Observation of nitrate ions at the air/water interface by UV-second harmonic generation

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Abstract

Nitrate ions have been observed by resonant second harmonic generation in the air/water interface of sodium nitrate solutions when the nitrate mole fraction exceeds $10^{-2}$ at ambient conditions. The surface propensity of nitrate is weak compared to those of other small anions determined by the same methodology, in qualitative agreement with recent simulations, experiments, and the position of nitrate in the Hofmeister anion series. The presence of nitrate ions in the interface of aqueous solutions has potential implications for chemical processes occurring in both natural and anthropogenic aqueous systems.

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1. Introduction

A growing body of recent experimental and theoretical results is challenging the traditional view that small inorganic ions are excluded from the air/water interface [1]. This rapidly evolving picture of interfacial electrolyte partitioning is developing through the interpretation of increasingly sophisticated simulations [2–6], and through the application of more selective and innovative experimental techniques [7–11]. Recent simulations and experiments indicate both the presence and concentration enhancement of specific anions, including $I^-$, $N_3^-$, SCN$^-$, Fe(CN)$_6^{3-}$, and even hydronium, at the air/solution interface [9,10,12–14]. In some remarkable cases (e.g. $I^-$ and Fe(CN)$_6^{3-}$), strong interfacial adsorption appears even in the dilute (millimolar) regime where one expects the Wagner–Onsager–Samaras (WOS) theory to hold, as well as at higher (molar) concentrations, which are technically beyond the scope of WOS theory [12,13]. We refer the reader to recent reviews [15–18] for further details.

While this departure from classical electrolyte behavior is undoubtedly due to the neglect of specific molecular properties (e.g. size, polarizability, dehydration energy, surface charge density, etc.) in WOS theory and its adaptations, the strongest current arguments as to which specific effects drive ions to an interface against the repulsion of image charges are derived predominantly from the microscopic pictures generated through computational modeling. Jungwirth and Tobias have demonstrated the propensity of highly polarizable anions for the outermost liquid layer [3,19], where induction forces are implicated as playing the significant role [20]. Archontis and Leontidis have also suggested that hydrophobic (steric exclusion) forces are also significant in driving larger atomic ions such as iodide to the interface [21], while more recent work points to dehydration energy and/or surface charge density as an alternative order parameter for surface activity [11,22]. It is noted by Pegram and Record in their analysis that this order parameter is valid only across the anion series and take this as evidence that anion and cation surface propensities are thus driven by different mechanisms. Much of the more recent results and conclusions on this topic are reviewed by Collins et al. [23].

While the investigation of chemical forces driving ion surface enhancement is ongoing, efforts in our group are also focused on expanding the experimental data to test some of the most ubiquitous and environmentally relevant
ions as to their surface activity. To this end, we report here the results of a study of the interfacial aqueous nitrate anion that, like chloride, bromide and sulfate, is among the most abundant charged species present in atmospheric aerosols and terrestrial water sources. Excepting the vibrational sum-frequency generation (VSFG) of Schnitzer et al. [24], and the mass-spectrometric/electro-spray study of Cheng et al. [11], little experimental investigation of the nitrate anion at the air/water interface has been performed, and to the best of our knowledge, no direct experimental detection of the nitrate anion at the air/water interface has previously been performed. Two polarizable MD simulations have produced conflicting results concerning the propensity of the nitrate anion to the interface [5,25]. Dang et al.’s model suggests low surface affinity, while Salvador et al.’s model suggests a higher propensity. The differing results are possibly attributable to the different localization and magnitudes of polarizable centers used in the two simulations [25]. A very recent simulation by Thomas et al. [26] concludes that the nitrate ion resides primarily in the bulk, but does exhibit a low probability to exist in the interfacial region. In the present study, we directly probe the relative number density of the aqueous nitrate anion in the interfacial region as a function of bulk sodium nitrate concentration as a means to establish the surface affinity of the nitrate anion in water via resonant UV-SHG experiments.

2. Experimental

Our procedure follows that described elsewhere [12], and only the salient and altered details are presented here. The samples were prepared fresh from >99% purity sodium nitrate dissolved in 18.2 MΩ water from a Millipore Milli-Q A-10 system with <4 ppb total organic content. The water was sparged with nitrogen for at least 1 h before use. The various concentrations studied were generated by successive dilutions of either stock 6 M or 1 M sodium nitrate solutions, following a rigorous protocol for minimizing surface contamination. The samples themselves are contained in a Petri dish during analysis and kept in a nitrogen atmosphere at atmospheric pressure and room temperature for the duration of analysis.

We collected the second harmonic response of 0–6 M aqueous sodium nitrate (0–0.1 NO$_3^-$ mole fraction) solutions at incident wavelengths of 510 nm, 485 nm, and 400 nm. The UV–Vis absorption spectrum of nitrate at varying concentrations over a 1 mm path length is provided in Fig. 2. The anticipated resonant SHG wavelengths are shifted due to the differing polar environment of the interface relative to that of the bulk [27]. The wavelengths were chosen such that the second harmonic of 510 nm (255 nm) is strongly in resonance with the $\pi^* \leftrightarrow \pi$ transition of surface nitrate, that of 485 nm (243 nm) is slightly off the resonance peak, and that of 400 nm (200 nm) is far off-resonance. The resonance enhancement of the nitrate response in the SHG spectrum is evident in Fig. 1, where the 485 nm and 510 nm signals are considerably enhanced over the off-resonant 400 nm signal.

The optical system was used as described previously [13]. Briefly, the incident light was generated as the output of a tunable femtosecond optical parametric amplifier and focused onto the sample surface at a 45° angle with respect to the surface normal. The pulse FWHM have been previously determined to be $\sim$100 fs [9], and average power energies were varied from 0.2 µJ to 5 µJ to verify the appropriate second order dependence of the SHG signal on input power. Focusing onto the sample resulted in a diffraction-limited spot diameter at the sample surface of $\sim$140 µm, with average power densities generally ranging from 1 to 30 mJ cm$^{-2}$ per pulse. Samples were probed using p-polarized light with respect to the sample surface.

The SHG signal is collected in reflection geometry and spatially filtered from the fundamental frequency through a fused-silica prism. Signal detection is performed using a solar-blind PMT (R7154PHA, Hamamatsu). All signals
are collected as 500-shot averages and normalized to the square of 500-shot averages of the fundamental intensity as detected by a photodiode. This power-normalized value is then collected a minimum of 200 times per sample and then averaged to formulate an individual data point for a given solution on a given day. Data points presented in Fig. 1 represent an average of at least three different days of collection, distributed over three months, and are normalized to the response of neat water collected and processed identically.

Errors bars presented in Fig. 1 represent the standard deviation of the power-normalized values for a given solution pooled over each day of collection, with the error propagated from both the neat water signal and the solution signal in formulation the water-normalized signal. The calculation of the water-normalized signal itself is presented explicitly in the discussion section below.

3. Results and discussion

The intensity of the second harmonic response is described in terms of the number of nitrate molecules present at the surface by [13]

\[ I_{2\nu} \propto |N_{\text{water}}(\beta_{\text{water}}) + N_{\text{nitrates}}(\beta_{\text{nitrates}})|^2 \text{I}_0, \]

wherein \( N_i \) is the number of species \( i \), and \( \langle \beta_i \rangle \) is the molecular hyperpolarizability of species \( i \) averaged over molecular orientations. As an even-order process under the dipole approximation, this average is zero for centrosymmetric media, such as within the bulk solution [28]. At the air/water interface, this inversion symmetry is necessarily broken and thus observed second harmonic is generated only from the interfacial region. Nevertheless, this region has a finite thickness, and current technology is not able to precisely locate the depth of the interface from where the signal is produced.

The molecular hyperpolarizability, \( \beta \), is in general a complex-valued function in which the non-resonant water term can be approximated as being entirely real. The nitrate molecular hyperpolarizability can then be divided into its real and imaginary components as

\[ S_N = \frac{I_{2\nu}}{I_\nu} \propto |N_{\text{water}}(\beta_{\text{water}}) + N_{\text{nitrates}} \text{Re}(\langle \beta_{\text{nitrates}} \rangle)|^2 
+ i \cdot N_{\text{nitrates}} \text{Im}(\langle \beta_{\text{nitrates}} \rangle)|^2 
= |N_{\text{water}}(\beta_{\text{water}}) + N_{\text{nitrates}} \text{Re}(\langle \beta_{\text{nitrates}} \rangle)|^2 
+ |N_{\text{nitrates}} \text{Im}(\langle \beta_{\text{nitrates}} \rangle)|^2. \]

Assuming the number of water molecules and the hyperpolarizabilities remain approximately constant as nitrate is adsorbed to the interfacial region, the sample response can be normalized to the neat water response

\[ S_0 = |N_{\text{water}}(\beta_{\text{water}})|^2, \]
\[ S = \frac{S_N}{S_0} = (1 + B \cdot N_{\text{nitrates}})^2 + (C \cdot N_{\text{nitrates}})^2, \]

wherein \( S \) is a measure of the nitrate solution surface response in units of neat water response as a function of the number of nitrate molecules at the interface and two constants, \( B \) and \( C \).

The assumption that the non-resonant water response does not change as a function of sodium nitrate concentration is not explicitly valid in this case, as can be shown by the slight concentration dependence in the off-resonant signal. This behavior has been assumed to result from the perturbing presence of the ions in the interface, and is discussed below [17,24].

In the previous studies performed by our group, we have been able to successfully adapt the widely used Langmuir adsorption model to a bulk solution-to-surface adsorption model [9,10,12,13]. This model, in principle, facilitates the extraction of the Gibbs excess free energy of adsorption of nitrate to the interface. The Langmuir isotherm relating surface adsorbed nitrate to the Gibbs energy of adsorption as a function of bulk nitrate concentration is given by

\[ N_{\text{nitrates}}^{\text{surface max}} = \frac{N_{\text{nitrates}}^{\text{surface max}}}{[\text{H}_2\text{O}]} \cdot K^{-1} + [\text{NO}_3^-]. \]

Here \( N_{\text{nitrates}}^{\text{surface max}} \) is the number of nitrate molecules at the surface, \( N_{\text{nitrates}}^{\text{surface max}} \) is the maximum number of surface molecules, \([\text{NO}_3^-] \) is the bulk concentration of surfactant, \([\text{H}_2\text{O}] \) is the bulk concentration of water and \( K \) is the equilibrium constant for surface adsorption, given by

\[ K = \frac{[\text{H}_2\text{O}] \cdot N_{\text{nitrates}}^{\text{surface max}}}{[\text{NO}_3^-] \cdot N_{\text{nitrates}}^{\text{surface max}} - N_{\text{nitrates}}^{\text{surface max}}}. \]

and \( \Delta G_{\text{ads}} \) is the corresponding Gibbs surface excess adsorption energy. Substitution of the Langmuir expression (Eq. (4)) into Eq. (3) gives

\[ S = \left(1 + B \cdot \frac{N_{\text{nitrates}}^{\text{surface max}}}{[\text{H}_2\text{O}]} \cdot K^{-1} + [\text{NO}_3^-]\right)^2 
+ \left(C \cdot \frac{N_{\text{nitrates}}^{\text{surface max}}}{[\text{H}_2\text{O}]} \cdot K^{-1} + [\text{NO}_3^-]\right)^2 
= 1 + B' \frac{X}{\gamma + X} + \left(C \frac{X}{\gamma + X}\right)^2. \]

For clarity, we have redefined the fit parameters and labeled the bulk nitrate concentration as \( X \), and let \( \gamma \) be the product of the inverse equilibrium constant and water concentration.

When \( X \) is much smaller than \( \gamma \), this equation is approximated by

\[ S \approx 1 + B' \frac{X}{\gamma} + \left(C \frac{X}{\gamma}\right)^2, \]

intrinsically coupling the equilibrium constant with the fit parameters. Thus, as with the data presented here, the saturation concentration of bulk nitrate is significantly less than \( \gamma \), and \( X \) is never comparable in magnitude to \( \gamma \).
Hence, the Gibbs energy of adsorption becomes undeterminable in our experiment. This limitation is a direct result of the finite capacity of the aqueous phase for sodium nitrate whereas it is not a limitation for gas phase adsorption studies, wherein the pressure (proportional to \(X\)) can often be effectively increased without limit.

While precise determination of the adsorption free energy for the nitrate ion is not possible from our current data (due to a combination of relatively weak transition strength and weak surface adsorption), a best fit of the data yields a value of \(+15\ \text{kJ mol}^{-1}\) with an undefined upper bound and \(-2\ \text{kJ mol}^{-1}\) lower bound at 90% confidence. For the reasons discussed above, these results are best considered in qualitative terms under the conditions of this experiment. Thus, we conclude that our experiments demonstrate that strong absorption of this species to the interface does not occur, whereas the obvious resonant enhancement at 255 nm over 200 nm (Fig. 1) indicates that nitrate is present in readily detectable amounts at the air/water interface for sufficiently high bulk concentrations of sodium nitrate.

The three published nitrate/water slab molecular dynamics simulations of nitrate mentioned earlier provide mildly conflicting predictions for nitrate surface activity. Dang et al. found no strong evidence to indicate that nitrate exists as a surface solvated species [25], whereas Salvador et al. found that nitrate residence times in the interfacial region during their simulations were significant [5]. Similarly, Thomas et al.’s study predicts some surface population of nitrate anions in the interface at high (molar) bulk concentrations although nitrate densities in the outermost liquid layers were minimal [26]. While these studies differ in how polarizability was assigned to the nitrate anion, cationic presence, etc., our present experimental results suggest that the relative ambiguity in nitrate surface propensity is due to its approximately neutral adsorption free energy; i.e. there is no strong preference either for or against surface solvation.

In terms of the well-known Hofmeister series, the nitrate anion is the most strongly water-withdrawing species studied among the monovalent anions investigated thus far by our group using this UV-SHG approach (SCN\(^-\), N\(_3\), I\(^-\)). The surface propensity of nitrate is the weakest of this set and, as such, our results further corroborate the general correlation between greater water-withdrawing power and lesser surface propensity.

Not only do we observe optical resonance of nitrate anions in the interface, it is important to note that we also observe the non-resonant (200 nm) response of the interface increasing as a function of nitrate mole fraction. In fact, an increase over neat water of nearly 300% is observed over the nitrate mole fraction range studied here (up to 6 M) and, barring the possibility that this wavelength is not completely off-resonant with the nitrate moiety, the non-resonant signal can be predominately ascribed to water moieties alone. Thus we are effectively observing an increased magnitude of the observed average molecular hyperpolarizability (\(\langle\beta_{\text{water}}\rangle\), Eq. (1)) as a result of the perturbing influence of nitrate, which indicates a relative change in ordering at the interface and can be loosely interpreted as an indication of enhanced water structure. If the 200 nm signal is truly non-resonant, this implies that the change in net water-orientation in the interface may be quite significant in sodium nitrate solutions and that the perturbation of sodium nitrate on surface water net-orientation may be important, as previously suggested [24]. A complete UV–Vis SHG surface spectrum of the ion will be necessary to definitively establish on- and off-resonance conditions and is currently under investigation.

It also may be possible that undissociated nitric acid moieties may play a significant yet unexplored role in this system. Richmond and coworkers’ recent VSFG study of nitric acid at the air/water interface successfully detected undissociated nitric acid in the interfacial region at high bulk concentrations (>0.1 mole fraction), but did not report estimates of surface concentrations of this species [29]. Owing to the exceptionally low basicity of nitrate, it is not expected that undissociated nitric acid would exist in sufficiently high quantities to be detectable in the present study. However, in light of recent predictions of an acidic air/water interface [14,30], it will be interesting to pursue this in further work.

4. Conclusions

Qualitatively, this study establishes that appreciable concentrations of the nitrate anion do reside in the interfacial region at bulk nitrate mole fractions greater than 0.02, and thus provides another example of a small inorganic anion that is present at the air/water interface. While our results demonstrate that the nitrate anion concentration is not strongly enhanced at the aqueous interface, and the presence of nitrate in the interface significantly perturbs the interfacial water structure. Computational studies of nitrate surface adsorption have been somewhat ambiguous regarding the affinity of the ion for the surface, which we ascribe to the nearly neutral adsorption free energy (\(\Delta G_{\text{ads}} \equiv 0\)).

Considering the ubiquitous presence of nitrates in atmospheric aerosols and terrestrial water bodies, nitrate ions may engender significant yet presently unrecognized interfacial chemistry in aqueous systems. Similar surface-active halogens have already been shown to have dramatic effects on aqueous molecular bromine and chlorine production rates on aerosol surfaces in the presence of ozone [31,32]. Further exploration of potential consequences of the presence of nitrate ions at the surface of aqueous surfaces clearly seems warranted.

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References