

**NaCl, MgCl<sub>2</sub>, and AlCl<sub>3</sub> Surface Coverages on Fused Silica and Adsorption Free Energies****at pH 4 From Nonlinear Optics**

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**Abstract.** We employ amplitude- and phase-resolved SHG experiments to probe interactions of fused silica:aqueous interfaces with Al<sup>3+</sup>, Mg<sup>2+</sup>, and Na<sup>+</sup> cations at pH 4 and as a function of metal cation concentration. We quantify the second-order nonlinear susceptibility and the total potential in the presence and absence of 10 mM screening electrolyte to understand the influence of charge screening on cation adsorption. Strong cation:surface interactions are observed in the absence of screen electrolyte. The total potential is then employed to estimate the total number of adsorbed cations. The contributions to the total potential from the bound and mobile charge were separated using Gouy-Chapman-Stern model estimates. All three cations bind fully reversibly, indicating physisorption as the mode of interaction. Of the isotherm models tested, the K<sub>d</sub> adsorption model fits the data with binding constants of 3 to 30 mol<sup>-1</sup> and ~300 mol<sup>-1</sup> for the low (<0.1 mM) and high (0.1 -3 mM) concentration regimes, corresponding to adsorption free energies of -13 to -18 and -24 kJ mol<sup>-1</sup> at room temperature, respectively. The maximum surface coverages are around 10<sup>13</sup> cations cm<sup>-2</sup>, matching the number of deprotonated silanol groups on silica at pH 4. Clear signs of decoupled Stern and diffuse layer nonlinear optical responses are observed and found to be cation specific.

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**Introduction.** The interaction of inorganic cations with charged aqueous interfaces is important for a variety of settings relevant to environmental chemistry, nanotechnology, energy processes, as well as industrial and engineering applications.<sup>1-2</sup> A major challenge is to quantify the number of adsorbed ions per area under conditions of aqueous flow or as a function of ion concentration, and to assess the extent to which adsorption and desorption are reversible. Of the surface-selective experimental approaches that provide these capabilities, X-ray reflectivity,<sup>3-4</sup> quartz crystal microbalance mass estimates,<sup>5</sup> and nonlinear optical spectroscopy<sup>6-9</sup> are particularly powerful. The latter two techniques circumvent the strong absorber problem of water in the ultraviolet and mid-infrared regions, which prevents the probing of most inorganic ions at surfaces using conventional electronic or vibrational spectroscopic techniques (notable exceptions are oxyanions like arsenate,<sup>10-12</sup> chromate,<sup>13</sup> phosphate,<sup>14</sup> or sulfate.)<sup>15</sup> Interface-specific vibrational spectroscopies such as sum frequency generation probe the response of water's O-H oscillators in the interfacial region to the presence of oxy-<sup>16</sup> and non-oxy ions,<sup>17-21</sup> from which metal cation number densities, or even relative surface coverages, have not yet been quantified due to absorptive-dispersive mixing of the Stern and diffuse layer contributions to the nonlinear optical response.<sup>22-24</sup> Electronic spectroscopies are challenging as most common inorganic ions do not possess strong enough electronic transitions that are readily accessible at buried aqueous interfaces. A notable exception is what has been achieved at the air:water interface using second harmonic generation (SHG) measurements that access solvent to solute charge transfer resonances in the ultraviolet down to 210 nm.<sup>25-27</sup> Electronic resonances involving n- $\pi^*$  transitions of ions such as nitrate ( $\lambda_{\text{max, SHG}}=300$  nm)<sup>28</sup> or ligand-to-metal charge transfer processes of some select transition metal ions ( $\text{CrO}_4^{2-}$ ,

$\lambda_{\text{max, SHG}}=290 \text{ nm}$ )<sup>29-34</sup> or uranyl ( $\lambda_{\text{max, SHG}}=305\text{-}310 \text{ nm}$ )<sup>35</sup> at buried aqueous interfaces have also been detected in our laboratory using resonantly enhanced second harmonic generation (SHG).

We recently advanced non-resonant second order nonlinear spectroscopy to probe specific ion interactions at fused silica: aqueous interfaces via the SHG phase and amplitude.<sup>36-43</sup> The approach avoids the strong absorber problem of liquid water and provides the total potential as well as the second order nonlinear susceptibility of buried across interfaces in contact with ions of various chemical identity. We now employ this method to quantify the total number of adsorbed cations  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^{+}$  cations at fused silica surfaces maintained at pH 4 and during exposure to varying concentrations of the metal cation chlorides. Unlike in our recent work, here we work at pH 4, which simplifies the cation speciation so that hydroxides, important for alkaline earths and trivalent cations at elevated pH, are not prevalent.

**Experimental.** The solutions are prepared using inorganic salts and HCl (Fisher Scientific, ACS Plus, Part # A144, 36.5-38.0%). Stock solutions of 1 M and 10 mM NaCl (Sigma-Aldrich, anhydrous, part # 746398,  $\geq 99\%$  pure),  $\text{MgCl}_2$  (from  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , Sigma-Aldrich, part # M2670,  $\geq 99.0\%$  pure), and  $\text{AlCl}_3$  (from  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , Alfa Aesar, part # 10622, 99.9995% pure) were prepared to obtain solutions with concentration ranges between 1  $\mu\text{M}$  to 3 mM. This range was selected because the maximum  $\text{Al}^{3+}$  concentration that can be used while maintaining a pH of about 4 is 3 mM. 1 M HCl was used to set the pH to 4 as needed. Conductivity (Thermo Scientific, Orion 4-cell I think) and pH (Thermo Scientific, Orion ROSS Ultra Triode, 8107UWMMD) values were determined regularly (Thermo Scientific, Orion Star A325, pH/conductivity meter). Only one salt is tested per day to prevent contamination at the interface from unwanted ions. is tested per day to prevent contamination at the interface from unwanted ions.

We use a 1” diameter fused silica hemisphere (Hyperion Optics, Corning 7979, infrared grade) that is first rinsed in ultrapure water from a Milli-Q system (18.2 MOhm) and then placed in Nochromix solution (*CAUTION: working with Nochromix solution should only be done after reading and understanding the appropriate MSDS sheets*) for at least 1 hour before it is again rinsed with copious amounts of ultrapure water. Then the hemisphere is sonicated in methanol for at least 15 minutes, rinsed, sonicated for 15 minutes, and rinsed again, all with ultrapure water, and then dried using house nitrogen gas passed through a desiccator. The hemisphere is then plasma cleaned (Harrick Plasma) for about 30-60 seconds on "high" setting. The flow cell is then assembled by first dispensing ultrapure water into the flow cell, adding a Viton O-ring, and finally securing the cleaned hemisphere onto the sample cell using clamps.

In the amplitude and phase-resolved laser experiments, the s-polarized 1030 nm output from an amplifier laser system (10 W Pharos, Light Conversion, 200 fs, 200 kHz) is attenuated to 40 mW at the sample, directed onto the silica:water interface using a 100 mm focusing lens while ultrapure water equilibrated in laboratory air overnight ( $<2 \mu\text{S cm}^{-1}$ ) is flowed through the cell at a rate of  $2 \text{ mL min}^{-1}$  (Fig. 1A). A peristaltic pump is used to control the flow rate. A 100 mm off-axis parabolic mirror directs the fundamental and the SHG signal from the interface onto a set of optics for time and spatial overlap, and into a photon counter after passing through a short pass filter and a 520 nm bandpass (FWHM=40 nm) filter, as described earlier.<sup>42</sup> Nonlinear optical interference fringes are recorded using a 50  $\mu\text{m}$  thin quartz wafer on a 100 mm motorized translational stage as a local oscillator source from which the SHG amplitude and phase are determined as detailed in our prior work.<sup>42</sup> After recording a test fringe to ensure accurate alignment, system is allowed to equilibrate for at least 2 hours while ultrapure water continuously

flows through the cell at a rate of 2 mL min<sup>-1</sup>, after which the SHG phase and amplitude are stable.

Then, SHG fringes are collected in fourfold replicates for each solution condition. After each set of four fringes, the next solution is introduced to the system and is flowed for at least 30 minutes at 2 mL min<sup>-1</sup>. Due to well established hysteresis effects,<sup>40</sup> fringes are recorded in order of increasing ion concentration. For the SHG phase referencing, we use a freshly prepared pH 2.5, 500 mM NaCl aqueous solution each day (*vide infra*).

The SHG intensity measurements employed in our time-dependent experiments are carried out using the same standard sample cell and flow system described above but at a flow rate of 10 mL min<sup>-1</sup> now the interface is probed by the 1035 nm output of a Light Conversion Flint Oscillator (90 fs pulse duration at 80 MHz repetition rate) attenuated to 0.5 W. We use the p-in/p-out polarization combination and record the SHG intensity using a time resolution of 100 ms. Under these conditions, the fused silica:pH 4 solution interface yields several hundred counts per 100 ms.

**Results and Discussion.** Fig. 1B shows an example of nonlinear optical interference fringes recorded while flowing ultrapure water first, then an aqueous pH4 solution at MgCl<sub>2</sub> concentrations ranging from 1 μM to 1 mM, and finally a pH 2.5 0.5 M salt solution across a fused silica hemisphere. Clear shifts in the fringe amplitude and phase are evident in the data and quantified using a simple cosine fit function of the form  $y_0 + E \cdot \cos(\kappa x + \varphi)$ . This equation accounts for the signal offset,  $y_0$ , the SHG amplitude,  $E$ , and its phase,  $\varphi$ . The constant  $\kappa = 3.14^\circ \text{ mm}^{-1}$  arises from the group velocity dispersion and the 100-millimeter-long time delay stage we use to record the nonlinear optical fringes.<sup>42</sup> Like in our earlier work,<sup>42</sup> we reference the SHG phase to the one we obtain at the high ionic strength and the pH of zero charge (500 mM, pH 2.5),

where we expect the surface potential to be minimized and where the SHG response is therefore purely real-valued ( $E \propto e^{i\phi}$ , where  $\phi=0^\circ$ ), and the total surface potential,  $\Phi_{\text{tot}}$ , and the nonlinear second order susceptibility,  $\chi^{(2)}$ , as detailed earlier.<sup>38, 40</sup>

Fig. 2 shows  $\Phi_{\text{tot}}$  and  $\chi^{(2)}$  as a function of cation concentration for the three chloride salts we surveyed. When the salts are added with 10 mM screening electrolyte present (Fig. 2A), we find negligible changes in  $\Phi_{\text{tot}}$  and  $\chi^{(2)}$ . We find that even the trivalent  $\text{Al}^{3+}$  cation does not possess a sufficiently large enough driving force to adsorb to the interface when the negative surface charges from the deprotonated silanol groups are screened by 10 mM electrolyte concentration. In other words, surface charge screening from the 10 mM background electrolyte requires too much work for specific adsorption to occur. This situation is quite different when we perform the adsorption isotherm measurement without any added screening electrolyte (Fig. 2B). Here, we find that the magnitudes of the total potential and the second order nonlinear susceptibility both decrease with increasing metal cation concentration. The decrease is more pronounced for  $\text{Al}^{3+}$  when compared to  $\text{Mg}^{2+}$  or  $\text{Na}^+$ . Among all three cations, the sodium cation requires the largest concentration to reduce the magnitude of the total surface potential to a given level, as anticipated given it has the lowest charge density in the series. The nonlinear susceptibility, at a given ion concentration, is smallest for the hardest cation and highest for the softest cation, as perhaps expected from a cation polarizability argument.<sup>44</sup>

In Fig. 3A we show the total number of adsorbed cations per square centimeter,  $N_{\text{ads}}$ , which we compute by first multiplying the difference of the total potential,  $\Phi_{\text{tot}}$ , relative to the lowest metal cation concentration,  $\Phi_{\text{tot},0}$ , with the Faraday constant,  $F$ , and the cation valency,  $n$ ,<sup>45-46</sup> then dividing by the thermal energy,  $RT$ , and then employing this value as the argument in a Boltzmann

term that we multiply into the bulk cation concentration,  $C_{bulk}$  with units of mol L<sup>-1</sup>. Raising this product to the power of 2/3 yields the number of cations per unit area, and a factor of 1/100 converts from decimeters squared to centimeters squared, as shown in the following equation:

$$N_{ads} = C_{bulk} \cdot \left[ e^{-n[\Phi_{tot} - \Phi_{tot,0}]F(RT)^{-1}} \right]^{2/3} \cdot 10^{-2} cm^{-2} dm^{-2} \quad (1)$$

Here, R is the gas constant and T is the temperature (298K). Fig. 3 shows that for all cations we surveyed the surface coverages are quite similar, all the way up to 10<sup>12</sup> - 10<sup>13</sup> per square centimeter at the highest concentrations. This saturation level range roughly corresponds to roughly 1% to 10% of the number of silanol groups on fused silica (4.6 x 10<sup>14</sup> cm<sup>-2</sup>),<sup>47</sup> or the number of deprotonated silanol groups on a silica surface held at pH 4.<sup>48</sup> The similarity in the overall surface coverages at a given ion concentration seems to indicate that local field effects, such as lateral cation-cation interactions, are not detectable within the uncertainty and intra-sample variation of the data.

Fig. 3B shows the number of adsorbed ions for Na<sup>+</sup> vs Mg<sup>2+</sup> and Al<sup>3+</sup> when plotting the x-axis as ionic strength as opposed to cation concentration, signaling a detectable ion specific effect, similar to what is observed in the  $\chi^{(2)}$  values shown in Fig. 2B. The Al<sup>3+</sup> surface coverage at the highest concentration used is in good agreement with results from quartz crystal microbalance measurements reported by the Kabengi group (at 1 mM Al(NO<sub>3</sub>)<sub>3</sub> and a pH of ~4, a mass of 18 to 19 ng cm<sup>-2</sup> was detected on silica-terminated sensors, which corresponds to 1.5 x 10<sup>13</sup> Al<sup>3+</sup> ions cm<sup>-2</sup> if all the mass detected is due to the metal cation).<sup>49</sup>

The total potential,  $\Phi_{tot}$ , contains the contributions from the mobile charges (the anion and cation valency, commonly modeled using Gouy-Chapman and/or Gouy-Chapman-Stern, or GCS, electrical double layer models, or EDLs) as well as from the bound charges (those on the water

molecules, the silanol groups, the Si-O-Si bonds, and the ions) that are present in the SHG active region. Subtracting the GCS contribution from  $\Phi_{tot}$  yields the contribution from the bound charges, according to

$$\Phi(0)_{tot} - \left\{ \frac{2k_B T}{ze} \sinh^{-1} \left[ \frac{\sigma_{diffuse}}{\sqrt{8k_B T \epsilon_0 \epsilon_r C}} \right] + \frac{\sigma_{Stern}}{C_{Stern}} \right\} = -\Phi_{dipole,quad. etc}^{non-GCS} \quad (2).$$

Here,  $z$  is the ion valence (1:1 for NaCl),  $C$  is the ion concentration in the EDL,  $k_B T$  is the thermal energy, the  $\sigma$ 's are the charge density in the diffuse and Stern layers,  $e$  is the elementary charge,  $\epsilon_0$  and  $\epsilon_r$  are the vacuum permittivity and the relative permittivity of water, respectively, and the curly bracket indicates the GCS potential. We can evaluate eqn. 2 by using a Stern layer capacitance of  $0.2 \text{ F m}^{-2}$  from Sahai and Sverjensky,<sup>50</sup> a Stern layer thickness of  $2 \text{ \AA}$  from Brown and co-workers,<sup>51</sup> the ionic strength-dependent interfacial charge densities from Hore and co-workers,<sup>52</sup> and the notion that  $\sigma_{diffuse} = \sigma_{Stern}$  due to charge neutrality in the EDL. Fig. CC shows that in the ionic strength regime studied here, the GCS potential due to the mobile charges contributes only about 50% of  $\Phi(0)_{tot}$  for an aqueous salt solution in contact with fused silica at pH 5.8. For brine conditions, over 90 % of  $\Phi(0)_{tot}$  for silica is due to the contribution from the bound charges. In other words, the GCS model recapitulates only 50% (*resp.*, 10%) of the total surface potential at dilute (*resp.*, concentrated) solution conditions. A modified Poisson-Boltzmann model with hydration repulsion<sup>53-54</sup> may provide better agreement between experiment and theory, especially when further modified with effective ion diameters at charged interfaces,<sup>55</sup> as its good agreement with XPS measurements has been established for silica colloids<sup>53</sup> to account for non-ideal behavior (short-range ion correlations, site availability, etc.) of aqueous electrolytes at surfaces.<sup>55-59</sup> A related issue is the spatial variation of the (field-dependent) relative permittivity,  $\epsilon_r$ ,<sup>60</sup> which these models neglect, i.e. the solvent is modeled as a uniform continuum, despite large



differences in reported  $\epsilon_r$ .<sup>50, 55, 61-67</sup> These considerations point to the possibility that the total potential we employ to compute cation surface coverages from eqn. 1 should in fact be reduced by about 50%. Fig. 3D shows the resulting surface coverages, recomputed with eqn. 1 using half of the  $\Phi_{\text{tot}}$  values reported in Fig. 2 (*n.b.*,  $\Phi_{\text{tot},0}$  was kept unchanged in this calculation).

Fig. 4 shows fully reversible  $I_{\text{SHG}}$  vs time traces recorded without phase- or amplitude resolution. This outcome is in good agreement with the  $\text{Al}^{3+}$  reversibility study (also at pH  $\sim 4$ ) published by the Kabengi group.<sup>49</sup> These data indicate that the reversibility condition required for an adsorption isotherm analysis, described further below, is met for all three cations. Fig. 4 also shows the apparent signature of Stern and diffuse layer interactions we reported in 2021 for ionic strength jumps at constant pH.<sup>39</sup> In that work, we found that under certain experimental conditions, the SHG intensity recorded when jumping the ionic strength from 100 mM NaCl to 10  $\mu\text{M}$  NaCl at pH 5.8 undergoes a maximum at early times and then a signal reduction at longer times. Amplitude- and phase-resolved SHG measurements carried out in  $\sim 10$  sec time resolution led to  $\Phi_{\text{tot}}:\chi^{(2)}$  correlation plots that indicated nonlinear variations of the Stern and diffuse layer nonlinear optical properties. The results provided evidence for structural changes in the Stern and diffuse layers occurring in lockstep under some conditions of changing ionic strength but not others. Fig. 4 appears to indicate that these nonlinear variations of Stern and diffuse layer structure are cation specific. There appears to be a dependence on flow rate as well, given that the time traces shown in this work were recorded using a flow rate of  $10 \text{ ml min}^{-1}$ , whereas our previous study was carried out at  $5 \text{ mL min}^{-1}$  and showed less of a non-monotonic variation in the SHG signal intensity at early times when compared to the present work. These results will be pursued further in upcoming work that is beyond the scope of this study.

Having established that the interaction of our mono-divalent, and trivalent cations with the surface is fully reversible, we proceeded to analyze the adsorption isotherms shown in Fig. 3 using a variety of classical adsorption models.<sup>68-70</sup> Fig. 3 appears to indicate two interaction regimes, one for ion concentrations up to about 0.1 mM and a second regime for higher ion concentrations, as indicated by the dashed lines in Fig. 3A. Attempts to fit a single- or dual-site Langmuir adsorption isotherm model to the data failed, but a dual  $K_d$  model<sup>71</sup> of the form  $\theta_{ads,i} = K_{d,i} \cdot C_{bulk}$  (here,  $\theta_{ads,i}$  is the surface coverage in regime  $i$  relative to  $10^{13}$  cm<sup>-2</sup>, the saturation level) resulted in binding constants of 3 to 30 mol<sup>-1</sup> and  $\sim 300$  mol<sup>-1</sup> for the low and high concentration regime, respectively, from which we compute adsorption free energies of -13 to -18 and -24 kJ mol<sup>-1</sup> at room temperature, respectively (here, we used the 55.5 molarity of liquid water as a standard reference state<sup>72</sup> by which we multiply the binding constants, according to  $\Delta G_i = -RT \ln(55.5 \cdot K_{d,i})$ ). The range of binding constants and adsorption free energies in the low concentration regime are the result of using eqn. 1 with only 50% of the total potential to account for just the mobile charges (*c.f.* Fig. 3C) as opposed to 100% of the total potential.

**Conclusions.** In conclusion, we employed amplitude- and phase-resolved SHG experiments to probe interactions of fused silica:aqueous interfaces with Al<sup>3+</sup>, Mg<sup>2+</sup>, and Na<sup>+</sup> cations at pH 4 and as a function of metal cation concentration. We quantified the second-order nonlinear susceptibility and the total potential in the presence and absence of 10 mM screening electrolyte to understand the influence of charge screening on cation adsorption. Strong cation:surface interactions were observed in the absence of screen electrolyte. The total potential was then employed to estimate the total number of absorbed cations. The contributions to the total potential from the bound and mobile charge were separated using Gouy-Chapman-Stern model estimates.

We found that all three cations bind fully reversibly, indicating physisorption as the mode of interaction. Of the isotherm models tested, the  $K_d$  adsorption model fit the data with binding constants of 3 to 30  $\text{mol}^{-1}$  and  $\sim 300 \text{ mol}^{-1}$  for the low ( $<0.1 \text{ mM}$ ) and high (0.1 -3  $\text{mM}$ ) concentration regimes, corresponding to adsorption free energies of -13 to -18 and -24  $\text{kJ mol}^{-1}$  at room temperature, respectively. The maximum surface coverages are around  $10^{13} \text{ cations cm}^{-2}$ , matching the number of deprotonated silanol groups on silica at pH 4. Clear signs of decoupled Stern and diffuse layer nonlinear optical responses were observed and found to be cation specific.

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**Figure Captions**

**Fig. 1. (A)** Spectrometer used for heterodyne-detected second harmonic generation (HD-SHG). The orange and green pulses represent the 1030 nm fundamental and the 515 nm SHG signal (sig), respectively. LO = local oscillator, SO = short pass filter, BP = bandpass filter,  $\lambda/2$  = half-wave plate, Pol = polarizer, LP = long pass filter, FL = focusing lens, OAP = off-axis parabolic mirror, TDC = time-delay compensator, and PMT = photomultiplier tube. **(B)** Interference fringes for fused silica surface in contact with ultrapure water (pH 5.8), and 1  $\mu\text{M}$ , 10  $\mu\text{M}$ , 100  $\mu\text{M}$ , and 1 mM of  $\text{MgCl}_2$ , (lightest blue to darkest blue) held at pH 4, and reference solution of pH 2.5 and 500 mM NaCl (green). Vertical dashed lines indicate phase change.  $2\omega=515$  nm.

**Fig. 2. (A)** Nonlinear second-order susceptibility (squares) and the total surface potential (circles) for  $\text{MgCl}_2$  (gray) and  $\text{AlCl}_3$  (green) in the presence of 10 mM NaCl screening electrolyte. **(B)** Nonlinear second-order susceptibility (squares) and the total surface potential (circles) for NaCl (green),  $\text{MgCl}_2$  (gray), and  $\text{AlCl}_3$  (green) in the absence of 10 mM NaCl screening electrolyte.

**Fig. 3. (A)** Metal cation surface coverage as a function of metal cation concentration for  $\text{Na}^+$  (green circles),  $\text{Mg}^{2+}$  (gray circles) and  $\text{Al}^{3+}$  (empty circles). Dashed lines indicate the two interaction regimes described in the main text. **(B)** Metal cation surface coverage as a function of ionic strength for  $\text{Na}^+$  (green circles),  $\text{Mg}^{2+}$  (gray circles) and  $\text{Al}^{3+}$  (empty circles). **(C)** Total interfacial potential from HD-SHG over fused silica at pH 5.8 and varying ionic strength (white circles) and Gouy-Chapman and GC-Stern model results (solid and dashed lines, all bottom left axis) for various interfacial charge densities, and percent difference in non-GCS potential contribution to total interfacial potential (empty circles, left axis, top). Shading indicates uncertainties; horizontal dashed line indicates 50% level discussed in the main text. **(D)** Metal cation surface coverage as a

function of ionic strength for  $\text{Na}^+$  (green circles),  $\text{Mg}^{2+}$  (gray circles) and  $\text{Al}^{3+}$  (empty circles)

computed with 50% total interfacial potential. Please see text for detail.

**Fig. 4.** SHG Intensity vs time traces of fused silica hemispheres in contact with pH 4 aqueous solutions before ( $<0$  min) and during (0 min to 9 min) exposure to 17.7 mM ionic strength solution (17.7 mM NaCl (green), 5.8 mM  $\text{MgCl}_2$  (dark gray), and 3 mM  $\text{AlCl}_3$  (light gray)) and during pH 4 flush ( $>9$  min), normalized to the SHG intensity obtained at negative times.  $2\omega=515$  nm.











