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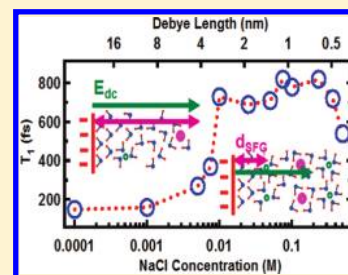
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S Supporting Information

ABSTRACT: The effect of the surface electric field on the ultrafast vibrational dynamics of interfacial water is studied using IR pump-sum frequency generation (SFG) probe spectroscopy. At very low salt concentrations, a vibrational lifetime (T_1) of ~ 200 fs, similar to bulk H_2O , is observed for the O–H stretch at the H_2O /silica interface at pH 6, where the silica surface is negatively charged. However, T_1 increases to ~ 700 fs by increasing the NaCl concentration to 0.01 M. The observation of similar dynamics for a range of salt concentrations, associated with different extensions of the electric field, suggest that the surface electric field is screened faster than predicted by classical electrical double-layer theories and that the Debye length may not be the appropriate measure of the depth sampling of the SFG response. An interfacial excess of cations is hypothesized to explain the faster decay of the static electric field than predicted by the Gouy–Chapman theory.

SECTION: Surfaces, Interfaces, Catalysis



The interaction of water with electrically charged surfaces is of great importance to areas such as heterogeneous catalysis, electrochemistry, biophysics, colloidal, and environmental science.^{1,2} Silica is one of the most widespread and important oxides on the planet. It has been the subject of much research mainly because of its applications in geochemistry and in semiconductor technology.^{3–5} In aqueous media, the origin of the surface charge is known to result from protonation–deprotonation of surface hydroxyls at the oxide surface.^{6,7} The structure and dynamics of water molecules close to the oxide surface can substantially modify the reactivity and functionality of the material.⁸ Bulk properties, such as pH, of the aqueous solution can greatly affect the structure and the dynamics of interfacial water following protonation–deprotonation of the surface hydroxyl groups.⁷ For example, the surface charge can be altered in the presence of aqueous salt solution, with resulting change in the structure of interfacial water.^{6,9–15} In addition, increasing the salt concentration reduces the Debye length and the penetration of the electric field into the aqueous bulk.⁶

Despite the broad impact of interfacial water, the lack of experimental techniques with interface specificity has been an obstacle to expanding our molecular level structural and dynamical understanding. In the past two decades, however, sum-frequency generation (SFG) has developed as a versatile vibrational spectroscopic tool to probe the structure of interfacial water.^{16–19} Surface vibrational SFG is a second-order nonlinear optical process where two incident laser beams, with frequencies ω_{IR} and ω_{vis} , spatially and temporally overlap at the surface and a third beam, whose frequency (ω_{SF}) is the sum of two incident frequencies ($\omega_{\text{SF}} = \omega_{\text{IR}} + \omega_{\text{vis}}$), is generated.

In the past, SFG spectra of water at solid oxide interfaces have provided information on the structure and orientation of interfacial water as a function of the electrolyte, pH, or both.^{20–26} In particular, the presence of ions at the oxide/water interface has been shown to affect SFG spectra of water/silica interface.^{4,7,13,14,23,27} However, it is challenging to interpret the SFG spectra to answer fundamental questions such as how deep the interface is and to what extent SFG is sensitive to the interface, rather than the bulk, at a charged interface because of known electric field effects on the nonlinear optical response.^{6,6}

Recently, SFG has been used to probe the ultrafast vibrational dynamics of interfacial water.^{28–37} We have shown that the measured vibrational lifetime of the O–H stretch of H_2O depends on the charge density at the silica surface.³⁴ One of the fundamental questions that arises from our previous work is whether it is the presence of the electric field, its penetration into the bulk water, or another characteristic of interfacial water that leads to the observation of vibrational dynamics similar to bulk water for the charged interface.³⁴ If the contributions to the SFG response of ordered and polarized water molecules are the primary reason for the observation of fast, bulk-like vibrational dynamics at the charged surface, then screening the electric field, so that it acts over a smaller distance, could lead to the observation of slower vibrational dynamics characteristic of interfacial water because the number of water molecules in

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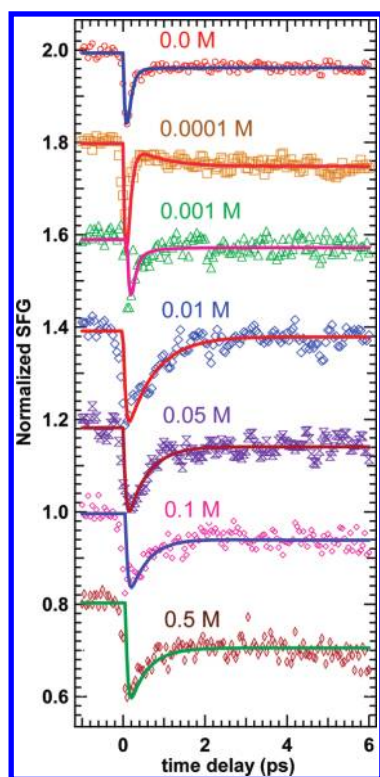


Figure 1. IR pump-SFG probe trace of O–H stretching of H₂O/silica for $\nu_{\text{probe}} = \nu_{\text{pump}} = 3200 \text{ cm}^{-1}$ at pH 6 with NaCl concentrations of 0, 0.0001, 0.001, 0.01, 0.05, 0.1, and 0.5 M. The solid lines are the fit (see text). The polarization combination for SFG, visible, IR is p,p,p.

bulk-like solvation environments that contribute to the signal can be reduced. Alternatively, water at a charged surface may actually have a vibrational lifetime that is different from that of water at a neutral surface.

In the present study, we investigate the effect of screening of the electric field on the vibrational relaxation of H₂O at a silica interface at pH 6 where the silica surface is negatively charged. Our results support our hypothesis that the reason for faster vibrational dynamics at the negatively charged surface is due to the penetration of the electric field into the bulk water and consequent sampling of bulk-like water response. We found that at low salt concentration (10^{-3} M and below) the vibrational dynamics is similar to the dynamics in the absence of the salt. An increase in the vibrational lifetime is observed at salt concentrations $>10^{-3}$ M, reaching a plateau at a concentration of 10^{-2} M. We postulate that in the plateau region, the hydrated cations accumulate near the silica surface with one or more layers of water sandwiched in between. The surface enrichment of cations further decreases the penetration of the electric field to distances shorter than the Debye length because the classical Gouy–Chapman model does not include molecular structural information nor does it allow for the surface enrichment of ions at the charged surface. In the plateau region ($>10^{-2}$ M), the dynamics is dominated by the first few layers of water molecules close to the silica surface.

The IR pump-SFG probe of vibrational dynamics of O–H stretch at 3200 cm^{-1} at the H₂O/silica interface at pH 6 for selected NaCl concentrations, are shown in Figure 1. A four-level system with two time constants, assigned to the vibrational lifetime (T_1) and the thermalization time (T_{th}), was used to fit the pump–probe data. Details of this model can be found

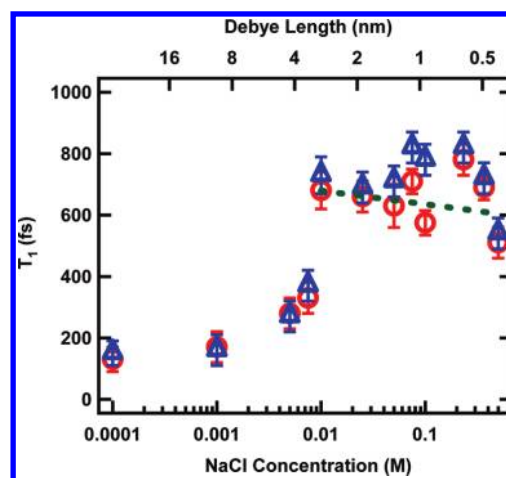


Figure 2. Vibrational lifetime (T_1) extracted from the fit to the IR pump-SFG probe of O–H stretching of H₂O/silica for $\nu_{\text{probe}} = \nu_{\text{pump}} = 3200 \text{ cm}^{-1}$ at pH 6 with different NaCl concentrations. The T_1 for two polarization combinations for the SFG, Vis, and IR probe are p,p,p (red circles) and s,s,p (blue triangles) are shown. All T_1 are listed for all concentrations studied even though only selected pump–probe traces are shown in Figure 1. The error bars for the dynamics at ppp polarization combination are the standard deviation of at least three different independent measurements. The solid dashed line is a linear fit to the ppp data for concentrations of 0.01 M and greater. The top x axis represents the Debye length for corresponding ionic strength in the bottom x axis.

elsewhere.^{30,33} In brief, the SFG signal was fit by a system of coupled differential equations that describe the transient populations of the ground, excited, and intermediate states. According to this model, the vibrational lifetime (T_1) is associated with the vibrational relaxation from the excited state to an intermediate state, a nonthermal combination of accepting modes. The time constant over which redistribution of energy occurs over all degrees of freedom and leads to full thermal equilibrium is described by the thermalization time constant (T_{th}).

The extracted values of T_1 and T_{th} from the fit are shown in Figures 2 and 3, respectively. It is apparent that whereas the T_1 undergoes a trend (rise and fall) as a function of salt concentration, the T_{th} does not change significantly within the error bars. Three regions can be identified for the values of T_1 . At very low salt concentration (0 to 1 mM), T_1 is almost constant with an average value of <200 fs. The first region is followed by a transition region where T_1 increases at concentrations >1 mM and reaches an asymptotic value at a concentration of 10 mM. Finally, a plateau region is observed where T_1 does not significantly change with increase in salt concentration up to 0.5 M.

In the absence of salt, the vibrational lifetime ($T_1 < 200$ fs) is similar to the T_1 of bulk water (~ 200 fs),³⁸ the T_1 reported for the H₂O/silica interface at pH 12 (~ 250 fs),³⁴ and also to the previous report for the H₂O/silica interface at pH 5.7 (~ 300 fs).²⁸ In the absence of NaCl, the electric field polarizes water molecules over a large distance, in principle, as long as the Debye length, into the bulk. The SFG then monitors the dynamics of water molecules that are, for the most part, completely solvated.³⁴ In the presence of surface charge, the SFG response has contributions from both the second- and third-order nonlinear susceptibilities⁶

$$I_{\text{SFG}} \propto (P^{(2)})^2 \propto (N_{\text{S}}\chi^{(2)}E_{\text{IR}}E_{\text{VIS}} + N_{\text{B}}\chi^{(3)}E_{\text{IR}}E_{\text{VIS}}E_{\text{dc}})^2 \quad (1)$$

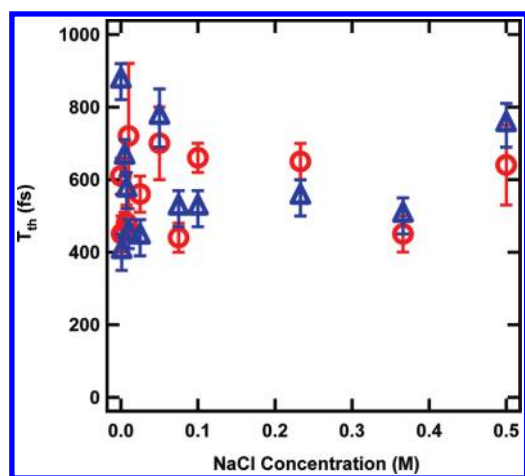


Figure 3. Thermalization time constant (T_{th}) extracted from the fit to the IR pump-SFG probe of O–H stretching of H₂O/silica for $\nu_{probe} = \nu_{pump} = 3200\text{ cm}^{-1}$ at pH 6 with different NaCl concentrations. The T_{th} for two polarization combinations for the SFG, Vis, and IR probe are p,p,p (red circles) and s,s,p (blue triangles) and are shown. All T_{th} are listed for all concentrations studied even though only selected pump–probe traces are shown in Figure 1. The error bars for the dynamics at ppp polarization combination are the standard deviation of at least three different independent measurements.

where N_S and N_B represent the number of water molecules contributing to the second- and third-order responses, respectively, and E_{dc} is the surface electric field. $\chi^{(2)}$ and $\chi^{(3)}$ are the second- and third-order susceptibilities, respectively. The third-order susceptibility, $\chi^{(3)}$, has the contributions from both polarized as well as aligned water molecules and can be written as⁶

$$\chi^{(3)} \propto \left(\alpha^{(3)} + \frac{\mu\alpha^{(2)}}{kT} \right) \quad (2)$$

where $\alpha^{(3)}$ and μ are the third-order polarizability and the permanent dipole moment, respectively. N_S is constant and has a value that depends on the surface specificity of SFG, i.e., the number of layers contribute to the $\chi^{(2)}$ response. N_B , however, depends on the depth through which polarized and aligned water contribute to the SFG and, in a crude approximation, is determined by the Debye length.

According to eq 1, the surface specificity of the SFG response is reduced if the third-order response, i.e., bulk contribution, dominates. However, because in the condensed phase the value of $\chi^{(2)}$ is several orders of magnitude greater than $\chi^{(3)}$,³⁹ the contribution of third-order should be negligible. However, for surface electric fields on the order of 10^7 V/m , such as those in the present experiment, and in the absence of the salt or at very low salt concentration, where the value of N_B is substantially greater than N_S , the relative importance of the surface contribution (first term in eq 1) and the bulk contribution (second term in eq 1) may become comparable. Hence, the observed SFG vibrational dynamics in the absence of salt or at very low salt concentration may reflect bulk-like water dynamics. Increasing the NaCl concentration up to 10^{-3} M does not change T_1 significantly; that is, T_1 remains $\sim 200\text{ fs}$, suggesting that the majority of water molecules sampled by SFG have bulk-like behavior. This explanation is consistent with the recent phase-sensitive SFG spectroscopic measurements of water at a charged surface, which suggests that the spectrum of water near a charged surface is similar to that of bulk water.^{40,41}

Above 10^{-3} M NaCl, the vibrational dynamics starts to slow down and T_1 reaches $\sim 700\text{ fs}$ at 0.01 M NaCl concentration. Further increase in NaCl concentration (up to 0.5 M) results in an apparent slight decrease in T_1 , indicated by a straight dotted line fit to the data in Figure 2, but on average it is similar to the value of T_1 ($\sim 570\text{ fs}$) that was observed at the H₂O/silica interface at pH 2.³⁴ The Debye length, calculated with the Gouy–Chapman theory, at 0.01 M NaCl is 3 nm , that is to say, ~ 10 layers of water molecules. Although the Debye length is not a measure of depth profiling of the SFG, it is still reasonable to state that compared with 0.001 M the number of completely solvated water molecules that contribute to the SFG signal at 0.01 M has been reduced. As a result, the dynamics samples fewer of the completely solvated bulk-like water, increasing the relative contribution of water molecules that are near the silica surface and have longer T_1 , as in the case of H₂O/silica interface at pH 2.³⁴

The reason for the longer T_1 at pH 2 was attributed to the incomplete solvation of first layer of water molecules near the silica surface, which provides the dominant contribution to the SFG response.³⁴ However, at pH 6, the classical Debye length varies from ~ 3.0 to $\sim 0.4\text{ nm}$ (i.e., 10 to 1 layers of water molecules) as the concentration increases from 0.01 to 0.5 M . The observation of T_1 of $\sim 700\text{--}500\text{ fs}$ for concentrations of 0.01 M and greater may then imply that the true depth probed by the SFG is less than the corresponding Debye length at each concentration. It should be noted that apart from increased screening of the electric field, i.e., reducing the distance over which it acts, adding salt can also result in the dissociation of intact SiOH groups by hydrated cations, creating extra surface charge.^{42–46} However, even with an increase in surface charge, the surface potential and its extension to the bulk decrease with increasing salt concentration. (See the Supporting Information).

Two distinct hypotheses can be advanced to explain the difference between the classical Debye length and the depth profiling revealed by the SFG response. In the first scenario, according to eq 1, the reduction of N_B (determined by the Debye length) renders the contribution of the third-order response (bulk water) negligible compared with the contribution of interfacial water. The long vibrational lifetime, similar to that of water at neutral silica surface ($\sim 570\text{ fs}$),³⁴ is consistent with this hypothesis. In other words, at 0.01 M , the measured vibrational lifetime is characteristic of interfacial water alone.

Alternatively, one can assume that the surface concentration of hydrated cations near the silica surface is enhanced (scheme in Supporting Information), thereby reducing the surface potential, the interfacial electric field, and the depth of bulk water sampled by SFG. This enhanced concentration near the surface can be estimated assuming that the surface charge is screened by the accumulation of counterions in the Debye volume. (See the Supporting Information.) Cations may retain their solvation shell, that is, accumulate at the Stern layer or outer Helmholtz plane, or specifically adsorb to the silica surface with loss of part of their solvation shell, that is, accumulate at the inner Helmholtz plane. The excess concentration, compared with bulk, of cations near the silica surface then reduces the penetration distance of the electric field into the bulk water and its contribution to the SFG. At 0.01 M NaCl and greater concentrations, the dynamics is therefore dominated by the first few layers of water molecules.

Extensive experimental results from spectroscopic techniques such as X-ray photoelectron spectroscopy (XPS),⁴⁷ second-harmonic generation (SHG),^{48,49} and SFG^{10,11} as well as MD simulation⁵⁰ have predicted enrichment of halide anions at the

air/water interface. However, the negative charge at the silica surface at pH 6 suggests that it is the accumulation of cations near the surface that occurs. A simple model (Supporting Information) allows for an estimation of the free energy of adsorption of Na^+ to the silica surface ($\sim 22 \pm 4$ kJ/mol). The difference between the classical Debye length and the depth profiling of the SFG, therefore, can be explained by either of these two hypotheses. However, on the basis of the current measurements, we are unable to favor one versus the other.

Although the average value of T_1 at concentrations greater than 0.01 M is ~ 650 fs, we observed shorter T_1 (~ 500 fs) at 0.5 M, where the Debye length is ~ 0.4 nm (1 to 2 layers of water molecules). The decrease in T_1 observed here for salt concentrations higher than 10^{-2} M is in contrast with the increase in T_1 observed in the dynamics of bulk water by adding salt. However, whereas the vibrational dynamics of bulk water do respond to the presence of salt, this only occurs at much higher concentrations and provides only a small contribution to the overall dynamics. (See the Supporting Information for further discussion.)

The faster T_1 observed at ~ 0.5 M can be explained by an increase in the local electric field resulting from the decrease in the penetration of the surface electric field, that in turn affects fewer water molecules near the silica surface at higher salt concentration. (This is discussed in more detail in the Supporting Information) Compared with 0.01 M, interfacial water molecules at 0.5 M experience an order of magnitude greater electric field, which results in a more ordered structure⁷ and can partially explain the shorter vibrational lifetime (Supporting Information).^{51,52} However, measurements with higher sensitivity and greater electric fields would be needed to conclude definitively as to the effect of the electric field. It is noted that the dependence of the vibrational lifetime on the surface potential (surface charge) has been observed for CN^- at electrode surfaces, where up to a factor of two change in lifetime was reported for surface potentials that were an order of magnitude greater than those at the silica/water interface system investigated here.⁵³

Although the analysis focuses on the vibrational dynamics, the orientational dynamics could, in principle, have some contribution to the observed dynamics as well. In the bulk, polarization anisotropy measurements are used to separate these two contributions. However, because of the symmetry at the interface, a different scheme should be applied to get insight into the surface orientational dynamics, as has been recently suggested.^{54,55} In a first approximation, the different polarization combinations sample different orientational distributions of the water molecules, which could show different orientational dynamics, for example, for in-plane and out-of-plane motions.⁵⁶ Within the error bars, the T_1 values at different salt concentrations are almost the same for PPP and SSP polarization combinations (Figure 2). Although the comparison of the T_1 for PPP and SSP does not give any quantitative measure of the orientational dynamics, it qualitatively suggests that the orientational dynamics is not significant on the time scale explored here. This is reasonable because the bulk water orientational time scale is >3 ps.^{57,58} Thus, unless a considerable acceleration in the interfacial dynamics occurred, we would not expect to see an orientational relaxation contribution to the observed dynamics. It should be noted that the orientational dynamics of water at micellar interfaces was observed to be even longer than that in the bulk.⁵⁹

The results presented here suggest that the primary reason for the similarity between the dynamics of interfacial water at the charged surface and that of bulk water is the dominant contribution of the

completely solvated water molecules to the SFG response due to the penetration of the electric field into bulk water. By decreasing the number of completely solvated water molecules sampled by SFG, the true vibrational relaxation rate specific to the interface can be obtained. This can be done either by limiting the penetration of the electric field to the first few layers of water next to the charged surface (by adding salt) or by removing the surface electric field (when the silica surface is neutral). The fact that the dynamics at the neutral silica surface and at the charged silica surface in the presence of salt concentrations greater than 10^{-2} M are the same supports the hypothesis that it is the interface rather than its chemical composition that leads to the longer vibrational lifetime of interfacial water compared with the bulk.⁵⁸ The shorter vibrational lifetime at pH 12 compared with that at pH 6, at same ionic strength, can be explained by the hypothesis that because of the higher charge density at pH 12 compared with that at pH 6, the same ionic strength (0.01 M) does not screen the penetration of the electric field equally. We are currently performing experiments to test this hypothesis. The distinction between the properties of bulk and those of interface water is of both fundamental and practical interest, given the many diverse areas where interfacial water is important, for example, biological, electrochemical, and geochemical interfaces.

In summary, we have studied the effect of the surface electric field and its penetration depth on the vibrational dynamics of the H_2O /silica interface at pH 6 by varying the concentration of salt. These experiments also probe the interfacial thickness and the depth to which SFG probes interfacial water. In the absence of NaCl and at low concentrations (up to 0.001 M), T_1 is short, similar to the dynamics of H_2O /silica at high pH and also the T_1 of bulk H_2O . A 10-fold increase in the concentration of NaCl from 0.001 to 0.01 M results in an approximately three times increase in T_1 from 200 to 700 fs. T_1 does not change significantly after further increasing the NaCl concentration up to 0.5 M, implying that the dynamics is dominated by the first few layers of water molecules close to the silica surface. This suggests that the effect of the interfacial electric field extends only a few molecular layers into the bulk at concentrations as low as 0.01 M, a significant deviation from what is predicted by Debye theory (3 nm or ~ 10 molecular layers). This deviation can be explained by the surface enrichment of the cations near the silica surface, reducing the penetration depth of the electric field into the bulk water at a rate faster than that predicted by the classical Debye length. Alternatively, for classical Debye lengths of 3 nm and less, the contribution of bulk-like water, via a $\chi^{(3)}$ response, is reduced to the point where it is negligible compared with the $\chi^{(2)}$ response that samples truly interfacial water. Classical electrical double-layer theory and the Debye length do not include molecular information, and as such the results reported here represent a benchmark for next generation models.

EXPERIMENTAL SECTION

The IR fused silica prism (ISP optics) and Teflon sample holder were cleaned by piranha solution (3:1 (v/v), concentrated sulfuric acid and 30% hydrogen peroxide) prior to experiment (Caution! Piranha solution is a very strong oxidant and is extremely dangerous to work with; gloves, goggles, and a face shield should be worn.) Solutions with different ionic strength were prepared by adding NaCl (Fisher, ACS certified) to distilled Millipore water (>18.2 M Ω .cm resistivity). Hereafter, we refer to the solution as pH 6. To remove the organic impurities, we heated the as-received NaCl (Fisher, ACS certified) to ~ 550 °C

overnight.⁴⁹ After the baking, the absence of the C–H peak in the SFG spectrum in the C–H stretching region was an indication of the successful removal of the organic impurities. Metal impurities such as calcium and magnesium can adsorb to the silica and change the surface charge.⁶⁰ However, we note that such impurities are <0.001% and so their concentration (compared to the sodium) is considerably smaller and should not affect our measurements. It should be noted that our Millipore water filtration unit is equipped with a UV lamp that decomposes any residual organics that might remain after the filtration stage. The details of the optical and IR pump-SFG probe setup can be found elsewhere.³⁵ In brief, a femtosecond IR pulse, generated from a commercial OPA (TOPAS, light conversion) is split in two with a 4:1 ratio to form the IR pump and IR probe beams. The TOPAS was pumped by 90% of the output of a femtosecond regenerative amplifier (Quantronix, Integra-E; central wavelength 810 nm, repetition rate 1 kHz, pulsewidth ~130 fs fwhm, pulse energy ~3 mJ). The remaining 10% of amplifier output was used as a visible pulse. The IR pump, IR probe, and visible beams with energies of ~8, 2, and 2 μ J/pulse, incident at the surface with angles of 72, 58, and 65°, were focused to beam waists of 250, 200, and 200 μ m, respectively. The third-order cross-correlation between IR pump, IR probe, and visible was used to optimize the signal and to define the position of $t = 0$. The SFG (IR probe + visible) as a function of time between IR pump and IR probe was recorded and was normalized (with and without the IR pump). The IR pump (~3200 cm^{-1}) and IR probe (~3200 cm^{-1}) were p-polarized, whereas the visible and SFG beams were either s- or p-polarized, as described in the text.

■ ASSOCIATED CONTENT

S Supporting Information. Details of the comparison of the dynamics of interfacial and bulk water in the presence of salt, adsorption isotherm for the estimation of the cation adsorption, and the acceleration of the dynamics at high salt concentration. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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