

Spectroscopic Studies of Solvated Hydrogen and Hydroxide Ions at Aqueous Surfaces

Teresa L. Tarbuck, Stephanie T. Ota, and Geraldine L. Richmond*

Contribution from the Materials Science Institute and Department of Chemistry,
University of Oregon, Eugene, Oregon 97403

Received May 6, 2006; E-mail: Richmond@oregon.uoregon.edu

Abstract: Measuring the molecular properties of the surface of acidic and basic aqueous solutions is essential to understanding a wide range of important biological, chemical, and environmental processes on our planet. In the present studies, vibrational sum-frequency spectroscopy (VSFS) is employed in combination with isotopic dilution experiments at the vapor/water interface to elucidate the interfacial water structure as the pH is varied with HCl and NaOH. In acidic solutions, solvated proton species are seen throughout the interfacial region, and they alter the hydrogen bonding between water molecules in ways that reflect their depth in the interfacial region. At the higher frequencies of the OH stretch region, there is spectral evidence for solvated proton species residing in the topmost layers of the interfacial region. As reported in previous VSF studies, more strongly bound solvated proton species are observed at lower OH stretching frequencies.^{1–4} The solvated proton species that have stronger hydrogen bonding are similar in structure to those found in bulk acid solutions and likely reside somewhat deeper in the interfacial region. There is also evidence of OH stretching from solvated protons and relatively strong hydrogen bonding in the solvation sphere that is similar to other solvated ions. In contrast, water molecules solvating OH⁻ ions show relatively weak hydrogen bonding and significantly less interfacial order. VSF spectra are acquired under multiple polarizations to provide crucial information for the interpretation of the spectra and for the determination of interfacial structure.

Introduction

The understanding of molecular arrangements and interactions at aqueous acidic and basic interfaces is important in many chemical systems including biological, chemical, and environmental processes. Because these solutions are so important, the bulk solvation of H⁺ and of OH⁻ has been studied extensively, primarily to understand the anomalously high rate of charge transfer in water.⁵ The mechanism of charge transfer for H⁺ in bulk solution is modeled as a continuous interconversion between H₃O⁺·(H₂O)₃ (the Eigen form) and [H₂O···H···OH₂]⁺ (the Zundel form), which is dependent on the inter-oxygen distance and a reduction in the coordination number for the accepting water molecule.⁶ It is unclear if one form is dominant or if it is concentration dependent.^{6–8} For OH⁻, the bulk solution structure is still being determined. New evidence from neutron scattering experiments^{9,10} and MD simulations⁵ suggests that OH⁻ accepts four hydrogen bonds and donates one hydrogen bond.

The orientation and solvation of H⁺ and OH⁻ at a surface are anticipated to be different from that in the bulk due to the anisotropy in the interfacial region. In general, properties at the surface of a solution differ from bulk properties because the concentration, geometry, and the distribution of charge are different at the interface from that in the bulk. These effects can be prominent for interfacial ions that have significant separation of charge. In addition, surface water properties are generally different even in the presence of ions of the same charge.^{11,12}

The surfaces of acidic and basic aqueous solutions, where a wealth of interesting chemistry occurs, are just beginning to be explored.^{3,13} The first surface studies using vibrational sum-frequency spectroscopy (VSFS) of acid solutions were conducted with H₂SO₄, by Raduge et al.⁴ and Baldelli et al.¹⁴ Surface studies of HCl solutions using VSFS followed, with the conclusion that field effects lead to increases in low-frequency OH vibrations due to strong hydration of the protons which leaves the water molecules less screened from the charge on the anion.^{1–3} These studies focused on increases in coopera-

- (1) Baldelli, S.; Schnitzer, C.; Shultz, M. J. *J. Chem. Phys.* **1998**, *108* (23), 9817–9820.
- (2) Schnitzer, C.; Baldelli, S.; Shultz, M. J. *J. Phys. Chem. B* **2000**, *104*, 585–590.
- (3) Mucha, M.; Frigato, T.; Levering, L. M.; Allen, H. C.; Tobias, D. J.; Dang, L. X.; Jungwirth, P. *J. Phys. Chem. B* **2005**, *109*, 7617–7623.
- (4) Raduge, C.; Pflumio, V.; Shen, Y. R. *Chem. Phys. Lett.* **1997**, *274*, 140–144.
- (5) Tuckerman, M. E.; Chandra, A.; Marx, D. *Acc. Chem. Res.* **2006**, *39* (2), 151–158.
- (6) Sillana, A. J.; Laasonen, K. *Phys. Chem. Chem. Phys.* **2004**, *6*, 555–565.
- (7) Botti, A.; Bruni, F.; Imberti, S.; Ricci, M. A.; Soper, A. K. *J. Chem. Phys.* **2004**, *121* (6), 7840–7845.
- (8) Agmon, N. *J. Phys. Chem. A* **1998**, *102*, 192–199.

- (9) Botti, A.; Bruni, F.; Imberti, S.; Ricci, M. A. *J. Chem. Phys.* **2003**, *119* (10), 5001–5004.
- (10) Imberti, S.; Botti, A.; Bruni, F.; Cappa, G.; Ricci, M. A. *J. Chem. Phys.* **2005**, *122*, 194509/1–94509/9.
- (11) Raymond, E. A.; Richmond, G. L. *J. Phys. Chem. B* **2004**, *108*, 5051–5059.
- (12) Tarbuck, T. L.; Richmond, G. L. *J. Am. Chem. Soc.* **2006**, *128* (10), 3256–3267.
- (13) Gopalakrishnan, S.; Liu, D.; Allen, H. C.; Kuo, M.; Shultz, M. J. *Chem. Rev.* **2006**, *106*, 1155–1175.
- (14) Baldelli, S.; Schnitzer, C.; Shultz, M. J.; Campbell, D. J. *J. Phys. Chem. B* **1997**, *101* (49), 10435–10441.

tive water stretching deduced from large increases in the lower frequency modes. Results from more recent surface anion studies, including SO_4^{2-} ^{12,15} and Cl^- ,^{11,16} showed that the interfacial water structure changes significantly and can be anion dependent. Therefore, the effect of protons on interfacial structure depends strongly on the solution composition.

Recently, three MD simulation studies have explored the location of protons within the interfacial region with different results.^{3,17,18} A quantum mechanical simulation using one HCl molecule suggested that the Eigen form ($\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$) of the proton will migrate to and reside in the upper most interfacial water layer with the chloride ion residing several molecules below.¹⁷ Classical MD simulations suggest both Eigen protons and Cl^- ions can be found in the top surface layer.³ And, classical calculations of the potential mean force to move a hydronium ion across the interface resulted in no significant minimum (or propensity to be at the surface).¹⁸

The surface properties of NaOH and HCl solutions are different from those of water, and each other as evidenced by surface tension measurements. NaOH behaves like a simple electrolyte, increasing the surface tension of water (the interfacial ion concentration is less than the bulk ion concentration), and OH^- is classified as a structure maker in the Hofmeister series, which ranks ions based on their effect on the surrounding water structure.¹⁹ HCl does not behave like a simple electrolyte; the surface tension is similar to neat water up to ~ 0.1 mole fraction, then decreases with increasing HCl concentration.¹ The interfacial ion concentration is higher than the bulk ion concentration. Recent second harmonic studies of solutions of I^- have shown significant concentration increases of interfacial I^- in the presence of H^+ (versus Na^+ or K^+) at concentrations greater than 2 M, consistent with the decrease in surface tension.²⁰

The focus of this investigation is to gain more molecular detail, predominately at higher OH frequencies, to determine how the acidic/basic interface is different from the neat interface. The natural starting point for understanding the surfaces of acidic or basic solutions is a clear understanding of the structure of the surface of neat water. The current understanding of the neat vapor/water interface includes the following five factors: (1) There is a decrease in the hydrogen bonding of and the coordination between water molecules as the interface is approached, particularly in the top surface layer.^{12,21–23} (2) Approximately 20% of the surface water molecules have a hydrogen atom directed into the vapor.²⁴ (3) The interfacial water molecules are very sensitive to dipoles at the surface and to electric field effects.²⁵ (4) The water dipole is oriented slightly into the bulk on average.^{26,27} (5) A wide range of hydrogen-bonding strengths and coordinations exist between surface water molecules.

- (15) Gopalakrishnan, S.; Jungwirth, P.; Tobias, D. J.; Allen, H. C. *J. Phys. Chem. B* **2005**, *109*, 8861–8872.
 (16) Liu, D.; Gang, M.; Levering, L. M.; Allen, H. C. *J. Phys. Chem. B* **2004**, *108*, 2252–2260.
 (17) Petersen, M. K.; Iyengar, S. S.; Day, T. J. F.; Voth, G. A. *J. Phys. Chem. B* **2004**, *108*, 14804–14806.
 (18) Dang, L. X. *J. Chem. Phys.* **2003**, *119* (12), 6351–6353.
 (19) Collins, K. D.; Washabaugh, M. W. *Q. Rev. Biophys.* **1985**, *18* (4), 323–422.
 (20) Petersen, P. B.; Saykally, R. J. *J. Phys. Chem. B* **2005**, *109*, 7976–7980.
 (21) Dang, L. X.; Chang, T.-M. *J. Chem. Phys.* **1997**, *106* (19), 8149–8159.
 (22) Walker, D.; Richmond, G. L. *J. Phys. Chem. B*, submitted.
 (23) Buch, V. J. *J. Phys. Chem. B* **2005**, *109*, 17771–17774.
 (24) Du, Q.; Superfine, R.; Freysz, E.; Shen, Y. R. *Phys. Rev. Lett.* **1993**, *70*, 2313–2316.
 (25) Gragson, D. E.; McCarty, B. M.; Richmond, G. L. *J. Am. Chem. Soc.* **1997**, *119* (26), 6144–6152.

This study provides new insight into the outstanding issues regarding the molecular structure of the surfaces of acidic and basic solutions, including identification of interfacial species not present at the neat aqueous interface, and the question of whether Eigen protons are in the top interfacial layer. Vibrational sum-frequency spectroscopy (VSFS) is used in a series of isotopic dilution and polarization experiments to answer these questions.

VSF spectroscopy is a powerful tool for interrogating liquid surfaces apart from the bulk since it probes only those molecules residing in the interfacial region.²⁸ The spectra are complicated due to the wide variety of water environments, which give rise to broad overlapping vibrational modes; however, isotopic dilution experiments simplify the assignment of the various overlapping OH stretching modes by decoupling intermolecular and intramolecular vibrations. In these studies, the presence of solvated proton species in the top layer of the interface is demonstrated. The behavior of solvated proton species is strikingly different from that of other solvated ions that have been studied at water interfaces. The solvating water molecules show anomalously strong water bonding interactions given their location at the topmost surface layer. Critical support for these conclusions comes from spectra collected under two different polarization schemes, which probe the in-plane and out-of-plane response.

Experimental Section

Laser System. The laser system has been described extensively in previous publications,^{29,30} so only a brief description is given here. The sum-frequency light is generated by overlapping 800 nm (2 ps, 1 kHz repetition rate) and tunable (2700–4000 cm^{-1}) infrared light in a copropagating geometry at 56° and 67° from the surface normal, respectively. The beams provide approximately 100 μJ of 800 nm light and 4–10 μJ of IR. After filtering any reflected 800 nm light, the sum-frequency response is collected every 0.0025 μm over the tunable range with a thermoelectrically cooled CCD camera (Princeton Instruments). In these experiments, two polarization combinations are utilized: *ssp* and *sps*. These polarization schemes denote the sum-frequency, visible, and infrared polarizations, respectively, which represent polarizations in the plane of incidence (*p*) and normal to the plane of incidence (*s*). The tensor elements probed in *ssp* and *sps* access the perpendicular and parallel transition dipole moments, respectively.

The spectroscopic samples are poured or injected via gastight syringes into scrupulously clean glass dishes. All glassware was soaked for at least 24 h in a mixture of sulfuric acid and NoChromix, rinsed in Nanopure water, soaked for at least 24 h in water, and rinsed again with copious amounts of Nanopure water. Surface active contaminants can affect the interface at lower than millimolar concentrations, whereas millimolar concentrations of inorganic contaminants do not affect the vapor/water interface. The glass dishes are enclosed in a nitrogen purged Teflon cell fitted with CaF_2 windows. The Teflon cell has three ports, two of which are used for gases and/or a pressure gauge, and the remaining port is a vent via Teflon tubing to a fume hood.

Sample Preparation and Analysis. Certified ACS grade HCl was purchased from Fisher Scientific (12.1 M), and NaOH (99.998%), from Aldrich. D_2O (d99.9%) was purchased from Cambridge Isotopes

- (26) Vassilev, P.; Hartnig, C.; Koper, M. T. M.; Frechard, F.; van Santen, R. A. *J. Chem. Phys.* **2001**, *115* (21), 9815–9820.
 (27) Raymond, E. A.; Tarbuck, T. L.; Brown, M. G.; Richmond, G. L. *J. Phys. Chem. B* **2003**, *107*, 546–556.
 (28) Shen, Y. R. *The Principles of Nonlinear Optics*; Wiley: New York, 1984.
 (29) Gragson, D. E.; McCarty, B. M.; Richmond, G. L.; Alavi, D. S. *J. Opt. Soc. Am. B* **1996**, *13*, 2075–2083.
 (30) Allen, H. C.; Raymond, E. A.; Richmond, G. L. *J. Phys. Chem. A* **2001**, *105*, 1649–1655.

Laboratories. DCl (35% in D₂O) and NaOD (40% in D₂O) were purchased from C/D/N Isotopes. No further purification of these materials was attempted. All samples were diluted to the experimental pH with high purity H₂O obtained from a Millipore Nanopure system (18 MΩ cm).

All spectra were normalized for variations in SF intensity. The spatial variation between the visible and IR beams when scanning the IR frequency, the temporal lengthening of the IR pulses by water vapor, and the frequency dependence of the optics used for filtering the sum-frequency were removed by dividing the spectra by the nonresonant response from an unprotected gold surface over the same frequency range. The presented spectra are averages of 2–8 spectra, taken over a series of days using fresh samples to ensure reproducibility.

Spectral Fitting. The sum-frequency intensity is proportional to the square of the second-order nonlinear susceptibility, $\chi^{(2)}$, and one of the distinguishing characteristics of nonlinear optical spectroscopies is coherence. The nonlinear susceptibility is complex, with each resonant component having an amplitude, A , and an associated phase, $e^{i\phi}$.

$$I_{\text{sf}} \propto |\chi_{\text{NR}}^{(2)} + \chi_{1\text{R}}^{(2)} + \chi_{2\text{R}}^{(2)} + \chi_{3\text{R}}^{(2)} + \dots|^2 \quad (1)$$

$$I_{\text{sf}} \propto |A_{\text{NR}}^{(2)} + A_{1\text{R}}^{(2)}e^{i\phi_1} + A_{2\text{R}}^{(2)}e^{i\phi_2} + A_{3\text{R}}^{(2)}e^{i\phi_3} + \dots|^2 \quad (2)$$

Interferences can arise between the resonances (and the nonresonant response), making the spectral interpretation more complicated. However, the interferences often result in unique line shapes that lend more certainty to the assignment of the vibrational frequencies and modes, because there are phase relationships. SF spectra must be fit in order to deconvolve the resonant modes from the nonresonant susceptibility. It is important to resolve the resonant modes because they contain the molecular information that helps to elucidate the strength of bonding, the orientation, and the environments of molecules.

Since all of the spectra are of condensed media, it is necessary to fit the data with a more complicated line shape than the simple Lorentzian lines that come from the treatment of individual molecules. The inhomogeneous broadening and the homogeneous line widths of the vibrational transitions are accounted for by employing a fitting routine first proposed by Bain:³¹

$$\chi^{(2)} = \chi_{\text{NR}}^{(2)} + \sum_v \int_{-\infty}^{+\infty} \frac{A_v e^{-[\omega_L - \omega_v]/\Gamma_v}]^2}{\omega_{\text{IR}} - \omega_L - i\Gamma_L} d\omega_L \quad (3)$$

The first term is the nonresonant second-order susceptibility. The second term is a sum over all resonant vibrational modes and is often given the symbol $\chi_{\text{R}(v)}^{(2)}$. It represents the convolution of the homogeneous line widths of the individual molecular transitions (HWHM, Γ_L) with inhomogeneous broadening (fwhm, $\sqrt{2\ln 2}\Gamma_v$). The transition strength, A_v , is proportional to the product of the number of molecules and their orientationally averaged IR and Raman transition probabilities. The frequency of the IR, the Lorentzian, and the resonant mode are ω_{IR} , ω_L , and ω_v , respectively.

The parameters used to fit the neat vapor/water interface in *ssp*-polarization were taken from previous isotopic dilution experiments.^{11,27,32} In these studies, spectra of pure H₂O, increasing concentrations of D₂O in H₂O (HOD), and pure D₂O were iteratively fit as a set allowing all the spectra to be fit with the same peak positions, Lorentzian widths, phases, and similar Gaussian widths. Lorentzian widths are fixed at 5 and 12 cm⁻¹ for the OH modes and free OH mode, respectively. The phase relationships are consistent with those reported in molecular dynamics simulations of the neat interface.^{27,33} At the neat water interface, the free OH and high frequency (>3600

cm⁻¹) stretching modes are out of phase with the lower frequency (<3500 cm⁻¹) modes. The Gaussian widths are broad, 100–135 wavenumbers, except for the free OH. The parameters used to fit the neat vapor/water interface in *sps*-polarization are the same parameters used for the neat vapor/water *ssp*-polarization spectrum with one exception, an additional resonance at ~3580 cm⁻¹.

Results and Discussion

The discussion begins with a review of the current understanding of the structure, orientation, and hydrogen bonding of water molecules at the neat vapor/water interface so that comparisons of the neat interfacial region may be made with the interfacial region in the presence of H⁺ and OH⁻. The extent of any contributions from Na⁺ and Cl⁻ are also examined. Next, the results from the isotopic dilution experiments, the concentration experiments, and the *sps*-polarization spectra of H⁺ and OH⁻ are presented. Finally, the overall effects of H⁺ and OH⁻ in the interfacial region are summarized.

Neat Vapor/Water Interface. The neat vapor/water interface has been explored in detail in recent experimental studies^{13,27,34,35} with excellent contributions from MD simulations.^{21,23,33,36,37} The interfacial region is very thin, 6–9 Å,^{27,38} with interfacial water molecules in a broad range of local environments, each corresponding to different numbers and/or strengths of hydrogen bonds whose vibrational frequencies often span several hundred wavenumbers. The interfacial region has a larger percentage of water molecules with fewer hydrogen-bonding opportunities in the top surface layer, and MD simulations suggest the vibrational modes of these water molecules also span several hundred wavenumbers.^{22,23} A continuum of water environments span the OH spectral region; however, experiments and MD simulations consistently indicate a dominance of certain species in distinct spectral regions and at different interfacial depths. In general, the topmost surface water molecules with the weakest neighboring bonding interactions appear around 3500–3700 cm⁻¹ in the spectrum. As the amount of cooperative OH stretching between adjacent water molecules increases, the vibrational frequency decreases. Water molecules exhibiting intensity up to ~3500 cm⁻¹ are often a few angstroms from the top surface layer, bond with additional coordination, have stronger individual bonds and cooperative interactions (compared to the top surface water molecules), and often change orientation and/or transition strength due to surface dipole and electric field effects. These effects can extend the surface region further into the bulk allowing more highly coordinated water molecules to contribute to the VSFS response. The opportunities for a water molecule to hydrogen bond are dependent on the location in the interface. The coordination and strength of hydrogen bonding of water molecules resemble those in the bulk just a few molecular layers away from the interface.

Effects of Na⁺ and Cl⁻ on the Neat Vapor/Water Interface. The largest changes to the neat vapor/water interface in the presence of HCl and NaOH are due to H⁺ and OH⁻. There is ample evidence that Na⁺ and Cl⁻ at the concentrations examined in these experiments (~1 M) have very little effect

(31) Bain, C. D.; Davies, P. B.; Ong, T. H.; Ward, R. N.; Brown, M. A. *Langmuir* **1991**, *7* (8), 1563–1566.

(32) Raymond, E. A.; Tarbuck, T. L.; Richmond, G. L. *J. Phys. Chem. B* **2002**, *106* (11), 2817–2820.

(33) Morita, A.; Hynes, J. T. *Chem. Phys.* **2000**, *258*, 371–390.

(34) Wei, X.; Shen, Y. R. *Phys. Rev. Lett.* **2001**, *86* (21), 4799–4802.

(35) Gan, W.; Wu, D.; Zhang, Z.; Feng, R.-r.; Wang, H.-f. *J. Chem. Phys.* **2006**, *124*, 114705/1–114705/15.

(36) Morita, A.; Hynes, J. T. *J. Phys. Chem. B* **2002**, *106*, 673–685.

(37) Perry, A.; Neipert, C.; Ridley, C.; Space, B.; Moore, P. B. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2005**, *71* (5–1), 050601/1–050601/4.

(38) Dang, L. X.; Chang, T.-M. *J. Chem. Phys.* **1997**, *106* (19), 8149–8159.

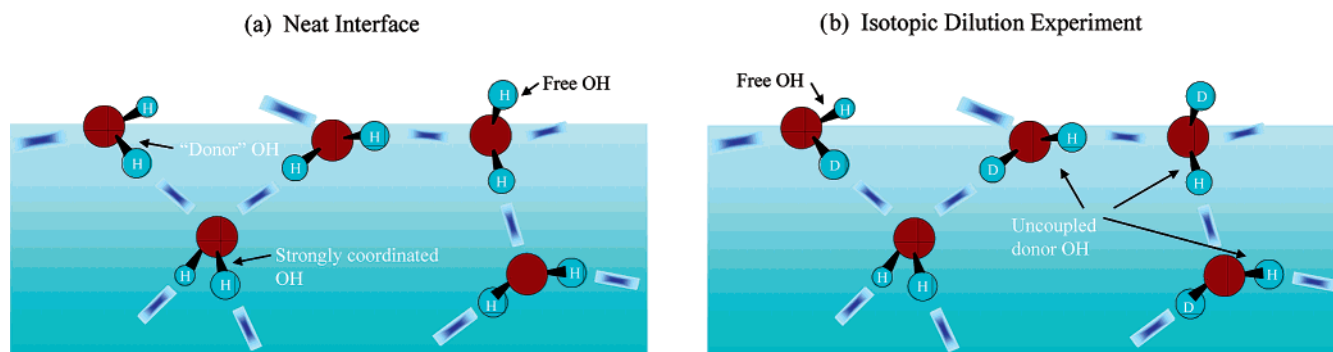


Figure 1. (a) A cartoon of the neat interface with many different OH stretching environments. (b) A cartoon with mostly interfacial HOD, the intra- and intermolecular coupling is removed, simplifying the spectra.

on the interfacial water structure in the presence of OH^- and H^+ .^{2,11,39,40} In addition, previous work in this laboratory concluded that there is little effect on the neat vapor/water interface from either the Cl^- anion or the Na^+ cation up to 1.7 M, because the strength, orientation, and coordination of hydrogen bonds at the NaCl/water interface at these concentrations is similar to that at the neat vapor/water interface.¹¹ Cl^- induces a small increase in intensity in the highly coordinated OH stretch at 3335 cm^{-1} (a slight blue shift from the same feature in neat water) and a solvation feature appears at 3650 cm^{-1} . For HCl , any changes beyond these are due to H^+ . In general, sodium ions have much less of an effect on the bulk water structure than anions which is not surprising because they are smaller and relatively unpolarizable.^{39,40} Sodium ions are also expected to have less of an effect on the neat vapor/water interface than protons, because they are not as strongly hydrated and they associate more with the anions (than H^+ does) resulting in a smaller separation of charge.² For NaOH , the changes to the water structure are assumed to be solely from the anion.

Effects of pH on the Neat Vapor/Water Interface. A. Isotopic Dilution Experiments. The isotopic dilution experiments for the neat vapor/water interface were briefly discussed in the spectral fitting section, and a cartoon representation of the experiment is shown in Figure 1. The neat interface, with various OH stretching environments, is depicted in part a, and the interface with mostly HOD without the intermolecular and intramolecular coupling is depicted in part b. With mostly HOD, the number of OH stretching environments is reduced, and therefore fewer species give rise to OH stretching vibrations. The isotopic dilution series also provides spectral constraints, because each OH spectrum (with different amounts of H_2O , D_2O , and HOD) must be fit with the same peak parameters. The smallest number of Gaussian features that can be iteratively fit to all the neat water spectra in an isotopic dilution series are four dominant OH stretching modes at ~ 3700 , 3460 , 3330 , and 3200 cm^{-1} in *ssp*-polarization, with one additional feature at $\sim 3580\text{ cm}^{-1}$ prominent only in the *sps*-polarization spectra. Except for the unbound OH stretch at 3700 cm^{-1} , there is some disagreement as to which water environments give rise to each spectral feature. However, most agree that water molecules in the top surface layers with fewer hydrogen-bonding interactions appear in the $3500\text{--}3700\text{ cm}^{-1}$ region,^{22,23,27,34,35,37} and bulklike environments are concentrated in the $3100\text{--}3500\text{ cm}^{-1}$ region

in agreement with IR and Raman studies of bulk water.^{41–43} For a more detailed discussion of the water assignments, refer to the supporting material and the recent MD simulations that have explored the contributions to these features in detail.^{22,23,37} Although not present at the neat vapor/water interface, strong hydrogen bonding and cooperative motion of hydrogen bonds give rise to a spectral feature at $\sim 3150\text{ cm}^{-1}$. This feature has been observed at the vapor/ice interface⁴⁴ as well as at the surface of strong acid solutions.²

Spectra were acquired in pure water from pH 0 to pH 15, employing solutions of HCl or NaOH to investigate the effect that pH has on the vapor/water interface. Significant changes from the neat vapor/water spectra were observed only below pH 2 and above pH 13, but the individual resonant contributions that comprised the spectral fit for the neat vapor/water interface could not produce the acidic or basic line shapes. The isotopic dilution series for H^+ or OH^- are fit with a similar set of parameters that capture the new spectral features, which are presented in Figures 2 and 3, respectively. In Figure 2, the overall fit is a solid line for each spectrum in the series. The contributing resonant peaks are shown to the right of two selected spectra and described below.

In the HCl isotopic dilution series, the concentration of HCl was held constant at 0.8 M while the amount of H_2O , D_2O , and HOD varied. The spectra are offset in Figure 2 and range from HCl in pure water (top spectrum) to DCl in pure D_2O (bottom spectrum). The bottom spectrum in the series, DCl in D_2O , is the simplest and provides the nonresonant amplitude in the fits because there are no vibrational resonances in this region.

The first spectrum in the series with a significant resonant contribution is the next spectrum higher in the series, HOD in D_2O ($\sim 0.2 \times \text{HOD}$ and $\sim 0.01 \times \text{H}_2\text{O}$), and consists primarily of the free OH at $\sim 3700\text{ cm}^{-1}$ and the uncoupled “donor” OH modes, which are centered at $\sim 3455\text{ cm}^{-1}$ and extend $\sim 90\text{ cm}^{-1}$ at fwhm. This is the simplest spectrum to understand and model because the intra- and intermolecular vibrations are decoupled. When the HOD solution is acidified, this peak, referred to as the donor OH, is slightly enhanced compared to neat HOD. This enhancement is attributed to HOD molecules near the top surface layer that are involved in the solvation of protonated species.

(41) Walrafen, G. E.; Fisher, M. R.; Hokmabadi, M. S.; Yang, W.-H. *J. Chem. Phys.* **1986**, *85* (12), 6970–6982.

(42) Walrafen, G. E.; Hokmabadi, M. S.; Yang, W.-H. *J. Chem. Phys.* **1986**, *85*, 6964–6969.

(43) Scherer, J. R. *Advances in Infrared and Raman Spectroscopy*; Heyden: London, 1978; Vol. 5, pp 149–216.

(44) Wei, X.; Miranda, P. B.; Shen, Y. R. *Phys. Rev. Lett.* **2001**, *86* (8), 1554–1557.

(39) Aqueous Solutions of Simple Electrolytes. In *Water a Comprehensive Treatise*; Franks, F., Ed. Plenum Press: New York, 1973; Vol. 3, pp 1–472.

(40) Cacace, M. G.; Landau, E. M.; Ramsden, J. J. *Q. Rev. Biophys.* **1997**, *30* (3), 241–277.

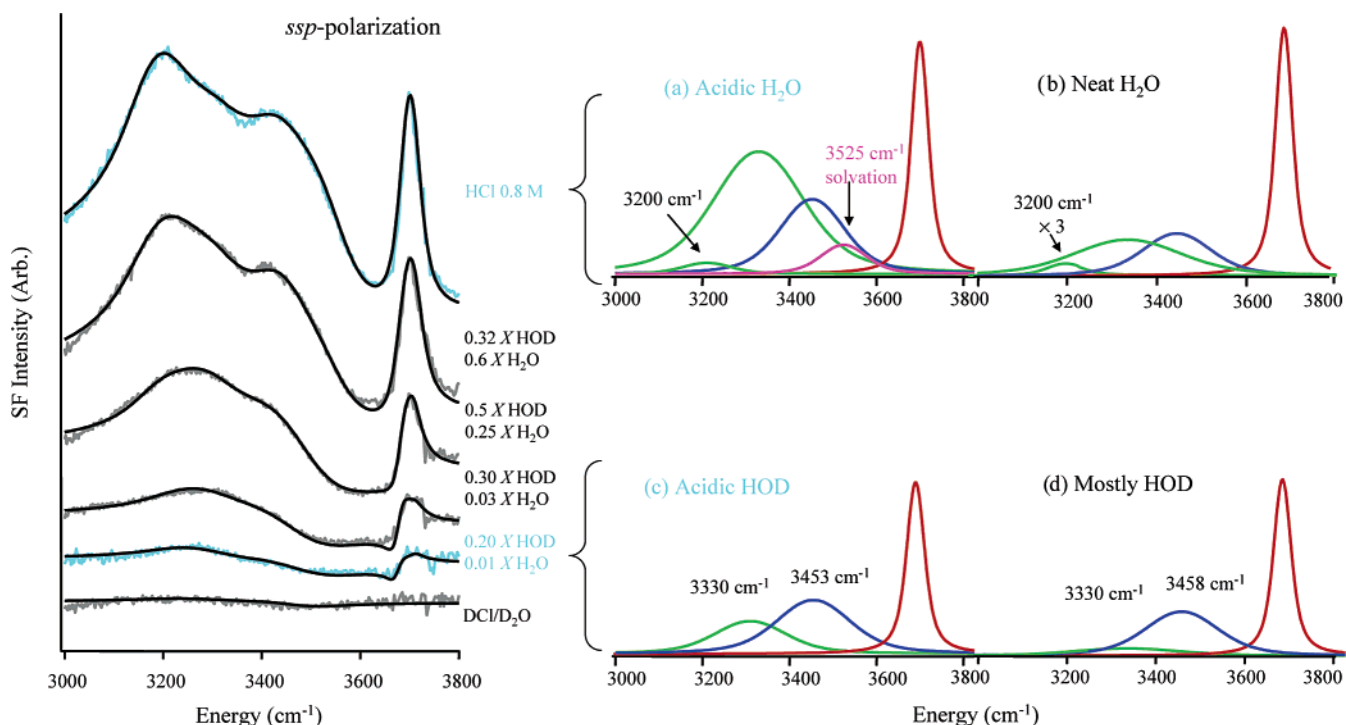


Figure 2. VSF spectra of the isotopic dilution series of 0.8 M HCl with the spectral fits. The spectra have been offset for clarity. Components to the resonant sum-frequency response from (a) 0.8 M HCl/ H_2O , (b) H_2O , (c) HOD in 0.8 M HCl/ D_2O , and (d) HOD in D_2O .

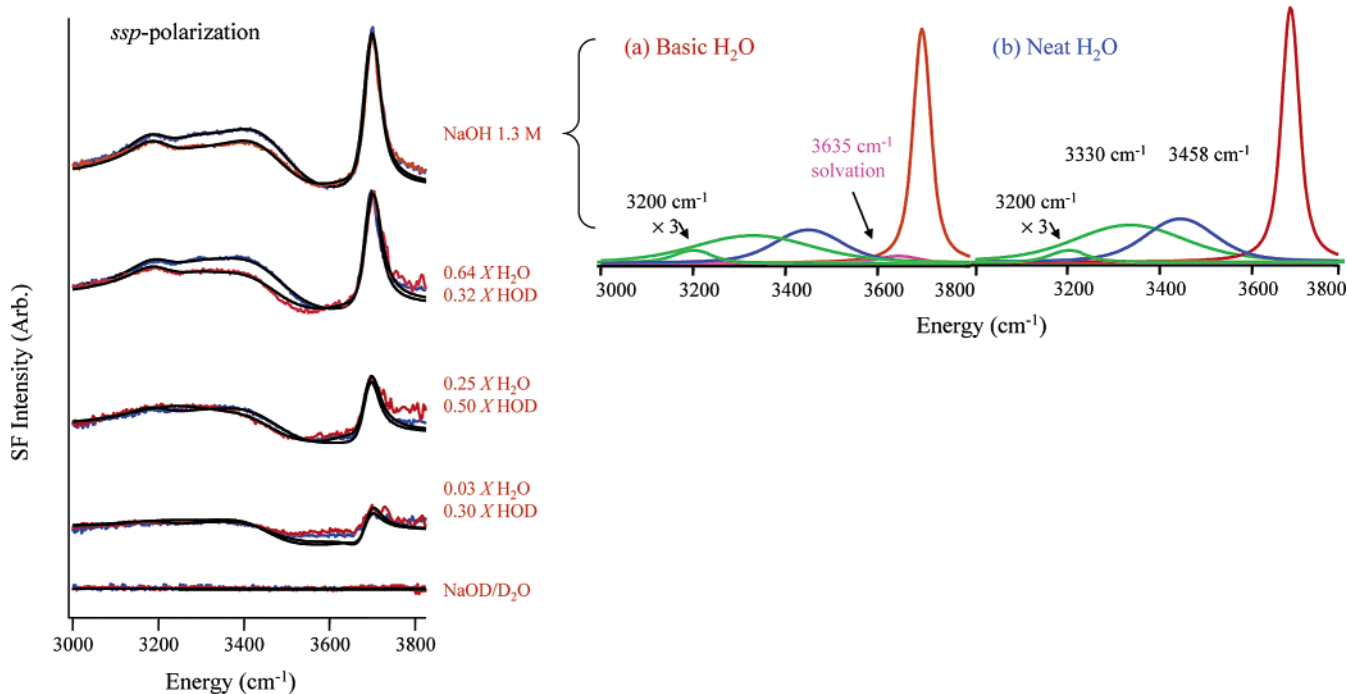


Figure 3. VSF spectra of the isotopic dilution series of 1.3 M NaOH (red) and neat H_2O (blue) with the spectral fits. Components to the resonant sum-frequency response from (a) 1.3 M NaOH and (b) the neat vapor/water interface.

In addition, the acidic spectrum shows an increased intensity from stronger hydrogen bonds or more oriented uncoupled OH stretches centered at 3330 cm^{-1} and extending $\sim 130\text{ cm}^{-1}$ at fwhm; this is significantly more intensity than that in the neat vapor/water spectrum from the small concentration of H_2O in solution ($0.03\text{ X }H_2O$). It is important to note that the HCl isotopic dilution spectra stand in stark contrast to the isotopic dilution studies of 1.7 M NaCl that show only a small increase in intensity at 3335 cm^{-1} and virtually no change in intensity

for the uncoupled donor OH modes.¹¹ This demonstrates that the structure-making H^+ effect dominates any contribution from the chloride ion.

The top spectrum in Figure 2 (left) shows increases in intensity upon acidification for all the resonant modes, except the free OH, compared to the neat vapor/water interface. H^+ has strong interactions with water molecules inducing more tetrahedral coordination and greater cooperative motion as discussed earlier and seen previously in other acid solutions^{2,4}

and with structure-making ions.^{12,15} For HCl, the enhancement of the lower frequency features (3200 and 3330 cm^{-1}) is attributed to solvated protons, to strong electrostatic interactions between water molecules and protons in solution, and to an enhanced electric field.^{1,2} OH stretching of solvated protons^{45–48} and from the Zundel adsorption continuum^{48,49} have been measured in bulk water near 3330 cm^{-1} . The coincidence of the resonances found for solvated proton species in bulk and in these surface studies indicates that the proton associated water species in the interfacial region are similar to those found in bulk acid solutions. The strong electrostatic interactions between water molecules and protons can induce cooperativity, a phenomenon in which water molecules with strong hydrogen bonds can induce stronger hydrogen bonding in the adjacent water molecules (that are hydrogen bonded to other water molecules). Although the hydrogen-bonding strength weakens as the connectivity number increases, the cooperativity of water molecules can be significant when strong hydrogen bonding is present.^{50,51} The electric field produced by charge separation can also induce stronger cooperative tetrahedral OH stretching, increase the transition strength of the vibrations of interfacial water molecules, cause greater water dipole alignment along the surface normal, and/or increase the interfacial depth that the VSF probes. Previous SF studies of acidic solutions attribute the increased intensity to an enhanced electric field boosting the SF response.²

Increases in the intensity in the 3400–3500 cm^{-1} region are extensive for the acid solutions compared with the neat vapor/water interface. In general, the OH environments that contribute to these modes are intermediate in range, with less coordination and bond strength than those for the lowest frequency modes (3200 and 3330 cm^{-1}), but with significant bond strength and coordination compared to OH stretching environments in the 3600–3700 cm^{-1} region. These spectra can be fit by taking two different approaches: either by incorporating an increased intensity to the donor OH mode at 3453 cm^{-1} accompanied by a small change in phase or by the addition of another mode at ~ 3525 cm^{-1} . (The fit with the additional mode is shown in Figure 2.) This suggests that the presence of protons induces additional strength, coordination, and/or orientation of water molecules. Mostly likely, water molecules in the top surface layers are solvating H^+ ions creating this new OH stretching environment. These solvating water molecules are likely to comprise the first and second hydration shells, although the solvation sphere appears to be extensive. This assignment is supported by studies of various ions at aqueous surfaces^{11–13,52,53} and MD simulations.^{22,23} The frequencies of the solvation features found here for H^+ are similar to those found for solutions of structure-making ions, SO_4^{2-} and HSO_4^- , for example.¹² These solvating water molecules show stronger hydrogen-bonding interactions as evidenced by their larger spectral red-shift than that found for the hydrogen-bonding

interactions of water molecules solvating structure-breaking anions, Cl^- , Br^- , and I^- . The surface water molecules solvating these ions appear at ~ 3650 cm^{-1} .¹¹

It may appear by inspection that there is a decrease in the free OH when protons are present. However, the areas from the fits show that any change is smaller than the error in the fits.

The spectra of the isotopic dilution series for 1.3 M NaOH solutions (red) show a striking resemblance to the spectra of the isotopic dilution series of the neat vapor/water interface (blue) in Figure 3. However, small differences arise in the amplitudes of the fitted peaks relative to the neat vapor/water interface, especially at higher OH^- concentrations, and a new feature appears in the spectra that we attribute to the solvating water molecules associated with OH^- . The nonresonant amplitude used in the fits is the amplitude from NaOD in pure D_2O taken from the bottom spectrum in the series.

The first spectrum in the series with a significant resonant contribution is the next spectrum higher in the series, HOD in D_2O ($\sim 0.3 \times \text{HOD}$ and $\sim 0.03 \times \text{H}_2\text{O}$), which consists primarily of the free OH and the uncoupled OH modes. The uncoupled modes are centered at ~ 3450 cm^{-1} and extend ~ 90 cm^{-1} at fwhm for the NaOH spectra which is a small red-shift (~ 8 cm^{-1}) from the frequency of this feature in the neat vapor/water spectrum.

As the H_2O concentration increases (from bottom to top), the strongly coordinated OH stretching region increases in intensity (3200 and 3330 cm^{-1} region), but the amplitude of the 3330 cm^{-1} mode remains less than that at the neat vapor/water interface. Overall, OH^- causes a loss of amplitude at 3450 and 3330 cm^{-1} , along with broadening in the 3330 cm^{-1} mode. The decrease is attributed to the solvation of OH^- inducing coordination and cooperation between water molecules similar to bulk solution environments, leading to a more random orientation of water molecules in the interfacial region and reducing the number of water molecules generating SF intensity. This change is similar to that seen in solutions of NaF at the vapor/water interface where strong tetrahedral coordination associated with the anion is present.¹¹ A small feature due to water molecules solvating OH^- also grows in at ~ 3635 cm^{-1} , also similar to NaF solutions. The free OH mode is unchanged from the neat vapor/water interface in 1.3 M NaOH. Although the changes in hydrogen bonding are small at 1.3 M concentration, the changes are greater at higher OH^- concentrations.

B. Concentration Series Experiments. Spectra of interfaces under *ssp*-polarization of low (pH ~ 0 –0.5) and high (pH ~ 14 –15) pH solutions are shown in Figure 4, and are compared with the spectrum of a neat vapor/water interface (blue). These spectra are shown to emphasize the significant changes at low (or high) pH as the pH increases (or decreases). The broad increases in intensity with increasing concentration when H^+ is present is very different from the decreases in intensity with increasing OH^- concentration. It is not surprising that the effects are dissimilar given that the size and solvation of the cation and anion are so different.⁵

As the acidity increases, the intensity increases throughout the entire OH stretching region; this is attributed to solvated protons, to strong electrostatic interactions between water molecules and protons in solution, and to an enhanced electric field at the interface. As discussed earlier, the electrostatic

(45) Bethell, D. E.; Sheppard, N. *J. Chem. Phys.* **1953**, *21*, 1421–1421.

(46) Stoyanov, E. S.; Hoffmann, S. P.; Kim, K.-C.; Tham, F. S.; Reed, C. A. *J. Am. Chem. Soc.* **2005**, *127*, 7664–7665.

(47) Falk, M.; Giguere, P. A. *Can. J. Chem.* **1957**, *35*, 1195–1204.

(48) Headrick, J. M.; Diken, E. G.; Walters, R. S.; Hammer, N. I.; Christie, R. A.; Cui, J.; Myshakin, E. M.; Duncan, M. A.; Johnson, M. A.; Jordan, K. D. *Science* **2005**, *308*, 1765–1769.

(49) Buch, V.; Sadlej, J.; Aytemiz-Uras, N.; Devlin, P. J. *J. Phys. Chem. A* **2002**, *106*, 9374–9389.

(50) Kleeberg, H.; Luck, W. A. P. *J. Phys. Chem.* **1989**, *270*, 613–625.

(51) Kammer, T.; Luck, W. A. P. *J. Chim. Phys.* **1993**, *90*, 1643–1655.

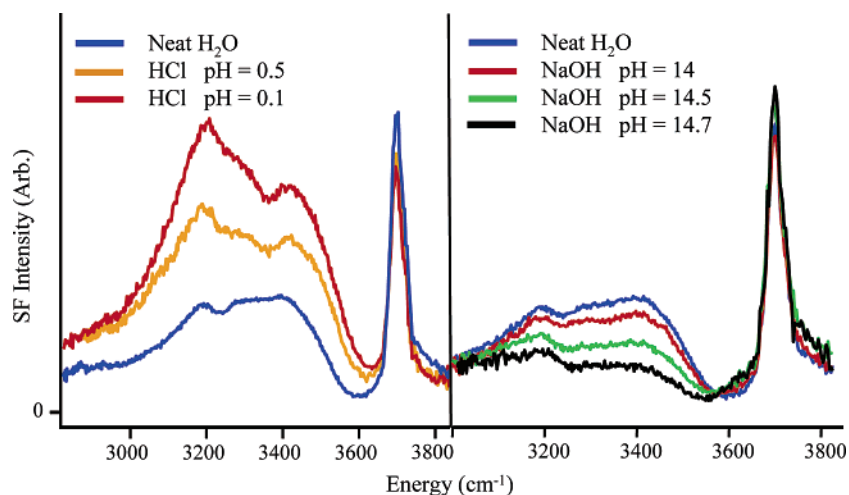


Figure 4. (Left) The neat vapor/water interface and the HCl/water interface at pH 0.5 and 0.1 (0.27 and 0.8 M), respectively. (Right) The neat vapor/water interface and the NaOH/water interface at pH 14, 14.5, and 14.7 (1.3, 3, and 5 M), respectively.

interaction and field effects not only increase the hydrogen-bonding strength but also change the orientation of the water dipole more toward the surface normal and/or increase the number of water molecules in the region of anisotropy. Although there appears to be a significant change in the free OH, the decrease in area is small and within the fitting error. The apparent decrease is due to the interference between the free OH out-of-plane mode and the broad OH modes.

For basic solutions, there is an obvious decrease in intensity in the highly coordinated OH stretching region with increasing OH^- concentration. The spectral fits show that there is a decrease in intensity in the modes at 3450 and 3330 cm^{-1} ; however, there is a small increase in the intensity in the 3200 cm^{-1} mode. The solvation environment of OH^- in the interfacial region is most likely similar to water molecules in bulk solution environments, leading to a more random orientation of water molecules in the interfacial region and reducing the number of water molecules generating SF intensity at ~ 3330 and 3450 cm^{-1} . The small increase in intensity at 3200 cm^{-1} is attributed to strong solvation of OH^- . The free OH is not affected, so either these effects do not extend to the top surface layer or the free OH is sufficiently uncoupled as to be unaffected. One feature does grow in, a solvation feature at 3635 cm^{-1} , similar to the solvation feature of F^- , which is ranked similarly to OH^- in the Hofmeister series.

C. *sps*-Polarization Analysis. The analysis of *sps*-polarized spectra is relatively new and is evolving with the assistance of MD simulations.^{22,23,33,36} This polarization scheme probes transition dipole moments in the plane of the interface. Analysis is difficult for two primary reasons: a low signal-to-noise ratio in the experimental data and the relatively large nonresonant intensity, which must be separated from the resonant contributions to the intensity. The nonresonant intensity can be 50% or more of the total SF intensity.

The *sps*-polarization spectra of HCl and NaOH interfaces are compared with a neat water spectrum in Figure 5. For the neat vapor/water interface, the largest contribution to the intensity is from water molecules in the top surface layer that have few hydrogen-bonding interactions (3500–3700 cm^{-1}), primarily weakly hydrogen-bonded water molecules that orient slightly away from the surface plane.^{22,27} Donor OH modes (3460 cm^{-1})

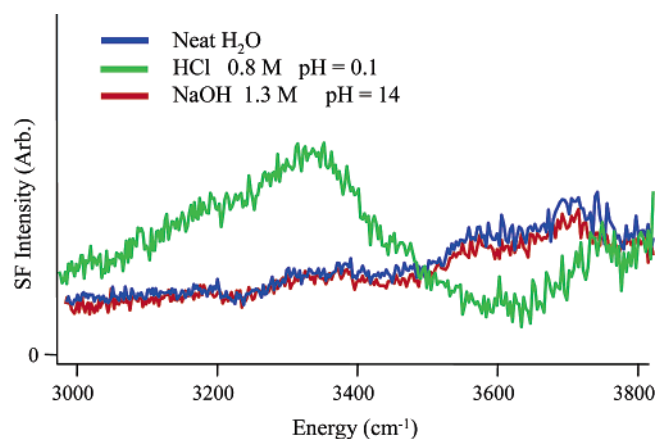


Figure 5. *sps*-Polarization spectra of the neat vapor/water interface and the vapor/water interface with 0.8 M HCl and 1.3 M NaOH.

and smaller contributions from the strongly coordinated OH stretching region (3200 and 3330 cm^{-1}) are also visible.

There are several significant differences between the neat vapor/water spectrum and the H^+ spectrum. First, there is an increase in spectral intensity for the surface of HCl containing solutions at 3330 cm^{-1} and the donor OH mode at 3453 cm^{-1} relative to the neat vapor/water interface due to relatively strongly bonded, multiply coordinated water molecules. The same increases were observed in the *ssp*-polarization spectra, so these spectra corroborate the earlier analysis. More importantly, there is a loss of intensity in the mode at ~ 3580 cm^{-1} , the region corresponding to weakly coordinated water molecules that are oriented in the interfacial plane. This loss is attributed to a change in orientation and/or hydrogen-bonding strength of these water molecules in the top surface layer due to the presence of H^+ in the interfacial region, in addition to interference between the mode at 3580 cm^{-1} and the broad modes at 3330 and 3460 cm^{-1} . Most likely, the top surface water molecules are increasing in hydrogen-bonding strength, orientation, and/or coordination resulting in a spectral red-shift from 3580 to 3525 cm^{-1} and lower OH stretching energies. Clearly, the topmost interfacial water structure has changed due to the presence of H^+ in solution. The HCl *sps*-spectra stand in stark contrast to spectra of 1.7 M NaCl (not shown), which closely resemble the neat vapor/water interface.⁵⁴

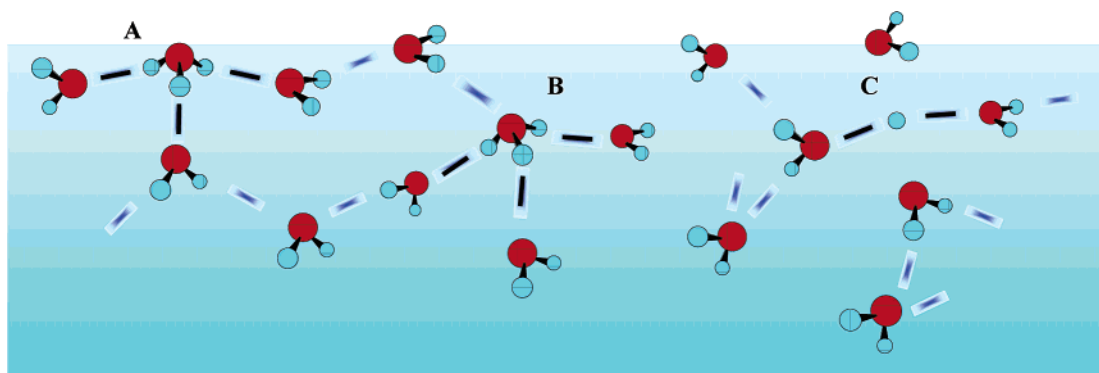


Figure 6. A cartoon of two Eigen and one Zundel form of solvated protons with locations A, B, and C, respectively, and orientations consistent with the spectral data.

sps-Polarization spectra suggest that H^+ induces interfacial structure, because there are similarities to *sps*-polarization spectra of 1.7 M Na_2SO_4 and NaHSO_4 .¹² The ions H^+ , SO_4^{2-} , and HSO_4^- induce some reorientation and/or loss of the weakly bound surface water molecules. If SO_4^{2-} anions reside deep in the interfacial layer as recent MD simulations suggest,¹⁵ with large solvation shells,⁵⁵ and still affect the top surface water molecules,¹² it is possible that the top surface layer of an acid solution can be affected without solvated H^+ present in the top surface layer. However, given that the protons are extremely small in comparison, the transition strength of solvating waters would have to significantly increase and/or protons would have to induce longer range effects. Most likely, protons are found throughout the interfacial region including the top water layer and clearly affect the topmost hydrogen bonding and structure.

Changes in spectral intensity are minimal throughout the OH stretching region for the NaOH interface compared with the neat vapor/water interface under *sps*-polarization. Small decreases in intensity in the higher frequency modes (3450 and 3580 cm^{-1}) are present, but no significant intensity changes appear in the 3330 and 3200 cm^{-1} modes. Similar to *ssp*-spectra, the changes are very subtle and the presence of OH^- has almost no effect on the water structure at pH 14. The basic *sps*-polarization spectrum is significant because it does not show large deviations from the *ssp*-polarization spectra and analysis. Given the already low signal-to-noise ratio, we hypothesize that spectral changes with increasing OH^- concentrations will be small with some decrease in spectral intensity.

Protons in the Interfacial Region. The results of the above experiments demonstrate that solvated H^+ is present in the interfacial region and its solvation affects both the topmost water molecules and water molecules deeper in the interfacial layer. In general, our results suggest that both the Eigen and Zundel forms can be present throughout the interfacial region. The Eigen and Zundel forms are shown in Figure 6 with locations in the interfacial structure that are consistent with the spectral intensities. The spectral intensities suggest water molecules with strong coordination and an average dipole orientation toward the bulk are located in the top surface layers (A) and deeper in the interfacial region (B and C). In position A, the Eigen form donates three hydrogen atoms to hydrogen bonds and the lone

pairs of electrons do not accept any hydrogen bonds. In position B, the Eigen form donates three hydrogen atoms to hydrogen bonds and can also accept a hydrogen bond through one lone pair. Recent MD simulations suggest that the oxygen of the Eigen form points toward the vapor phase,^{15,17,20} and our results suggest that this orientation is reasonable.

Conclusions

The effects of pH on hydrogen bonding at the vapor/water interface were investigated as a function of H^+/OH^- concentration and with isotopic dilution experiments utilizing sum-frequency vibrational spectroscopy. The OH stretching mode amplitudes and frequencies of neat interfacial water molecules are compared to those of water molecules in the presence of HCl, DCl, NaOH, and NaOD.

At low pH, water structure and bonding are significantly perturbed in *all* interfacial layers by the presence of protons. In the top surface layers, our studies indicate that solvated proton species are present. The orientation of these species contributing to the higher frequency OH stretches is consistent with water molecules in the top surface layer solvating both the Zundel form and the Eigen form with the oxygen atom pointing toward the vapor phase. The water molecules surrounding these ions compared to water in the presence of other ions have strong hydrogen bonds.

Protonated species that have stronger hydrogen bonds to other water molecules exhibit spectral signatures similar to those found for protonated species in bulk acid solutions. Because of the bulklike nature of these protonated species, they likely reside somewhat deeper in the interfacial region than those species found at higher frequencies. For water molecules providing a VSF signal in this lower frequency region, strong electrostatic interactions between water and hydrated protons in the interfacial region and the change in the surface potential cause an increase in the transition strength, water hydrogen bond strength and cooperativity, and/or interfacial depth. Spectral features for the solvation of the hydronium ion and Zundel form are consistent with the strong hydrogen bonding of solvating water molecules surrounding structure-making ions such as H^+ . Increased hydrogen-bonding strength extends to all types of interfacial water molecules similar to charged structure-making ions many times greater in size.

At high pH (~ 14 and higher), coordination and cooperative hydrogen bonding is enhanced only slightly relative to neat water. The surface (dipole) and field effects are similar to those

(52) Scatena, L. F.; Richmond, G. L. *Chem. Phys. Lett.* **2004**, *383*, 491–495.
 (53) Becraft, K. A.; Richmond, G. L. *J. Chem. Phys. B* **2005**, *109*, 5108–5117.
 (54) Tarbuck, T. L. University of Oregon: Eugene, OR, 2006.
 (55) Koga, Y.; Westh, P.; Davies, J. V.; Miki, K.; Nishikawa, K.; Katayanagi, H. *J. Phys. Chem. A* **2004**, *108*, 8533–8541.

at the neat vapor/water interface, with some additional randomization of water molecules, where the coordination, orientation, and strength of hydrogen bonds are the same as those found in bulk water. Water molecules solvating OH^- have weaker hydrogen-bonding interactions than those solvating H^+ .

Due to the important role that the surface of atmospheric aerosols plays in the chemistry of the atmosphere and the high acid concentration often present in these aerosols, understanding the role of acids in altering the surface structure and adsorption on these particles is crucial. These studies demonstrate further how the presence of acid alters the surface water structure. Recent studies in this laboratory also show that the presence of acids alters the adsorption of organic species at the water surface.⁵⁶ The effect that ions have on surface adsorption of

organics in general is a focus of several ongoing studies in our laboratory.

Acknowledgment. The authors thank the National Science Foundation (CHE 0243856) for supporting this research and the Office of Naval Research for instrumentation.

Supporting Information Available: Details of the water assignments with a table of the fitting parameters for the neat vapor/water interface, the HCl/water interface, and the NaOH/water interface. This information is available free of charge via the Internet at <http://pubs.acs.org>.

JA063184B

(56) Kido-Soule, M.; Richmond, G. L. Manuscript in preparation.