Monovalent Ion – Graphene Oxide Interactions are Controlled by Carboxylic Acid Groups: Sum Frequency Generation Spectroscopy Studies

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Abstract

Graphene oxide (GO) is a two dimensional, mechanically strong, and chemically tunable material for separations. Elucidating GO-ion-water interactions at the molecular scale is highly important for predictive understanding of separation systems. However, direct observations of the nanometer region by the GO surfaces under operando conditions is not trivial. Therefore, thin films of GO at the air/water interface can be used as model systems. With this approach, we study the effects of alkali metal ions on water organization near graphene oxide films at the air/water interface using vibrational sum frequency generation (SFG) spectroscopy. We also use an arachidic acid Langmuir monolayer as a benchmark for a pure carboxylic acid surface. Theoretical modeling of the concentration-dependent sum frequency signal from graphene oxide and arachidic acid surfaces reveals that the adsorption of monovalent ions is mainly controlled by the carboxylic acid groups on graphene oxide. An in-depth analysis of sum frequency spectra reveals at least three distinct water populations with different hydrogen bonding strengths. The origin of each population can be identified from the concentration dependent variations of their SFG signal. Interestingly, interfacial water structure seemed mostly insensitive to the character of the alkali cation, in contrast to similar studies conducted at the silica/water interface. However, we observed an ion-specific effect with lithium, whose strong hydration prevented direct interactions with the graphene oxide film.

1. Introduction

Graphene-based materials show great promise in separation technologies, including ion separations, [1-7] gas separations, [8-11] and electrochemical separations.[12] Graphene oxide (GO), an oxygenated graphene derivative that has amphiphilic properties due to the hydrophobic basal graphene area and hydrophilic functional groups, has shown great potential for desalination and molecular separations due to its aqueous dispersibility and durability.[13-16] The separation achieved through a GO membrane, made of stacked GO sheets, mainly depends on ion adsorption on the GO surface and exclusive sieving through the interlayer gaps of the stacked GO sheets.[17] The chemical and physical properties of GO can be tailored by varying the synthesis conditions, which affect the composition of oxygen functional groups on the GO surface.[18] The C/O ratio of GO is closely related to the separation performance.

Surface functional groups play a crucial role in ion adsorption at the interface.[19-21] Recent studies demonstrated that the carboxyl functional groups on GO dominate the interactions with cations relative to the hydroxyl/epoxy groups and play an important role in ion adsorption.[22-25] GO materials showed outstanding adsorption performance of heavy metal, actinide, and rare earth elements in bulk studies.[16, 23, 25-29] However, there is very little direct information available about molecular-scale details of ion adsorption onto GO surfaces.[30] Therefore, understanding the various factors governing ion adsorption is critical to develop GO as a practical separation material. GO thin films at the air/water interface serve as ideal model systems to study ion-water-GO interactions.[31-38]

Multivalent lanthanide and actinide ions are typical targets in GO studies.[16, 23-24, 26, 28, 39] However, monovalent salts are also present in most systems either unavoidably or as a part of the process conditions. It has also been demonstrated that Li^+, K^+, H^+ affect GO swelling in ion-specific way.[15] Also, alkali metals can significantly affect multivalent ion adsorption. For instance, Lee et al. reported background Na^+ ions decrease overall Y^{3+} adsorption at muscovite (100)-water interface.[40] Interestingly, Nayak et al. reported that background NaCl decreases Nd^{3+} adsorption at arachidic acid (AA) monolayers at air/water interface at low Nd^{3+} concentrations but increases adsorption at high Nd^{3+} concentrations.[41] Comparing these two studies suggests that the effects of background salts strongly depend on the surface structure and chemistry due to competing effects, such as competitive adsorption, surface deprotonation, and ion hydration. It is suggested that the surface functional groups can protonate/deprotonate differently upon adding salt, which directly affects surface charge and corresponding interfacial water behavior.[19-21] Hunger et al. also reported ion specificity of alkali metal ion adsorption at charged silica interfaces.[42] Such results highlight the importance of monovalent ions at GO interfaces, which directly affect interfacial water structure and multivalent ion adsorption. However, no systematic study of the effects of monovalent ions at GO surfaces has been reported.

Vibrational sum frequency generation (SFG) spectroscopy is one of the most effective surface specific techniques for studying ion and water behavior near charged surfaces.[36-37, 43-44] Recent SFG studies using carboxyl and amine groups have shown that the salt concentration in the subphase affects the protonation and deprotonation of charged headgroups.[19-21, 45-46] Tyrode et al. reported the deprotonation of AA monolayers upon the addition of salts to the subphase by monitoring the hydrated carboxylate vibration via SFG.[20] Sung et al. demonstrated that increasing ionic strength promotes protonation of amine groups of n-octadecylamine (ODA) monolayers at air/water interface using SFG.[19] Sthoer et al. reported an improved detection limit of the interactions between trivalent ions and the charged carboxylic acid groups upon adding monovalent ions to the subphase.[21]

SFG spectroscopy has also been used to investigate interfacial water structure near pristine graphene under electrochemical control.[44, 47-48] When graphene is on a solid substrate, such as CaF_2, it has been demonstrated that the pseudocapacitive charging/discharging of the substrate can significantly affect the SFG signal.[44] Therefore, creating a uniform large-area graphene film at the air/water interface has been shown to be a better approach to avoid substrate effects.[48]

SFG spectroscopy is highly surface-specific because the sum frequency generation process is forbidden in centrosymmetric media. Since the inversion symmetry is broken at the air/water interface, the SFG signal only originates from the interface. However, the thickness of the region with broken symmetry can vary with solution conditions. For instance, the static electric field from the surface charge may orient water molecules deeper into the bulk, thus enhancing the SFG signal. Interestingly, destructive interference between SFG signals originating from different depths may also decrease the total signal. The competition between these two factors is particularly important at low ion concentrations, leading to a non-monotonic SFG response as a function of bulk concentration. [20-21, 42]

We recently reported La^{3+}, Lu^{3+}, Y^{3+}, Sr^{2+}, Cs^{+} ion behaviors near GO thin films by combining synchrotron X-ray and SFG techniques.[31, 33, 49] Hong et al. studied water structure with SFG near GO thin films at different ionic strengths using NaCl.[36] While these studies offered valuable molecular-scale insights, they were limited to a narrow range of salt concentrations (> 0.05 mM) and did not explore the very low concentration regime where deprotonation and/or interference effects could be observed. A comprehensive study is necessary to understand the effect of alkali metal salts on water structure and ion interactions near the GO interface.

In this study, we investigate the effects of monovalent salts on interfacial water structure and surface functional groups using SFG spectroscopy on GO thin films at the air/water interface. Additionally, we employ AA monolayers as a benchmark to elucidate the carboxylic acid density of GO films. We explain the dissociation of the carboxylic acid groups and the corresponding surface charge of GO by using recently developed models that explicitly consider $\chi^{(3)}$ effects.[20, 50] Our results show that the ion-specific effects of alkali metal cations are significantly different at the GO surface compared to the silica surface.[42] Furthermore, we find that the water populations with Li^{+} near GO differ from other alkali cations, likely due to the strong hydration of Li^{+} preventing it from interacting with GO layers. In contrast, other ions dehydrate and can form cation-π binding interactions with the sp^2 carbon clusters of the GO.

2. Materials and methods

2.1. Materials

LiCl (99.999%, trace metals basis, anhydrous), NaCl (99.999%, trace metals basis), KCl (99.999%, trace metals basis), and CsCl (99.999%, trace metals basis), arachidic acid (eicosanoic acid, 99%), anhydrous methanol (99.8%, anhydrous), and chloroform (anhydrous grade, stabilized with ethanol) were purchased from Sigma Aldrich. Ultrapure water was obtained from Synergy Water Purification System (Millipore) with a resistivity of 18.2 MΩ. Graphene oxide (GO) solution (GO-V50, 1wt%) was purchased from Standard Graphene (South Korea). The company reported that they prepared the GO by using Hummer's method.

2.2. Sample preparation

Subphases were prepared by dissolving LiCl, NaCl, KCl, and CsCl in ultrapure water. GO and AA thin films were spread over the subphases by a micro syringe as described below and demonstrated in Figure S1.

The GO solutions were prepared by diluting the 10 mg/mL stock solution to 1 mg/mL with purified water. This solution was diluted with methanol/water (5:1) (v/v) and then sonicated for 1 hour. The resultant solution was filtered with a 1.2 μm syringe filter.[32] AA solution was prepared by dissolving AA at 1 mM in a chloroform/methanol (3:1) (v/v) solution.

For SFG experiments, GO films were prepared in a polytetrafluoroethylene (PTFE) dish with the inner diameter of 60 mm and the height of 20 mm, by slowly spreading GO dropwise onto the prepared liquid surface (Figure S1). The SFG spectra were collected at a constant pressure of 20 mN/m (Figure 1). The surface pressure was measured using a pressure sensor (Nima) equipped with a Wilhelmy plate by carefully adding the prepared GO solutions until the surface pressure reaches 20 mN/m. AA monolayer was prepared in the same PTFE dish, by spreading AA solution dropwise onto the liquid surface until the surface pressure reaches 20 mN/m, and all SFG experiments for AA were carried out in this condition. The solutions were not buffered and the pHs of all the solutions were ~ 6.2 ± 0.2.

2.3. Vibrational sum frequency spectroscopy

Vibrational sum frequency generation is a second-order, nonlinear interface sensitive technique. The general SFG spectrometer setup and measurement details are described elsewhere.[51-55] The tunable IR beam (ω_{IR}) is overlapped with a fixed visible beam (ω_{VIS}) on the liquid interface (Figure S2). These beams are directed to the same position of the surface and overlapped to produce a sum frequency ($\omega_{SFG} = \omega_{IR} + \omega_{VIS}$) signal. At a charged interface, the total SFG response in the -OH region originates from water molecules at the interface and within the diffuse double layer. SFG experiments were conducted using an amplified Nd:YAG laser system (EKSPLA) that generates light with a wavelength of 1064 nm at 50 Hz a pulse width of 29 ps and an energy of 28 mJ. A harmonic unit creates two 532 nm beams by doubling the 1064 nm beam with a KDP crystal. One of the 532 nm beams and the 1064 nm beam are used to generate a narrow-band IR pulse tunable from 1000 to 4000 cm^{-1} via an optical parametric generator and difference frequency generation. The incident angles of the 532 nm beam and IR beams were 60° and 55° to the surface normal, respectively. The pulse energy of the 532 nm beam is 200 µJ and the energy of the IR beam is 100 µJ. The resolution of the spectra was 4 cm^{-1}, and each point is an average of 300 laser shots. Spectra were recorded in an SSP polarization combination and normalized by the SFG measured signal from a reference quartz sample. The sample was rotated every three frequency steps to make sure the consistency of the data from the sample, so the spectra were not coming from the specific local position of GO film. This method not only ensures that our sample has homogeneous and reproducible quality but also the sample is not damaged from the repetitive exposure of the laser during the measurement.

The SFG intensity is composed of contributions from the visible beam, IR beam, and the second order non-linear susceptibility ($\chi^{(2)}$) presented in equation (1).

$$I_{SFG} \propto \left|\chi^{(2)}\right|^2 I_{Vis} I_{IR} \qquad (1)$$

$\chi^{(2)}$ consists of nonresonant and resonant terms (equation 2)

$$\left|\chi_{eff}^{(2)}\right|^2 \propto \left|\chi_{NR}^{(2)} + \sum_n \frac{A_n}{\omega_{IR}-\omega_n+i\Gamma_n}\right|^2 \tag{2}$$

where χ_{NR} is the nonresonant component of $\chi_{eff}^{(2)}$, A_n is the resonant amplitude, ω_{IR} is the IR beam frequency, ω_n is the resonant frequency, and Γ_n is the vibrational damping constant.

At charged interface, the SFG intensity can also be affected by the diffuse double layer referred to as the $\chi^{(3)}$ effect

$$\begin{aligned} I_{SF} &\propto I_{VIS}I_{IR}\left|\chi^{(2)} + \chi^{(3)}\int_0^{+\infty} E_{DZ}(z)e^{i\Delta \mathrm{k}_z z}dz\right|^2 \\ &\approx I_{VIS}I_{IR}\left|\chi^{(2)} + \chi^{(3)}\psi_0\frac{\kappa}{\kappa - i\Delta\kappa_z}\right|^2 \end{aligned} \tag{3}$$

where $\chi^{(3)}$ is the third order nonlinear susceptibility, ψ_0 is surface potential, κ is the inverse Debye screening length, and $\Delta\kappa$ is the inverse SFG coherence length.

The SFG intensity in all the spectra were fitted by 3 Lorentzian peak functions presented in eq (2). The peak width, frequency and $\chi_{NR}^{(2)}$ were fitted as global variables and the amplitudes were fitted individually for each spectrum.[31, 33]

3. Results and Discussion

3.1. Alkali metal ion interactions with GO films

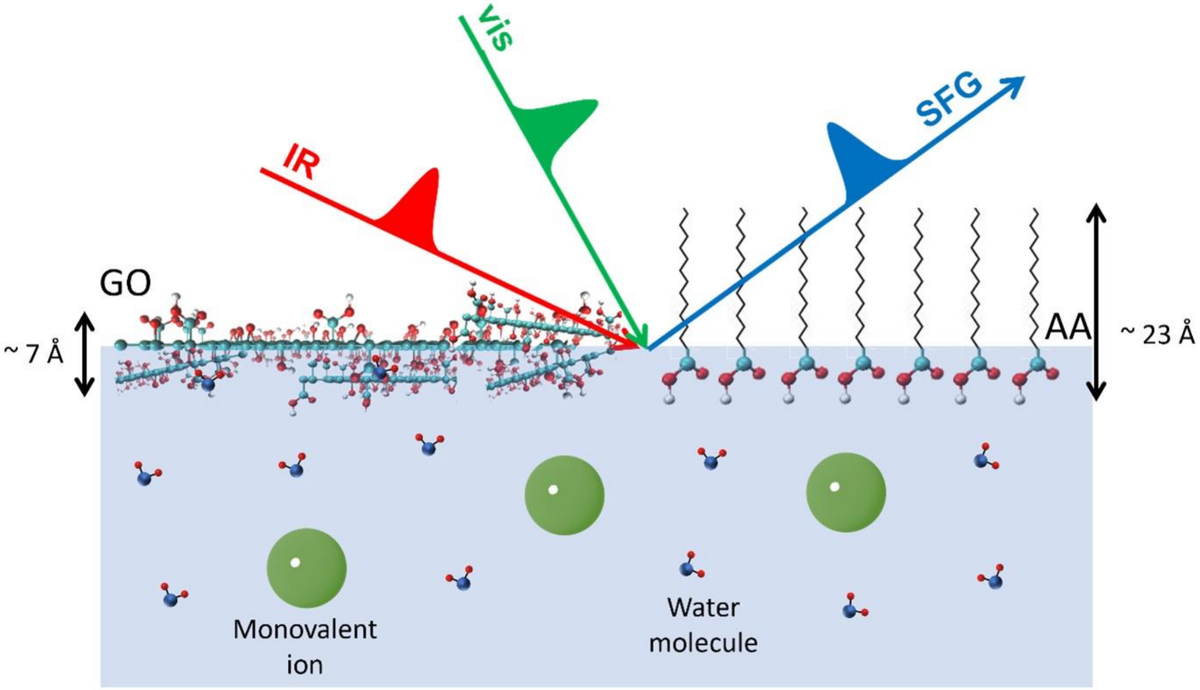

Figure 1. Experimental setup cartoon of sum frequency generation spectroscopy (SFG) measurements on a graphene oxide thin film and with arachidic acid monolayer at the air/water interface. (Not to the scale)

We studied the GO/aqueous interface with four alkali metal ions over a wide range of ionic strengths using SFG spectroscopy, under SSP polarization configuration (Figure 1). The SFG intensity in the OH stretching region near the GO thin film is shown in Figure 2. The SFG signal in this region provides information on orientational ordering and relative number density of water populations with varying hydrogen bond strengths. Generally, the ordering of water molecules originates due to the electric field created by the charged GO interface or from the interactions with the GO film. The SFG signal mainly consists of two broad bands centered at ~3200 cm^{-1} and ~3400 cm^{-1}, which are assigned to stronger hydrogen bonded and weaker hydrogen bonded water populations at the interface, respectively.[56] The quantitative definition of hydrogen bonding strength is an active topic of discussion.[57] Also, relatively weaker but distinct band around 3600 cm^{-1} was observed. We attribute this band to the water molecules intercalated between GO layers, as discussed below and in previous studies.[32-33, 49] The free -OH peak at 3700 cm^{-1} was not observed indicating that the GO film covers the surface completely.[36]

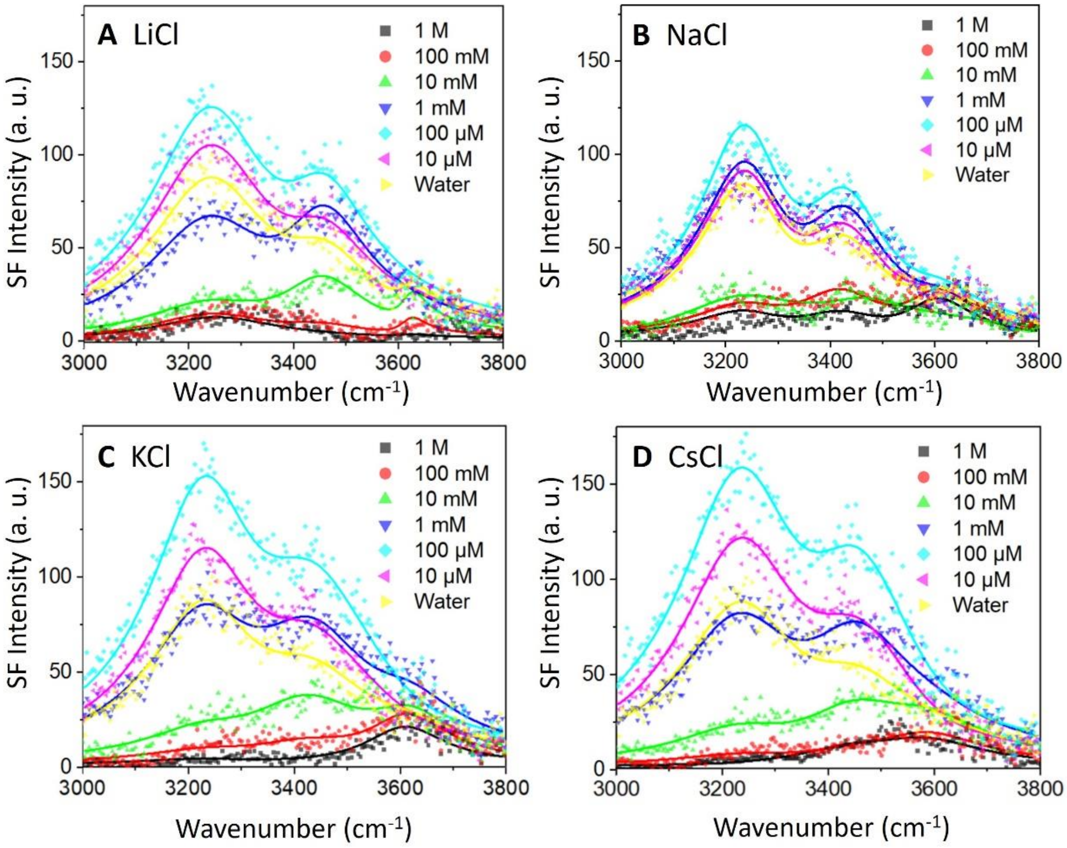

Figure 2. SFG spectra intensity from GO thin films on a (A) LiCl subphase, (B) NaCl subphase, (C) KCl subphase, and (D) CsCl subphase in different salt concentrations under SSP polarization. The surface pressure of the GO was 20 mN/m. Solid lines show the SFG intensities fitted using equation (2).

The variation of -OH stretching bands with the addition of LiCl, NaCl, KCl and CsCl from 10 µM to 1 M is qualitatively similar for all salts (Figure 2). To visualize the variations more clearly, the integrated SFG intensities over the -OH stretching band as a function of the salt concentration are shown in Figure 3. The SFG intensities increase noticeably from plain water to 100 µM for all salts and start decreasing when the subphase concentration is further increased. Previous SFG studies of the GO/aqueous interface only covered the latter of this concentration range that shows the decreasing SFG signal.[36] A recent study at the silica/water interface using lower concentrations demonstrated a similar increasing and decreasing trend.[42] However, the overall SFG intensity showed stronger cation specific effects due to significantly different chemistry and structure of the silica surface compared to GO.

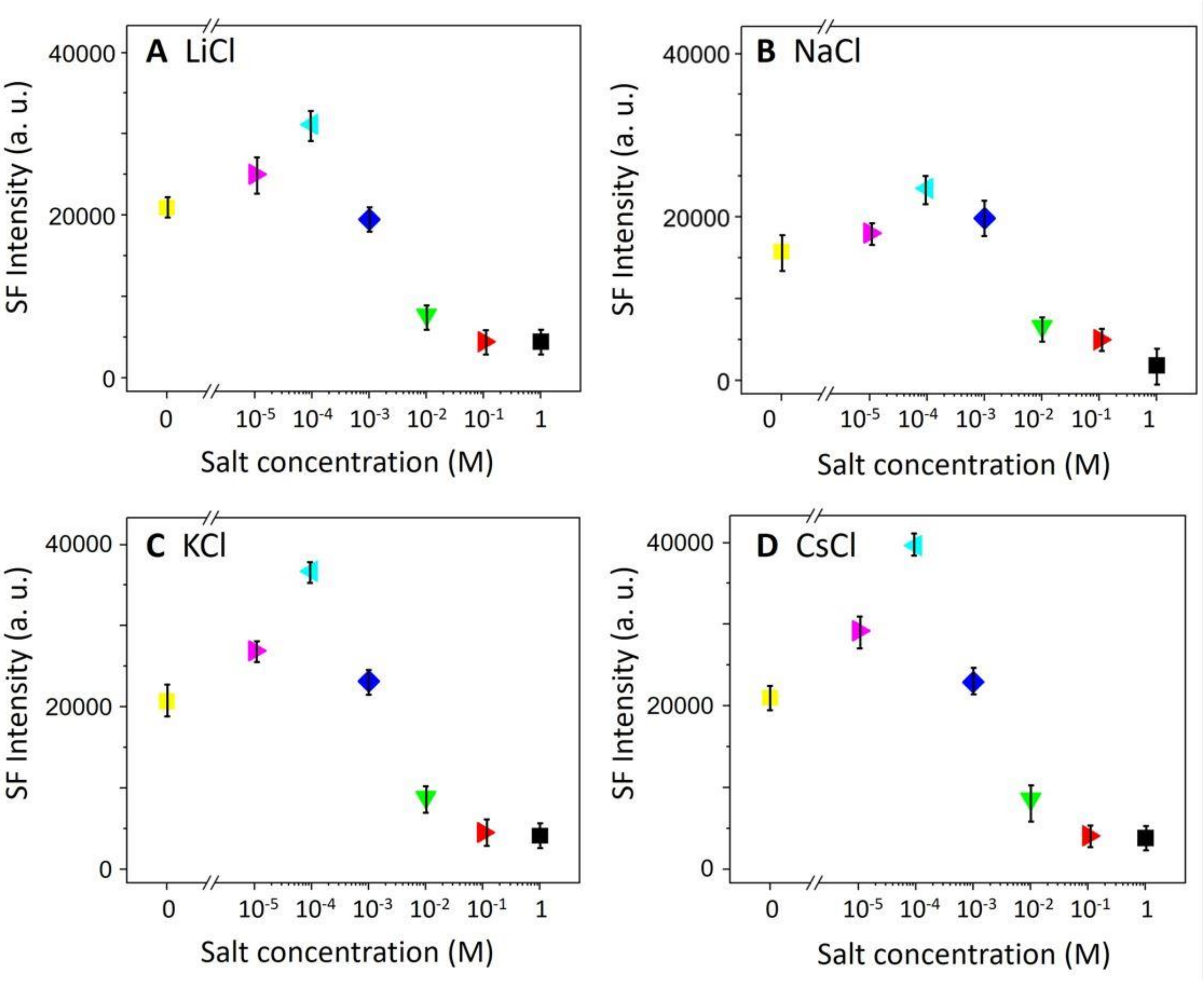

Figure 3. Integrated SFG intensity of the water OH stretch (3000 – 3550 cm^{-1}) for GO thin film on salt solutions as a function of subphase concentration for (A) LiCl, (B) NaCl, (C) KCl, and (D) CsCl.

The decrease in SFG signal at higher salt concentrations can be explained by the disruption of water alignment due to the screening effect of the counterions. The counterions screen the surface charge induced by the deprotonated functional groups of GO, which weakens the intensity of the electric field perpendicular to the interface and hence the orientational ordering of the water molecules. This is generally referred to as the $\chi^{(3)}$ effect (Equation 3). The interactions between ions, water, and GO become stronger at higher concentrations because the Debye screening length decreases thus disrupting the water ordering in the vicinity of the GO thin films by directly affecting the $\chi^{(2)}$ term in Equation 3. By probing Cs^+, Sr^{2+}, and Y^{3+} ions directly with X-ray fluorescence near total reflection, we have previously shown that the decrease in SFG signal in this regime can be correlated to the stronger adsorption of the cations.[31]

The increasing SFG signal with the increasing salt concentration below 100 μM (Figure 3) is counterintuitive based on the above explanation and requires further investigation. First, we show that the surface charge of the GO film mainly originates from the carboxylic acid groups. XPS results show that our GO contains ~8 % carboxylic acid groups[32] (Figure S5). The role of the carboxylic acid groups and their protonation level to the surface charge can also be confirmed by pH dependent SFG measurements (Figure S3).[33] The increase in SFG signal as the pH increases is induced by the deprotonation of the carboxylic acid groups on the GO surface. As the carboxylic acid groups deprotonate, the surface charge of GO thin film becomes more negative. Therefore, the population of water molecules aligned by the generated electric field increases, which enhances the SFG signal.

SFG studies of carboxyl and amine groups suggested that the salt concentration in the subphase can affect their protonation.[19-21, 45-46] In principle, the relation between deprotonation and surface charge as a function of the salt concentration can be explained by the Gouy-Chapman model.[19-21] Also, the variation in the interference effects due to the decreasing Debye length is important. In both cases, the surface charge is a very important parameter. We estimated the effective surface charge induced by the carboxylic acid groups of GO based on the ratio of O-C=O and C-C bonds characterized by XPS.[32] This was compared to the surface charge of AA Langmuir monolayer composed of pure carboxylic acid groups.

There are multiple advantages of using AA as a benchmark for a pure carboxylic acid film. AA forms a very stable monolayer over a wide range of subphase concentrations allowing easy interpretation of the changes in the interfacial water structure with varying subphase concentration. AA structure has been studied extensively on pure water,[58] and on salt solutions.[20-21, 41, 45, 59] Therefore, comparing GO to AA will allow us to determine the role of carboxylic acid groups in GO clearly.

3.2 Interference effect and deprotonation of carboxylic acid groups

AA forms a closely packed monolayer of carboxylic acid groups at the air/water interface. SFG spectra from AA were collected at various concentrations of NaCl under SSP polarization combination. All SFG measurements were carried out at a constant surface pressure of 20 mN/m, which corresponds to an average area per molecule of ~20 Å^2.[20, 58] The general SFG intensity trend shown in Figure 4A agrees well with the previous studies.[20, 45] The SFG intensity in the water region increases until reaching a maximum around 1 mM bulk concentration and decreases with further increasing concentration.

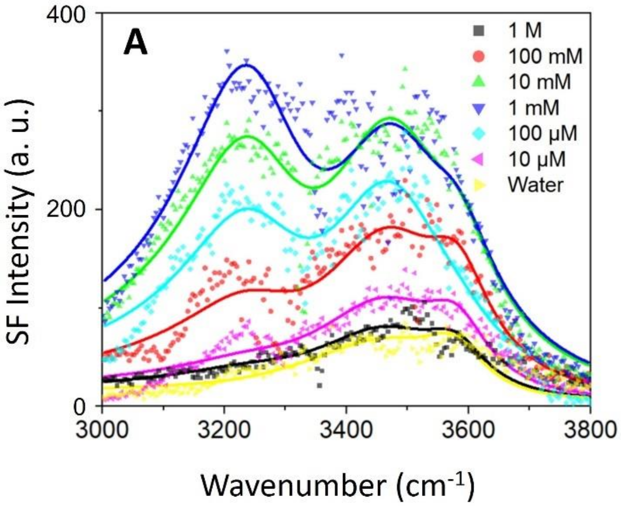

Figure 4. (A) SFG spectra intensity from AA monolayers on NaCl subphase with different concentrations under SSP polarization. AA was compressed to 20 mN/m and the average area per molecule was 20 Å^2.[20] Solid lines show the SFG intensities fitted using equation (2). (B) SFG data of -OH stretching band at

3200 cm^{-1} for GO and AA interface with varying salt concentrations. Symbols are binned experimental data for each concentration, and solid lines show fit according to equation (3).

Figure 4B compares the SFG intensities as a function of the bulk concentration, as previously done for the NaCl/GO data (Figure 2B). The SFG intensities for AA are significantly stronger than those measured with GO at all salt concentrations (Figure 2 and Figure 4A). The smaller intensity for GO is due to the significantly smaller density of the surface charge compared to AA. The overall trends of the GO and AA data look similar but the SFG intensity for GO reaches a maximum value at a lower concentration (100 μM) compared to AA (1 mM). This difference can also be explained by the lower surface charge of GO.

We fitted the SFG intensities of -OH stretching band at 3200 cm^{-1} for GO and AA using equation 3 and the Grahame equation (equation S2), which considers the different surface charge of GO and AA (Figure 4B). Using the C=O to C-C bonds ratio from our previous XPS data, we assume that the surface charge of GO is about 8 % of an AA monolayer, corresponding to 250 Å^2 per carboxylic acid group.[32] Indeed, this assumption in the calculation leads to a good agreement with the experimentally observed SFG trend as a function of salt concentration (Figure 4B). The $\chi^{(3)}$ term is directly associated with a weak surface potential (see equation (3)). The smaller magnitude of surface potential of GO film weakens the $\chi^{(3)}$ contribution and reduces the interference effect, which results in a maximum SFG intensity for GO at a lower salt subphase concentration. This analysis is done with all the salts for GO films and with NaCl for AA films, since the trends in concentration dependent SFG data are similar for all cations investigated in this study (Figure 4B, dashed lines).

These data suggest that the monovalent ion interactions near GO are mainly controlled by the surface charge induced by the deprotonation of carboxylic acid groups of GO. Interestingly, trivalent ions show different adsorption behavior, as evidenced by our recent work.[49] Our Surface X-ray fluorescence near total reflection (XFNTR) data revealed that the quantity of La^{3+} ions adsorbed onto GO is approximately 1/3 of that adsorbed onto AA. This is significantly greater than the expected charge compensation, considering that the carboxylic acid groups on GO is only ~ 8 % of those on AA. Taken together, the adsorption of trivalent ions cannot be simply explained by the carboxylic acid groups of GO, in contrast to the monovalent ions, which appear to be governed by the surface charge of GO. It is possible that the presence of other functional groups on GO surface or the flexible structure of GO film at the interface contribute to an enhanced adsorption capability of trivalent ions onto GO surface.

These experiments were conducted at pH = 6.2, where carboxylic acid groups are fully deprotonated. Control experiments at low pH, eliminating the formation of surface charges would be useful to identify the subtle effects of other functional groups. However, SFG signal at low pH is too low to obtain meaningful variations in SFG signal as a function of the subphase concentration. (Figure S3).

3.3 Identifying water populations with different hydrogen bonding strengths

The -OH stretching band is a probe of the orientational ordering of water molecules in close proximity to the GO thin films. This signal can be fitted using three peaks, each of which is attributed to different hydrogen bonding environments. We note the AA spectra only show two major contributions, but for completeness we included a peak centered at 3600 cm^{-1} to our model and showed that its amplitude is indeed negligible for AA. Figure 5 shows the variation of fitted SFG peak amplitudes (Equation 2) at 3200 cm^{-1}, 3400 cm^{-1}, and 3600 cm^{-1} for AA monolayers and GO thin films on subphases with varying salt concentrations. We discuss how the relative changes in different populations influence the SFG signal.

For GO, the 3200 cm^{-1} peak amplitude (Figure 5A-D, blue circles) shows a similar trend to the integrated intensities in Figure 3. At concentrations less than 100 µM, the SFG signal is dominated by the 3200 cm^{-1} peak. After reaching a maximum value at 100 µM, this peak amplitude shows a sharp decrease. The trends for the 3400 cm^{-1} peak are different overall. The variations in its amplitude are less significant and the decrease in intensity starts at 10-100 times higher bulk concentrations. The 3600 cm^{-1} peak becomes more visible at high concentrations. For AA, the 3200 cm^{-1} peak from 100 µM is similar to that from pure water and then then reaches a maximum amplitude at 1 mM before decreasing sharply. The 3400 cm^{-1}

follows a similar trend but with smaller slopes and a plateau between 0.1 mM – 10 mM instead of a sharp maximum. There is no 3600 cm^{-1} peak with AA.

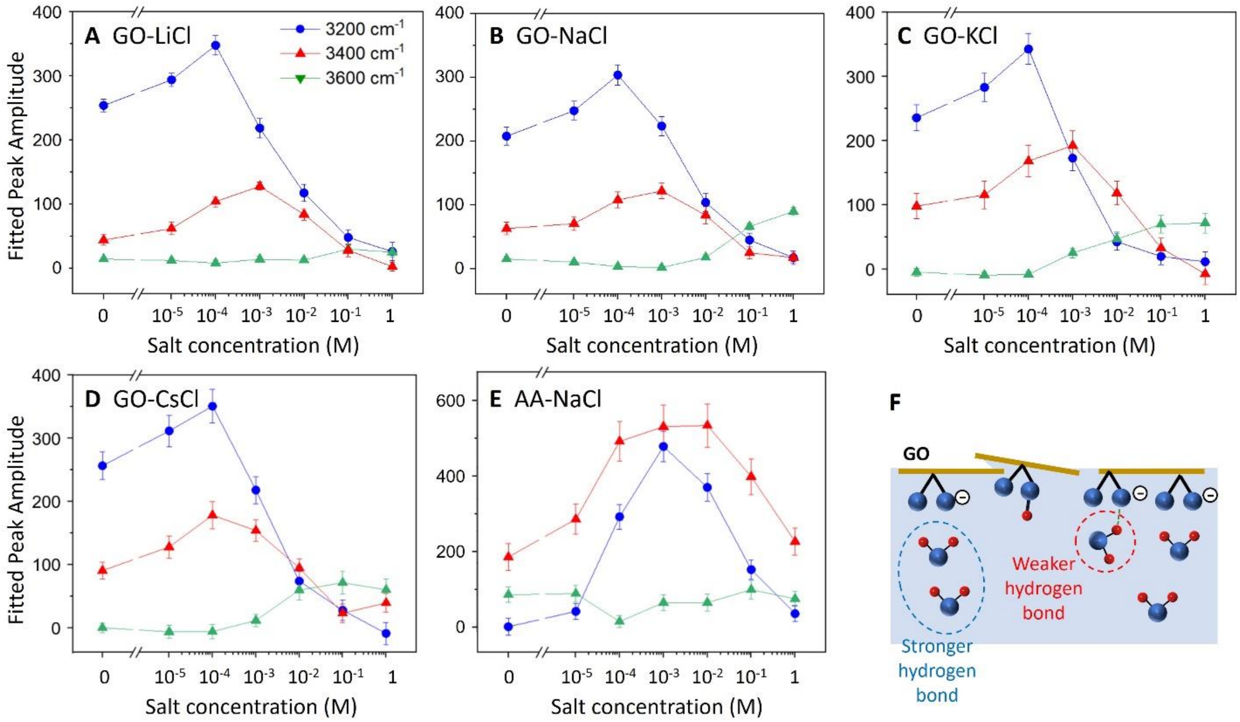

Figure 5. Fitted $\chi^{(2)}$ peak amplitudes of SFG data of GO thin films for the 3200 cm^{-1}, 3400 cm^{-1}, and 3600 cm^{-1} water signal features as a function of (A) LiCl, (B) NaCl, (C) KCl, and (D) CsCl subphases with different concentrations. Fitted $\chi^{(2)}$ peak amplitudes of SFG data of AA monolayers for the 3200 cm^{-1}, 3400 cm^{-1}, and 3600 cm^{-1} water signal features as a function of NaCl subphase concentrations (E). Cartoon showing the water alignment near GO thin films (F). Stronger hydrogen bonds originate from the water molecules aligned by the electric field generated by the negative surface charge and weaker hydrogen bonds stem from the formation of hydrogen bonds between water molecules and functional groups of GO.

The assignment of these peaks to the exact water populations had been debated and most studies preferred to make interpretations based on the integrated intensities.[19, 45] It is possible that the origin and distribution of these peaks are also surface dependent. In other words, the 3400 cm^{-1} peak at the free air/water interface may have a different origin than the 3400 cm^{-1} peak at the GO/water interface.[60] Nevertheless, the presented data and their comparison to previous studies allow us to gain important physical insights.

It is reasonable to assume that stronger hydrogen bonded water populations are farther into the bulk and weaker hydrogen bonded water populations are closer to the surface.[42] Indeed, we suggest that the 3400 cm^{-1} population is very close to the surface and possibly interacting with the GO, and 3600 cm^{-1} peak originates from the water molecules mostly trapped between the GO sheets. It is not possible to get a clear separation between these two populations. For instance, with lower quality GO films, a separate 3600 cm^{-1} peak was not observed, and 3400 cm^{-1} peak showed weaker concentration dependence in comparison to what we observed here.[31-32, 36] The absence of the 3600 cm^{-1} peak with AA also supports this explanation, as water molecules cannot intercalate within the densely packed lipid monolayer.

The concentration dependent trends for both the integrated and fitted SFG peaks look mostly independent from specific cation. This is in contrast to the strong ion specific trends observed at the silica interface but agrees well with the indistinguishable behavior of these salts at AA monolayers.[20] In recent years, many studies demonstrated that the surface characteristics play an important role in ion-specific effects, and it is not trivial to generalize the observations in one specific system to others.[41, 61]

The most significant ion-specific effect we observe is the absence of 3600 cm^{-1} peak with LiCl while with other salts, the peak becomes more prominent as the concentration gets higher. We suggest that the 3600 cm^{-1} peak is not visible for GO on LiCl because Li^+ retains its hydration shell and cannot intercalate between the GO layers of the thin film. The 3600 cm^{-1} peaks observed for the other metals likely stems from these ions' partial dehydration and intercalation between the GO sheets.[62] It is possible that the other cations undergo partial dehydration during intercalation, and also be stabilized by favorable cation-π interactions between the metal and the aromatic sp^2 carbon areas of the GO.

This hypothesis is supported by ultraviolet (UV) absorption experiments (Figure S4). The UV spectrum of GO at ~ 230 nm is assigned to a conjugate double bond of the aromatic rings that can be generated π- π* transition.[63-67] The UV intensity of GO drastically decreases with the addition of Na, K, and Cs salts, but the intensity of GO with Li salt is almost identical with that from pure GO. This implies that Li^+ barely affects the water organization near interfacial GO while the other ions strongly affect the aromatic groups of GO. Indeed, previous studies have reported cation-π interactions with GO[68] and these interactions are thought to significantly affect ion transport behavior through GO membranes.[68-70]

4. Conclusion

The presence of monovalent ions in aqueous solutions is known to strongly affect the interfacial water structure at aqueous interfaces.[19-21, 40-42] Despite the importance of monovalent ions near graphene oxide surfaces, a comprehensive molecular-scale study was lacking. We conducted sum frequency generation spectroscopy studies demonstrating the water behavior near interfacial graphene oxide and considered the contributions of monovalent ions and ionic strength. The -OH stretching band near the graphene oxide thin film at the air/water interface was observed as a function of salt concentration. The SFG signal reached to a maximum intensity at an intermediate salt concentration (~100 μM). We demonstrated that carboxylic acid groups on graphene oxide can explain major trends in the data. The density of carboxylic acid groups estimated from X-ray photoelectron spectroscopy studies matched the interfacial model. These results are consistent with recently proposed theoretical models accounting for both the deprotonation of the surface and the interference effect.[20-21, 42] The lower surface charge magnitude derived by the smaller amount of carboxylic acid groups of graphene oxide weakens the $\chi^{(3)}$ contribution, which in turn reduces the interference effect, as demonstrated experimentally by the maximum achieved sum frequency generation intensity at a relatively lower ionic strength for a graphene oxide film in comparison to arachidic acid. These results demonstrate that monovalent ion – GO interactions are controlled by carboxylic acid groups in contrast to the trivalent ion – GO interactions reported previously.

The sensitivity of monovalent and trivalent ions to different functional groups on GO can be exploited in separation applications.

The sum frequency generation signal trends showed minimal variation with specific ions. This was in contrast to the strong ion specific effects on silica surface, which was attributed to the cation size variation affecting the interference between different water populations at the very interface.[42] Apparently, significantly rougher GO surface smears out such effects. The only significant ion specific effect was the behavior of 3600 cm^{-1} peak with the Li^+ ion. The strong hydration of Li^+ ions prevented them intercalating between the graphene oxide layers. However, this qualitative difference in ion adsorption did not affect the trends in other water populations represented by 3200 and 3400 cm^{-1} peaks. These results suggest that background ions can help controlling the hydration around the graphene oxide which is highly important in selective ion adsorption and transport in membrane applications.[1-3] Furthermore, the success of the theoretical modelling of experimental data paves the way for future studies to determine mixture of monovalent and trivalent salts at GO interfaces which will aid understanding more complex separation systems.

Supplementary Material

Gouy-Chapman model, GO thin film preparation, SFG configuration, pH-dependent SFG measurements, UV absorption spectra, XPS analysis, and SFG fit parameters.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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