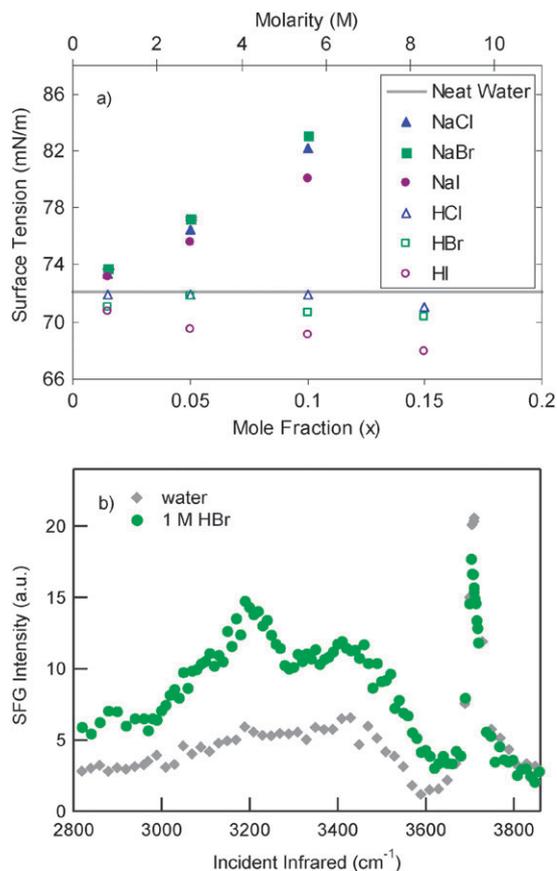


Fig. 6 (a) Surface tension values of sodium salts and monoprotic acids as a function of concentration. (b) ssp-polarized VSFG spectra of aqueous 1 M HBr and neat water.

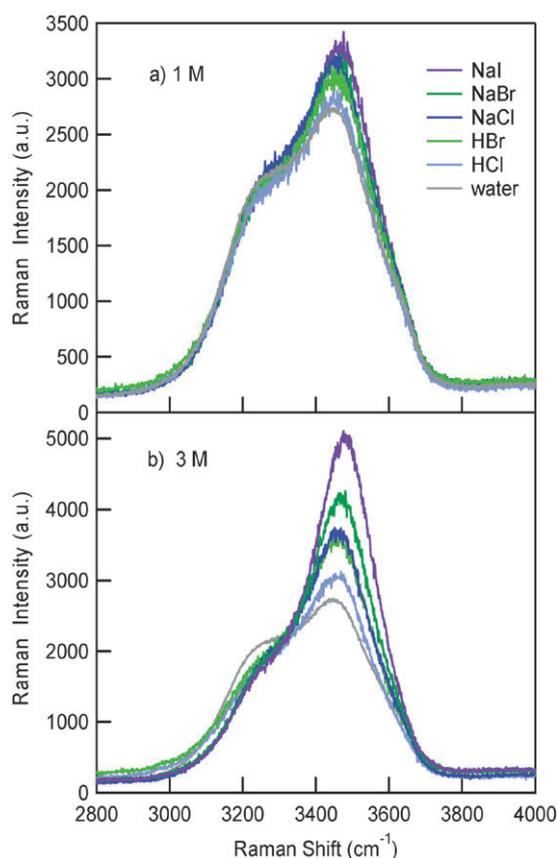


Fig. 7 Unpolarized Raman spectra of (a) 1 M and (b) 3 M aqueous sodium salts and monoprotic acid solutions. Unpolarized Raman spectra of neat water are shown in gray for reference.

spectra. Shown in Fig. 7 for reference are Raman spectra in the OH stretch region of aqueous bulk solutions. Here it is clear that the 3400 cm^{-1} region increases with the number of salt ions, and with increase in size and polarizability of the anion. It is also clear that the acids only reveal an increase due to the presence of the salt ions, not the hydrated protons. Thus, the VSFG spectra^{83,102} show unique spectral signatures from the interfacial region compared to the bulk. The free OH intensity decrease is also counter to what is observed for the salt solutions (no detectable decrease in the 1–2 M range). New ssp and ppp VSFG data, as shown in Fig. 8, reveal that the ratio of the ssp to the ppp intensity in the free OH peak is relatively constant for two different aqueous HBr concentrations.

According to previous reports,^{78,107} the orientation fluctuation of the free OH oscillator may occur in a time scale that could match its vibrational relaxation time or even shorter. Under the fast reorientation motion scenario, reorientation is known to affect the SFG intensity response of the free OH oscillator as demonstrated by Wei and Shen.⁷⁸ However, this effect is considered to be relatively modest under the ssp and ppp polarization conditions. Moreover, in addition to the fast reorientation motion effect, the applied orientation angle distribution can also affect the SFG intensity response. For instance, to better represent an average orientational angle, a Gaussian weighting function is often employed to represent the orientation angle distribution. As demonstrated by Fourkas *et al.*, the larger the spread in the orientation angle distribution,

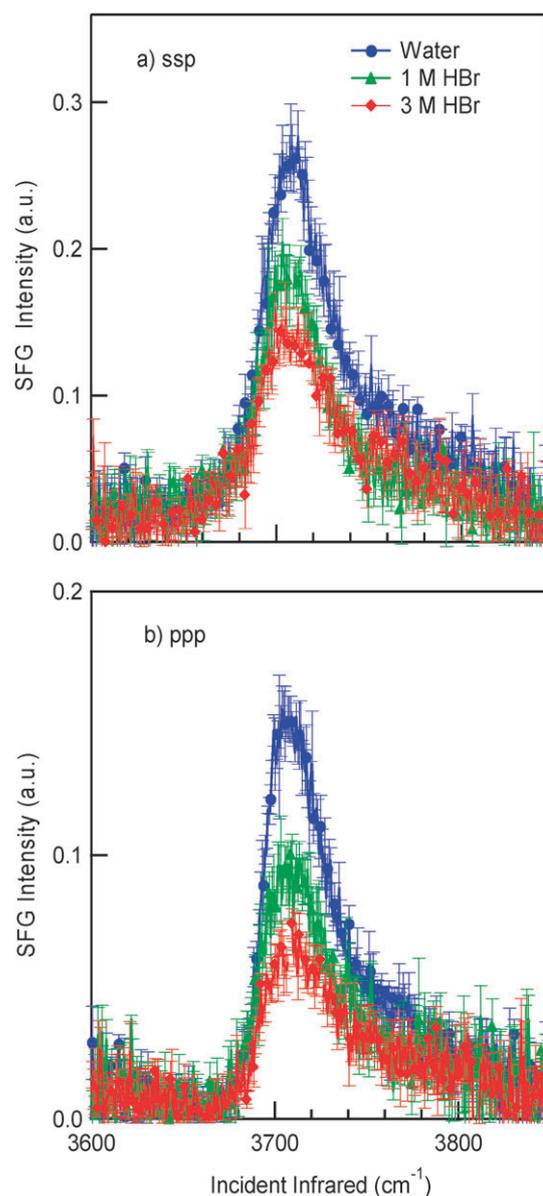


Fig. 8 VSFG spectra of 1 M and 3 M aqueous HBr under (a) ssp and (b) ppp polarization combinations. Incident angles of the infrared and visible radiations from the surface normal are 68° and 53° , respectively. Error bars show the range (± 1 standard deviation) of the intensities. Spectra obtained with the broad bandwidth SFG system.

the greater the effect of the reorientation results in the SFG signal.⁷¹ Yet, for a modest spread of the orientation angle distribution ($\sim 10^\circ$), reorientation has little effect on the free OH SFG spectra for the ssp and ppp polarization conditions. Based on the recent study by Wang and co-workers, the average orientation angle of the free OH oscillator on the neat water surface is 33° with respect to the surface normal with a constrained orientation distribution less than 15° assuming a Gaussian distribution.^{62,107} In order to fulfill the same degree of intensity loss found in the spectra, the orientation angle distribution has to encompass a much wider spread, which is physically unreasonable. This is consistent with an intensity decrease due to a number density decrease of free OH oscillators at the surface and not a change of orientation angle and/or

orientation angle distribution width. Recall from above that only the nitrates with divalent counter cations revealed a change in number density, and a significant increase in the average tilt angle relative to the surface normal.

To summarize the acids, aqueous surfaces of halogen acids are different relative to their corresponding sodium salts with respect to their effect on surface water structure.^{19,20,25} It is also observed that the surface activity of the anion plays a role in the surface activity of H_3O^+ as revealed from the increasing enhancement with polarizability and size of the anion, a similar trend to that found for the sodium halides, but more significant. Phase measurements indicate a flip in orientation of the OH oscillators in most of the hydrogen bonding region, particularly in the lower spectral region. Thus, H_3O^+ and water hydrogens point toward the bulk phase.^{79,80} Recent theoretical studies²⁶ predict that neat water is more acidic at the air–water interface relative to the bulk, consistent with our findings that suggest that H_3O^+ is surface active in the acid studies. Additionally, we conclude that the halide polarizability plays a key role in the interfacial surface activity of the anions, and helps to increase the surface activity of the hydrated protons.

Discussion on interfacial depth

In our interpretation of the VSFG intensity, Raman and infrared spectral response from bulk solution is an important comparison.^{19,59,82,83} In most cases, the Raman and infrared intensity changes relative to water were smaller than what was observed for the VSFG surface spectra. In fact, there are several chemical systems, specifically the halogen acids, sulfate, and nitrate with divalent cations, where the Raman and infrared bulk spectroscopies provided a very different picture when used to predict VSFG spectra. It is these differences and the selection rules for the SFG, Raman, and infrared that point to information of concentration gradients in the subsurface regions.

It is clear that any soluble solute creates a structure below the water surface, giving rise to an increase in interfacial depth relative to that of neat water. The structures, either in the form of two separate concentration gradients, or a complex set of concentration gradients, can only be theoretically postulated at this time. There are fewer assumptions for the quantification of interfacial depth in the sodium halide systems⁵⁹ (relative to other electrolyte systems) and therefore interfacial depth can be experimentally determined, as we have done. For these systems we find that the interfacial depth is as a minimum 2 times deeper (for 1 M NaBr and NaI) relative to neat water. For other systems studied, interfacial depth was difficult to quantify due to enhancements in regions other than the solvation shell 3400 cm^{-1} region, which undercounts water molecules within the centrosymmetric environment of the sphere-like hydration environment.

Lipids and surface water; confinement of the free OH

In addition to surface water structure of electrolyte aqueous solutions, it is of interest to understand an organic film on an aqueous surface. We have recently delved into the area of fatty

acid and lipid films on purely aqueous and on aqueous electrolyte solutions.^{87,108,109} There has been a small body of

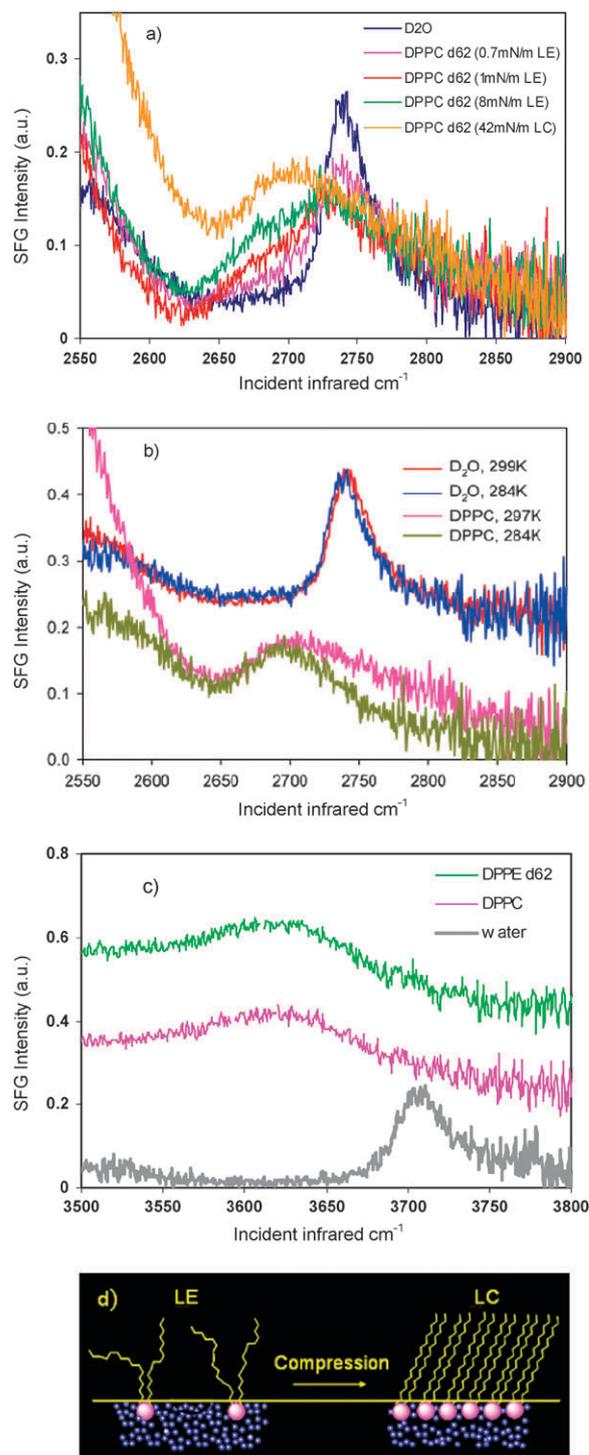


Fig. 9 ssp VSFG spectra of (a) DPPC d62 monolayer on D_2O at different surface pressures (free OD region), (b) DPPC monolayer on D_2O at different temperatures (free OD region), and (c) DPPE d62 monolayer and DPPC monolayer on water (free OH region). Neat D_2O and H_2O spectra are included in the corresponding regions. (d) Model depiction of water (blue spheres) at the interface being strongly disturbed by DPPC monolayer in condensed phase (LC, all-*trans* conformation). Spectra obtained with the broad bandwidth SFG system.

work on understanding the underlying OH hydrogen bonding region of lipid films;^{56,110,111} however, the free OH of surface water had not been of interest previously. This may have been from the assumption that the free OH was not present in the presence of a lipid monolayer or fatty acid film. Surprisingly, the free OH continues to exist even when a full monolayer of lipid or fatty acid is spread on the water surface. We have shown that the dangling nature of the bond persists under monolayer conditions.⁸⁴ A very recent study¹¹² has also observed a similar phenomenon. Fig. 9 reveals this result. In Fig. 9a, as one compresses a surface film, the free OD (proxy for free OH) shifts to lower frequency, implying a possible interaction with surrounding surface molecules. This is consistent with studies of CO₂ and SO₂ adsorption on water surfaces,¹¹³ and methane on ice surfaces.¹¹⁴ In Fig. 9b, temperature studies reveal that the OH is clearly not hydrogen bonded. In Fig. 9c, it is shown that this also occurs for other lipids such as dipalmitoyl phosphatidyl ethanolamine (DPPE) in addition to dipalmitoyl phosphatidylcholine (DPPC) indicating that the dangling OH is at the base of the lipid chain and is not affected by differing head groups. Fatty acids have also been tested and the free OD shows similar behavior. Additionally, the free OD and the free OH also show the same behavior as revealed in Fig. 9c. Work in this area continues in our group and has expanded into the investigation of other electrolyte and non-electrolyte aqueous solutions. This observation seems to be general in nature, yet more work is needed to understand more complex surface films. There are possible biological implications for this phenomenon, particularly as it relates to surface activity and understanding the mechanism of water transport in lipid films.

Future direction

Water organization and structure at aqueous surfaces is a fascinating area of science that has a multitude of implications for biological systems, atmospheric aerosol science, and materials. VSFG spectroscopy has tremendously increased our knowledge in this area, with the help of other important experimental^{9,11,13,105,115–129} and theoretical tools.^{130–148} VSFG, although very useful, lacks in its ability to be highly quantifiable; it averages molecular responses. VSFG deuteration schemes^{149–151} are helpful in providing additional information about water structures by decoupling vibrational modes, but also suffer from the same lack of quantification. VSFG has advanced significantly over the past 10 or more years, yet quantification continues to be an issue since all data, inclusive of the phase measurements and new polarization techniques, are averaged in one or more ways. However, phase sensitive and polarized VSFG experiments will likely further contribute to the clarification of water spectral assignments, which continue to be debated. The role that dynamics^{62,71,78,152,153} plays in the spectral shape is another area in need of additional advances. New VSFG (and second harmonic¹⁵⁴) approaches and variations of existing approaches, in addition to complementary experimental and theoretical tools, continue to be needed to further our understanding of aqueous surface structure.

Acknowledgements

The NSF, DOE-BES, Beckman, Dreyfus, and Sloan foundations have contributed funding for the research presented and discussed here. The SFG and surface science communities, our experimental and theoretical colleagues, are also acknowledged. This work would not be possible without the insights of others from the scientific community, the US and abroad.

References

- 1 S. S. Xantheas and T. H. Dunning, *J. Chem. Phys.*, 1993, **99**, 8774.
- 2 S. S. Xantheas, *J. Chem. Phys.*, 1994, **100**, 7523.
- 3 A. K. Soper, *J. Chem. Phys.*, 1994, **101**, 6888.
- 4 A. Luzar and D. Chandler, *Nature*, 1996, **379**, 55.
- 5 K. Liu, J. D. Cruzan and R. J. Saykally, *Science*, 1996, **271**, 929.
- 6 L. X. Dang and T. M. Chang, *J. Chem. Phys.*, 1997, **106**, 8149.
- 7 U. Buck and F. Huisken, *Chem. Rev.*, 2000, **100**, 3863.
- 8 R. Ludwig, *Angew. Chem., Int. Ed.*, 2001, **40**, 1808.
- 9 C. J. Fecko, J. D. Eaves, J. J. Loparo, A. Tokmakoff and P. L. Geissler, *Science*, 2003, **301**, 1698.
- 10 M. Miyazaki, A. Fujii, T. Ebata and N. Mikami, *Science*, 2004, **304**, 1134.
- 11 P. Wernet, D. Nordlund, U. Bergmann, M. Cavalleri, M. Odelius, H. Ogasawara, L. A. Naslund, T. K. Hirsch, L. Ojamae, P. Glatzel, L. G. M. Pettersson and A. Nilsson, *Science*, 2004, **304**, 995.
- 12 M. L. Cowan, B. D. Bruner, N. Huse, J. R. Dwyer, B. Chugh, E. T. J. Nibbering, T. Elsaesser and R. J. D. Miller, *Nature*, 2005, **434**, 199.
- 13 J. D. Eaves, J. J. Loparo, C. J. Fecko, S. T. Roberts, A. Tokmakoff and P. L. Geissler, *Proc. Natl. Acad. Sci. U. S. A.*, 2005, **102**, 13019.
- 14 H. Papid, N. Agmon, M. K. Petersen and G. A. Voth, *J. Chem. Phys.*, 2005, **122**, 014506.
- 15 P. Perera, M. Wyche, Y. Loethen and D. Ben-Amotz, *J. Am. Chem. Soc.*, 2008, **130**, 4576.
- 16 Q. Du, R. Superfine, E. Freysz and Y. R. Shen, *Phys. Rev. Lett.*, 1993, **70**, 2313.
- 17 K. B. Eisenthal, *Chem. Rev.*, 1996, **96**, 1343.
- 18 G. L. Richmond, *Chem. Rev.*, 2002, **102**, 2693.
- 19 S. Gopalakrishnan, D. Liu, H. C. Allen, M. Kuo and M. J. Shultz, *Chem. Rev.*, 2006, **106**, 1155.
- 20 Y. R. Shen and V. Ostroverkhov, *Chem. Rev.*, 2006, **106**, 1140.
- 21 K. Lum, D. Chandler and J. D. Weeks, *J. Phys. Chem. B*, 1999, **103**, 4570.
- 22 P. Jungwirth and D. J. Tobias, *J. Phys. Chem. B*, 2001, **105**, 10468.
- 23 P. Jungwirth and D. J. Tobias, *J. Phys. Chem. B*, 2002, **106**, 6361.
- 24 M. K. Petersen, S. S. Iyengar, T. J. F. Day and G. A. Voth, *J. Phys. Chem. B*, 2004, **108**, 14804.
- 25 M. Mucha, T. Frigato, L. M. Levering, H. C. Allen, D. J. Tobias, L. X. Dang and P. Jungwirth, *J. Phys. Chem. B*, 2005, **109**, 7617.
- 26 V. Buch, A. Milet, R. Vacha, P. Jungwirth and J. P. Devlin, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 7342.
- 27 B. C. Garrett, *Science*, 2004, **303**, 1146.
- 28 H. C. Allen, J. M. Laux, R. Vogt, B. J. Finlayson Pitts and J. C. Hemminger, *J. Phys. Chem.*, 1996, **100**, 6371.
- 29 T. M. Miller and V. H. Grassian, *Geophys. Res. Lett.*, 1998, **25**, 3835.
- 30 J. S. Lighty, J. M. Veranth and A. F. Sarofim, *J. Air Waste Manage. Assoc.*, 2000, **50**, 1565.
- 31 M. Kendall, B. M. Hutton, T. D. Tetley, M. J. Nieuwenhuijsen, E. Wigzell and F. H. Jones, *Appl. Surf. Sci.*, 2001, **178**, 27.
- 32 U. Poschl, *J. Aerosol Med.*, 2002, **15**, 203.
- 33 F. Dominici, R. D. Peng, M. L. Bell, L. Pham, A. McDermott, S. L. Zeger and J. M. Samet, *JAMA, J. Am. Med. Assoc.*, 2006, **295**, 1127.
- 34 N. Bloembergen and P. S. Pershan, *Phys. Rev.*, 1962, **128**, 606.
- 35 P. A. Franken and J. F. Ward, *Rev. Mod. Phys.*, 1963, **35**, 23.

- 36 J. H. Hunt, P. Guyotsonnest and Y. R. Shen, *Chem. Phys. Lett.*, 1987, **133**, 189.
- 37 P. Guyotsonnest, J. H. Hunt and Y. R. Shen, *Phys. Rev. Lett.*, 1987, **59**, 1597.
- 38 X. D. Zhu, H. J. Suhr and Y. R. Shen, *J. Opt. Soc. Am. B*, 1986, **3**, P252.
- 39 V. Buch and J. P. Devlin, *J. Chem. Phys.*, 1991, **94**, 4091.
- 40 Y. R. Shen, *Surf. Sci.*, 1994, **299/300**, 551.
- 41 C. D. Bain, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 1281.
- 42 G. A. Somorjai and G. Rupprechter, *J. Phys. Chem. B*, 1999, **103**, 1623.
- 43 R. Braun, B. D. Casson, C. D. Bain, E. W. M. van der Ham, Q. H. F. Vrethen, E. R. Eliel, A. M. Briggs and P. B. Davies, *J. Chem. Phys.*, 1999, **110**, 4634.
- 44 M. Himmelhaus, F. Eisert, M. Buck and M. Grunze, *J. Phys. Chem. B*, 2000, **104**, 576.
- 45 S. Nihonyanagi, Y. Shen, K. Uosaki, L. Dreesen, C. Humbert, P. Thiry and A. Peremans, *Surf. Sci.*, 2004, **573**, 11.
- 46 C. M. Johnson, E. Tyrode and C. Leygraf, *J. Electrochem. Soc.*, 2006, **153**, B113.
- 47 X. L. Lu, N. Shephard, J. L. Han, G. Xue and Z. Chen, *Macromolecules*, 2008, **41**, 8770.
- 48 S. Baldelli, *Acc. Chem. Res.*, 2008, **41**, 421.
- 49 M. C. Goh, J. M. Hicks, K. Kemnitz, G. R. Pinto, K. Bhattacharyya, T. F. Heinz and K. B. Eisenthal, *J. Phys. Chem.*, 1988, **92**, 5074.
- 50 Q. Du, E. Freysz and Y. R. Shen, *Science*, 1994, **264**, 826.
- 51 S. Baldelli, C. Schnitzer, M. J. Shultz and D. J. Campbell, *J. Phys. Chem. B*, 1997, **101**, 10435.
- 52 D. E. Gragson, B. M. McCarty and G. L. Richmond, *J. Am. Chem. Soc.*, 1997, **119**, 6144.
- 53 D. Zhang, J. Gutow and K. B. Eisenthal, *J. Phys. Chem.*, 1994, **98**, 13729.
- 54 G. R. Bell, C. D. Bain and R. N. Ward, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 515.
- 55 J. Kim and P. S. Cremer, *J. Am. Chem. Soc.*, 2000, **122**, 12371.
- 56 S. Ye, S. Nihonyanagi and K. Uosaki, *Phys. Chem. Chem. Phys.*, 2001, **3**, 3463.
- 57 B. A. Fitchett and J. C. Conboy, *J. Phys. Chem. B*, 2004, **108**, 20255.
- 58 S. Rivera-Rubero and S. Baldelli, *J. Am. Chem. Soc.*, 2004, **126**, 11788.
- 59 D. F. Liu, G. Ma, L. M. Levering and H. C. Allen, *J. Phys. Chem. B*, 2004, **108**, 2252.
- 60 A. N. Bordenyuk and A. V. Benderskii, *J. Chem. Phys.*, 2005, **122**, 134713.
- 61 E. Tyrode, C. M. Johnson, A. Kumpulainen, M. W. Rutland and P. M. Claesson, *J. Am. Chem. Soc.*, 2005, **127**, 16848.
- 62 W. Gan, D. Wu, Z. Zhang, R. R. Feng and H. F. Wang, *J. Chem. Phys.*, 2006, **124**, 114705.
- 63 M. Sovago, R. K. Campen, G. W. H. Wurpel, M. Muller, H. J. Bakker and M. Bonn, *Phys. Rev. Lett.*, 2008, **100**, 173901.
- 64 C. Hirose, N. Akamatsu and K. Domen, *Appl. Spectrosc.*, 1992, **46**, 1051.
- 65 C. Hirose, H. Yamamoto, N. Akamatsu and K. Domen, *J. Phys. Chem.*, 1993, **97**, 10064.
- 66 A. Morita and J. T. Hynes, *Chem. Phys.*, 2000, **258**, 371.
- 67 A. J. Moad and G. J. Simpson, *J. Phys. Chem. B*, 2004, **108**, 3548.
- 68 H.-F. Wang, W. Gan, R. Lu, Y. Rao and B.-H. Wu, *Int. Rev. Phys. Chem.*, 2005, **24**, 191.
- 69 A. G. Lambert and P. B. Davies, *Appl. Spectrosc. Rev.*, 2005, **40**, 103.
- 70 A. Perry, C. Neipert, B. Space and P. B. Moore, *Chem. Rev.*, 2006, **106**, 1234.
- 71 J. T. Fourkas, R. A. Walker, S. Z. Can and E. Gershgoren, *J. Phys. Chem. C*, 2007, **111**, 8902.
- 72 I. V. Stiopkin, H. D. Jayathilake, A. N. Bordenyuk and A. V. Benderskii, *J. Am. Chem. Soc.*, 2008, **130**, 2271.
- 73 H. Groenzin, I. Li and M. J. Shultz, *J. Chem. Phys.*, 2008, **128**, 214510.
- 74 E. L. Hommel and H. C. Allen, *Analyst*, 2003, **128**, 750.
- 75 J. Holman, D. J. Neivandt and P. B. Davies, *Chem. Phys. Lett.*, 2004, **386**, 60.
- 76 Z. H. Wang, Y. S. Pang and D. D. Dlott, *J. Phys. Chem. A*, 2007, **111**, 3196.
- 77 Y. Rao, D. H. Song, N. J. Turro and K. B. Eisenthal, *J. Phys. Chem. B*, 2008, **112**, 13572.
- 78 X. Wei and Y. R. Shen, *Phys. Rev. Lett.*, 2001, **86**, 4799.
- 79 N. Ji, V. Ostroverkhov, C. S. Tian and Y. R. Shen, *Phys. Rev. Lett.*, 2008, **100**, 096102.
- 80 C. S. Tian, N. Ji, G. A. Waychunas and Y. R. Shen, *J. Am. Chem. Soc.*, 2008, **130**, 13033.
- 81 E. L. Hommel and H. C. Allen, *Anal. Sci.*, 2001, **17**, 137.
- 82 S. Gopalakrishnan, P. Jungwirth, D. J. Tobias and H. C. Allen, *J. Phys. Chem. B*, 2005, **109**, 8861.
- 83 L. M. Levering, M. R. Sierra-Hernández and H. C. Allen, *J. Phys. Chem. C*, 2007, **111**, 8814.
- 84 G. Ma, X. K. Chen and H. C. Allen, *J. Am. Chem. Soc.*, 2007, **129**, 14053.
- 85 C. Y. Tang and H. C. Allen, *J. Phys. Chem. A*, 2009, accepted.
- 86 D. K. Hore, D. K. Beaman, D. H. Parks and G. L. Richmond, *J. Phys. Chem. B*, 2005, **109**, 16846.
- 87 G. Ma and H. C. Allen, *Langmuir*, 2006, **22**, 5341.
- 88 E. Tyrode, C. M. Johnson, M. W. Rutland, J. P. R. Day and C. D. Bain, *J. Phys. Chem. C*, 2007, **111**, 316.
- 89 T. Miyamae, A. Morita and Y. Ouchi, *Phys. Chem. Chem. Phys.*, 2008, **10**, 2010.
- 90 A. B. Sugiharto, C. M. Johnson, I. E. Dunlop and S. Roke, *J. Phys. Chem. C*, 2008, **112**, 7531.
- 91 M. Xu, C. Y. Tang, A. M. Jubb, X. K. Chen and H. C. Allen, *J. Phys. Chem. C*, 2009, **113**, 2082.
- 92 J. D. Smith, C. D. Cappa, K. R. Wilson, R. C. Cohen, P. L. Geissler and R. J. Saykally, *Proc. Natl. Acad. Sci. U. S. A.*, 2005, **102**, 14171.
- 93 R. L. C. Wang, H. J. Kreuzer and M. Grunze, *Phys. Chem. Chem. Phys.*, 2006, **8**, 4744.
- 94 C. S. Tian and Y. R. Shen, *Phys. Rev. Lett.*, 2008, **101**, 139401.
- 95 M. Sovago, R. K. Campen, G. W. H. Wurpel, M. Muller, H. J. Bakker and M. Bonn, *Phys. Rev. Lett.*, 2008, **101**, 139402.
- 96 K. M. Callahan, N. N. Casillas-Ituarte, M. Xu, M. Roeselova, H. C. Allen and D. J. Tobias, 2009, to be submitted.
- 97 E. A. Raymond and G. L. Richmond, *J. Phys. Chem. B*, 2004, **108**, 5051.
- 98 C. Schnitzer, S. Baldelli and M. J. Shultz, *J. Phys. Chem. B*, 2000, **104**, 585.
- 99 M. J. Shultz, C. Schnitzer, D. Simonelli and S. Baldelli, *Int. Rev. Phys. Chem.*, 2000, **19**, 123.
- 100 M. J. Shultz, S. Baldelli, C. Schnitzer and D. Simonelli, *J. Phys. Chem. B*, 2002, **106**, 5313.
- 101 H. T. Bian, R. R. Feng, Y. Y. Xu, Y. Guo and H. F. Wang, *Phys. Chem. Chem. Phys.*, 2008, **10**, 4920.
- 102 M. Xu, R. Spinney and H. C. Allen, *J. Phys. Chem. B*, 2009, **113**, 4102.
- 103 M. Xu, J. P. Larentzos, M. Roshdy, L. J. Criscenti and H. C. Allen, *Phys. Chem. Chem. Phys.*, 2008, **10**, 4793.
- 104 E. M. Knipping, M. J. Lakin, K. L. Foster, P. Jungwirth, D. J. Tobias, R. B. Gerber, D. Dabdub and B. J. Finlayson-Pitts, *Science*, 2000, **288**, 301.
- 105 S. Ghosal, J. C. Hemminger, H. Bluhm, B. S. Mun, E. L. D. Hebenstreit, G. Ketteler, D. F. Ogletree, F. G. Requejo and M. Salmeron, *Science*, 2005, **307**, 563.
- 106 P. B. Petersen, R. J. Saykally, M. Mucha and P. Jungwirth, *J. Phys. Chem. B*, 2005, **109**, 10915.
- 107 W. Gan, D. Wu, Z. Zhang, Y. Guo and H. F. Wang, *Huaxue Wuli Xuebao*, 2006, **19**, 20.
- 108 L. F. Voss, C. M. Hadad and H. C. Allen, *J. Phys. Chem. B*, 2006, **110**, 19487.
- 109 L. F. Voss, M. F. Bazerbashi, C. P. Beekman, C. M. Hadad and H. C. Allen, *J. Geophys. Res., [Atmos.]*, 2007, **112**, D06209.
- 110 M. R. Watry, T. L. Tarbuck and G. I. Richmond, *J. Phys. Chem. B*, 2003, **107**, 512.
- 111 Z. S. Nickolov, D. W. Britt and J. D. Miller, *J. Phys. Chem. B*, 2006, **110**, 15506.
- 112 Z. Zhang, D. S. Zheng, Y. Guo and H. F. Wang, *Phys. Chem. Chem. Phys.*, 2009, **11**, 991.
- 113 T. L. Tarbuck and G. L. Richmond, *J. Am. Chem. Soc.*, 2006, **128**, 3256.
- 114 B. Rowland, M. Fisher and J. P. Devlin, *J. Chem. Phys.*, 1991, **95**, 1378.

- 115 C. J. Gruenloh, J. R. Carney, F. C. Hagemester, C. A. Arrington, T. S. Zwier, S. Y. Fredericks, J. T. I. Wood and K. D. Jordan, *J. Chem. Phys.*, 1998, **109**, 6601.
- 116 J. L. Duncan, L. R. Schindler and J. T. Roberts, *J. Phys. Chem. B*, 1999, **103**, 7247.
- 117 A. W. Omta, M. F. Kropman, S. Woutersen and H. J. Bakker, *Science*, 2003, **301**, 347.
- 118 J. M. Headrick, E. G. Diken, R. S. Walters, N. I. Hammer, R. A. Christie, J. Cui, E. M. Myshakin, M. A. Duncan, M. A. Johnson and K. D. Jordan, *Science*, 2005, **308**, 1765.
- 119 U. Heugen, G. Schwaab, E. Brundermann, M. Heyden, X. Yu, D. M. Leitner and M. Havenith, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 12301.
- 120 T. Head-Gordon and M. E. Johnson, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 7973.
- 121 J. Teixeira, A. Luzar and S. Longeville, *J. Phys.: Condens. Matter*, 2006, **18**, S2353.
- 122 J. Cheng, C. D. Vecitis, M. R. Hoffmann and A. J. Colussi, *J. Phys. Chem. B*, 2006, **110**, 25598.
- 123 B. Jagoda-Cwiklik, P. Jungwirth, L. Rulisek, P. Milko, J. Roithova, J. Lemaire, P. Maitre, J. M. Ortega and D. Schroder, *ChemPhysChem*, 2007, **8**, 1629.
- 124 Y. Miller, G. M. Chaban, J. Zhou, K. R. Asmis, D. M. Neumark and R. B. Gerber, *J. Chem. Phys.*, 2007, **127**, 094305.
- 125 R. Mancinelli, A. Botti, F. Bruni, M. A. Ricci and A. K. Soper, *J. Phys. Chem. B*, 2007, **111**, 13570.
- 126 A. Tokmakoff, *Science*, 2007, **317**, 54.
- 127 J. Cheng, M. R. Hoffmann and A. J. Colussi, *J. Phys. Chem. B*, 2008, **112**, 7157.
- 128 D. E. Moilanen, E. E. Fenn, Y. S. Lin, J. L. Skinner, B. Bagchi and M. D. Fayer, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 5295.
- 129 P. B. Petersen and R. J. Saykally, *Chem. Phys. Lett.*, 2008, **458**, 255.
- 130 D. Asthagiri, L. R. Pratt, J. D. Kress and M. A. Gomez, *Proc. Natl. Acad. Sci. U. S. A.*, 2004, **101**, 7229.
- 131 J. A. Poulsen, G. Nyman and P. J. Rossky, *Proc. Natl. Acad. Sci. U. S. A.*, 2005, **102**, 6709.
- 132 D. Chandler, *Nature*, 2005, **437**, 640.
- 133 A. B. McCoy, X. C. Huang, S. Carter and J. M. Bowman, *J. Chem. Phys.*, 2005, **123**, 064317.
- 134 J. Chowdhary and B. M. Ladanyi, *J. Phys. Chem. B*, 2006, **110**, 15442.
- 135 D. Laage and J. T. Hynes, *Science*, 2006, **311**, 832.
- 136 T. Sommerfeld and K. D. Jordan, *J. Am. Chem. Soc.*, 2006, **128**, 5828.
- 137 S. Bulusu, S. Yoo, E. Apra, S. Xantheas and X. C. Zeng, *J. Phys. Chem. A*, 2006, **110**, 11781.
- 138 T. Todorova, A. P. Seitsonen, J. Hutter, I. F. W. Kuo and C. J. Mundy, *J. Phys. Chem. B*, 2006, **110**, 3685.
- 139 H. S. Lee and M. E. Tuckerman, *J. Chem. Phys.*, 2006, **125**, 154507.
- 140 J. L. Thomas, M. Roeselova, L. X. Dang and D. J. Tobias, *J. Phys. Chem. A*, 2007, **111**, 3091.
- 141 J. D. Smith, R. J. Saykally and P. L. Geissler, *J. Am. Chem. Soc.*, 2007, **129**, 13847.
- 142 F. Paesani, S. Iuchi and G. A. Voth, *J. Chem. Phys.*, 2007, **127**, 074506.
- 143 V. Buch, T. Tarbuck, G. L. Richmond, H. Groenzin, I. Li and M. J. Shultz, *J. Chem. Phys.*, 2007, **127**, 204710.
- 144 R. Bukowski, K. Szalewicz, G. C. Groenenboom and A. van der Avoird, *Science*, 2007, **315**, 1249.
- 145 B. Auer, R. Kumar, J. R. Schmidt and J. L. Skinner, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 14215.
- 146 A. Morita and T. Ishiyama, *Phys. Chem. Chem. Phys.*, 2008, **10**, 5801.
- 147 M. Leetmaa, K. T. Wikfeldt, M. P. Ljungberg, M. Odelius, J. Swenson, A. Nilsson and L. G. M. Pettersson, *J. Chem. Phys.*, 2008, **129**, 084502.
- 148 B. M. Auer and J. L. Skinner, *J. Chem. Phys.*, 2008, **128**, 224511.
- 149 B. M. Auer and J. L. Skinner, *J. Chem. Phys.*, 2008, **129**, 214705.
- 150 R. A. Raymond, T. L. Tarbuck, M. G. Brown and G. L. Richmond, *J. Phys. Chem. B*, 2003, **107**, 546.
- 151 D. S. Walker and G. L. Richmond, *J. Phys. Chem. C*, 2007, **111**, 8321.
- 152 J. A. McGuire and Y. R. Shen, *Science*, 2006, **313**, 1945.
- 153 A. Ghosh, M. Smits, M. Sovago, J. Bredenbeck, M. Muller and M. Bonn, *Chem. Phys.*, 2008, **350**, 23.
- 154 P. L. Hayes, J. N. Malin, C. T. Konek and F. M. Geiger, *J. Phys. Chem. A*, 2008, **112**, 660.