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Sum Frequency Generation of O−H Vibrations on the Surface of H_2O/HNO_3 Solutions and Liquid HNO_3

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The surfaces of aqueous HNO_3 solutions and liquid HNO_3 are examined using sum frequency generation (SFG). A molecular-level picture of these atmospherically relevant systems is developed. Consistent with previous interpretations, an electric double layer comprised of subsurface anions and cations develops in $0.005x$ and $0.01x$ HNO_3 solutions, where x = mole fraction. Compared to pure water, these solutions generate more SFG signal in the hydrogen-bonded region as water molecules respond to the subsurface electric field by aligning with the surface normal. At higher concentrations, $0.05x$ and $0.4x$ HNO_3, ionic complexes or molecules sufficiently approach the surface to disrupt the hydrogen-bonding network and perturb the first water layer. Neither liquid nitric acid nor its solutions show a clear O−H.

Introduction

Nitric acid is a key player in atmospheric processes. In the troposphere, it is scavenged by water droplets, resulting in acid precipitation. In the stratosphere, it is the primary component of type I polar stratospheric clouds which comprise surfaces on which ozone-depleting reactions occur.[1−8] A molecular-level understanding of H_2O/HNO_3 surfaces is important for modeling these atmospheric processes. Sum frequency generation (SFG) is an ideal technique for this application because it is only sensitive to molecules at the interface where the inversion symmetry of the bulk phases is not present. It is found that at $0.005x$ (x = mole fraction) and $0.01x$ HNO_3 an electric double layer comprised of subsurface ions reorients surface water. As the concentration of HNO_3 increases, its degree of association increases, resulting in contact ion pairs and molecular species which complex surface water.

In the nonlinear surface-specific process of SFG, the molecular vibrations of interest must be both Raman and IR active in accordance with

$$\beta^{(2)} = \langle \mathrm{g}|\alpha|\nu\rangle\langle\nu|\mu|\mathrm{g}\rangle \qquad (1)$$

where $\beta^{(2)}$ is the molecular hyperpolarizability, α is the Raman polarizability tensor, μ is the infrared transition dipole, and g and ν are the ground and excited vibrational states, respectively.[9,10] The macroscopic nonlinear susceptibility tensor, $\chi^{(2)}$, is equal to the number of molecules contributing to the SFG signal multiplied by the orientational average of β. The SFG signal intensity is proportional to the square of the induced polarization,

$$I_{\mathrm{SFG}} \propto \vec{P}\mathrm{s}_{\mathrm{I}}^{\,2} = [\sum_{J,K} \chi_{IJK}(\vec{E}_J(\omega_1)\,\vec{E}_K(\omega_2) + \vec{E}_J(\omega_2)\,\vec{E}_K(\omega_1))]^2 \qquad (2)$$

where $\vec{E}_J$ and $\vec{E}_K$ are the incident infrared and visible light fields, respectively, and I, J, and K are the Cartesian coordinates in the laboratory frame. The first term in parentheses contains the resonant contribution, while the second contributes to the nonresonant signal background. The nonresonant signal is negligible for dielectric substrates such as the aqueous solutions examined in this work.[11−14]

Experimental Section

Details of the sum frequency generation experimental setup have been described previously.[15−17] To summarize, the 532 nm and tunable infrared light are generated in a KTP-based OPO/OPA (LaserVision), pumped by a 10 Hz nanosecond Nd:YAG laser (Spectra-Physics). The infrared light is tunable from 2500 to 4000 cm^{-1}, and depending on the wavelength, its energy is 0.5−5.0 mJ/pulse with a bandwidth of 4 cm^{-1}. The energy densities of the visible and infrared beams are about 400 and 100 mJ/cm^2, respectively. The polarization combination is *ssp* for the sum frequency, visible, and infrared beams, respectively. The SFG signal is selected with a Jarrell-Ash monochromator and detected by a Hamamatsu R3443 photomultiplier tube. Then, the signal is sent to a gated boxcar averager and a computer for processing. All data points are normalized to the infrared beam intensity and referenced to the 3700 cm^{-1} peak of H_2O.

The HNO_3 solutions were prepared with spectral grade HNO_3 from GFS Chemicals and 18 MΩ cm water from a Barnstead/Nanopure Infinity Base Unit. Aqueous samples were maintained at 273 K with the sample cell in an ice−water bath. The liquid HNO_3 was held at 257 ± 2 K with a custom-built temperature controller. It was prepared by condensing solid HNO_3 in the sample cell placed in liquid nitrogen and then slowly warming it until it liquefied. Nitric acid vapor was prepared[18] by gently bubbling UHP N_2(g) through a mixture of one part concentrated HNO_3 (GFS Chemicals) and three parts concentrated H_2SO_4 (Fisher Scientific) (9 wt % H_2O, 18 wt % HNO_3, 73 wt % H_2SO_4) in a sidearm flask connected to the cell via an inverted U-tube at atmospheric pressure. H_2SO_4 and H_2O remained in the flask due to the low vapor pressure of H_2SO_4 and the

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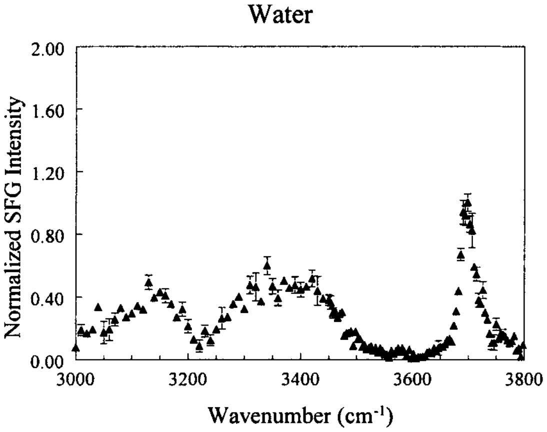

Figure 1. SFG spectrum of the neat liquid interface of water. The polarization is *ssp*, and the temperature is 277 K. The spectrum is normalized to the free-OH peak intensity at 3700 cm^{-1}.

extensive hydrogen bonding between H_2O and H_2SO_4. The purity of HNO_3 was checked by melting point. To avert photolysis, HNO_3 samples were prepared daily under yellow or red light and kept in the dark.

Results

The SFG spectrum of H_2O (Figure 1) is in good agreement with those presented previously.[19-21] The vibrational contributions to the peaks in the 3000−3600 cm^{-1} region have been discussed extensively in the literature. The following interpretation is adopted for this discussion based on findings from infrared and Raman spectroscopy on bulk water.[22-28] The lowest energy peak ca. 3150 cm^{-1} is associated with the symmetric stretch of H_2O symmetrically hydrogen bonded. The peak about 3400 cm^{-1} is a convolution of several resonances including asymmetrically hydrogen-bonded water and the asymmetric stretch of symmetrically bonded water and therefore is not the focus of this paper. The relatively narrow peak at 3700 cm^{-1} is assigned to a free-OH group projecting out of the bulk solution into the vapor phase, free of hydrogen bonding. Shen and coworkers estimate that about 20% of surface water molecules contribute to this free-OH peak.[19] The intensity of this peak for neat H_2O is assigned the value of 1 in our work, and the other SFG spectra are referenced to this peak.

The HNO_3 solution spectra of Figure 2 illustrate how HNO_3 alters the environment of surface water molecules; compared to the neat water surface (Figure 1), the 3150 cm^{-1} peak of $0.005x$ and $0.01x$ HNO_3 approximately doubles. By $0.05x$ HNO_3, however, the peaks associated with hydrogen-bonded water decrease in intensity. The free-OH peak at 3700 cm^{-1} remains the same intensity as H_2O for $0.005x$ HNO_3, despite the increased intensity of the hydrogen-bonded peaks. The 3700 cm^{-1} peak intensity diminishes with increasing HNO_3 concentration ($0.01x$ and $0.05x$) and finally is below the detection limit by $0.4x$ HNO_3. A clear O−H resonance from HNO_3 is not observed for either liquid HNO_3 or its solutions, although a weak hydrogen-bonded resonance may be convoluted with that of water.

Discussion

A. Electric Double Layer Model. The SFG spectra of H_2O on the surface of inorganic acid and salt solutions as a function of concentration are consistent with an electric double layer model. Both experimental observations and theoretical calculations indicate that an electric double layer comprised of subsurface anions and cations develops at the surface of aqueous ionic solutions.[29-31] The double layer is due to a lower energetic cost for the larger, more polarizable ions, usually anions, to approach the surface than the less polarizable cations. This distribution, in which the anions approach closer to the surface and the cations lag behind toward the bulk phase, creates an electric double layer. Surface water molecules respond to the excess negative charge toward the surface by pointing their hydrogen atoms more into the bulk solution. This increased alignment of water molecules with the surface normal results in an enhanced SFG signal in the hydrogen-bonded region compared to pure water.

It has been observed previously that at low inorganic acid and salt concentrations, i.e., below $0.05x$ solute, the SFG intensity in the hydrogen-bonded region reaches a maximum value compared to the other concentrations.[16,17,20,32] For example, the 3150 cm^{-1} peak for water at the surface of $0.01x$ H_2SO_4[16] and $0.05x$ HCl[32] solutions increases to about 4 times the intensity of neat H_2O. At the same concentration, the free-OH peak intensity remains comparable to pure water, indicating the first layer of water is not significantly perturbed by this electric field. The increased SFG intensity at 3150 cm^{-1} must therefore arise from reoriented subsurface water molecules.

At higher concentrations of inorganic acids and salts, i.e., above about $0.2x$ solute, the electric double layer collapses due to the increased association between the anions and cations. The 3150 cm^{-1} peak intensity diminishes due to this collapse. Further, the free-OH peak diminishes as surface water is bound in hydrated complexes.

B. Low HNO_3 Concentrations: Ions in Solution. The electric double layer model is now applied to the SFG spectra of nitric acid solutions. Similar to the other inorganic acid and salt solutions examined with SFG, there is an increase in SFG intensity in the hydrogen-bonded region of $0.005x$ and $0.01x$ HNO_3 (Figure 2) compared to the neat H_2O spectrum (Figure 1). Furthermore, the free-OH intensity decreases between $0.005x$ and $0.01x$ HNO_3. These observations imply there is increased alignment of hydrogen-bonded water or more water layers ordered compared to the neat H_2O surface. At $0.01x$ HNO_3, the decreased free-OH intensity indicates that the effect of HNO_3 has penetrated to the very first layer of the solution. Nonetheless, the hydrogen-bonded intensity remains relatively high. The electric double layer model is consistent with these observations.

The SFG spectra of $0.005x$ and $0.01x$ HNO_3 (Figure 2) reflect the ionic nature of HNO_3 solutions:

$$HNO_3 + H_2O \rightleftarrows [H_3O]^+ + [NO_3]^- \qquad (3)$$

Raman and NMR studies indicate that nitric acid is completely dissociated below $0.01x$ HNO_3 at 273 K, as shown in Figure 3.[33-36] In fact, the tendency for nitric acid to dissociate is so great that, even when as little as 6−10 wt % of water (0.7−$0.8x$ HNO_3) is present, Ritzhaupt and Devlin found that H_3O^+ and NO_3^- still are present.[37]

These subsurface ions in the electric double layer reorient interfacial water molecules, increasing the H_2O alignment with the surface normal. Thus, the SFG signal in the hydrogen-bonded region is enhanced compared to the neat H_2O surface. It is clear that the electric field does not extend to the surface of $0.005x$ HNO_3 solutions since the free-OH intensity is the same as that of pure water. The decrease in the free-OH intensity as the concentration of HNO_3 increases to $0.01x$ (Figure 2), however, suggests that the subsurface electric field penetrates the aqueous surface at this slightly higher HNO_3 concentration.

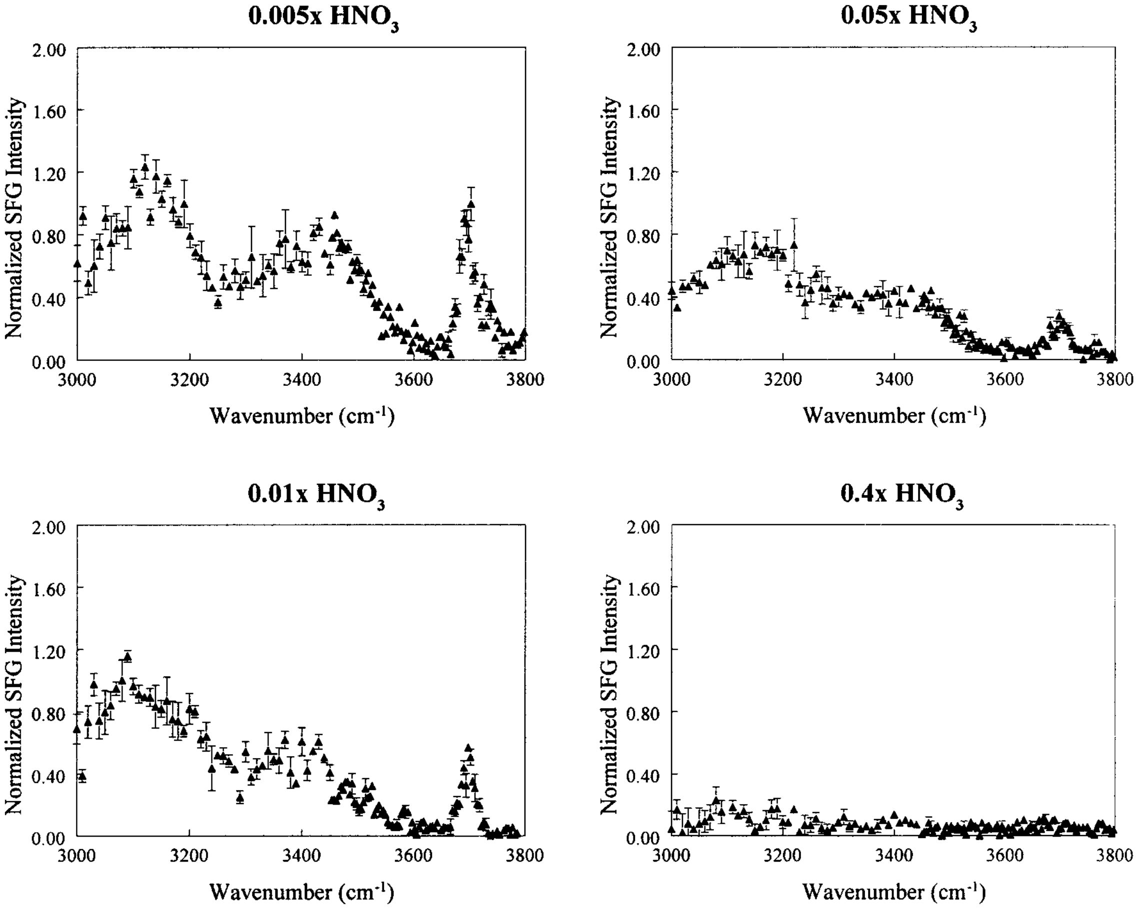

Figure 2. SFG spectra of the H_2O/HNO_3 solutions. The polarization is *ssp* and the temperature is 277 K. The spectra are referenced to the 3700 cm^{-1} SFG peak of neat H_2O.

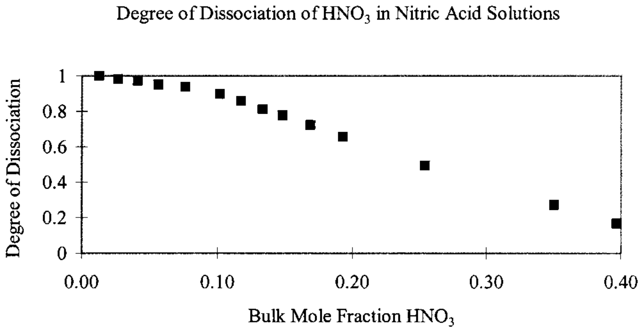

Figure 3. The degree of dissociation of HNO_3 as a function of concentration at 273 K.[33]

C. Higher HNO_3 Concentrations: Molecular Complexes and Contact Ion Pairs. The SFG intensity in the hydrogen-bonded region decreases when the nitric acid concentration increases to 0.05*x* (Figure 2). The free-OH intensity also decreases substantially. These observations imply that ionic complexes or molecules approach the surface sufficiently to perturb the first water layer, disrupting the hydrogen-bonding network and bringing the free-OH groups into solution. Surface tension measurements support this assertion in that the surface tension of HNO_3 solutions decreases as the concentration of HNO_3 increases.[38] This indicates that HNO_3 species adsorb into the surface region more than H_2O molecules, and thus there is an excess of HNO_3 at the surface.[31]

The change in the solution surface at higher concentrations results from the collapse of the electric double layer due to contact ion pairs, e.g., $H_3O^+NO_3^-$, and molecular species disrupting the hydrogen-bonded water. There is precedent for contact ion pairs in HNO_3 solutions since even the monohydrate of HNO_3 is ionic in its crystal form[39,40] and gas phase (HNO_3)-$(H_2O)_y$ clusters form solvated ion pairs when at least five H_2O molecules are present to hydrate HNO_3.[41] There is also precedent for the formation of molecular species.[42] For example, the degree of association increases slightly by 0.05*x* HNO_3 (Figure 3) and experimental[43] and theoretical[44] results suggest that nitric acid is molecular in the 1:1 binary HNO_3−H_2O complex.

D. Concentrated HNO_3 Solutions. By 0.4*x* HNO_3 (Figure 2), the intensity of hydrogen-bonded water is scarcely discernible and there is no SFG intensity at 3700 cm^{-1}. The lack of free-OH intensity suggests that water is complexed and/or displaced from the surface. The marginal intensity from 3100 to 3600 cm^{-1} implies that hydrogen-bonded water has been displaced from the surface. This is consistent with contact ion pairs or molecular nitric acid at the surface. If the surface concentration equals the bulk concentration at 0.4*x* HNO_3, HNO_3 occupies three times more surface space than H_2O due to the larger surface area of HNO_3 (30 $Å^2$)[45] compared to H_2O (10 $Å^2$).[46] Considering the number of water molecules is proportional to the square root of the SFG intensity, the signal from water would be about 5% of water which is near the detection limit. Therefore, no conclusion can be drawn about the detailed structure of water on the surface of this concentrated solution.

E. Liquid Nitric Acid. The SFG spectra of liquid HNO_3 and aqueous HNO_3 solutions reveal no nitric acid O−H resonances. The free-OH vibration of HNO_3 is predicted to be near the gas-phase molecular absorption at 3560 cm^{-1}.[47] There is no resonance observed in that region, hence there are negligible HNO_3 free-OH vibrations. Alternatively, if HNO_3 hydrogenbonds, an intense vibration at 3400 cm^{-1} is expected.[48] Scanning the region 3000−3600 cm^{-1}, however, reveals no sign of molecular nitric acid. The lack of SFG resonances for HNO_3 reflects the complicated nature of this system in which HNO_3 decomposes spontaneously and undergoes self-ionization.[49] Using SFG to examine the N−O stretches on the surface of HNO_3 will help resolve the specific nature of nitric acid in the surface region.

Conclusion

Compared to the neat H_2O spectrum (Figure 1), the enhanced SFG intensity in the 3000−3600 cm^{-1} region of 0.005x and 0.01x HNO_3 solutions (Figure 2) indicates increased alignment of hydrogen-bonded water with the surface normal. Further, the decreased free-OH intensity between 0.005x and 0.01x HNO_3 signifies that the first layer of water molecules is perturbed. The presence of an electric double layer comprised of subsurface anions and cations is consistent with the SFG spectra. At higher concentrations, the association of anions and cations in contact ion pairs and molecular complexes collapses the electric double layer, observed as decreased SFG intensity of both hydrogen-bonded and free-OH water. There are no O−H vibrations observed for HNO_3, reflecting its complicated nature.

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