THE JOURNAL OF
PHYSICAL CHEMISTRY C

Article

pubs.acs.org/JPCC

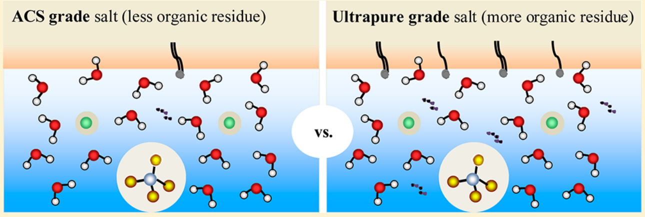
Impact of Salt Purity on Interfacial Water Organization Revealed by Conventional and Heterodyne-Detected Vibrational Sum Frequency Generation Spectroscopy

Wei Hua, Dominique Verreault, Ellen M. Adams, Zishuai Huang, and Heather C. Allen*

Department of Chemistry & Biochemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio 43210, United States

Ⓢ *Supporting Information*

ABSTRACT: Water organization and ion distribution at air/aqueous interfaces investigated by nonlinear vibrational spectroscopy as well as by other surface-sensitive techniques depend critically on the purity grade and purification processing of the chosen salts and their solutions. This is true not only for the ACS grade salts but also for the ultrapure (UP) grade, even though both have <1% impurities. It is shown here by means of conventional vibrational sum frequency generation (VSFG) and heterodyne-detected VSFG (HD-VSFG) spectroscopy that salt purity grade and pretreatment has a tremendous impact on the interfacial water spectrum of aqueous salt solutions. Our spectroscopic results indicate that salt solutions prepared from ACS and UP grade salts (NaCl, Na_2CO_3, Na_2SO_4, and $(NH_4)_2SO_4$) display highly similar conventional VSFG and HD-VSFG spectra, provided that their solutions undergo pretreatment, that is, either salt baking followed by solution filtration or simply filtration for low melting point salts. In addition, untreated $(NH_4)_2SO_4$ and NaCl salt solutions prepared from ACS grade salts show no significant spectral difference compared with pretreated ones. However, the corresponding untreated solutions made from UP grade salts show a remarkably higher content in organic impurities, which perturb greatly the conventional VSFG spectra in the water OH stretching region. Only in the case of high melting point halide salts such as chlorides, was it found that salt baking has an effect comparable to solution filtration. However, this was not always true for all salts, particularly those having oxyanions. Overall, to avoid spectral distortion introduced by the presence of organic contamination, it is strongly recommended that metal halide salts should be baked, yet all other molecular ion-based salts should be first baked (depending on the salt melting point), followed by filtration of their solutions before being used by VSFG spectroscopy and, most likely, in any other surface-sensitive spectroscopic studies of water organization at air/aqueous interfaces.



1. INTRODUCTION

The impact of inorganic ions on interfacial water organization at air/aqueous interfaces has been a topic of sustained interest, particularly because of its relevance in atmospheric aerosol chemistry,[1−4] geochemistry,[5−7] and oceanic chemistry,[8] among others. In recent years, intensive efforts have been invested through both computational and experimental methods in the understanding of the surface of aqueous salt solutions.[9−15] For instance, the combination of molecular dynamics (MD) simulations and surface-specific nonlinear optical techniques, such as second harmonic generation (SHG),[16,17] conventional,[18−21] and (more recently) phase-sensitive and heterodyne-detected vibrational sum frequency generation (HD-VSFG) spectroscopy,[22−26] as well as two-dimensional (2D)-VSFG spectroscopy,[27−29] have allowed unprecedented access to the molecular-level picture of water organization and ion distributions at air/aqueous interfaces.

In the past decade, numerous conventional VSFG and HD-VSFG spectroscopic studies have systematically investigated the surface propensity and influence of common inorganic salts, such as chlorides and other halides,[19,30−37] carbonates,[35,38,39] nitrates,[30,40−42] and sulfates,[30,33,35,43] on the interfacial water organization. Although there is some relative agreement on the effects of inorganic ions on the interfacial water spectrum and on their relative location within the interface, a lack of reproducibility between conventional VSFG and HD-VSFG spectra from different research groups as well as with other surface-sensitive techniques[44,45] still exists in the literature. Aside from instrumental and methodological factors, a possible explanation for this discrepancy could come from the use of commercial salts of different grades or from salts and salt solutions that have undergone different processing (e.g., being used as-received, baking, filtering, baking and then filtering, etc.; see Table 1).[17,19,21,30,31,33,35,38−43] However, aside from sporadic reports regarding halide salts,[17,37] to the authors' knowledge, no study using conventional VSFG and HD-VSFG spectroscopy has so far systematically compared the influence of salt purity and different prior treatments of salts and their solutions on the spectrum in the water OH stretching region for a variety of salts, particularly molecular ion-based ones.

To assess the impact of salt purity on the interfacial water organization and to establish a standardized pretreatment

Received: August 14, 2013
Revised: August 20, 2013
Published: August 21, 2013

Table 1. Comparative List of Purity of Salts Used in Previously Published SHG, Conventional VSFG and HD-VSFG Studies at the Air/Solution Interface

salt	supplier	grade and purity	salt baking	solution filtration	ref
Halides					
NaCl	GFS Chemicals	n/a	no	yes[a,d]	21
NaF, NaCl, NaBr, NaI	Sigma-Aldrich	ACS reagent, 99%+	no	no	19
NaF, NaCl, NaBr, NaI	Fisher Scientific	ACS certified	no	yes[b,d,e]	32
NH_4Cl	n/a	n/a	no	yes[b,d]	33
NaCl, NaBr, NaI	Acros Organics	ACS reagent, 99%+	yes (500 °C, >6 h)	no[d]	17
$MgCl_2{\cdot}6H_2O$	Fisher Scientific	ACS certified	no	yes[b]	31
NaCl, KCl, NH_4Cl	Sigma-Aldrich	TMB, 99.999% (NaCl, KCl), 99.998% (NH_4Cl)	yes (NaCl, KCl, 500 °C)	yes[a]	30
NaCl, $CaCl_2$	Fisher Scientific	ACS certified, 99%	yes (650 °C, >10 h)	yes[b,d]	35
NaI	Sigma-Aldrich	99.999%	yes	yes[c]	37
Carbonates					
Na_2CO_3, $NaHCO_3$	Aldrich	99.995% (Na_2CO_3), ≥99.5% ($NaHCO_3$)	no	no	43
Na_2CO_3	Spectrum Chemical	99%	no	no	38
$NaHCO_3$	Mallinckrodt Chemicals	99.7–100.3%	no	no	
Na_2CO_3	Fisher Scientific	ACS certified, 99.5–100.5%	yes (650 °C, >10 h)	yes[b,d]	39
$NaHCO_3$	Fisher Scientific	ACS certified, 99.7–100.3%	yes (650 °C, >10 h)	yes[b,d]	
Nitrates					
$NaNO_3$ (HNO_3 + NaOH)	GFS Chemicals	n/a	n/a	yes[a,d]	21
$Mg(NO_3)_2$, $Ca(NO_3)_2$, $Sr(NO_3)_2$	Fisher Scientific	n/a	no	yes[b,d]	40
$Mg(NO_3)_2{\cdot}H_2O$, $Ca(NO_3)_2{\cdot}4H_2O$, $Sr(NO_3)_2$	Fisher Scientific	ACS certified, 98.0–102.0%, 99.0–103.0%, 99.0%	no	yes[b,d]	41
$NaNO_3$	Sigma-Aldrich	TMB, 99.995%	no	yes[a]	30
$LiNO_3$, $NaNO_3$, $Mg(NO_3)_2{\cdot}6H_2O$	Fisher Scientific	Fisher Bioreagents, ≥99.0%, ACS grade, 98–102%	no	yes[b,d]	42
NH_4NO_3	MP Biomedicals	UP grade, >99%			
Sulfates					
$KHSO_4$	GFS Chemicals	n/a	no	yes[a,d]	21
Na_2SO_4, $(NH_4)_2SO_4$	n/a	n/a	no	yes[b,d]	33
Na_2SO_4, $NaHSO_4{\cdot}H_2O$	Aldrich	99.99% (Na_2SO_4), 99% ($NaHSO_4$)	no	no	43
Na_2SO_4, $(NH_4)_2SO_4$	Sigma-Aldrich	TMB, 99.99% (Na_2SO_4) 99.999% ($(NH_4)_2SO_4$)	yes (Na_2SO_4, 500 °C)	yes[a]	30
Na_2SO_4	Acros Organics	≥99%	yes (650 °C, >10 h)	yes[b,d]	35
$(NH_4)_2SO_4$	Sigma-Aldrich	ACS reagent, ≥99%			

[a] Purification using syringe filters. [b] Purification using activated carbon filters. [c] Purification using the Lunkenheimer method.[53] [d] Salt solutions were checked for organic contamination with VSFG spectra in the CH stretching region (2800–3000 cm^{-1}). [e] NaF was purified only by recrystallization. n/a, not available; TMB, trace metals basis.

procedure, conventional VSFG spectra were measured in the water OH stretching (3000–3800 cm^{-1}) and in the surfactant CH stretching (2800–3000 cm^{-1}) regions and HD-VSFG spectra in the OH stretching region from the aqueous interfaces of solutions made with ACS and ultrapure (UP) grade commercial salts, with and without prior treatment. In the case of salts with high melting points (NaCl), VSFG spectra were also obtained for solutions made from baked-only ACS and UP grade salts. The results regarding carbonate, sulfate, and chloride salts reveal that for the same chemical species, UP grade salts (>99.99%) versus ACS grade ones (≥99%) display highly similar conventional VSFG and HD-VSFG spectra in the OH stretching region, provided that the solutions be treated beforehand. However, untreated solutions from UP grade salts show a greater amount of organic impurities in comparison with ACS grade salts and greatly distort the spectrum in the water OH stretching region such that they should be used with caution in any study of interfacial water organization on aqueous solutions.

2. EXPERIMENTAL DETAILS

2.1. Materials. ACS grade (purity ≥99%) and UP grade salts (purity ranging from 99.99% to 99.999%) were purchased from several suppliers: NaCl (ACS certified, ≥99%, Fisher Scientific; trace metals basis, 99.999%, Acros Organics), Na_2CO_3 (ACS certified, Primary Standard, Mallinckrodt Chemicals; trace metals basis, 99.999%, Acros Organics), Na_2SO_4 (ACS certified, ≥99%; trace metals basis, ≥99.99%, Sigma-Aldrich), $(NH_4)_2SO_4$ (ACS reagent, ≥99%, Acros Organics; trace metals basis, 99.9999%, Acros Organics), and $LiNO_3$ (ACS certified powder, Fisher Scientific). Ultrapure water (not purged of CO_2) with a resistivity of 18.2–18.3 MΩ·cm and a measured pH of 5.6 was obtained from a Barnstead Nanopure system (model D4741, Thermolyne Corporation) equipped with additional organic-removing cartridges (D5026 Type I ORGANICfree Cartridge Kit; Pretreat Feed).

2.2. Preparation of Salt Solutions. Stock salt solutions for VSFG measurements were prepared by dissolving ACS and UP grade salts in ultrapure water. Owing to its ultrahigh sensitivity, VSFG spectra obtained in the surfactant CH stretching region (2800–3000 cm^{-1}) were utilized as a probe to verify the presence of trace amount organic residues. As revealed in these spectra, organic contamination was found in all stock salt solutions prior to any pretreatment. To completely eliminate organic impurities, as-received salts and their stock solutions underwent either one of the following pretreatments: (1) salt baking first followed by solution filtration or (2) filtration only (see Table 2). Baking was applied only for salts with a high melting point (e.g., $T_m \geq 650$ °C for carbonate, sulfate, and chloride salts), and the temperature chosen was at least 50 °C lower than the melting point. Most salts (except $(NH_4)_2SO_4$ and $LiNO_3$) were baked at ~600 °C for 10 h in a muffle furnace (Isotemp model 550-14, Fisher Scientific). Stock salt solutions were then filtered using activated carbon filters (Whatman Carbon Cap 75, Fisher Scientific).

Table 2. Standardized Pretreatment Procedure for Inorganic Salts Purification

	salt		
	metal halides	molecular ion-based	
pretreatment	high T_m (e.g., NaCl)	high T_m (e.g., Na_2CO_3, Na_2SO_4)	low T_m (e.g., $(NH_4)_2SO_4$, $LiNO_3$)
salt baking + solution filtration	+	+	−
solution filtration only	+	+	+
salt baking only	+	−	−

Depending on the abundance of organics in each salt, two or more filtration steps were performed: chloride solutions, 2 times; carbonate and sulfate solutions, 2−4 times; and nitrate solutions, 4−6 times. For salts with a low melting point (<500 °C), pretreatment only refers to filtration. Salts from several different batches were tested and compared in this work, and no appreciable disparities were observed. Raman calibration curves were obtained to determine the concentration of carbonate, sulfate, and nitrate after filtration based on their vibrational symmetric stretch ion mode (Supporting Information Figure S1), while chloride solutions were standardized by Mohr titration.[46]

The measured pH of most solutions was found to fall in the range 5−7 (except Na_2CO_3 which had a pH~12). All pretreated salt solutions were shown to be free of organic impurities as revealed by the conventional VSFG spectra obtained in the surfactant CH stretching region (see Supporting Information). All solutions were thermally equilibrated to room temperature (23 ± 1 °C) over 24 h before use. No degassing or N_2-purging has been applied on them.

2.3. Conventional and Heterodyne-Detected Vibrational Sum-Frequency Generation Spectroscopy. Conventional VSFG spectroscopy measurements were performed on a broad-bandwidth VSFG spectrometer setup that has been described in detail elsewhere.[20,47−49] The HD-VSFG spectroscopy setup is based mostly on the conventional one, with the optical configuration in the sample stage area redesigned for the new application.[50,51] The latter setup is similar to the system reported by Tahara and co-workers,[24,25] which is based on heterodyne detection of broad-bandwidth signals and Fourier transform analysis. The HD-VSFG setup and the data processing procedure have been described elsewhere in detail.[35,39,50] Here, only the modifications made to the experimental setup and calculated parameters are presented. Briefly, the full spectral bandwidth of the generated broadband infrared beam has been expanded from 3000 to 3600 cm^{-1} (~600 cm^{-1}) in the current HD-VSFG setup in the OH stretching region. The average incident energy of the visible (s-

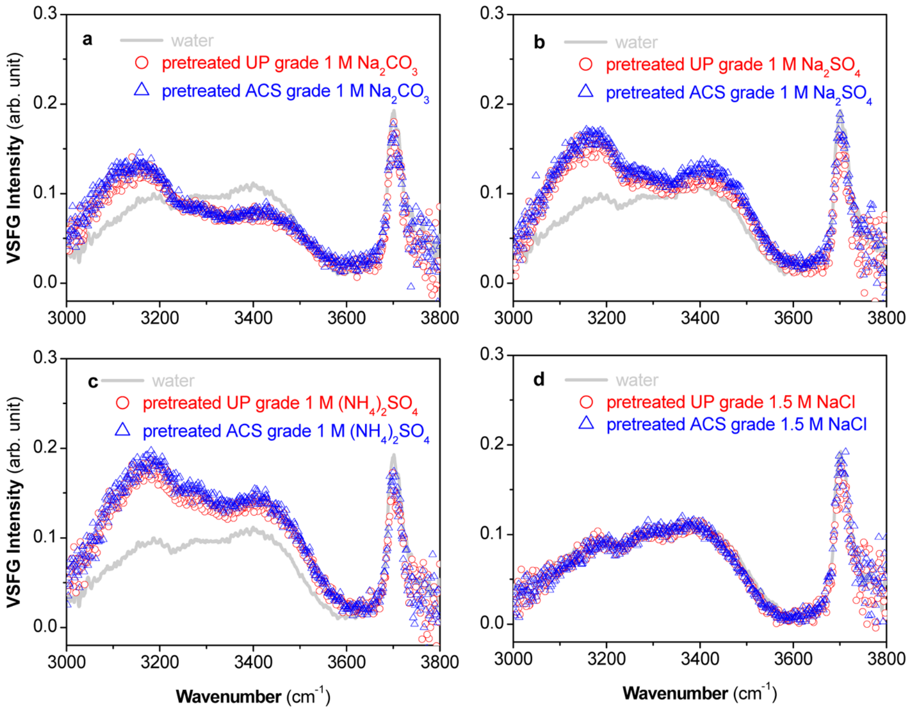


Figure 1. Comparison between conventional VSFG spectra from ACS and UP grade salt solutions in the OH stretching region (3000−3800 cm^{-1}) after pretreatment. (a) 1 M Na_2CO_3, (b) 1 M Na_2SO_4, (c) 1 M $(NH_4)_2SO_4$, and (d) 1.5 M NaCl. The VSFG spectrum of neat water is also shown as a reference by a gray line.

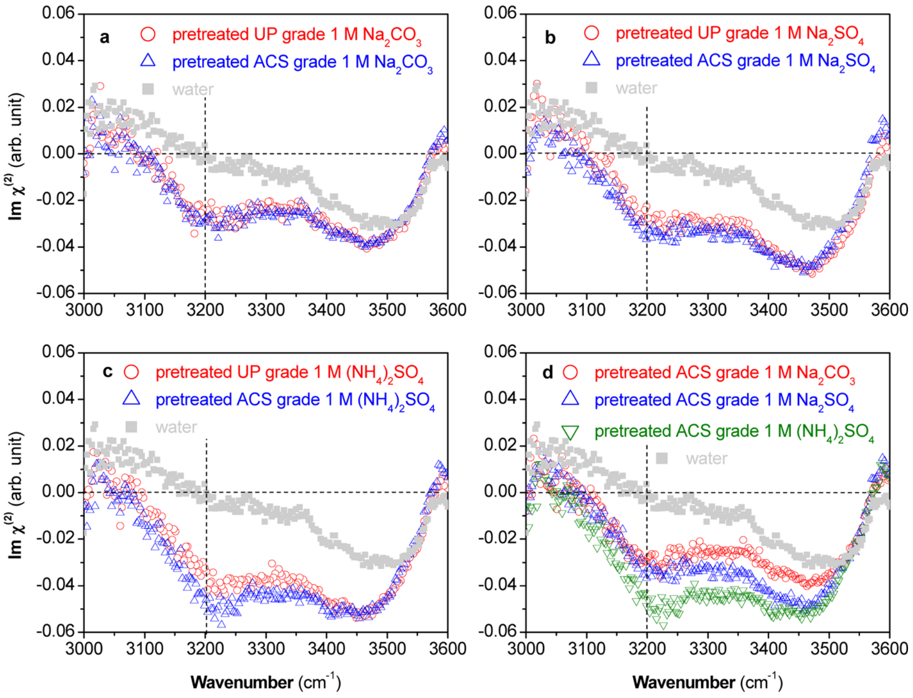


Figure 2. Comparison between HD-VSFG spectra from ACS and UP grade salt solutions after pretreatment. (a) 1 M Na_2CO_3, (b) 1 M Na_2SO_4, (c) 1 M $(NH_4)_2SO_4$, and (d) comparison of all 1 M salt solutions. The HD-VSFG spectrum of neat water is also shown as a reference.

polarized, 800 nm) and infrared (p-polarized, OH stretching region) beams prior to the sample stage was reduced to 260 and 8 μJ, respectively. The primary sum-frequency beam is time-delayed by 1.7 ps by its passage through a thin silica plate (<1 mm). Neat water spectra were used as a reference for salt comparison to assess reproducibility during the whole experimental period. The reproducibility for both conventional VSFG and HD-VSFG (Im $|\chi^{(2)}|$) spectra of neat water is demonstrated in the Supporting Information. Critical here is that all Im $\chi^{(2)}$ spectra of salt solutions are compared with that of neat water. Thus, our interpretation is based on the *relative* difference between neat water and the salt solutions. To check the validity in the general trend of these spectra, the deduced power $|\chi^{(2)}|^2$ spectra of each salt solution (see Supporting Information) reconstructed from the HD-VSFG results are compared with those measured directly by conventional VSFG spectroscopy. Only every second and fourth data points are plotted in the conventional VSFG and HD-VSFG and spectra, respectively, to avoid spectral clutter.

3. RESULTS AND DISCUSSION

3.1. Conventional and Heterodyne-Detected VSFG Spectra of Pretreated Salt Solutions for Different Purity Grade Salts.

Figure 1 shows the comparison between conventional VSFG spectra in the OH stretching region of pretreated 1 M Na_2CO_3, Na_2SO_4, $(NH_4)_2SO_4$, and NaCl salt solutions made from ACS and UP grade salts. A typical VSFG spectrum of the neat air/water interface is also shown as a reference for all salt solution spectra. This spectrum spans a large spectral region from 3000 to 3800 cm^{-1} and consists of a very broad band ranging from 3000 to ~3600 cm^{-1} and a narrow band centered at around 3700 cm^{-1}. The broad spectral band reflects the collective OH stretching modes of hydrogen-bonded surface and subsurface (i.e., a few Å away from the surface) water molecules with a broad continuum of geometries and strengths;[10,23,31] the hydrogen bonding strength weakens as one goes from low to high frequencies. The narrow band at 3700 cm^{-1} is assigned to the dangling OH stretching of the topmost surface water molecules with their OH bonds protruding into the vapor phase.[52]

The conventional VSFG spectra of pretreated Na_2SO_4 and $(NH_4)_2SO_4$ salt solutions show greater SFG signal intensity over the entire broad region relative to that of neat water, whereas that of the Na_2CO_3 solution displays signal enhancement only below 3200 cm^{-1}, with a weakened intensity for the higher frequency region (~3200–3450 cm^{-1}). In contrast, the conventional VSFG spectrum of NaCl remains practically unchanged compared with that of neat water. No appreciable differences are observed for the SFG signal of the dangling OH peak for all salts studied. The observed changes in the broad region for carbonate and sulfate solutions have been interpreted as an increase in the electric field magnitude normal to the interface caused by the preferential distribution of CO_3^{2-} and SO_4^{2-} ions within the interface.[33]

Moreover, it can be seen from Figure 1 that there is no significant intensity and shape differences between corresponding conventional VSFG spectra of pretreated ACS and UP grade salt solutions studied ($LiNO_3$ spectrum in Supporting Information). The relative trend observed here between the conventional VSFG spectra from sulfate salts and water is in good agreement with those previously reported on solutions made from as-received UP grade salts[43] and with pretreated solutions from ACS[33,35] and UP grade salts.[30] Noteworthy is the fact that despite using as-received UP grade salts (e.g., Na_2CO_3, 99.95%; Na_2SO_4, 99.99%), Tarbuck and Richmond observed no CH signal in their conventional VSFG spectra that would indicate the presence of organic contamination.[43] However, a similar situation was not found by Koelsch et al. in their comparison of VSFG spectra of as-received and purified 1 M NaI solution (in this case "surface chemical purity" was assessed using a surface tension-based purification method)[53] made from as-purchased UP grade salt (99.999%) nor for the case of untreated UP grade salts shown here (see Section 3.2).[37] This apparent discrepancy is not surprising because it may well reflect the variations in organic impurity over time among salt batches, among suppliers, and even from the same supplier. Also notable is the reversal of signal intensity in the conventional VSFG spectra of Na_2SO_4 and $(NH_4)_2SO_4$ pretreated solutions (see Figure 1a, c) from Allen and co-workers[33,35] relative to those reported by Tian et al.[30] An explanation for this discrepancy could come from the difference in the applied solution filtration methods. It is possible that the method privileged by Tian et al., primarily used for the removal of insoluble microparticles,[17] could have been less effective in the thorough elimination of organic contaminants.

The change in the overall shape of the hydrogen-bonded region with salt addition suggests that the presence and distribution of the ions within the interfacial region perturb water organization to different extents and force a rearrangement of the hydrogen-bonding network. However, little information concerning the relative distributions of cations and anions in the interface can be inferred from conventional VSFG spectra because of the loss of phase information (i.e., OH transition dipole moment orientation) inherent to conventional VSFG spectroscopy. To gain further insight into the effects of ions on the orientation of water molecules and, in turn, on the relative ion distribution, HD-VSFG spectroscopy is utilized. In contrast to conventional VSFG spectroscopy, this technique provides directly the sign (i.e., orientation) and magnitude of the net water transition dipole moment for each vibrational mode.

HD-VSFG spectra in the hydrogen-bonded stretching region (3000−3600 cm^{-1}) from the pretreated solutions of each salt are shown in Figure 2. Again, the Im $|\chi^{(2)}|$ spectrum of neat water serves here as reference and is similar to the ones reported previously.[22,24,25] This spectrum displays positive and negative bands located below and above a zero crossing point at ~3200 cm^{-1}, which represent water molecules with a net OH transition dipole moment oriented toward and away from the vapor phase, respectively. In contrast to the higher frequency region, the assignment of absolute orientation in the lower frequency still remains debated because of recent computational analysis.[54−56]

As can be seen in Figure 2, similar to conventional VSFG spectra, no significant difference can be observed in the intensity and the shape of the HD-VSFG spectra between ACS and UP grade salt solutions after pretreatment (e.g., filtration). These serve as evidence that pretreated UP grade salts have a negligible effect in the study of water structure for aqueous salt solutions. (This is not necessarily true for studies of lipids on salt subphase.[57−59]) HD-VSFG spectra of Na_2CO_3, Na_2SO_4, and $(NH_4)_2SO_4$ pretreated salt solutions all show greater negative intensity in the ~3050−3500 cm^{-1} spectral region compared with neat water. This negative enhancement can be attributed to the presence of an ion-induced electric field in the interfacial region (e.g., carbonate and sulfate anions residing closer to the isotropic aqueous bulk with their cations located above them), which then causes water molecules to reorganize and to have a net orientation toward the bulk solution. A comparison of the Im $|\chi^{(2)}|$ spectra for the pretreated solutions made with ACS grade salts indicates clearly that the magnitude of this electric field from largest to smallest and, therefore, the extent of water reorganization, follows the series $(NH_4)_2SO_4$ > Na_2SO_4 > Na_2CO_3 (Figure 1d). This trend is also consistent with the one observed previously with pretreated solutions from ACS grade salts.[35]

3.2. Conventional VSFG Spectra of Pretreated and Untreated Salts of Different Purity Grades.

To emphasize the importance and to assess the effectiveness of solution pretreatment, a direct comparison was made between conventional VSFG spectra in the OH stretching region of 1 M $(NH_4)_2SO_4$ solutions made from ACS and UP grade salts, *before* and *after* pretreatment (Figure 3a). Conventional VSFG spectroscopy has been preferred here over its more involved heterodyne-detected variant because the focus here is not about the change of water transition moment orientation caused by the presence of specific salts but, instead, the spectral perturbations introduced by their impurities. As shown previously, there is no observable spectral difference between the VSFG spectra of pretreated ACS and UP grade $(NH_4)_2SO_4$ solutions. Interestingly, the HD-VSFG spectrum for the untreated ACS grade $(NH_4)_2SO_4$ solution overlaps very well with the pretreated ones, indicating that the low amount of organic impurities present in the ACS grade salt does not affect the interfacial water organization. In contrast, the untreated UP grade $(NH_4)_2SO_4$ solution exhibits remarkable differences in its VSFG spectrum with a marked intensity increase in the lower frequency region, a small decrease in the higher frequency region, and a complete disappearance of the dangling OH peak at 3700 cm^{-1}. The suppression of the water dangling OH peak has been observed previously for surfactant systems, such as insoluble alcohols, fatty acids, and phospholipids monolayers, and has been attributed to the presence of adsorbed surfactants replacing surface water molecules at the interface.[52,60]

To verify the presence of possible surfactant species, conventional VSFG spectra partially encompassing the surfactant CH stretching region (~2850−3000 cm^{-1}) have

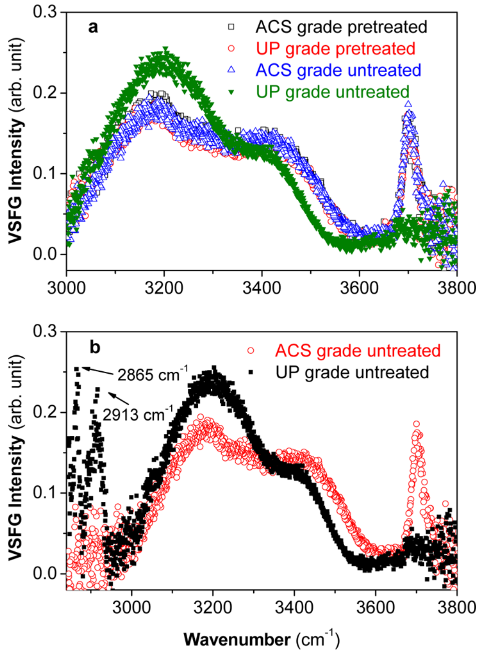


Figure 3. (a) Comparison between conventional VSFG spectra of untreated and pretreated 1 M $(NH_4)_2SO_4$ solutions made from ACS and UP grade salts. (b) Comparison between conventional VSFG spectra of untreated 1 M $(NH_4)_2SO_4$ solutions made from ACS and UP grade salts.

been obtained for untreated 1 M $(NH_4)_2SO_4$ solutions made from ACS and UP grade salts (Figure 3b). Despite the lower signal-to-noise ratio at the edge of this broad spectral window, two distinctive peaks associated with CH_3 and terminal CH_2 symmetric (~2865 cm^{-1}), and CH_2 asymmetric (~2913 cm^{-1}) stretching modes can be distinguished in the VSFG spectrum of untreated UP grade $(NH_4)_2SO_4$ solution, thus confirming the presence of surfactants. In comparison, untreated ACS grade $(NH_4)_2SO_4$ solution shows very little to no organic contamination in the same spectral region. This result clearly demonstrates that prior to pretreatment, the UP grade $(NH_4)_2SO_4$ contains much more organic impurities than its ACS grade equivalent. This could possibly be due to the different industrial processes employed in the purification of UP (trace metals basis) and ACS grade salts, the former presumably using chelating surfactant compounds for the precipitation or retention of unwanted inorganic ions.[61−63]

In the case of high melting point halide salts, one could also resort to salt baking as a suitable and easy-to-use alternative to solution filtration in the removal of organic impurities. Baking also limits the salt loss due to filtration and the need for subsequent concentration calibration. Figure 4a shows, for instance, a comparison between conventional VSFG spectra in the OH stretching region of 1.5 M NaCl solutions made from ACS and UP grade salts that underwent either baking or filtration steps. It can be seen that both treatment on ACS and UP grade NaCl solutions give nearly identical spectra in the OH region. In other words, salt baking and solution filtration appear to be comparable methods when it comes to organics removal. This is also the case for 2 M NaBr solution (data not shown).

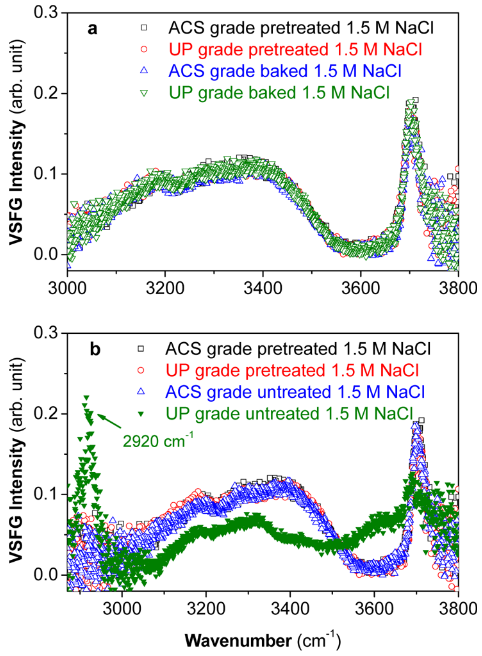


Figure 4. (a) Comparison between conventional VSFG spectra of baked or filtered 1.5 M NaCl solutions made from ACS and UP grade salts. (b) Comparison between conventional VSFG spectra of pretreated and untreated 1.5 M NaCl solutions made from ACS and UP grade salts.

A complete removal of organic contaminants has also been demonstrated previously by Bian et al. by comparing the VSFG spectrum in the surfactant CH stretching region of concentrated NaBr solutions made from unbaked and baked salt.[17] However, in the case of Na_2CO_3 and Na_2SO_4, two high melting point molecular ion-based salts, similar VSFG measurements performed on baked and filtered solutions indicate that baking, even over an extended time period, proved to be less effective (data not shown). Solutions made from baked ACS grade Na_2CO_3 and Na_2SO_4 salts still showed the presence of organic impurities in the CH region and were often slightly cloudy, which resulted in poorly reproducible VSFG spectra in the OH region. This could be due to the presence of floating microparticles (submicrometer-sized) in these solutions, which could only be removed through filtration.[17] It has been reported that such microparticles act as a secondary source of contamination and exist at the surface of sodium halide solutions, whether the salt has been baked or not. It was hypothesized that these particles could possibly originate from carbonized organic contaminants that cannot be detected in the surfactant CH stretching region by conventional VSFG spectroscopy but, instead, with nonresonant SHG fluctuation measurements on the solution surface. However, the conventional VSFG results obtained here in the CH region on ACS grade Na_2CO_3 and Na_2SO_4 salt solutions could be due, in fact, to insoluble microparticles or aggregates containing organic contaminants that survived the baking process and that would be detectable.

Similar to the case of $(NH_4)_2SO_4$ (Figure 3b), the untreated 1.5 M NaCl solution made from ACS grade salts displays a VSFG spectrum nearly identical to those of pretreated solutions (Figure 4b). The untreated UP grade NaCl, on the other hand, shows a significantly different spectrum over the entire OH stretching region, although with less dramatic changes than those observed for unfiltered $(NH_4)_2SO_4$ solution. For instance, the intensity of the dangling OH peak is still reduced, but to a lesser extent, mostly because of the smaller amount of surfactants contained in untreated NaCl salt. These results somewhat differ from those of Tarbuck and Richmond, who used UP salts as-received and showed no evidence of organic contamination in the surfactant CH stretching region.[43] As mentioned above, this could be an indication of the variability in organic impurities between suppliers. Hence, to avoid such potential contamination, solutions made from UP grade salts *must* be treated by filtration or, preferably, by salt baking (depending on the melting point) followed by solution filtration, before being used in surface-sensitive spectroscopic studies of bare air/aqueous salt solution interfaces.

4. CONCLUSIONS

It is shown in this work that no apparent difference is observed in the OH stretching region of conventional VSFG and HD-VSFG spectra between ACS and UP grade salts after pretreatment (either salt baking followed by solution filtration or simply filtration for low melting point salts). It is demonstrated that UP grade salts contain much more organic impurities than the corresponding ACS grade salts, and these impurities largely affect the salt solution spectra in the water OH stretching region. This presumably results from the industrial use of chelating surfactants for the removal of trace metals.

For halide salts, such as chlorides, baking serves as a suitable alternative to solution filtration in the removal of organic impurities. In contrast, the similarity in conventional VSFG and HD-VSFG spectra between pretreated ACS and UP grade salt solutions suggests that the ACS grade salts are adequate for the spectroscopic investigation of water organization at air/aqueous salt solution interfaces. This result is of significance because it should ensure greater reproducibility and better comparison of VSFG measurements at the air/solution interface between different research groups and provide a more defined benchmark for computational models.

Although it was not shown in the current work, it is likely that organic contamination is predominant at higher salt concentrations. The question on the minimal level at which organic impurities begin to have an effect on interfacial water spectral features still needs to be carefully examined by further concentration studies. Furthermore, for studies that investigate binding effects of ions to surfactants (e.g., fatty acids and phospholipids monolayers) on aqueous salt solution subphases, the impact of salt purity is currently not well established. However, recent results suggest that for surfactant surface studies, organic contaminants are not as critical as trace metal impurities.

Considering the variation in the production methods from any given supplier, or between several suppliers or between product batches, there is no guarantee that a given salt will have the same level of organic impurities over time. Since organic impurities are not usually specifically tested, one cannot rely on the specifications as an infallible guide for surface-chemical purity. Hence, regardless of the salt source, unless the specific batch has been tested and shown to be free of surface-active impurities, it is strongly recommended to filter salt solutions but preferably bake the salts (depending on the salt melting point) and then filter the solutions before studying interfacial water organization of aqueous salt solutions. In addition, the use of complementary techniques (as already shown by few research groups), such as non-resonant SHG for floating microparticle detection and surface tension, can serve as valuable indicators of surface chemical cleanliness. Even though these recommendations could be simply viewed as "common good standard analytical practice", it is still not widely recognized and adopted throughout the nonlinear surface spectroscopy community. The current work should hopefully serve as a cautionary warning for future studies on aqueous surfaces.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Raman spectra and calibration curve of $NaSO_4$ solutions. Conventional VSFG spectra of all salt solutions examined in the surfactant CH stretching region showing the absence of organic contamination after pretreatment. Conventional VSFG and HD-VSFG spectra of neat water in the OH stretching region obtained during the entire experimental period demonstrating system and phase stability. Conventional VSFG spectra of $LiNO_3$ salt solution in the OH stretching region before and after pretreatment. Deduced $|\chi^{(2)}|^2$ power spectra of ACS and UP grade salt solutions in the OH stretching region. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: allen@chemistry.ohio-state.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge the NSF-CHE (Grant No. 1111762) and the DOE-BES Geochemistry (Grant No. DE-FG02-04ER15495) for funding this work. W.H. acknowledges a Presidential Fellowship from The Ohio State University.

■ REFERENCES

(1) Finlayson-Pitts, B. J. The Tropospheric Chemistry of Sea Salt: A Molecular-Level View of the Chemistry of NaCl and NaBr. *Chem. Rev.* **2003**, *103*, 4801−4822.

(2) Finlayson-Pitts, B. J.; Pitts, J. N., Jr. *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments and Applications*; Academic Press: San Diego, CA, 2000.

(3) Finlayson-Pitts, B. J. Reactions at Surfaces in the Atmosphere: Integration of Experiments and Theory as Necessary (but Not Necessarily Sufficient) for Predicting the Physical Chemistry of Aerosols. *Phys. Chem. Chem. Phys.* **2009**, *11*, 7760−7779.

(4) Usher, C. R.; Michel, A. E.; Grassian, V. H. Reactions on Mineral Dust. *Chem. Rev.* **2003**, *103*, 4883−4939.

(5) Brown, G. E.; Parks, G. A. Sorption of Trace Elements on Mineral Surfaces: Modern Perspectives from Spectroscopic Studies, and Comments on Sorption in the Marine Environment. *Int. Geol. Rev.* **2001**, *43*, 963−1073.

(6) Michot, L. J.; Villiéras, F.; François, M.; Bihannic, I.; Pelletier, M.; Cases, J. M. Water Organisation at the Solid-Aqueous Solution Interface. *C. R. Geosci.* **2002**, *334*, 611−631.

(7) Schrödle, S.; Richmond, G. L. In Situ Non-Linear Spectroscopic Approaches to Understanding Adsorption at Mineral−Water Interfaces. *J. Phys. D: Appl. Phys.* **2008**, *41*, 033001/1−033001/14.

(8) Laß, K.; Kleber, J.; Friedrichs, G. Vibrational Sum-Frequency Generation as a Probe for Composition, Chemical Reactivity, and Film Formation Dynamics of the Sea Surface Nanolayer. *Limnol. Oceanogr.: Methods* **2010**, *8*, 216−228.

(9) Chang, T. M.; Dang, L. X. Recent Advances in Molecular Simulations of Ion Solvation at Liquid Interfaces. *Chem. Rev.* **2006**, *106*, 1305−1322.

(10) Gopalakrishnan, S.; Liu, D. F.; Allen, H. C.; Kuo, M.; Shultz, M. J. Vibrational Spectroscopic Studies of Aqueous Interfaces: Salts, Acids, Bases, and Nanodrops. *Chem. Rev.* **2006**, *106*, 1155−1175.

(11) Petersen, P. B.; Saykally, R. J. On the Nature of Ions at the Liquid Water Surface. *Annu. Rev. Phys. Chem.* **2006**, *57*, 333−364.

(12) Jungwirth, P.; Tobias, D. J. Specific Ion Effects at the Air/Water Interface. *Chem. Rev.* **2006**, *106*, 1259−1281.

(13) Jungwirth, P. Spiers Memorial Lecture Ions at Aqueous Interfaces. *Faraday Discuss.* **2009**, *141*, 9−30.

(14) Jungwirth, P.; Winter, B. Ions at Aqueous Interfaces: From Water Surface to Hydrated Proteins. *Annu. Rev. Phys. Chem.* **2008**, *59*, 343−366.

(15) Jubb, A. M.; Hua, W.; Allen, H. C. Organization of Water and Atmospherically Relevant Ions and Solutes: Vibrational Sum Frequency Spectroscopy at the Vapor/Liquid and Liquid/Solid Interfaces. *Acc. Chem. Res.* **2012**, *45*, 110−119.

(16) Otten, D. E.; Petersen, P. B.; Saykally, R. J. Observation of Nitrate Ions at the Air/Water Interface by UV-Second Harmonic Generation. *Chem. Phys. Lett.* **2007**, *449*, 261−265.

(17) Bian, H.-t.; Feng, R.-r.; Xu, Y.-y.; Guo, Y.; Wang, H.-f. Increased Interfacial Thickness of the NaF, NaCl and NaBr Salt Aqueous Solutions Probed with Non-Resonant Surface Second Harmonic Generation (SHG). *Phys. Chem. Chem. Phys.* **2008**, *10*, 4920−4931.

(18) Shen, Y. R.; Ostroverkhov, V. Sum-Frequency Vibrational Spectroscopy on Water Interfaces: Polar Orientation of Water Molecules at Interfaces. *Chem. Rev.* **2006**, *106*, 1140−1154.

(19) Raymond, E. A.; Richmond, G. L. Probing the Molecular Structure and Bonding of the Surface of Aqueous Salt Solutions. *J. Phys. Chem. B* **2004**, *108*, 5051−5059.

(20) Allen, H. C.; Casillas-Ituarte, N. N.; Sierra-Hernandez, M. R.; Chen, X. K.; Tang, C. Y. Shedding Light on Water Structure at Air−

Aqueous Interfaces: Ions, Lipids, and Hydration. *Phys. Chem. Chem. Phys.* **2009**, *11*, 5538−5549.

(21) Schnitzer, C. S.; Baldelli, S.; Shultz, M. J. Sum Frequency Generation of Water on NaCl, $NaNO_3$, $KHSO_4$, HCl, HNO_3, and H_2SO_4 Aqueous Solutions. *J. Phys. Chem. B* **2000**, *104*, 585−590.

(22) Ji, N.; Ostroverkhov, V.; Tian, C. S.; Shen, Y. R. Characterization of Vibrational Resonances of Water−Vapor Interfaces by Phase-Sensitive Sum-Frequency Spectroscopy. *Phys. Rev. Lett.* **2008**, *100*, 096102/1−096102/4.

(23) Tian, C. S.; Ji, N.; Waychunas, G. A.; Shen, Y. R. Interfacial Structures of Acidic and Basic Aqueous Solutions. *J. Am. Chem. Soc.* **2008**, *130*, 13033−13039.

(24) Nihonyanagi, S.; Yamaguchi, S.; Tahara, T. Direct Evidence for Orientational Flip-Flop of Water Molecules at Charged Interfaces: A Heterodyne-Detected Vibrational Sum Frequency Generation Study. *J. Chem. Phys.* **2009**, *130*, 204704/1−204704/5.

(25) Nihonyanagi, S.; Yamaguchi, S.; Tahara, T. Water Hydrogen Bond Structure near Highly Charged Interfaces Is Not Like Ice. *J. Am. Chem. Soc.* **2010**, *132*, 6867−6869.

(26) Stiopkin, I. V.; Weeraman, C.; Pieniazek, P. A.; Shalhout, F. Y.; Skinner, J. L.; Benderskii, A. V. Hydrogen Bonding at the Water Surface Revealed by Isotopic Dilution Spectroscopy. *Nature* **2011**, *474*, 192−195.

(27) Zhang, Z.; Piatkowski, L.; Bakker, H. J.; Bonn, M. Communication: Interfacial Water Structure Revealed by Ultrafast Two-Dimensional Surface Vibrational Spectroscopy. *J. Chem. Phys.* **2011**, *135*, 021101/1−021101/3.

(28) Zhang, Z.; Piatkowski, L.; Bakker, H. J.; Bonn, M. Ultrafast Vibrational Energy Transfer at the Water/Air Interface Revealed by Two-Dimensional Surface Vibrational Spectroscopy. *Nat. Chem.* **2011**, *3*, 888−893.

(29) Singh, P. C.; Nihonyanagi, S.; Yamaguchi, S.; Tahara, T. Ultrafast Vibrational Dynamics of Water at a Charged Interface Revealed by Two-Dimensional Heterodyne-Detected Vibrational Sum Frequency Generation. *J. Chem. Phys.* **2012**, *137*, 094706/1−094706/6.

(30) Tian, C. S.; Byrnes, S. J.; Han, H. L.; Shen, Y. R. Surface Propensities of Atmospherically Relevant Ions in Salt Solutions Revealed by Phase-Sensitive Sum Frequency Vibrational Spectroscopy. *J. Phys. Chem. Lett.* **2011**, *2*, 1946−1949.

(31) Casillas-Ituarte, N. N.; Callahan, K. M.; Tang, C. Y.; Chen, X. K.; Roeselova, M.; Tobias, D. J.; Allen, H. C. Surface Organization of Aqueous $MgCl_2$ and Application to Atmospheric Marine Aerosol Chemistry. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 6616−6621.

(32) Liu, D. F.; Ma, G.; Levering, L. M.; Allen, H. C. Vibrational Spectroscopy of Aqueous Sodium Halide Solutions and Air−Liquid Interfaces: Observation of Increased Interfacial Depth. *J. Phys. Chem. B* **2004**, *108*, 2252−2260.

(33) Gopalakrishnan, S.; Jungwirth, P.; Tobias, D. J.; Allen, H. C. Air−Liquid Interfaces of Aqueous Solution Containing Ammonium and Sulfate: Spectroscopic and Molecular Dynamics Studies. *J. Phys. Chem. B* **2005**, *109*, 8861−8872.

(34) Ishiyama, T.; Morita, A. Molecular Dynamics Study of Gas-Liquid Aqueous Sodium Halide Interfaces. II. Analysis of Vibrational Sum Frequency Generation Spectra. *J. Phys. Chem. C* **2007**, *111*, 738−748.

(35) Hua, W.; Jubb, A. M.; Allen, H. C. Electric Field Reversal of Na_2SO_4, $(NH_4)_2SO_4$, and Na_2CO_3 Relative to $CaCl_2$ and NaCl at the Air/Aqueous Interface Revealed by Heterodyne Detected Phase-Sensitive Sum Frequency. *J. Phys. Chem. Lett.* **2011**, *2*, 2515−2520.

(36) Feng, R.-r.; Bian, H.-t.; Guo, Y.; Wang, H.-f. Spectroscopic Evidence for the Specific Na^+ and K^+ Interactions with the Hydrogen-Bonded Water Molecules at the Electrolyte Aqueous Solution Surfaces. *J. Chem. Phys.* **2009**, *130*, 134710/1−134710/6.

(37) Koelsch, P.; Viswanath, P.; Motschmann, H.; Shapovalov, V. L.; Brezesinski, G.; Mohwald, H.; Horinek, D.; Netz, R. R.; Giewekemeyer, K.; Alditt, T. S.; et al. Specific Ion Effects in Physicochemical and Biological Systems: Simulations, Theory and Experiments. *Colloids Surf., A* **2007**, *303*, 110−136.

(38) Du, H.; Liu, J.; Ozdemir, O.; Nguyen, A. V.; Miller, J. D. Molecular Features of the Air/Carbonate Solution Interface. *J. Colloid Interface Sci.* **2008**, *318*, 271−277.

(39) Hua, W.; Chen, X. K.; Allen, H. C. Phase-Sensitive Sum Frequency Revealing Accommodation of Bicarbonate Ions, and Charge Separation of Sodium and Carbonate Ions within the Air/Water Interface. *J. Phys. Chem. A* **2011**, *115*, 6233−6238.

(40) Xu, M.; Tang, C. Y.; Jubb, A. M.; Chen, X. K.; Allen, H. C. Nitrate Anions and Ion Pairing at the Air−Aqueous Interface. *J. Phys. Chem. C* **2009**, *113*, 2082−2087.

(41) Xu, M.; Spinney, R.; Allen, H. C. Water Structure at the Air−Aqueous Interface of Divalent Cation and Nitrate Solutions. *J. Phys. Chem. B* **2009**, *113*, 4102−4110.

(42) Hua, W.; Verreault, D.; Allen, H. C. Cation Effects on Water Organization at the Air/Aqueous Nitrate Solution Interfaces. *submitted.*

(43) Tarbuck, T. L.; Richmond, G. L. Adsorption and Reaction of CO_2 and SO_2 at a Water Surface. *J. Am. Chem. Soc.* **2006**, *128*, 3256−3267.

(44) Ghosal, S.; Hemminger, J. C.; Bluhm, H.; Mun, B. S.; Hebenstreit, E. L. D.; Ketteler, G.; Ogletree, D. F.; Requejo, F. G.; Salmeron, M. Electron Spectroscopy of Aqueous Solution Interfaces Reveals Surface Enhancement of Halides. *Science* **2005**, *307*, 563−566.

(45) Sloutskin, E.; Baumert, J.; Ocko, B. M.; Kuzmenko, I.; Checco, A.; Tamam, L.; Ofer, E.; Gog, T.; Gang, O.; Deutsch, M. The Surface Structure of Concentrated Aqueous Salt Solutions. *J. Chem. Phys.* **2007**, *126*, 054704/1−054704/10.

(46) Finlayson, A. C. The pH Range of the Mohr Titration for Chloride-Ion Can Be Usefully Extended to 4−10.5. *J. Chem. Educ.* **1992**, *69*, 559.

(47) Hommel, E. L.; Allen, H. C. Broadband Sum Frequency Generation with Two Regenerative Amplifiers: Temporal Overlap of Femtosecond and Picosecond Light Pulses. *Anal. Sci.* **2001**, *17*, 137−139.

(48) Ma, G.; Allen, H. C. Surface Studies of Aqueous Methanol Solutions by Vibrational Broad Bandwidth Sum Frequency Generation Spectroscopy. *J. Phys. Chem. B* **2003**, *107*, 6343−6349.

(49) Tang, C. Y.; Allen, H. C. Ionic Binding of Na^+ Versus K^+ to the Carboxylic Acid Headgroup of Palmitic Acid Monolayers Studied by Vibrational Sum Frequency Generation Spectroscopy. *J. Phys. Chem. A* **2009**, *113*, 7383−7393.

(50) Chen, X. K.; Hua, W.; Huang, Z. S.; Allen, H. C. Interfacial Water Structure Associated with Phospholipid Membranes Studied by Phase-Sensitive Vibrational Sum Frequency Generation Spectroscopy. *J. Am. Chem. Soc.* **2010**, *132*, 11336−11342.

(51) Chen, X. K.; Allen, H. C. Water Structure at Aqueous Solution Surfaces of Atmospherically Relevant Dimethyl Sulfoxide and Methanesulfonic Acid Revealed by Phase-Sensitive Sum Frequency Spectroscopy. *J. Phys. Chem. B* **2010**, *114*, 14983−14988.

(52) Du, Q.; Superfine, R.; Freysz, E.; Shen, Y. R. Vibrational Spectroscopy of Water at the Vapor Water Interface. *Phys. Rev. Lett.* **1993**, *70*, 2313−2316.

(53) Lunkenheimer, K.; Pergande, H. J.; Kruger, H. Apparatus for Programmed High-Performance Purification of Surfactant Solutions. *Rev. Sci. Instrum.* **1987**, *58*, 2313−2316.

(54) Ishiyama, T.; Morita, A. Analysis of Anisotropic Local Field in Sum Frequency Generation Spectroscopy with the Charge Response Kernel Water Model. *J. Chem. Phys.* **2009**, *131*, 244714−244717.

(55) Ishiyama, T.; Morita, A. Vibrational Spectroscopic Response of Intermolecular Orientational Correlation at the Water Surface. *J. Phys. Chem. C* **2009**, *113*, 16299−16302.

(56) Pieniazek, P. A.; Tainter, C. J.; Skinner, J. L. Surface of Liquid Water: Three-Body Interactions and Vibrational Sum-Frequency Spectroscopy. *J. Am. Chem. Soc.* **2011**, *133*, 10360−10363.

(57) Okur, H. I.; Kherb, J.; Cremer, P. S. Cations Bind Only Weakly to Amides in Aqueous Solutions. *J. Am. Chem. Soc.* **2013**, *135*, 5062−5067.

(58) Kherb, J.; Flores, S. C.; Cremer, P. S. Role of Carboxylate Side Chains in the Cation Hofmeister Series. *J. Phys. Chem. B* **2012**, *116*, 7389−7397.

(59) Huang, Z. S.; Hua, W.; Verreault, D.; Allen, H. C. Influence of Salt Purity on Na^+ and Palmitic Acid Interactions. *J. Phys. Chem. A* **2013**, under revision.

(60) Watry, M. R.; Tarbuck, T. L.; Richmond, G. L. Vibrational Sum-Frequency Studies of a Series of Phospholipid Monolayers and the Associated Water Structure at the Vapor/Water Interface. *J. Phys. Chem. B* **2003**, *107*, 512−518.

(61) Keil, O.; Dahmen, J.; Volmer, D. A. Automated Matrix Separation and Preconcentration for the Trace Level Determination of Metal Impurities in Ultrapure Inorganic Salts by High-Resolution ICP-MS. *Fresenius' J. Anal. Chem.* **1999**, *364*, 694−699.

(62) Maeda, S.; Pham, H. Q.; Young, T. C.; Young, T.; Pham, H.; Ha Kyu, P.; Shuuji, M. Purification of Solid Salt Composition for Industrial Processes, Comprises Separating Solid Salt from Organic Liquid with Resin and Epihalohydrin, Washing with Solvents and Removing Insoluble Material or Soluble Organic Contaminants. U.S. Patent Application 2010331494-A1, 2009.

(63) Kikuchi, T.; Furusho, S.; Sato, Y. Purification of Brine for Electrolysis, Involves Dissolving Industrial Salt in Water, Adding Sodium Hydroxide, Controlling pH, Processing Filtered Product with Chelate Resin, and Removing Divalent-Metal Ion in Crude Brine. WO2007122781-A1, 2008.