State of Water in Supersaturated Nitrate Aerosols Disclosed by the Raman Difference Spectra

Li-Jun Zhao,[†,‡] **Qing-Xuan Zeng,**[‡] **and Yun-Hong Zhang***[,†]

The Institute of Chemical Physics, School of Science, and School of Aerospace Science and Engineering, Beijing Institute of Technology, Beijing 100081, P. R. China

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The hygroscopic properties of supersaturated aerosols as a function of relative humidity (RH) can be determined on the molecular level by the solutes with varied structures, as well as the solvent in the state of solvated water or free water. Although the former has been investigated by FTIR and Raman spectroscopy, the latter has gone mostly unnoticed. In this work, the state of water in supersaturated $Mg(NO_3)_2$ and $NaNO_3$ aerosols were investigated through the application of the Raman difference spectra with respect to pure water. This technique could be developed from the observation that the Raman scattering and infrared absorbance cross sections of the molecular vibrations of interest remain practically unchanged from diluted solutions to supersaturated aerosols at low RHs. The results were expressed in terms of the percentage of free water (W_{free}) as a function of RH, as well as the solvated water-to-solute ratio ($W_{solvated}SR$) and the free water-to-solute ratio ($W_{free}SR$) as a function of the total water-to-solute ratio (WSR). Solvated water observed in the Raman difference spectra was primarily related to the first hydration layers. In $Mg(NO_3)_2$ aerosols, three phases were identified with distinct mechanisms for the transition of the state of water. One unique structure with $W_{solvated}SR = 4$ was proposed to occur in supersaturated $Mg(NO_3)_2$ aerosols at low RHs. In $NaNO_3$ aerosols, it was found that the equality of solvated and free water could not provide a necessary condition for efflorescence, in contrast to the recent investigations by fluorescence spectroscopy. According to this investigation, solvated water could be more abundant than free water not only prior to the efflorescence of supersaturated $NaNO_3$ aerosols, but also in relatively diluted droplets.

Introduction

Atmospheric hygroscopic aerosols are usually expected to experience deliquescence and efflorescence processes in response to the changing ambient relative humidity (RH).[1] The hysteresis evident from the two processes corresponds to supersaturated aerosols,[1] which occur ubiquitously in the atmosphere.[2,3] The aerosols in supersaturated states have been studied by FTIR and Raman spectroscopy to allow for an understanding of their hygroscopic properties.[4−6] In these investigations, complicated solute structures like isolated hydrated ions and various ion pairs attracted much of the attention, while the water in aerosols was only partially analyzed on the evolution of strong and weak hydrogen bonds.

Recently, it was claimed that the water in supersaturated aerosols could be investigated by fluorescence spectroscopy using pyranine as a probe,[7−9] whose two emission bands were believed to arise from free water and solvated water, respectively. However, the mechanism was proposed only intuitively,[7−9] and it could not explain why it is pyranine that differentiates between free water and solvated water instead of 2-napthol series probes,[10,11] whose emission bands respond to the change of microenvironments in a way very similar to pyranine. Moreover, the two band intensities for calculating the relative amount of free water and solvated water in aerosols were not previously corrected for the overlapping effect in the emission spectra of pyranine.[8,9,12] Despite these criticisms, the investigations of supersaturated aerosols by pyranine could still come up with a few interesting observations, such as the spatial heterogeneity of supersaturated aerosols at low RHs.[8,9] In addition to fluorescence spectroscopy, other techniques may also contribute to the study of the state of water in supersaturated aerosols.

The FTIR/ATR (attenuated total reflection) difference spectra, which could be obtained by subtracting an aliquot of reference solutions from proper solutions, have been used to identify the unique features of the first hydration layers of isolated ions.[13] By using the double difference technique,[14,15] ionic hydration behaviors have been unambiguously derived from the infrared spectra of HDO as a probe in various aqueous solutions. Factor analysis suggested that pure water (i.e., free water) and solvated water should coexist from diluted to saturated bulk solutions.[16] By assuming further that the solution density changes linearly with the concentration, the FTIR/ATR spectra of “pure” solvated water could be obtained by subtracting an appropriate amount of pure water from aqueous salt solutions.[16,17] Despite the fact that various salts were assigned to fixed hydration numbers in these investigations,[16,17] which should not be the case in increasingly concentrated solutions,[8,9,14] the method based on the difference spectra can still shed light on the study of water in supersaturated aerosols. In particular, the idea of subtracting pure water from aqueous solution for solvated water is very important, leading finally to the development of the technique for investigating the state of water in supersaturated aerosols.

The technique can be firmly founded upon the hypothesis that the infrared absorption and Raman scattering cross sections

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[*] To whom correspondence should be addressed. Telephone: 86-10-86668406. Fax: 86-10-68913596. E-mail: yhz@bit.edu.cn.

[†] The Institute of Chemical Physics, School of Science, Beijing Institute of Technology.

[‡] School of Aerospace Science and Engineering, Beijing Institute of Technology.

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of the molecular vibrations of interest remain relatively constant from diluted to supersaturated solutions. According to the hypothesis, diluted solutions (e.g., 0.5 M $NaNO_3$ solution), whose water-to-solute molar ratios (WSRs) can be readily known, may act as some references for more concentrated ones. With the υ_1-NO_3^- bands being normalized in area to that in 0.5 M $NaNO_3$ solution, the areas of the water O−H stretching envelopes in supersaturated nitrate aerosols should be proportional to the WSRs. The calculated WSRs can thus provide a measure for the hypothesis. In fact, the infrared absorption cross sections of υ_3-SO_4^{2-}, υ_3-NO_3^- and υ_s-OH in diluted solutions were previously shown to approximate well those in supersaturated and effloresced aerosols,[18] and the Raman scattering cross sections of υ_1-SO_4^{2-} and υ_1-HSO_4^- were also found independent of temperature and concentration over a wide range.[19] With the hypothesis being approved, the residues after subtracting free water should be due to solvated water, and the state of water in supersaturated aerosols can be accordingly investigated.

Experimental Section

The experimental setup for confocal Raman measurements of aerosol particles has been detailed in several of our previous publications, and similar experimental procedures were also used.[5,6] In addition, the Raman spectra used in this work for investigating the state of water in supersaturated $Mg(NO_3)_2$ and $NaNO_3$ aerosols at various RHs were partially adopted from those published previously.[5,6]

Preparation of Aerosols and Bulk Solutions for Measurements. Without further purification, weighted crystal powders of $Mg(NO_3)_2 \cdot 6H_2O$ and anhydrous $NaNO_3$ of analytical grade were dissolved in triply distilled water (pure water) to prepare 0.5 M $Mg(NO_3)_2$ and $NaNO_3$ solutions, respectively. A syringe was used to inject a few aerosol droplets onto a quartz substrate fixed to the bottom of a sample chamber, which was then swiftly sealed with a piece of thin transparent polyethylene (PE) film. The RH in the chamber was adjusted by mixing two flows of dry N_2 and water vapor saturated N_2 at controlled rates, and was monitored at an interval of 2 s by a humidity temperature meter (Centertek Center 310) with accuracies of ±2.5% RH and ±0.7 °C. To prepare supersaturated aerosols at low RHs, the RH in the chamber was gradually decreased in steps of ~5%. Prior to the measurements, more than 30 min were always allowed for aerosol droplets to completely equilibrate with the ambient RH.

The slopes for the hygroscopic curves of $Mg(NO_3)_2$ and $NaNO_3$ aerosols as a function of RH were found to get increasingly steep at RH > ~80%. Due to the limited RH accuracy (±2.5%), enormously large uncertainties can be expected for aerosol compositions at these high RHs. Therefore, additional bulk solutions of 1.0 and 2.0 M were accurately prepared for $Mg(NO_3)_2$ and $NaNO_3$, respectively.

Confocal Raman Measurements of Aerosols and Bulk Solutions. A confocal Raman system (Renishaw InVia) equipped with a Leica DMLM microscope was used to acquire the Raman spectra of supersaturated $Mg(NO_3)_2$ and $NaNO_3$ aerosols at various RHs, which were about 20−80 μm in diameter. A beam from a 514.5 nm argon ion laser (LS-514 model, Laserphysics) adjusted to the pinhole-in mode was used to excite the aerosols at an output power of 20 mw. The focus of the laser beam was about 1 μm in diameter. The backscattering light signals, after passing through an 1800 g/mm grating, were detected by a charge-coupled device (CCD). A 514.5 nm notch filter was used to remove the strong Rayleigh scatterings. Spectral calibration was always made with respect to the silicon band at 520 ± 0.05 cm^{-1} prior to the measurements. By accumulation of 5 scans each with an exposure time of 10 s, the Raman spectra were acquired by the Wire 2.0 program in the range of 200−4000 cm^{-1} with a resolution of 1 cm^{-1}. All measurements were made at room temperatures of 22−24 °C.

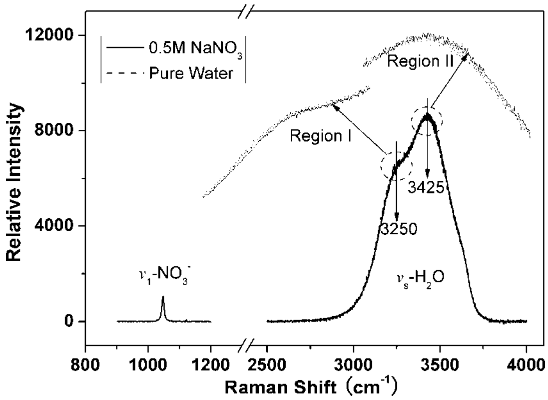

Figure 1. Comparisons of water O−H stretching envelopes in 0.5 M $NaNO_3$ solution and pure water.

Pure water, 1 M $Mg(NO_3)_2$ solution, and 0.5 and 2 M $NaNO_3$ solutions were placed into four quartz cuvettes, respectively, and their Raman spectra were collected by the same confocal Raman system. Because higher or lower concentrations were found to either distort noticeably the water O−H stretching envelope or produce relatively weak υ_1-NO_3 signals, 0.5 M $NaNO_3$ solution with known WSR was used in this work as a reference for calculating the WSRs of nitrate aerosols as a function of RH.

Results and Discussion

The Raman spectra of 0.5 M $NaNO_3$ solution and pure water are displayed by the solid and dashed lines in Figure 1, respectively. Generally, the two spectra are in good accordance with each other in their water O−H stretching envelopes, meaning that the structures of water in 0.5 M $NaNO_3$ solution resemble nicely those of pure water. Nevertheless, slight differences can still be observed in the two regions around the shoulder at 3250 cm^{-1} (region I) and the main peak at 3425 cm^{-1} (region II), respectively, on magnifying the two spectra according to Figure 1. The spectrum of 0.5 M $NaNO_3$ solution can be found to have slightly lower and higher intensities than that of pure water in region I and region II, respectively. Under the water O−H stretching envelope, it was generally agreed that small or large Raman shifts should hint at strong or weak hydrogen bonds, respectively, in pure water and aqueous solutions.[4−6] Therefore, these differences clearly show that weak hydrogen bonds increase at expense of strong ones on the addition of small amount of $NaNO_3$ in pure water, which can be largely attributed to the "structure-breaking" effect of NO_3^- in aqueous solutions.

Procedures to Extract the State of Water in Supersaturated Nitrate Aerosols. The Raman spectra should be first checked for the hypothesis of practically unchanged Raman scattering cross sections as a function of RH in supersaturated nitrate aerosols. In Figure 2a, the Raman spectra of supersaturated $Mg(NO_3)_2$ aerosols were normalized in area with respect to the υ_1-NO_3^- band in that of 0.5 M $NaNO_3$ solution, which is displayed in Figure 1. The WSRs of supersaturated $Mg(NO_3)_2$ aerosols could be accordingly calculated, according to the direct proportionality of the WSRs with the areas of normalized water O−H stretching envelopes. Within the uncertainties due to RH

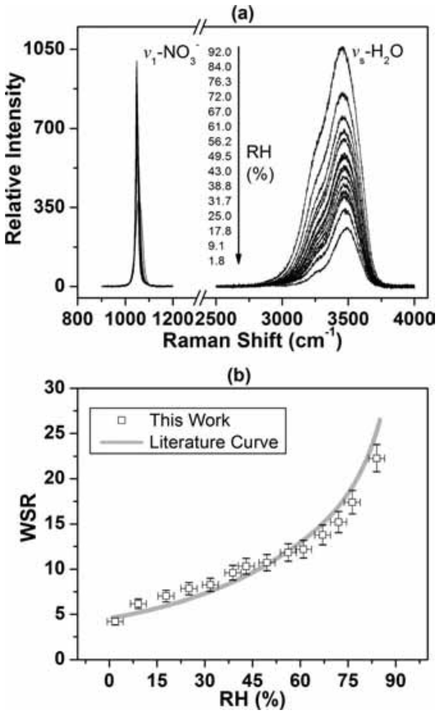

Figure 2. (a) Normalized Raman spectra of supersaturated $Mg(NO_3)_2$ aerosols to the ν_1-NO_3^- band; (b) Comparisons of calculated WSRs (black squares, error bars due to RH and subtraction are added) and those (thick gray line) obtained from the measurements[20] by an electrodynamic balance (EDB).

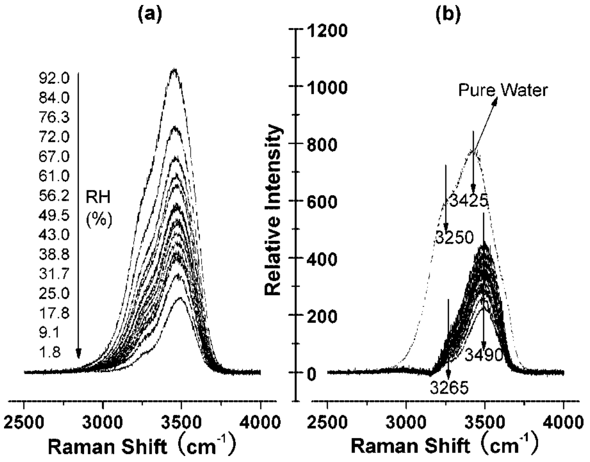

Figure 3. (a) Water O−H stretching envelopes in normalized Raman spectra of supersaturated $Mg(NO_3)_2$ aerosols at various RHs. (b) Spectra of solvated water obtained by subtracting the spectrum of pure water from those shown in part a, respectively. Dashed line in part b corresponds to pure water.

and subtraction, the calculated WSRs in Figure 2b can be found to agree well with the literature curve converted from the expression of mass fraction of solute (mfs) as a function of RH.[20] The available Raman spectra of $NaNO_3$ aerosols do not have the same high quality as those of $Mg(NO_3)_2$ aerosols, as apparent from Figures 3a and 4a. Therefore, similar results (no shown) but not as good as those for supersaturated $Mg(NO_3)_2$ aerosols have also be obtained for supersaturated $NaNO_3$ aerosols. The calculated WSRs in good accordance with those published previously show that the Raman scattering cross sections do retain relatively constant values from diluted solutions to supersaturated aerosols.[18−20]

The spectra of solvated water were obtained by subtracting the water O−H stretching envelope of pure water multiplied by proper factors from those of supersaturated $Mg(NO_3)_2$ and $NaNO_3$ aerosols. The proper factors could be determined by carefully tuning the multiplying factors until negative bands just began to appear in the difference spectra. Similar subtraction standards have been frequently used in the difference spectra for investigating aqueous solutions.[17,21] The normalized spectra prior to subtraction and the resulting spectra of solvated water for supersaturated $Mg(NO_3)_2$ aerosols are shown in Figure 3, parts a and b, and those for supersaturated $NaNO_3$ aerosols are displayed in Figure 4, parts a and b, respectively. The subtracted free water in area percentage (W_{free}) is plotted as a function of RH in Figures 5a and 7a for supersaturated $Mg(NO_3)_2$ and $NaNO_3$ aerosols, respectively. Multiplying the WSR by the corresponding W_{free} can yield the free water-to-solute molar ratio ($W_{free}SR$). The $W_{free}SR$ is plotted as a function of the WSR in Figures 5b and 7b, as well as the solvated water-to-solute molar ratio ($W_{solvated}SR$), for supersaturated $Mg(NO_3)_2$ and $NaNO_3$ aerosols, respectively.

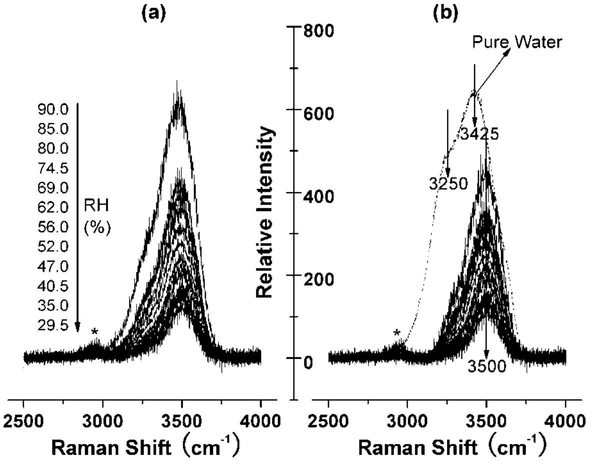

Figure 4. (a) Water O−H stretching envelopes in normalized Raman spectra of supersaturated $NaNO_3$ aerosols at various RHs. (b) Spectra of solvated water obtained by subtracting the spectrum of pure water from those shown in part a, respectively. Dashed line in part b corresponds to pure water. Residues indicated by asterisks in parts a and b are due to the PE film.

Investigations can accordingly be made possible of solvated water and free water in supersaturated aerosols. The unique features of solvated water in supersaturated $Mg(NO_3)_2$ and $NaNO_3$ aerosols can be identified in Figures 3b and 4b, respectively. The results displayed in Figures 5 and 7 can be analyzed for the state of water in supersaturated $Mg(NO_3)_2$ and $NaNO_3$ aerosols as a function of RH.

Raman Spectra of Solvated Water in Supersaturated Nitrate Aerosols. By subtracting free water from supersaturated $Mg(NO_3)_2$ and $NaNO_3$ aerosols, the spectra of solvated water can be obtained, as shown in Figures 3b and 4b, respectively. In contrast to pure water, whose O−H stretching envelope peaks at 3425 cm^{-1} with a shoulder at 3250 cm^{-1}, solvated water in supersaturated $Mg(NO_3)_2$ aerosols produces a main peak at 3490 cm^{-1} with a shoulder at 3265 cm^{-1} occurring especially at low RHs, and that in supersaturated $NaNO_3$ aerosols generates only a main peak at 3500 cm^{-1}. The spectra of isotopically diluted HDO in H_2O could avoid many experimental and interpretative problems connected with H_2O spectra, and were widely used to study ion hydrations in aqueous solutions.[21,22] By comparison with the double difference technique,[14,15,21,22] intermolecular couplings can not be excluded by this technique, therefore, the spectra of solvated water could be more complicated.

In concentrated aerosols with decreasing the RH, a transition has been clearly observed from isolated hydrated ions to various

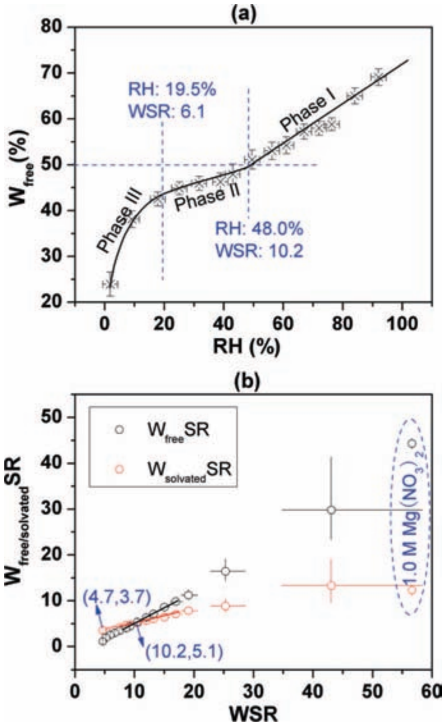

Figure 5. (a) Evolution of free water in percentage (W_{free}) as a function of RH. (b) W_{free}SR (black circles) and $W_{solvated}$SR (red circles) as a function of WSR for supersaturated $Mg(NO_3)_2$ aerosols and 1.0 M bulk solution. Error bars due to RH and subtraction are added. Enormously large uncertainties at high WSRs are mainly due to rapidly growing errors for aerosol compositions at higher RHs. Black solid line in part a and black and red solid lines in part b are used to guide the eye.

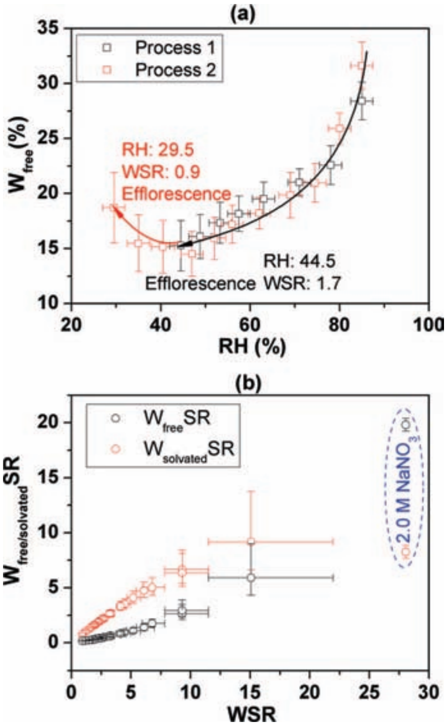

Figure 7. (a) Evolution of free water in percentage (W_{free}) as a function of RH. (b) W_{free}SR (black circles) and $W_{solvated}$SR (red circles) as a function of WSR for supersaturated $NaNO_3$ aerosols and 2.0 M bulk solution. Error bars due to RH and subtraction are added. Enormously large uncertainties at high WSRs are mainly due to rapidly growing errors for aerosol compositions at higher RHs. Black and red solid lines in part a are used to guide the eye.

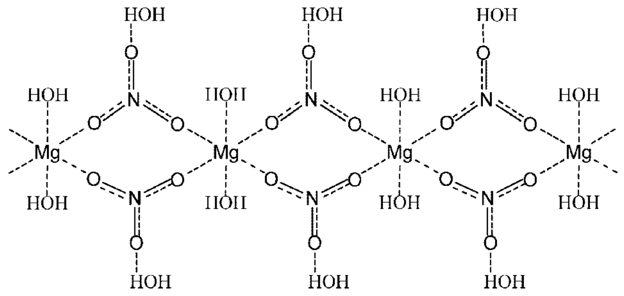

Figure 6. Chain structure with $W_{solvated}SR = 4$ proposed for supersaturated $Mg(NO_3)_2$ aerosols.

ions pairs, such as solvent separated ion pairs (2SIPs), solvent shared ion pairs (SIPs), and contact ion pairs (CIPs).[4-6] Therefore, solvated water in supersaturated aerosols can be expected to experience varying microenvironments as a function of RH. In concentrated $Ca(ClO_4)_2$ solutions, the two bands for cation and anion-affected water in the form of HOD have been found to approach each other, and become finally "cation+anion-affected in character" with increasing the concentration,[14] probably due to the formation of various ion pairs. In the FTIR/ATR difference spectra,[13,23] the hydrations of Mg^{2+} and Na^+ were mainly characterized by the two bands at around 3143 and 3440 cm^{-1}, while those of ClO_4^- and NO_3^- were primarily featured by the two bands at around 3585 and 3566 cm^{-1}, respectively. The interplay between cations and anions was further observed to generate bands different from those of isolated ions. For NO_3^-, the band peaking at 3566 cm^{-1} in the FTIR/ATR difference spectra was very broad, ranging from below 3400 to 3600 cm^{-1}. By comparison, the O−H stretching envelope of pure water peaking at 3300 cm^{-1} can extend from below 3000 to 3600 cm^{-1} in the FTIR/ATR spectra.[13,23] These results on NO_3^- hydration are in good agreement with previous theoretical investigations,[24] according to which NO_3^- can form both strong (comparable with the ones in pure water) and weak hydrogen bonds with water molecules in the first hydration layer.

The main peaks at 3490 and 3500 cm^{-1} in Figures 3b and 4b occur between the bands for Mg^{2+} (3143 cm^{-1}) and NO_3^- (3566 cm^{-1}), and those for Na^+ (3440 cm^{-1}) and NO_3^-, respectively. Therefore, the features could be assigned to solvated water in the first hydration layers of various ion pairs as 2SIPs, SIPs, and CIPs,[13,23] in agreement with the observation of solvated water affected by cations and anions in concentrated $Ca(ClO_4)_2$ solutions.[14] For the shoulder at 3265 cm^{-1} in supersaturated $Mg(NO_3)_2$ aerosols, which is very close to the band for Mg^{2+} compared with NO_3^-, it could be attributed to the Mg^{2+} hydration partially influenced by NO_3^-. The spectra of solvated water in bulk solutions were generally found to shift to higher frequency relative to that of pure water.[16,17]

State of Water in Supersaturated $Mg(NO_3)_2$ Aerosols. Supersaturated $Mg(NO_3)_2$ aerosols have been extensively investigated by Raman spectroscopy in several publications.[5,25] However, the emphasis was previously placed on the identification of various ion pairs with decreasing the RH, as well as the observation for the evolution of strong and weak hydrogen bonds. Decomposing the water O−H stretching envelope into the two components of strong and weak hydrogen bonds can help to quantify the hydrogen bond features of water at various RHs, without providing direct information on the state of water, i.e., solvated water and free water in supersaturated $Mg(NO_3)_2$ aerosols.

The evolution of free water in percentage (W_{free}) as a function of RH, according to Figure 5a, can be roughly divided into the three phases as I, II, and III, respectively. In phase I, with the

RHs above 48.0% (WSR = 10.2), the W_{free} decreases almost linearly with the decline of RH. In phase II, with the RHs between 48.0% (WSR = 10.2) and 19.5% (WSR = 6.1), the W_{free} reduces only slightly with decreasing the RH. In phase III, with the RHs below 19.5% (WSR = 6.1), the W_{free} descends sharply even for small decreases of RH. Three mechanisms should be responsible for the decrease of W_{free} as a function of RH. In phase I, with WSR > 10.2, the linear decrease of W_{free} could be attributed to the steady formation of SIPs between Mg^{2+} and NO_3^-. In phase II, with 6.1 < WSR < 10.2, the simple CIPs between Mg^{2+} and NO_3^-, or some aggregation of SIPs may account for the slow decrease of W_{free}.[5,26] In phase III, with WSR < 6.1, even the stable first hydration layer of Mg^{2+} must be broken, allowing for the abundant formation of complicated chains of CIPs, and the W_{free} can thus be rapidly reduced.

The W_{solvated}SR and W_{free}SR are given in Figure 5b as a function of WSR for supersaturated $Mg(NO_3)_2$ aerosols. Enormously large uncertainties occur at high WSRs in Figure 5b, mainly caused by the limited RH accuracy (±2.5%) resulting in rapidly growing WSR errors at RH > ~80%, which can be evident from Figure 2b.[20] Therefore, a bulk solution of 1.0 M was additionally prepared for analysis, as shown in Figure 5b. A gentle slope can be found for the W_{solvated}SR as a function of WSR, attaining a value of ~13.3 with large uncertainty at the highest RH in this investigation of $Mg(NO_3)_2$ aerosols, which can be regarded as consistent with the W_{solvated}SR of ~12.3 in 1.0 M $Mg(NO_3)_2$ solution. Raman spectroscopy was generally considered only sensitive to the first hydration layers,[27] therefore, the W_{solvated}SR of ~12.3 can be expected to reflect the total water molecules in the first hydration layers for one $Mg(NO_3)_2$ molecule dissolved in aqueous solutions. Theoretic calculations have shown that the first hydration layers of Mg^{2+} and NO_3^- hold 6 and 3 water molecules, respectively.[5,24] As a result, about 12 water molecules are required to fill in the first hydration layers of one Mg^{2+} and two NO_3^-. The good agreement on the hydration number in dilute $Mg(NO_3)_2$ solutions indicates that this technique can be safely used to extract the information on solvated water in the first hydration layers.

In Figure 5b, the W_{solvated}SR and W_{free}SR decrease linearly with the WSR prior to WSR = 10.2, at which the two become equal. With decreasing further the WSR to 4.7, corresponding to the supersaturated $Mg(NO_3)_2$ aerosols at 1.8% RH, the W_{solvated}SR and W_{free}SR reach 3.7 and 1.0, respectively. According to the Eigen mechanism,[28] CIPs can be formed by successively removing solvated water in the hydration layers of isolated ions until direct contact is achieved. Because direct contact between ions tends to increase in more concentrated solutions, CIPs can occur in great abundance in supersaturated aerosols with decreasing the RH, resulting in the formation of complicated structures. In Figure 6, one chain with W_{solvated}SR = 4 that is built upon "bridge bidentate CIPs" should be typical of structures in supersaturated $Mg(NO_3)_2$ aerosols at low RHs. In previous investigations by FTIR and Raman spectroscopy,[4,29,30] supersaturated $MgSO_4$ aerosols at the RHs below 60−40% were found to exist mainly as gels causing mass transfer limitations, for which one chain structure was proposed without considering the state of water.[30] Through the analysis of the state of water as a function of RH, the chain structure shown in Figure 6 was suggested to occur in supersaturated $Mg(NO_3)_2$ aerosols at the RHs below ~20%, which may partially account for the few investigations in the past.[5,25]

Solvated water and free water were reported to become equal at WSR = 6.0 in supersaturated $MgSO_4$ and $Mg(NO_3)_2$ aerosols, according to the study of aerosols by pyranine fluorescence spectroscopy.[8,9] For supersaturated $Mg(NO_3)_2$ aerosols, however, the wrong WSR as a function of RH was used in these investigations, which can be corrected by multiplying a factor of 148/86.[9,25] The corrected WSR for the equality of solvated water and free water is ~10.3, coinciding closely with the WSR (10.2) for 50% W_{free} in Figure 5. This means that the previous method by using pyranine as a probe for the state of water can somehow yield reasonable observations, despite the lack of a complete theory. Therefore, efforts are required in future to explore the mechanism behind the measurements.

State of Water in Supersaturated $NaNO_3$ Aerosols. Supersaturated $NaNO_3$ aerosols have been found to follow different phase transitions with the decrease of RH.[6,18,31−33] Small $NaNO_3$ particles generally retained residual water without efflorescence till the lowest RHs, and solid crystals could be obtained by heating the aerosol particles in an oven.[18,31] In contrast, large $NaNO_3$ particles were frequently observed to effloresce into anhydrous crystals at different RHs.[6,32,33] According to Figure 7a, the $NaNO_3$ aerosol droplets deposited on the quartz substrate can lose water at different RHs to become anhydrous solids. The aerosol efflorescence in process 1 occurs at around the lower limit of W_{free} as a function RH. By contrast, the aerosols in process 2 become more supersaturated prior to the efflorescence, and the W_{free} even increases slightly with decreasing further the RH.

Due to the same reason discussed for $Mg(NO_3)_2$ aerosols,[32,33] enormously large uncertainties also occur at high WSRs in Figure 7b, and a bulk solution of 2.0 M was accordingly prepared for analysis. According to Figure 7b, the W_{solvated}SR reaches 9.2 with large uncertainty at the highest RH, which can also be considered as consistent with the W_{solvated}SR of 8.3 for 2.0 M $NaNO_3$ solution. Because the first hydration layers of Na^+ and NO_3^- were reported to hold 5.2 and 3 water molecules,[24,34] respectively, solvated water can be related once again to the first hydration layers.

The equality of solvated and free water was previously concluded as a necessary but not sufficient condition for efflorescence, according to the studies of NaCl, Na_2SO_4 and $(NH_4)_2SO_4$ aerosols.[8,9] These observations are interesting but hard to rationalize by the proposed mechanism,[7−9] according to which the relative amount of protonated pyranine and deprotonated pyranine is determined by the hindered proton transfer in aqueous solutions. As a matter of fact, the two forms of pyranine are in an equilibrium charactrized by an apparent dissociation constant k_a, which can change to varying enviroments.[35]

Supersaturated aerosols should be stabilized by many factors, among which the state of water may play a role, but probably not a major one. Unlike what was observed for several aerosols,[8,9] solvated water can be more abundant than free water not only in supersaturated $NaNO_3$ aerosols, but also in relatively diluted droplets, according to Figure 7. On the basis of this observation, the relative amount of solvated water and free water can not provide a condition for aerosol efflorescence.

Conclusions

Supersaturated aerosols are ubiquitously present in the atmosphere. The properties of hygroscopic aerosols in supersaturated states depend not only upon the solutes with changing structures as a function of RH, but are also influenced by the state of water, which has rarely been investigated. The recent study of the state of water in supersaturated aerosols by pyranine fluorescence spectroscopy, for which a complete theory has yet to be established, has provided many interesting observations.[8,9]

In this work, one alternative technique has been developed for that purpose, by applying the scientific results about the practically unchanged Raman scattering and infrared cross sections of the molecular vibrations of interest from diluted to supersaturated solutions, as revealed by many investigations. By taking advantage of the Raman difference spectra, the state of water was quantitatively analyzed to gain an insight into the supersaturated structures in $Mg(NO_3)_2$ and $NaNO_3$ aerosols. Solvated water obtained by this technique was related to the first hydration layers for supersaturated $Mg(NO_3)_2$ and $NaNO_3$ aerosols. In $Mg(NO_3)_2$ aerosols, three distinctive mechanisms were envisaged for the transition of the state of water as a function of RH, and one chain structure of CIPs was constructed by considering the state of water in supersaturated aerosols. In $NaNO_3$ aerosols, solvated water was found more abundant than free water even in relatively diluted droplets at high RHs, and the state of water could not be accordingly related to aerosol efflorescence. This is in contrast to the previous aerosol investigations by employing pyranine to distinguish between solvated water and free water. The study of the state of water can help to understand the hygroscopic properties of atmospheric aerosols.

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