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Title

An investigation of aqueous ammonium nitrate aerosols with soft X-ray spectroscopy

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An Investigation of Aqueous Ammonium Nitrate Aerosols with Soft X-ray Spectroscopy

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Abstract

Aqueous aerosols are important in atmospheric chemistry, drug delivery, and in human health. X-ray photoelectron spectroscopy (XPS), a surface sensitive technique and near-edge X-ray fine structure (NEXAFS) spectroscopy which informs on the bulk, is deployed to study the solvation of ammonium nitrate (NH_4NO_3). Aerosolized solutions of NH_4NO_3 were introduced into a photoelectron spectrometer via an aerodynamic lens, and interrogated with soft X-ray photons, the resulting electrons were imaged via velocity map imaging. Density functional theory calculations were performed to compare with the measured binding energies of NH_4^+ and NO_3^- solvated in water. The results reveal that the nitrate anion has a slight propensity for the surface, while both ammonium and nitrate ions are present in equal measure in the bulk.

[Graphical Abstract]

Keywords: Ammonium Nitrate, X-ray photoelectron spectroscopy, Near-edge X-ray absorption spectroscopy, Velocity map imaging

Introduction

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Ammonium nitrate (NH_4NO_3), a nitrate (NO_3^-) salt is a major constituent in atmospheric aerosols with an impact on global climate system [1]. It is formed in the atmosphere by neutralizing ammonia (NH_3) with nitric acid (HNO_3) [2]. NH_3 is released by agricultural excreta and synthetic fertilizer [3] and HNO_3 is the photoproduct of nitric oxide (NO_x) oxidation [4]. It is also abundantly found in marine atmospheric aerosols [5,6]. This system has been studied extensively both experimentally and theoretically [7-9]. There are numerous studies on the behavior of separate cation and anion species in the solvent environment [10-12]. Ammonium (NH_4^+) ion is important for chemical and biological processes and its complex hydration structure with water was investigated to understand the nature of the hydrogen bonding and its implications to properties such as rotational dynamics [12-19].

X-ray spectroscopy has proven to be an effective technique for probing aqueous systems with the advent of liquid jets. It is a highly sensitive, robust technique which registers information about the local electronic structure of complex molecular systems. The hydrogen bonding nature of NH_4^+ and NO_3^- ions with water has been studied with X-ray absorption spectroscopy [11,20]. Ekimova and coworkers [20], studied the aqueous solvation of NH_4^+ ions, their results suggest that NH_4^+ forms weak hydrogen bonds with five water molecules in the first hydration shell. The influence of hydrogen bonding to the pre-, main-, and post-edge features of the X-ray absorption spectrum, was observed via spectral frequency shift and peak broadening caused by solvent-solute interactions. They also calculated the photoelectron spectrum of NH_4^+ at the valence level, which showed hybridization with H_2O ($3a_1$) and H_2O ($1b_1$) orbitals. The NO_3^- ion was studied with X-ray absorption spectroscopy by Smith et al. [11] with both theory and experiment. Their spectra showed two peaks, a sharp intense peak corresponding to the $\square^*$

transition and a broader less intense peak corresponding to the □* transition. According to their molecular dynamics (MD) calculations, the hydration core of the NO_3^- ion consisted of an average of 11.8 water molecules. However, this value depended on the calculation method, since previous work had reported different hydration numbers. For instance, the MD simulations performed by Dang and coworkers reported a coordination number of 10 around NO_3^- [21], while *ab initio* calculations by Vchirawongkwi et al. found an average coordination number of 7.9 [22,23].

The propensity of the anions and cations of NO_3^- salts towards the bulk or the interface of the solution is of great interest in a number of fields, particularly atmospheric chemistry [8-10]. This separation of the ionic pairs can create a double layer which can give rise to an interfacial electric field. Brown and coworkers studied the spatial distribution of NO_3^- in an aqueous liquid jet of $NaNO_3$ using photoelectron spectroscopy of N 1s and O 1s levels [10]. Their photoelectron spectroscopy measurements at different depths suggested anions prefer bulk solvation and a depletion of anion were noticed near the interface. Much later, Hua and coworkers measured the ion propensity of air-aqueous interface for a series of NO_3^- salts including NH_4NO_3 using phase-resolved vibrational sum frequency generation experiments [8]. They observed that NO_3^- has more tendency to segregate near the surface whereas the counter cation does not show a surface preference. However, they are not completely absent from the interface and compared to other alkali cations, a small population of NH_4^+ ion can still be present. A similar observation focused on NH_4NO_3 at different molar concentrations was reported in a recent theoretical molecular dynamics study by Mosallaneja and coworkers [9].

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However, to date, we are not aware of an X-ray spectroscopic study of aqueous ammonium nitrate. Here, we present an X-ray photoelectron and X-ray absorption spectroscopy study of 0.5 M NH_4NO_3 in an aerosol beam. Photoelectron spectroscopy studies of unsupported aerosol nanoparticles using synchrotron radiation in conjunction with velocity map imaging (VMI) provided a convenient and unique way to probe solvation of organic and salt-based aerosols [24-26]. In contrast to the conventional hemispherical analyzer method, typically used with liquid jets, this technique has the capability of simultaneous measurement of energy and the angular distribution with 4 collection efficiency of the photoelectrons. The VMI apparatus is capable of measuring both X-ray photoelectron spectroscopy (XPS) and near-edge absorption fine structure (NEXAFS) spectroscopy [27]. We collected XPS spectra at two photon energies (430 eV and 440 eV) of N 1s level, while the NEXAFS spectrum was collected at the N edge by scanning the photon energy range between 390 eV- 430 eV. XPS is a surface sensitive method and NEXAFS probes the bulk of the nanoparticle. Therefore, by combining the relative peak intensities from XPS, angular distribution information, NEXAFS measurements and theoretical calculations, we can get an understanding of the anion and cation distribution in the surface and bulk of the aerosol.

Experimental Method

A solution of 0.5 M NH_4NO_3 (Sigma-Aldrich, 99.0%) is prepared with highly purified water. A beam of aerosols is produced by nebulization of the solution through a constant output atomizer (TSI Model 3076) with Ar as the carrier gas. These aerosols then flow into the aerodynamics lens system through a 150 m nozzle and are focused to the VMI spectrometer

where they interact with the photon beam propagating orthogonal to the aerosol beam direction. This study is conducted at the soft X-ray beamline (9.0.1) of the Advanced Light Source synchrotron facility at Lawrence Berkeley National Laboratory. N 1s level XPS is collected at photon energies 430 eV and 440 eV. The NEXAFS spectrum is collected by scanning the photon energy between 390 eV – 430 eV.

After ionization in the VMI spectrometer, the photoelectrons are accelerated towards a microchannel plate (MCP) detector which is coupled to a phosphor screen. Under optimized conditions, electrons with kinetic energy up to 100 eV can be detected with ~2 eV energy resolution. For XPS, images are collected by a CMOS camera which records illuminations on the phosphor screen. A LabVIEW program is used for data acquisition. For each measurement, a background image is collected with the aerosol beam passing through an in-line nanoparticle filter. Images are reconstructed by the pBASEX algorithm [28] and FinA [29,30] program to get the photoelectron spectrum and the angular distribution information. The photoelectron spectra are calibrated using N_2 gas. The NEXAFS spectrum is collected by replacing the camera with the photomultiplier tube (PMT). The PMT collects only the intense secondary electron signal in the central part of the image. The photon energy is scanned while collecting the signal intensity and normalized by the photon flux detected from the photodiode. Similar to the XPS measurements, two data sets are acquired here as well for the signal and background.

Results and Discussion

[Figure 1]

[Table 1]

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The velocity map image and the photoelectron spectra of NH_4NO_3 at N 1s level is shown in Figure 1. In the image, the intense center spot corresponds to the secondary electron signal and the outer rings occur from primary photoelectrons. After reconstruction, the XPS signal for the primary electrons are shown in Figure 1 b) and c) for two different photon energies. The spectra are fitted with Gaussian distributions to separate the contribution of each ion. The higher binding energy peak is fitted to one Gaussian since it has a symmetric distribution and it is assigned to N 1s of NO_3^-. The low binding energy peak has an asymmetric distribution therefore it has a contribution from two Gaussian distributions, peak at 406 eV is NH_4^+ and the ~405 eV peak could be either gas phase NH_3 or an amide. The resolution of our apparatus does not allow us to separate these peaks. Comparing the NH_4^+ peak to previous XPS measurements in liquid jets [31] of NH_4Cl (binding energy 406.74 eV and FWHM 1.57 eV), we deduce very similar numbers as can be seen in Table 1. In a similar manner, we can compare our nitrate anion spectra to that measured by Pham et al. [32] in a liquid jet of 0.7 M nitric acid solution. Their binding energy of NO_3^- is 412.0 eV, and Gaussian peak width of 1.9 eV compares well with that measured here. In a similar study with 3M $NaNO_3$ by Brown et al., they also observed NO_3^- binding energy at 412 eV [10].

Additionally, we extracted the photoelectron angular distribution information from these images. The angular distribution for single-photon absorption can be characterized by the photoelectron differential cross section: $d\sigma_{ion}(hv)/d\Omega(\theta) = \sigma_{ion}(hv)/4\pi[1+\beta(hv)P_2(cos\theta)]$, where $\sigma_{ion}(hv)$ is the total photoionization cross section, P_2 is the second order Legendre polynomial, θ is the angle between polarization axis of the light and velocity of photoelectron. The photoelectron angular distribution is fully characterized by the anisotropy parameter ⬚. This

depends on the subshell in which the photoelectron is generated and for gas phase atoms in collision-less conditions, β has the limiting values of -1 and 2 for perpendicular and parallel transitions, respectively. For isotropic photoelectron distribution β =0. For condensed phase molecular systems, β can deviate from the limiting values mainly due to two reasons; orbital hybridization resulting from hydrogen bonding and elastic scattering. β values for NO_3^- and NH_4^+ at each photon energy are reported in Table 1. At both photon energies, the β parameter has a value closer to the isotropic distribution. Ionizing from the 1s level of N atoms (where the photoelectrons are generated from a 1s orbital), therefore, under ideal conditions, a *p-wave* distribution should lead to β = 2. However, the anisotropy is largely lost when the electron exits the aerosol particle. Since NH_4^+ can only form a weak hydrogen bond with surrounding waters, the loss of the initial anisotropy could occur due to elastic scattering. The slight increase in β upon increase in kinetic energy release is in agreement with what has been in our previous work on squalene [33] and boric acid [26] nanoparticles. Squalene was probed at C 1s and boric acid at B 1s levels, the consistency of those beta values to our data probed at N 1s level may indicate that local electronic structure does not affect the degree of elastic collisions in condensed phase systems. In future work, it would be interesting to quantify these changes in angular distributions by exploring both <10 eV, and >30 eV kinetic energy trends as recently discussed in the case of water by Gozem et al. [34] The photoelectron angular distributions of pure water, both in valence band and core levels [34,35], is of enormous interest in the community. Our method could be further extended to investigate how a change in the solvent environment can influence the electronic properties of water.

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To confirm our binding energy assignments and to understand the solvation dynamics and electronic structure, we performed theoretical calculations using the Q-Chem computational chemistry package [36]. Calculations were performed with different levels of theory: HF/6-311+G** and ωB97X-D/6-311+G**. The XPS peak positions and corresponding chemical shifts are obtained using the ΔSCF method or its variation applied to DFT. In this method, the binding energy is found as the difference between the neutral and core-ionized states. The solvent in calculations was simulated either by the polarizable continuum model (PCM) or explicitly by introducing 20 water molecules around NH_4NO_3. For comparison we also studied the isolated ions surrounded by 14 water molecules. Previously it was demonstrated that up to 20 water molecules are necessary to replicate experimental data in calculation for acetate in water[37]. Initial structures were modeled by arbitrarily placing water molecules around NH_4NO_3 or the isolated ions (NH_4^+ or NO_3^-). The obtained geometry optimized structures are presented in Figure 2 and the calculated binding energies are summarized in Table 2. Figure 1 d) shows the simulated photoelectron spectrum with binding energies calculated with the HF/6-311+G** PCM model convoluted with a Gaussian of FWHM = 2 eV. The binding energies do not show a significant difference with different levels of theory and solvent model, however they are consistent with our experimental data. Moreover, the calculations performed on isolated ions demonstrate the binding energies of ions are very similar to those of NH_4NO_3. This suggests that in our experiment we cannot separate signals arising from ions from those coming from a molecule. For completeness we would like to point out that earlier theoretical calculations suggest that the ammonium ion solvation shell has 6 water molecules [12] and the nitrate ion forms solvent cluster with 64 water molecules [38].

[Table 2]

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[Figure 2]

By combining XPS spectra with NEXAFS measurements, we hope to gain an understanding of the ion distribution in aqueous aerosols. XPS is surface sensitive while NEXAFS is sensitive to the bulk. The N edge NEXAFS spectrum collected by scanning the photon energy between 390 – 430 eV is shown in the green shaded region of Figure 3. We can compare our NEXAFS for 0.5 M solution to those measured for NH_4Cl [39] and $NaNO_3$ [11]. The linear combination of these two gives a spectrum (dash line) with a perfect agreement to the experimental spectrum and their coefficients are used to extract the respective contributions of NH_4^+ and NO_3^- to our NEXAFS spectrum. To a first approximation, as can be seen in Figure 3, they are present in a 1:1 ratio. The dip in the broad peak of NO_3^- around 415 eV is due to an experimental artifact.

[Figure 3]

In the photoelectron spectra, the area under the curve can be taken as a measurement of number of species in the probing area. Relative areas under NH_4^+ and NO_3^- peaks are shown in Table 1, and at 430 eV, NO_3^- is ~1.4 times higher than NH_4^+ while at 440 eV it is ~1.3 times higher. This observation indicates that NO_3^- has a greater tendency to be present at the surface than NH_4^+. Previous work has suggested [40], that the probing depth of photoelectrons in the kinetic energy range between 10-100 eV is relatively flat, and the two measurements in our experiment are within this range. However, the NEXAFS measurements shows, that in the bulk of the aerosol particle, both NO_3^- and NH_4^+ are present in the same amount. This surface and bulk separation of cations and anions agrees well with previous studies. Phase-resolved vibrational sum frequency generation experiments by Hua and coworkers [8] and molecular dynamics simulations performed by Mosallanejad and coworkers [9] for NH_4NO_3 aqueous solutions

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observed surface propensity of NO_3^- ion compared to the NH_4^+ ion. Pruitt et al. investigated this NO_3^- surface tendency using *ab initio* calculations, where they concluded that it forms strongly bound clusters with water through a hydrogen bonding network at the surface and breaking this cluster to penetrate into the bulk is difficult [38].

This initial survey of the X-ray spectroscopy of aqueous ammonium nitrate aerosols sets the stage for an in-depth study of its solvation dynamics. As mentioned earlier, extracting photoelectron spectra at different kinetic energies should allow us have a better sense of the surface propensity of these ions. Another very interesting topic would be the study of rotational dynamics of the NH_4^+ ion, which is postulated to occur due to bifurcated hydrogen bonding networks [12,15]. Only recently we have developed a combined X-ray spectroscopy of aqueous glycerol aerosols coupled to solution based terahertz and infrared spectroscopy to disentangle the elaborate hydrogen bond networks that are formed in co-solvent systems [41]. Moreover, we have used X-ray spectroscopy to study the local electronic structure of histidine which shows the applicability of this method to biologically important molecules [42]. It is anticipated that this methodology will find increased application in probing micro-heterogeneity in aqueous co-solvent and ionic solutions and will also become a tool in the arsenal of probing chemistry on surfaces of atmospherically and biologically relevant aerosols.

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Figure Captions:

Figure 1: Photoelectron spectroscopy of NH_4NO_3 at N 1s level. a) Raw velocity map image. Arrow indicates the polarization direction of the X-ray radiation. b) Photoelectron spectrum at 430 eV. c) Photoelectron spectrum at 440 eV. Peaks correspond to NO_3^- and NH_4^+ are in blue and pink, respectively. The orange peak is an additional feature resulting from either NH_3 or amide. d) Calculated photoelectron spectrum.

Figure 2: Optimized structures of NH_4^+, NO_3^-, and NH_4NO_3 with surrounding water molecules used to calculate binding energies.

Figure 3: X-ray absorption spectrum of NH_4NO_3 at the N edge obtained by tuning the photon energy from 390 eV - 430 eV. $NaNO_3$ NEXAFS spectrum (blue) is digitized from Figure 1 of Ref [11]., NH_4Cl NEXAFS spectrum (red) is digitized from Figure 4 of Ref [20], dash line gives the linear combination of these two spectra. Area ratio of NO_3^-: NH_4^+ is ~1:1.

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Table1: Binding energy, area, and FWHM of the XPS spectra and the angular distribution extracted from the images.

Ion	XPS – 430 eV			XPS – 440 eV		

	Binding energy (eV)	Area	FWHM (eV)	Beta	Binding energy (eV)	Area	FWHM (eV)	Beta
NO_3^-	411.5	1092.59	2.86	0.1	411.0	540.47	1.67	0.2
NH_4^+	406.1	763.55	1.81	0.1	406.5	423.97	1.54	0.2
Amide/NH_3	404.7	508.64	2.52	-	405.1	570.79	2.20	-

Table 2: Binding energies in eV calculated with different levels of theory and solvent models.

		HF/6-311+G**	ωB97X-D /6-311+G**
PCM Model	NO_3^-	411.67	410.66
	NH_4^+	405.95	405.83
NO_3^- + 14 H_2O		411.78	411.07
NH_4^+ + 14 H_2O		405.46	404.91
NH_4NO_3 + 20 H_2O	NO_3^-	411.71	410.82
	NH_4^+	405.51	405.13

Graphical Abstract

Figure
and NH
used to

Figure
at N 1s

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