Surface Charge Affects the Structure of Interfacial Ice

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Supporting Information

ABSTRACT: We have conducted studies on the freezing of water molecules next to charged surfaces to elucidate the effect of water orientation on the structure of ice using sum frequency generation spectroscopy. We observed that when water is frozen next to a positively charged sapphire surface, the signal intensity of ice is higher than that of liquid water as expected from previous theoretical studies. However, when water is frozen next to a negatively charged sapphire surface (using NaOH as pH adjuster), the signal intensity decreases. The same signal attenuation upon freezing is obtained when cesium hydroxide (CsOH) and tetramethylammonium hydroxide (N(CH\textsubscript{3})\textsubscript{4}OH) are used as pH adjusters. Since Na\textsuperscript{+}, Cs\textsuperscript{+}, and N(CH\textsubscript{3})\textsubscript{4}\textsuperscript{+} ions have different hydration properties, the cation specific effect for this attenuation in signal intensity for ice is ruled out. Experiments on a mica surface (inherently negatively charged) also showed similar attenuation in signal intensity for ice as negatively charged sapphire surface. We conclude that the orientation of the water molecules next to a surface plays an important role in the structure of ice. These results have important implications in understanding the strength of ice nucleation and strength of ice adhesion next to charged surfaces.

INTRODUCTION

Water is the most important liquid on Earth, and its interaction with charged surfaces influences key processes in biology, electrochemistry, geology, and technology.\textsuperscript{1–3} For biomolecular self-assembly, it has been shown that aggregation of protein molecules is controlled by the orientation of water molecules, which is influenced by the net charge on the protein surface and not by the protein–protein interactions.\textsuperscript{2} The interactions of water molecules with positively and negatively charged surfaces are not the same.\textsuperscript{4,5} In a dielectric continuum, the strength of an electric field should not depend on the sign of the charge. However, it has been pointed out that the orientation of water does make a difference, and coincidentally, most macromolecules and lipid bilayers in the cells are partially negatively charged. In addition, the other most important interfaces, oil/water or hydrophobic/water interfaces, are also suggested to be negatively charged due to adsorption of OH\textsuperscript{−}.\textsuperscript{6–9} Scheu et al.\textsuperscript{4} recently reported an intriguing asymmetry for tetracyanoborate\textsuperscript{(−)} and tetraphenylarsonium\textsuperscript{(+) } ions in water. Although these two ions are very similar in size and hydrophobic character, because of the charge differences, water molecules form stronger hydrogen bonds with negatively charged TBP\textsuperscript{−} ions compared with TPA\textsuperscript{+} ions.\textsuperscript{5,9}

Recently, Ehre et al.\textsuperscript{5} explored the role of charged surfaces in freezing of water and showed using specular X-ray diffraction (XRD) that the ice nucleates differently on positively and negatively charged surfaces. These differences resulted in a lower freezing temperature of water next to negatively charged surfaces. This experiment also suggested that the water molecules pointing with hydrogen facing toward or away from the surface influence the formation of ice and the differences in freezing temperatures.\textsuperscript{5} We also reported recently on the direct measurement of the freezing of water next to charged Al\textsubscript{2}O\textsubscript{3} (sapphire) surface using sum frequency generation (SFG) spectroscopy.\textsuperscript{10} SFG, a second-order nonlinear technique, is only active where there is a breakdown in inversion symmetry, which makes this technique useful to study the structure of water molecules near surfaces and interfaces.\textsuperscript{11–21} In these studies, NaOH and HCl were used to adjust the pH so that we could measure the freezing behavior of water next to negatively and positively charged sapphire surfaces, respectively. We observed that, on negatively charged surface, the SFG intensity of ice was attenuated in comparison with water signals before freezing. This was opposite of what was observed next to positively charged sapphire surfaces. We concluded that protons were disordered in the ice crystals next to negatively charged surfaces. However, the origin of proton disorder was not identified. Two hypotheses were suggested. First, there is a possibility of Na\textsuperscript{+} ions migrating to the sapphire interface and influencing the ordering of frozen water molecules. The second possibility could be due to the orientation of water and the fact that the freezing of water when the hydrogen atoms are pointing toward the surface is inherently different than that where hydrogens are pointing inward. Experiments using phase-sensitive SFG (PS-SFG), which is sensitive to the average orientation of water molecules at interfaces, observed a flip of the OH bonds toward the silica surface after melting of ice.\textsuperscript{22} Therefore, in a situation where...
the water molecules are strongly bonded to a negatively charged surface, such as a flip of the water dipoles during freezing could also cause the protons to disorder. The orientation of water can create a barrier in forming proton-ordered ice crystals because it has to overcome the strong electrostatic interactions to rearrange the water molecules.

To distinguish whether the ions or water orientation is a dominant factor in attenuation of the ice signals, we present here experimental data on two other ions which are known to be weak disrupters of water structure based on the Hofmeister series, cesium (Cs⁺) and tetracylammonium (N-(CH₄)₂) ions. We use hydroxides of these two ions to adjust the pH such that the sapphire surface is negatively charged. In addition, we studied an ammonia/water solution next to sapphire surface because it is known that ammonia is able to bond to the aluminol groups and polar order water molecules with the OH groups of the ice facing toward the bulk. This control of water orientation should exhibit strong proton-ordered ice structure and a high intensity of the ice peak. Finally, we will discuss SFG spectra for water and ice next to a positively charged mica surface. Since mica is negatively charged, we can test the effect of surface charge on ice without any interference from ions, and the structure of ice should be directly related to the surface charge.

**EXPERIMENTAL SECTION**

Ultrapure water with a resistance of 18.2 MΩ·cm (Millipore filtration system with deionizing and organic removal columns) was used in these experiments. CaOH (≥99.9% purity, Sigma-Aldrich), N(CH₃)₂OH (25 wt % in H₂O, Sigma-Aldrich), and NH₄OH (≥28–30% NH₃ basis, Sigma-Aldrich) were used as obtained for pH adjustments. The pH measurements were performed with an Oakton pH meter with an epoxy-body pH electrode.

Sapphire has a high surface energy, and it is easier for adventitious carbon to adsorb on the surface. Care was taken to clean the sapphire surfaces by sequentially sonicating in acetone, ethanol, and deionized water for 1 h each. The sapphire prisms were then thoroughly rinsed in deionized water and blow-dried with dry nitrogen gas. The prisms were then plasma treated for 4 min. We used a stainless steel cell to hold the sapphire prisms and water. The volume and surface area of the cell are ~300 μL and 0.3 cm², respectively. The cell was cleaned using the same procedure we used for sapphire prisms just before the experiments. Our cooling and heating experimental setup has been described earlier, and the diagram of this setup is provided in the Supporting Information (Figure S1). The temperature stage was purchased from Instec Inc. and modified in-house to hold the sapphire prisms. We have used 0.3 °C/min cooling or heating rate in most cases, and for some selected exceptions, the cooling or heating rates are provided in the text or figure captions. The process used to calibrate the temperature of the sample cell has been provided in earlier publication.

Muscovite mica was obtained from Lawrence Company, New Bedford, MA. To perform total internal reflection geometry experiment, mica was adhered onto a sapphire prism by first spin coating a polystyrene film on a clean sapphire prism. Then a drop of toluene was placed on the top of the film. A thin sheet of mica, cut to the size of the sapphire, was carefully placed on the toluene-soaked PS film. This tacky film was a good adhesive to hold the mica in place. The sample was then annealed at 120 °C for 12 h. Prior to performing an experiment, a thin sheet of mica was peeled off from a thicker mica sheet stuck to the PS film. This prevented contamination of the mica surface. The study of mica/water interface in a total internal reflection geometry using index matching layer was inspired by the recent paper by Abdelmonem et al. Here we have used deuterated polystyrene instead of index matching gels.

The details of the SFG system used in this work have been described in previous publications. In brief, a picosecond Spectra Physics laser system with tunable ~3.5 μJ IR beam ~2000–3800 cm⁻¹, 1 ps pulse width, 1 kHz repetition rate, and a diameter of 100–200 μm is overlapped with a ~70 μJ visible beam of 800 nm in wavelength, with a 1 ps pulse width, 1 kHz repetition rate, and a diameter of 1 mm. A home-built computer-controlled motorized delay stage is used to maintain the temporal delay as the IR beam is scanned from 2700 to 3800 cm⁻¹. The SFG signals were acquired using a 5 s averaging time and at intervals of 10 cm⁻¹. Due to the low IR beam energy used in the water experiments, laser heating of ice was negligible. The melting temperature of the ice was close to 0 °C and served as a good way to calibrate the temperature.

The SFG experiments were performed using equilateral 60° angle sapphire prisms at or near total internal reflection. The sapphire prisms are cut with the crystal axis to avoid any birefringence effect. A photomultiplier tube connected to a spectrometer 0.5 m in length was used to collect the SFG signals. The spectra were collected at an IR incidence angle of 16° with respect to the normal of the sapphire prism face. The incident angle of the visible laser beam was ~1.5° lower than the incident angles for the tunable IR laser. The polarization combinations reported in this work are SSP (s-polarized SFG output, s-polarized visible input, and p-polarized IR input) and PPP (p-polarized SFG output, p-polarized visible input, and p-polarized IR input). The SSP and PPP polarizations provide complementary information about the molecular susceptibility tensor and are useful in interpreting the orientation of molecules. A model to interpret SSP polarization results in internal reflection geometry has been provided in a previous publication.

We have used a Lorentzian fitting function to fit our data (eq 1).

\[
I_{SFG} \propto |\chi_{d\text{ENR}} + \sum q \omega_{IR} - \omega_q - i \Gamma_q|^2
\]

In eq 1, \(\chi_{d\text{ENR}}\) describes the nonresonant contribution. \(\omega_{IR}\), \(\omega_q\), and \(\Gamma_q\) are the amplitude, damping constant, and angular frequency of the qth vibrational resonance, respectively.

The use of total internal reflection geometry and scanning the IR beam over a broad range of wavelength could result in Fresnel factors that are a function of wavelength. The changes in SFG intensity (SSP polarization) due to the Fresnel factors are provided in the Supporting Information (Figures S2 and S3). The calculation predicts the SFG intensity for ice to be a factor of 2 higher than water. The comparison of the SFG data reported here is not corrected for the changes in Fresnel factors. However, to understand the influence of the changes in the SFG intensity due to Fresnel factors, we have shown the ratios of the amplitude strength and SFG intensities before and after correcting for the Fresnel factors (Table S1). The incident angles used in these experiments are provided in Table S2.
RESULTS AND DISCUSSIONS

Figure 1 shows the spectra of water and ice next to positively (a) and negatively (b, c, and d) charged sapphire surfaces. The empty squares and solid circles represent spectra of water and ice, respectively. The positively charge sapphire was prepared using HCl solution to adjust the pH to 3.3. The negatively charged sapphire surfaces were prepared using NaOH, CsOH, and N(CH₃)₄OH. The data for HCl and NaOH were discussed in our previous publication; here we briefly describe the peak assignments for water and ice next to the sapphire interface. The water spectrum (Figure 1a) has two peaks in the hydrogen-bonded region (3000–3600 cm⁻¹). The peak at 3200 cm⁻¹ corresponds to strong hydrogen-bonding OH stretching modes of water molecules at the solid surface, and the 3450 cm⁻¹ peak is assigned to weak hydrogen-bonding OH stretching modes of water near the interface.¹¹,²²,²³ These peaks are similar to those observed at the water/air interface. The only difference is the peak at 3720 cm⁻¹. At the water/air interface, this peak is assigned to "dangling" OH stretching mode.²⁴ However, at the sapphire/water interface, such a peak is attributed to free surface OH groups.¹⁶,²⁶,²⁹,³⁵ These free surface OH groups form very strong bonds and hence do not participate in hydrogen bonding with the interfacial water molecules.²⁶ These groups are only deprotonated at relatively high pH.¹⁰ This is very unlike the silica silanol groups which, when immersed in water, even at low pH, are easily deprotonated (due to silica's low isoelectric point).¹¹ Recently, it was reported that, while the assignment for the sapphire
surface OH is correct, some portion of the peak should be attributed to free water OH oscillators at the sapphire surface.\textsuperscript{32} We would like to note that there are various interpretations of the water peaks, especially at the water/air interface.\textsuperscript{36}−\textsuperscript{39} However, at the solid/water interface, water molecules have been shown to structure even in the absence of charge.\textsuperscript{40} In the presence of charge, the local electric field extends further and orients water molecules deeper in the bulk.\textsuperscript{40,41}

For the CsOH system, the water spectrum is similar to that of NaOH solution, and the 3450 cm\textsuperscript{−1} peak is absent (Figure 1c). There is, however, a small rise at around 3720 cm\textsuperscript{−1} due to partial deprotonation of alumnol groups at pH 10. Figures 1d and 2 show the SFG spectra for a N(CH\textsubscript{3})\textsubscript{4}OH solution with a partial deprotonation of ammonium groups at pH 10. The data were collected with (empty squares) and ice (solid circles) spectra are collected during the cooling cycle using a solution of pH 10. The liquid spectra in both polarizations are similar except for the shoulder at 3450 cm\textsuperscript{−1} due to hydrogen atoms that were facing the bulk.\textsuperscript{22} This was explained due to ammonia molecules hydrogen bonding with the surface silanol groups and orienting the water molecules with the protons facing the bulk.\textsuperscript{22} When an ammonia/water solution was frozen next to a silica substrate, Wei et al. reported that the freezing was initiated at the water/vapor and water/LiTaO\textsubscript{3} interfaces on negatively and positively charged surfaces, respectively. They attributed this difference in nucleation sites to the orientation of water molecules on the LiTaO\textsubscript{3} surface. Though this ice Ih is crystalline, there remains some residual entropy that allows the water molecules to rotate.\textsuperscript{48} This leads to protons being disordered in the ice crystal. Pauling\textsuperscript{48} produced a statistical model for the position of the hydrogen atoms based on the suggestions by Bernal and Fowler.\textsuperscript{49} According to the Bernal–Fowler ice rule, a large number of configurations exist in ice Ih due to the many different distribution of hydrogens in relation to oxygen atoms. Based on the SFG results, we conclude that the protons are ordered next to positively charged surfaces while they could be disordered next to the negatively charged surfaces. Since these results are similar for both strong and weak ions, we believe that the surface disorder of ice is not due to a specific cation effect.

We believe that the decrease in the SFG signal for ice suggests an intriguing possibility that the orientation of protons toward the negatively charged sapphire substrate may result in surface ice layer with disordered protons. Ehre et al.\textsuperscript{22} reported on the freezing of water molecules on negatively and positively charged LiTaO\textsubscript{3} surface. Using XRD, the authors observed that freezing was initiated at the water/vapor and water/LiTaO\textsubscript{3} interfaces on negatively and positively charged surfaces, respectively. They attributed this difference in nucleation sites to the orientation of water molecules on the LiTaO\textsubscript{3} surface. Although we have not directly measured the orientation of the water molecules next to the sapphire substrate, Wei et al.\textsuperscript{22} have used a phase-sensitive SFG to show that, upon melting, the hydrogen atoms that were facing the bulk flip to point toward the silica substrate. This implies that for negative charged surfaces, the water has to flip its orientation upon freezing. We believe this would lead to a proton disorder, and this is reflected in a weaker SFG intensity for ice next to negatively charged surfaces.

To confirm that orientation is playing an important role and not the cations used to increase pH of the solution, we have collected SFG spectra for the freezing of water for two additional systems: an ammonia/water solution and a negatively charged mica surface. Wei et al. reported that when an ammonia/water solution was frozen next to a silica surface, there was a threefold increase in the ice SFG signal intensity.\textsuperscript{22} This was explained due to ammonia molecules hydrogen bonding with the surface silanol groups and orienting the water molecules with the protons facing the bulk. Su et al. used similar explanation to describe the strong SFG signal observed for ice grown on Pt(111) surface.\textsuperscript{13} Figure 3 shows the ammonia/water solution and ice spectra next to sapphire surface. The water spectrum (empty squares) shows highly ordered water molecules. In aqueous solution, ammonia deprotonates a small amount of water to form ammonium hydroxide. These OH\textsuperscript{−} ions deprotonate some of the sapphire

![Figure 2. SFG spectra collected in PPP polarization during cooling of tetramethylammonium hydroxide solution (N(CH\textsubscript{3})\textsubscript{4}OH). The water (empty squares) and ice (solid circles) spectra are collected during the cooling cycle using a solution of pH 10. The data were collected with temperature increment of 1 °C (using a 0.3 °C/min cooling rate) and a 30 min equilibration time, before collecting the SFG spectra. The ice spectrum has been offset for clarity.](image-url)
hydroxyl groups to make the surface negatively charged. When the solution is cooled to form ice, the ice SFG signal intensity rises, contrary to what is observed on negatively charged surfaces. This further suggests that for the strong ice peak at 3150 cm\(^{-1}\) to be observed, water molecules have to orient with their OH bonds pointed toward the bulk. This is consistent with the hypothesis that some of the NH\(_3\) molecules are able to hydrogen bond to aluminol groups and orient water molecules at the interface.\(^{22}\) We also find that the incorporation of ammonia molecules into the ice is rate dependent and the SFG intensity for ice was higher with a faster freezing rate (Figure 3).\(^{22}\) We have not directly observed the N–H symmetric peak (at 3312 cm\(^{-1}\)) possibly due the high intensity of the ice signal which may have overshadowed the N–H peak. In Figure 4, we show an illustration of how ammonia is able to order water molecules in ice at the sapphire surface.

To emphasize the role of negatively charged surface in controlling the ice formation, we performed experiments on muscovite mica surface. Mica is an atomically smooth surface with an intrinsic negative charge density of \(-0.33 \text{ C/m}^2\) due to the isomorphic substitution of silicon by aluminum atoms.\(^{51}\) In air, the charge is compensated by potassium and, to a lesser extent, sodium ions. In aqueous solution, the surface charge is considerably less than \(-0.33 \text{ C/m}^2\) due to the adsorption of counterions to the surface charge sites.\(^{51}\) However, in water with considerably less ions (deionized water), potassium ions become hydrated and dissociate from the mica surface.\(^{52,53}\) The surface charge decreases with decreasing pH. The point of zero charge (PZC) for mica is still under debate, but it is generally assumed to be 3.\(^{54}\) Based on this, we studied both the water and ice structures on muscovite mica using deionized water of pH around 6. The slight acidity is derived from dissolved carbon dioxide in the solution. Figure 5a shows the spectra of water on mica in SSP and PPP polarizations. There are two main peaks. The red-shifted peak at 3150 cm\(^{-1}\) is attributed to strong hydrogen-bonded water molecules normally referred to as icelike, and the peak at 3450 cm\(^{-1}\) is assigned to the weak three- or low-coordinated liquidlike water molecules, similar to water on sapphire surface. The PPP polarization (empty squares), which is sensitive to both symmetric and asymmetric water stretching modes, shows both icelike and liquidlike water molecules. The SSP polarization (empty circles), which corresponds to molecules normal to the surface, shows highly ordered water next to the mica surface. This assessment is in line with data from scanning polarization force microscopy (SPFM)\(^{55,56}\) and first principles molecular dynamics simulation (MD)\(^{57}\) where water molecules adsorbed on mica form stable icelike monolayers. In the SSP water spectrum (Figure 5a), we observe an upturn in intensity from 3700–3800 cm\(^{-1}\), and because this observation is not reproducible (Figure 5b) we do not assign this upturn to a free OH vibration.

SFG measurement of adsorbed water molecules was first performed by Miranda et al.\(^{58}\) The authors observed that at 90% RH (relative humidity), the monolayer formed on the mica surface was an ordered icelike structure similar to what was predicted by molecular dynamics simulation.\(^{57,58}\) A recent study of the water/muscovite mica interface using SFG also reported the observation of icelike water molecules next to mica surface, and the trend is consistent with the results reported here.\(^{59}\) A shoulder near 3400 cm\(^{-1}\) has also been observed for water next to mica surface, which was not observed in these results\(^{58,59}\) and this could be due to differences in experimental geometry. Figure 5b shows the SFG results for water and the ice structure next to the mica surface using SFG. Upon freezing, the SFG signal intensity decreases and the peak is slightly blue-shifted. This sudden decrease in signal intensity is consistent with the hypothesis that proton disordering next to negatively charged surface reduces the intensity of ice. It is interesting that liquid water next to negatively charged surfaces is highly ordered due to the surface electric field. However, molecules in ice are proton disordered due to the strong interaction of water with the surface and the mechanism of ice formation. We would like to comment on the structure of water next to mica just before freezing. Very recently, Abdelmonem et al. reported, using second harmonic generation (SHG), that water next to mica increases its structural order before the freezing transition.\(^{20}\) We show in Figure 5c the SFG signal intensity at mica/water interface as a function of temperature during cooling (blue curve) and heating (red curve) at 0.3 °C/min.

Figure 3. SFG spectra collected in SSP polarization during cooling of ammonia/water solution. The changes in the SFG spectra were measured for pH 10. Two freezing rates are presented: 5 °C/min (empty circles) and 10 °C/min (solid circles). For each rate, the solution is cooled from 20 to −40 °C. The water spectrum (empty squares) was collected at 20 °C. This figure shows that the incorporation of ammonia into the ice structure at the sapphire surface is rate dependent.

Figure 4. Illustration of NH\(_3\)-doped ice near sapphire/ice interface. The bound ammonia molecules are able to order water molecules, significantly increasing the SFG signal intensity of ice next to sapphire substrate. This illustration is based on work in ref 22.
Our experiment shows no apparent increase in signal intensity as the temperature is decreased and is different from the SHG results. Perhaps this subtle change in SHG intensity is not observed in the SFG experiments. Finally, we would like to comment on the melting temperature of ice. In all cases studied here, the melting temperature is close to 0 °C. Although surprising, this implies that the proton order or disorder has no effect on melting temperature.

Finally, we would like to comment on the freezing temperature observed here for sapphire and mica surfaces in comparison to published work in the literature. These studies used different volume, surface area, cooling rates, and experimental approach, and this could influence the nucleation process. Campbell et al. studied freezing of water droplets on three substrates (silicon, glass, and mica), and they measured the number of droplets frozen as the sample was cooled below −15 °C at a cooling rate of 1 °C/min. They reported median transition temperatures that were very close to homogeneous nucleation temperature of water (−35 °C), indicating a very weak influence of the substrate on the nucleation process. Atkinson et al. also reported that K-feldspar is a better nucleator than mica sheets. In comparison, Steinke et al. observed a higher freezing temperature on mica (−22 °C). Because these studies were conducted using droplets with smaller volume, smaller surface area (4 × 10^{-9}−4 × 10^{-6} mL and 3 × 10^{-6}−3 × 10^{-4} cm^2), and faster cooling rates, this could be the reason for lower freezing temperature reported in these studies. The results by Abdelmonem et al. using similar experimental conditions reported freezing transition temperature of around −12 °C for mica and sapphire substrates, which are similar to the freezing temperatures reported here. Experiments are in progress to understand the influence of surface energy and volume of the sample cell on freezing transition temperatures.
CONCLUSIONS

Water and ice in contact with charged surfaces are ubiquitous on Earth, and here we show how the orientation of water molecules next to negatively charged surfaces has a profound effect on the surface structure of ice. By using surface-sensitive infrared—visible sum frequency generation spectroscopy (SFG), we show that at high pH the ice signals are attenuated compared to the water signals. This attenuation is not due to the cations added to increase the pH. However, it is due to the orientation of water molecules in contact with negatively charged surfaces, which leads to a proton disordered ice phase. We have shown using ammonia that if this orientation of water was reversed and in the same direction as neutral and positively charged surfaces, the ice signals are actually enhanced several orders of magnitude compared to water. On mica, which is inherently negatively charged, the ice signals were again attenuated compared to liquid water, indicating that it is negative charge which is responsible for the attenuation rather than the cations added to increase the pH. In comparison, the ice signals are much larger than water signals next to positively charged surfaces. These results have important implications in designing surfaces to reduce ice adhesion, understanding processes involved in cloud seeding, and movement of glaciers.

ASSOCIATED CONTENT

Supporting Information
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Notes
The authors declare no competing financial interest.

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