S1. Preparation of Optical Cell and Silica Substrates. Samples were prepared as previously reported.1-3 Fused silica hemispheres (Hyperion Optics Corning 7979 IR Grade) were clamped onto a custom-built aluminum flow cell with a removable PTFE interior. This Teflon portion of the cell was sealed to the hemisphere with a fluororubber o-ring. The silica substrates were cleaned by soaking in Alnochromix (Alconox) cleaning solution for an hour. The hemispheres were then rinsed with copious amounts of ultrapure water (Millipore), sonicated in HPLC-grade methanol for 15 minutes, rinsed again with ultrapure water, dried under flowing house N₂, plasma cleaned (Harrick Plasma) for another 10 minutes, and immediately stored in ultrapure water inside a glass beaker covered with parafilm. Substrates were left overnight in water prior to measurements. Only ultrapure water (Milli Q, Millipore Inc., 18.2 MΩ*cm) was utilized in substrate and solution preparation. NaCl (Sigma Aldrich (#746398, >99% purity)) solutions were
Ma et al. prepared at relevant concentrations (100mM, 1mM, 10μM). Solutions were made the day prior and left overnight to equilibrate with atmospheric CO₂ in Erlenmeyer flasks partially covered with Parafilm to reach a pH 5.7 (± 0.2) on the day of the laboratory measurements. No filtration was carried out prior to experiments.

S2. Conductivity Measurements. The conductivity of the solution exiting the flow cell was measured on an AKTA Pure (GE HealthSciences) chromatography system equipped with a C9 conductivity probe (GE HealthSciences). The C9 conductivity probe has a reading range of 0.01 to 999.99 mS/cm, and samples from the eluent a volume 22μL of flowing solution with an accuracy of ±0.01 mS/cm at a rate of ~3 Hz. The pumps were flushed with the solutions of interest before experimentation by flowing 50 mL of the starting solution through the wetted parts of the system. For these experiments, the AKTA system was rerouted such that the flow from the solution pumps (GE HeathSciences peristaltic pump P9) directly entered the sample flow cell through a 25μL total volume tubing (0.5mm diameter, ~6 inches long). The solution exiting the cell was then routed directly to the conductivity probe through an identical length of tubing. Experimental flow rates were set to 5mL per minute to recapitulate the flow rate used in the HD-SHG experiments. Fig. S1 shows the data from Fig. 2 in the main text replotted with logarithmic scale for the conductivity measured in-line using the GE AKTA probe to demonstrate the discontinuity at 420 seconds, where the in-line AKTA probe reaches it sensitivity limit and we use the conductivity measured with the more sensitive but less compact conductivity meter (Termo Fisher Orion A235) in the 10 μM eluent off-line.
Figure S1. Fig. 2 in the main text replotted with logarithmic scale for the conductivity measured in-line using the GE AKTA probe.
S3. SHG Measurements and Fitting Procedures. Our heterodyne-SHG set-up has been described previously. Briefly, SHG interference patterns were recorded in a continuous series by moving a piece of α-quartz along an automated 100 mm translational stage. Fringes were collected in forward and backwards-moving directions at approximately 12 seconds per collection period (Fig. S1). To verify stability of the signal and phase, fringes were collected for 15 minutes at each salt concentration. The pumps for the two aqueous solutions were stopped and started in tandem to reach the lower salt concentration from the higher one, and vice versa, for the return jump. We then wait for approximately 15 minutes while recording HD-SHG fringes at the target concentration, before initiating the return jump to the original salt concentration. The quartz reference was also removed, and homodyne-detected SHG intensities throughout the same process were recorded as well (Fig. S1). All measurements were performed at creeping (low shear) flow rates (~5-20mL min⁻¹, cell volume is ~ 3 mL).

S4. Fitting and Calculation of Δφₚᵣₑₜ and Eₚᵣₑₜ. Details regarding data collection and analysis have been previously reported. Briefly, the detected total signal intensity I_SHG, produced by coherent interference from the sample signal and α-quartz local oscillator is governed by:

\[ I_{SHG} \propto |E_{sig} + E_{LO}|^2 = |E_{sig}|^2 + |E_{LO}|^2 + 2E_{sig}E_{LO}\alpha \cos(\varphi) \]  

eqn. S1.

Here, \( \alpha \) accounts for the degree of spatial and temporal overlap between the sample and fundamental beams, and \( \varphi = \varphi_{LO} + \varphi_{sig} + \varphi_{PSU} \) comprises the contributions from the phase of the local oscillator, sample signal, and the change introduced by the phase shifting unit, or the controlled translation of the α-quartz unit along the beam path.
**Figure S2.** Interference fringes continuously generated from translation of alpha-quartz local oscillator along 100 mm, mapping salt concentration jump from high salt solution (green) to low salt solution (blue) at A) 100mM NaCl to 10μM NaCl, B) 100mM NaCl to 1mM NaCl, and C) 1mM NaCl to 10μM NaCl.

The following expression is fit to the generated interference pattern:

\[ I_{SHG} = I_0 + A \cos(\pi x + \varphi_{fit}) \]  

eqn. S2

which provides \( E_{sig} \), which is proportional to \( A \), the amplitude of the fringe along with \( \Delta \varphi_{sig} = \Delta \varphi_{fit} \) since \( \varphi_{PSU} \) and \( \varphi_{LO} \) are effectively constant across all measurements.

**S5. Flow Dependence.** Measurements of the SHG amplitude and phase using HD-SHG (Fig. S3) as well as homodyne-detected SHG intensity measurements (Fig. S4) show the rate of change in the measurables increases slightly when the aqueous solution flow rate is increased fourfold. The initial peak in the SHG amplitude Fig. S3) and intensity (Fig. S4) is observed at all three flow rates.
Figure S3 A) SHG amplitude and B) phase from experimental data mapping transition immediately after valve change, from 100mM NaCl to 10uM NaCl at 20mL/min (dark purple), 10mL/min (purple), and 5mL/min (light purple).

Figure S4. A) SHG intensity recorded for a jump from 100mM NaCl to 10uM NaCl at 20mL/min (dark purple), 10mL/min (purple), and 5mL/min (light purple) and B) for the return jump.
S5. Control Studies of Reference Crystal. Fig. S5 shows the relative contribution of the local oscillator (z-cut α-quartz only, SHG signal from the fused silica:water interface blocked with a 515 nm filter) to the total heterodyned SHG signal intensity (515 nm filter removed) at two salt concentrations. The interference between the SHG signal and the LO is due to the absolute phase of the local oscillator (the z-cut α-quartz) phase shifting by 180° every 60° around the z-axis. As previously shown,\textsuperscript{1,3} shifting the phase by 180° or rotating the crystal 60° results in a negative SHG vs LO(position) fringe pattern.

**Figure S5.** SHG intensity as a function of local oscillator (z-cut α-quartz) azimuthal rotation angle (along optical axis) at A) 100mM (green) and B) 10μM NaCl (blue). Bottom trace in each graph shows LO signal only.
S6. Additional Homodyne-Detected Studies. Homodyne-detected SHG signals collected during various ionic strength jumps show no hysteresis for the conditions indicated when the fused silica substrate had not been pre-exposed to salt, as shown in the two Figures below.

**Figure S6.** Top) Homodyne SHG intensity from the silica:water interface collected during ionic strength jumps from 1mM NaCl to 10μM NaCl (light grey) and 100mM NaCl to 10μM NaCl (dark grey). Bottom) SHG intensity from the silica:water interface collected during ionic strength jumps from 100 mM NaCl to 10μM NaCl (grey) and to 1 mM NaCl (black trace). Right panel shows the SHG intensity for the corresponding return jump.
**Figure S7.** Left) Homodyne SHG intensity from the silica:water interface collected during ionic strength transitions from 500mM NaCl to 100mM NaCl (grey) and 1M to 100mM (black) and return jump (right).

**S8.** Left) Correlation plot between $\chi^{(2)}:\Phi(0)$, for all jumps studied in this work. Graph shows $\chi^{(2)}$ varies significantly depending on initial experimental conditions. Right) SHG amplitude $E_{\text{sig}}$ (purple) and phase $\phi_{\text{sig}}$ (grey) as a function of NaCl concentration transition from 10uM to 100mM, indicated by the measured conductivity (green), without pre-exposure to salt.
**S8. MD Simulation Model Details.** Atoms in the inert substrate are fixed in a face-centered cubic structure with a lattice parameter of 0.392 nm and a (111) termination at the interface. The orthorhombic simulation cell is oriented such that the z coordinate is perpendicular to the silica surface, and the simulation cell is periodically replicated only in the x and y coordinates. In all simulations, the length of the simulation cell in the x and y coordinates is 2.77 nm and 2.88 nm, respectively, such that each of the silica inert substrates is described using four layers of inert atoms, with each inert layer containing 120 atoms (for a total of 960 inert atoms). A representative snapshot of our simulation box is shown in Fig. S8.

![Simulation snapshot](image)

**Figure S9.** A simulation snapshot with 0.1 M NaCl with $\sigma_0 = -0.041\ \text{C/m}^2$. The inert layers are grey spheres, on top of which are hydroxyl groups. Water molecules are in blue. Yellow and green spheres are Na$^+$ and Cl$^-$ ions, respectively.

**S9. Semipermeable Boundaries for Interfacial Na$^+$ Ions.** For the charged surface with no contact or solvent-separated ion pairs, semipermeable boundaries are introduced to interact only with Na$^+$ ions. The boundaries are located at $z = \pm 5.5$ nm in the case of solvent-separated ion pairs or at $z = \pm 5.175$ nm in case of no ion pairs. The purely repulsive boundaries for Na$^+$ ions are described by a truncated LJ interaction having an $\epsilon$ of 7.9597 kcal/mol, a $\sigma$ of 0.235 nm, and a cutoff of 0.235 nm. Lennard-Jones parameters and atomic charges used are listed in Table S1.
|                      | $\sigma$ (nm) | $\varepsilon$ (kcal/mol) | $q$ (e) |
|----------------------|---------------|--------------------------|--------|
| **NaCl ions**        |               |                          |        |
| Na$^+$               | 0.235         | 0.13                     | +1     |
| Cl$^-$               | 0.44          | 0.1                      | -1     |
| **SPC/E water**      |               |                          |        |
| O                    | 0.3166        | 0.1554                   | -0.8476|
| H                    | 0             | 0                        | 0.4238 |
| **Model silica substrate** |       |                          |        |
| Inert neutral atom$^i$ | 0.2534       | 7.8                      | 0      |
| **Protonated hydroxyl group (Si-OH)$^i$** | | | |
| Si                   | 0.2534        | 7.8                      | 0.265  |
| O                    | 0.3166        | 0.1554                   | -0.7   |
| H                    | 0             | 0                        | 0.435  |
| **Deprotonated hydroxyl group (Si-O)$^i$** | | | |
| O                    | 0.3166        | 0.1554                   | -0.9825|
| Si                   | 0.2534        | 7.8                      | -0.0175|

**Table S1.** Lennard-Jones parameters and atomic charge of water, ions and model silica atoms.
**S10. Variation of $\chi_{S_iOH}^{(2)}$ with Si-OH**

**Tilt Angle.** The four different sets of hyperpolarizabilities of an OH oscillator are considered in Figure SX, borrowed from Cyran et al.\textsuperscript{8} The tile angle ($\theta_0$) is the angle of the OH bond relative to the surface normal that is antiparallel to the associated Si-O bond. Each configuration exhibits distinct interaction between the OH bond in the silicic acid and water molecules. Configuration 1 is for an So-bound OH oscillator that is donates the hydrogen bond, while configuration 2 is for the H-bond accepting OH oscillator. In configuration 4, one Si-bound OH oscillator interacts with two water molecules, both donating and accepting an H-bond from water molecules. The average over each configuration was calculated using the relative population (0.59 for config.-1, 0.01 for config. -2 and 0.4 for config.-4), according to Cyran et al.\textsuperscript{8} In the main text (Table I), SiOH contributions are calculated using config.-4, which is the most relevant to conditions of model silica surface.

![Graph](image)

**Figure S10.** Second-order nonlinear susceptibility of a single SiOH group, $\chi_{S_iOH}^{(2)}$, as a function of the tilt angle, $\theta_0$. 

---

Ma et al.

S12
References.

1. Ohno, P. E.; Chang, H.; Spencer, A. P.; Liu, Y.; Boamah, M. D.; Wang, H.-f.; Geiger, F. M., Beyond the Gouy–Chapman Model with Heterodyne-Detected Second Harmonic Generation. *The Journal of Physical Chemistry Letters* **2019**, *10*(10), 2328-2334.

2. Boamah, M. D.; Ohno, P. E.; Lozier, E.; Van Ardenne, J.; Geiger, F. M., Specifics about Specific Ion Adsorption from Heterodyne-Detected Second Harmonic Generation. *J. Phys. Chem. B* **2019**, *123*, 5848-56.

3. Chang, H.; Ohno, P. E.; Liu, L.; Geiger, F. M., Direct Measurement of Charge Reversal on Lipid Bilayers using Heterodyne-Detected Second Harmonic Generation Spectroscopy. *chemRxiv.8678450.v1* **2019**.

4. Boamah, M. D.; Lozier, E. H.; Kim, J.; Ohno, P. E.; Walker, C. E.; Miller, T. F.; Geiger, F. M., Energy conversion via metal nanolayers. *Proceedings of the National Academy of Sciences* **2019**, *116* (33), 16210-16215.

5. Smith, D. E.; Dang, L. X., Computer simulations of NaCl association in polarizable water. *The Journal of Chemical Physics* **1994**, *100* (5), 3757-3766.

6. Berendsen, H.; Grigera, J.; Straatsma, T., The missing term in effective pair potentials. *Journal of Physical Chemistry* **1987**, *91* (24), 6269-6271.

7. Janeček, J.; Netz, R. R., Interfacial water at hydrophobic and hydrophilic surfaces: Depletion versus adsorption. *Langmuir* **2007**, *23* (16), 8417-8429.

8. Cyran, J. D.; Donovan, M. A.; Vollmer, D.; Siro Brigiano, F.; Pezzotti, S.; Galimberti, D. R.; Gaigeot, M.-P.; Bonn, M.; Backus, E. H. G., Molecular hydrophobicity at a macroscopically hydrophilic surface. *Proceedings of the National Academy of Sciences* **2019**, *116* (5), 1520-1525.