[Article]

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共聚焦拉曼光谱研究过饱和硝酸铵液滴中 NH_4^+ , NO_3^- 和 H_2O 之间的相互作用

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摘要: 将硝酸铵液滴沉积在石英基底上, 通过降低该液滴周围环境的相对湿度, 测定了该液滴由低浓度直至过饱和状态下高信噪比的拉曼光谱. 其中, 相对湿度的变化可以精确控制液滴浓度的改变. 在相对湿度(RH)由 72.1% 降低至 37.9% 的过程中, 硝酸铵液滴 $\nu_1\text{-NO}_3^-$ 峰位保持在 1048 cm^{-1} , 半峰宽为 10 cm^{-1} . 该现象表明 NO_3^- 周围的水分子被 NH_4^+ 取代后不会对 $\nu_1\text{-NO}_3^-$ 造成影响, 说明水分子和 NH_4^+ 所形成的氢键具有相同的强度. 对 $2500\text{--}4000\text{ cm}^{-1}$ 范围内的拉曼光谱进行成分分析, 2890 、 3090 、 3140 、 3220 、 3402 及 3507 cm^{-1} 分别被指认为 NH_4^+ 伞状弯曲振动的泛频、 NH_4^+ 伞状弯曲振动与摇摆振动的组合谱带、 NH_4^+ 的对称伸缩振动、 NH_4^+ 的反对称伸缩振动、水峰中强氢键成分和弱氢键成分. 从拟合结果得出: 强氢键在氢键结构中所占百分含量随液滴相对湿度的降低而减少, 弱氢键所占百分含量随液滴相对湿度的降低而增加. 该变化趋势是 NO_3^- 和 NH_4^+ 之间复杂相互作用的结果.

关键词: 拉曼光谱; 过饱和液滴; 氢键成分; 相对湿度; 光谱拟合

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Confocal Raman Spectroscopy Studies on the Interactions between NH_4^+ , NO_3^- and H_2O in Supersaturated NH_4NO_3 Droplets

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Abstract: High signal to noise (S/N) ratio Raman spectra of NH_4NO_3 droplets deposited on a quartz substrate were obtained from dilute to supersaturated states by reducing the relative humidity (RH) of the environment, allowing for accurate control over the concentration of solute within the droplet. When the RH was reduced from 72.1% to 37.9%, the peak position of the $\nu_1\text{-NO}_3^-$ band of the NH_4NO_3 droplet did not shift from its original position at 1048 cm^{-1} and a similar full width at half-maximum (FWHM) of 10 cm^{-1} was also observed. It was concluded that the replacement of H_2O molecules hydrogen-bonded with the O atoms of NO_3^- with NH_4^+ ions leaves the frequency of $\nu_1\text{-NO}_3^-$ relatively unchanged, indicating that both H_2O and NH_4^+ forming hydrogen bonds have the same strength. From component band analysis in the spectral range of $2500\text{--}4000\text{ cm}^{-1}$, six peaks at 2890 , 3090 , 3140 , 3220 , 3402 , 3507 cm^{-1} were identified and assigned. The first four components were assigned to the second overtone of NH_4^+ umbrella bending, the combination band of NH_4^+ umbrella bending and rocking vibrations, the NH_4^+ symmetric stretching vibration, and the NH_4^+ antisymmetric stretching vibration. The latter two peaks originated from strong and weak hydrogen bonds. The signature of the strong hydrogen bonding component was observed to decrease in intensity with the decrease in RH over the full range from 72.1% to 37.9%, while the signature of the weak hydrogen bonding component was shown to increase as the RH was reduced. The observed trend in the hydrogen bonding component resulted from the interactions between NH_4^+ and NO_3^- .

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Key Words: Raman spectrum; Supersaturated droplet; Hydrogen bonding component; Relative humidity; Spectral fitting

1 Introduction

Ammonium nitrate has long been known to be one of the most common constituents of atmospheric aerosols, accounting for 10%–30% of aerosol mass.^{1–3} There are two mechanisms for ammonium nitrate to form in the atmosphere. One is that OH oxidizes NO_x to nitric acid, and then nitric acid is neutralized to ammonium nitrate in the presence of ammonia; another mechanism is that NO_2 can react with NO_3 to form N_2O_5 without sunlight, which is heterogeneously converted to nitric acid in the presence of hydrated aerosols.⁴ Because of its ubiquity and environmental impacts, the properties of NH_4NO_3 particles attract much interest of chemists, aerologists, physicists, and biochemists.^{5–7}

How to understand the efflorescence and deliquescence processes at the molecular level is a focus of atmospheric science, solution chemistry, and crystallography. Yeung and Chan⁸ observed the efflorescence point of ammonium nitrate at ~30% RH, which is in agreement with the reported efflorescence range of 25%–32% RH by Tang.⁹ In contrast, Richardson and Hightower¹⁰ have claimed that the ammonium nitrate particles do not exhibit crystallization. Obviously, the phase transitions which occur in the NH_4NO_3 droplet are complicated, which deserves a more detailed investigation.

Even though the efflorescence and deliquescence processes of ammonium nitrate have ever been investigated with spectroscopic method, detailed interactions of $\text{NH}_4^+ - \text{NO}_3^-$, $\text{NH}_4^+ - \text{H}_2\text{O}$, and $\text{NO}_3^- - \text{H}_2\text{O}$ under supersaturated state are not clear, which basically determine the hygroscopic properties of the supersaturated NH_4NO_3 aerosols. The hydration structure of NO_3^- has been investigated by X-ray diffraction. However, this method is considerably difficult to deduce detailed hydration structure of NO_3^- .^{11,12} With the time-of-flight neutron diffraction, Kameda *et al.*¹³ determined the hydration numbers and the intermolecular bond distance of 10% (molar fraction) NaNO_3 solution in D_2O . Waterland and Kelley¹⁴ studied the structures of nitrate-water complexes by using resonance Raman spectra. Our experiment of depositing the ammonium nitrate droplets on a substrate allows accurate analysis on the chemical components of various association species since there is no morphology resonance disturbance on the Raman band.^{15,16}

Here we use micro-Raman technique to study the interactions between ions as well as interactions between water molecules and ions in NH_4NO_3 droplets especially in supersaturated state on a molecular level.

2 Experimental

2.1 Droplet preparation

The NH_4NO_3 solution ($1.0 \text{ mol} \cdot \text{L}^{-1}$) was prepared from ammonium nitrate (analytical reagent) and triply distilled water.

Droplets of this solution were injected onto a quartz substrate which was fixed to the bottom of a chamber by using a syringe. The diameters of these droplets were varied from ca 5 to 20 μm . The chamber was then sealed by a thin transparent polyethylene film (Xiongxian Dongjiang Hui Ze Products Corporation, with a thickness of 0.09 mm) and the RH in the chamber was adjusted by mixing a stream of water-saturated N_2 and another of dry N_2 at controlled flow rates. A humidity/temperature meter (Centertek Center310) was used to record the RH with an accuracy of $\pm 2.5\%$ near the exit of the chamber.

2.2 Raman spectral measurement of NH_4NO_3 droplets

Fig.1 shows the experimental apparatus used to study the solution droplets. The technique used in this work has been described elsewhere.^{17–21} The central part is a micro-Raman system (Renishaw Invia, U.K.) for measuring Raman spectra and imaging morphological changes of the droplets deposited on the substrate. Before the droplet measurement, a spectral calibration was made by using the 520 cm^{-1} silicon band as a reference. Spectroscopic measurements were then made on droplets observed with a $50\times$ objective of Leica DMLM microscope after being stabilized for about 1 h at a designated chamber RH. The 514.5 nm line of an argon-ion laser was used as the excitation source with a power of 20 mW. A notch filter was used to remove the strong Rayleigh scattering, and a charge-coupled device (CCD) was used to record backscattering signals dispersed by an $1800 \text{ g} \cdot \text{mm}^{-1}$ grating. The Raman spectra of NaClO_4 droplets from 100 to 4000 cm^{-1} were obtained with 5 spectral scans, and each with an accumulation time of 10 s. All the Raman spectral measurements were kept at ambient temperature of 23°C .

Fig.1 Sketch of the experimental apparatus for the confocal Raman measurements of droplets on quartz substrate

2.3 Band component analysis

By band component analysis, the band contour of the vibration bands of NH_4^+ ions and the O—H stretching envelope of water can be used to investigate the interactions between NH_4^+ , NO_3^- , and H_2O in the supersaturated droplets.²² This approach has been applied previously in the analysis of spectral bands arising from non-degenerate vibrations of solutes in aqueous solutions.^{23–25} In this work, each band component analyzed in the range of 2500–4000 cm^{-1} is described by a Gaussian/Lorentzian mixing function as follows.

$$y=y_0+A\left[m_u\frac{2}{\pi}\frac{w}{4(x-x_c)^2+w^2}+(1-m_u)\frac{\sqrt{4\ln 2}}{\sqrt{\pi}w}e^{-\frac{4\ln 2}{w^2}(x-x_c)^2}\right]$$

where, y_0 is the baseline offset, A is the total area, x_c is the center of the peak, w is 2σ , approximately 0.849 of the full width of the peak at half maximum (FWHM), and m_u is the profile shape factor. The spectral weight A of each component is the sole parameter which is allowed to vary in the fitting process, while the values of x_c and w remain unchanged. The aim of fitting is to find out those values of the parameters which best describe the experimental Raman spectra.

3 Results and discussion

3.1 Hygroscopic properties of NH_4NO_3 droplets

Fig.2 shows the molar water-to-solute ratios (WSRs) in NH_4NO_3 droplets at various RHs throughout the dehumidifying processes. The WSRs at given RHs can be obtained from literature.¹⁹ Meanwhile, the WSRs of NH_4NO_3 calculated from the E-AIM model are also included in this figure for comparison.²⁶ The solubility limit or saturation RH is determined to be at a RH of 61%.⁵ When the RH is lower than the saturation point, the droplet enters into the supersaturated region. The supersaturated state facilitates effectively the formation of ion pairs, which can be monitored *in situ* by micro-Raman spectroscopy. In this work, although the NH_4NO_3 droplet is deposited on the quartz substrate, it enters into the supersaturated region and reaches a fairly low RH (38%). Based on the WSR–RH curve, the NH_4NO_3 droplet at 38% RH was found to have a WSR of 0.76, at which one NH_4^+ and one NO_3^- share only one water mol-

Fig.2 Molar water-to-solute ratios (WSRs) of NH_4NO_3 droplets at various RHs in the dehumidifying process

ecule. At a RH of 34%, the NH_4NO_3 droplet crystallizes to an anhydrous particle. More supersaturated states can be achieved in the levitated droplets (with the RH of 30% and even lower) than in the deposited ones (with the lowest RH of 34%), because the levitated droplets in the center of an electrodynamic balance (EDB) can eliminate the heterogeneous nucleation to a great extent.²⁷ Despite its great success, one disadvantage inherent in Raman/EDB is that the sharp peaks caused by morphology-dependent resonances frequently overlap with the Raman spectra of single levitated droplets. This optical effect has not only caused difficulty in the identification of the minute features of spectra, but also complicated the broad water O—H stretching envelope of aerosol droplets. Our experiment with the ammonium nitrate droplets on a substrate which is free from this optical effect allows accurate analysis on the chemical components of various association species.

3.2 Raman spectra of the NH_4NO_3 droplets

The spectra of NH_4NO_3 at various RHs in the dehumidifying process are included in Fig.3. Four predicted bands of NO_3^- , identified as the totally symmetric mode ν_1 (A_1) at $\sim 1048 \text{ cm}^{-1}$, the anti-symmetric stretching mode ν_3 (F_2) at $\sim 1384 \text{ cm}^{-1}$, the bending modes $2\nu_2$ (E) at $\sim 1659 \text{ cm}^{-1}$, and ν_4 (F_2) at $\sim 718 \text{ cm}^{-1}$, respectively, are clearly observed in the spectra of dilute droplets at 72% RH as shown in Fig.3. For comparison, the spectrum of NH_4NO_3 crystal formed in this work is also displayed and marked with “Solid”. The ν_1 - NO_3^- , ν_2 - NO_3^- , and ν_4 - NO_3^- which center at 1048, 1654, and 713 cm^{-1} were labeled, respectively. However, ν_3 - NO_3^- became three peaks of 1288, 1415, and 1460 cm^{-1} . The complicated spectral region of 2500–4000 cm^{-1} is from the total contribution of O—H and N—H stretching vibrations.

Fig.4 shows the peak position and the FWHM of the ν_1 - NO_3^- band for NH_4NO_3 droplets as a function of RH, and those of $\text{Mg}(\text{NO}_3)_2$ droplets are given in Fig.4 for comparison. The ν_1 - NO_3^- band of NH_4NO_3 droplet has no shift in peak position of 1048 cm^{-1} and the similar FWHM of 10 cm^{-1} is noticed when the RH decreases from 72% to 38%. Vollmar²⁸ used the similarity between the ammonium ion and water molecule to explain the relatively unchanged ν_1 - NO_3^- of NH_4NO_3 . He

Fig.3 Vibrational bands of NH_4NO_3 droplets at various RHs in the dehumidifying process

Fig.4 Peak position and FWHM of the $\nu_1\text{-NO}_3^-$ band of NH_4NO_3 and $\text{Mg}(\text{NO}_3)_2$ droplets as a function of RH

showed that NH_4^+ and H_2O have almost identical masses and partial molar volumes and very similar bond angles and inter-atomic distances and then concluded that replacement of H_2O molecules hydrogen-bonded with O of NO_3^- by NH_4^+ ions would leave the frequency of $\nu_1\text{-NO}_3^-$ relatively unchanged.²⁸ Several studies have found that the formation of hydrogen bond resulted in a red shift of the frequency of the symmetric vibration. For both H_2O and NH_4^+ forming hydrogen bonds of about the same strength, it is rational to say that the peak position of the $\nu_1\text{-NO}_3^-$ band keeps unchanged when the H_2O molecules hydrated with NO_3^- are replaced by NH_4^+ .

In order to understand the interactions between NH_4^+ and NO_3^- , we also show the detail change of $\nu_1\text{-NO}_3^-$ band of $\text{Mg}(\text{NO}_3)_2$ droplets in Fig.4. The peak position of the $\nu_1\text{-NO}_3^-$ band of dilute $\text{Mg}(\text{NO}_3)_2$ droplet centers around 1050 cm^{-1} . As the RH decreases from 72% to 29%, the $\nu_1\text{-NO}_3^-$ band of $\text{Mg}(\text{NO}_3)_2$ shows a blue shift of 1 cm^{-1} from 1049 to 1050 cm^{-1} , and an increase in its FWHM from 11 to 14 cm^{-1} , both of which are bigger than that of NH_4NO_3 droplet.

Due to a larger hydrated radius of Mg^{2+} (0.428 nm) compared to NH_4^+ (0.331 nm), Mg^{2+} tends to break down the structure of the solution, creating a more variable environment for the nitrate ions. Any disordering influences seem to broaden a Raman band. Hence, the Mg^{2+} is able to induce a greater increase in the FWHM of ν_1 band than that of NH_4^+ .

Magnesium is an alkali earth metal element in the third period which possesses a large charge-to-radius ratio. It can form various contact ion pairs (CIPs) with NO_3^- in concentrated $\text{Mg}(\text{NO}_3)_2$ solutions, i.e., monodentate CIPs, bidentate CIPs, and more complex structures such as chain structures. The formation of these ion pairs between nitrate and magnesium involves the breaking of the hydrogen bond between the nitrate and H_2O , and then decreases the effective mass of the vibrating units (the oxygen atoms in the case of nitrate). For this reason, the replacement by a cation incapable of forming a hydrogen bond, i.e., ion-pair formation between the nitrate and the cation, causes the reduction of the frequency of $\nu_1\text{-NO}_3^-$ in $\text{Mg}(\text{NO}_3)_2$ droplets. Meanwhile, the replacement of hydrogen-bonded H_2O molecules by similarly hydrogen-bonded NH_4^+ ions would be expected to leave the nitrate ν_1 frequency rela-

tively unchanged as discussed before.

Compared with Mg^{2+} , NH_4^+ ion has a lower charge-to-radius ratio and a less electrostrictive effect on water. When the WSR is smaller than the number of water molecule in the first hydration shell of NH_4^+ , CIPs between NH_4^+ and NO_3^- are expected to form. Since there are no peak position shift and limited broadening (0.3 cm^{-1}) of the $\nu_1\text{-NO}_3^-$ band, it can be concluded that the formation of CIPs between NH_4^+ and NO_3^- has negligible effect on the $\nu_1\text{-NO}_3^-$ band. In other words, there is minor difference between NH_4^+ and H_2O interacting with NO_3^- . It proves that the model of free NO_3^- in NH_4NO_3 is rational not only in dilute solutions but also in supersaturated solutions.

3.3 Assignments of the fitted bands

Free NH_4^+ ion has T_d symmetry and nine internal vibrations ($T_d = A_1 + E + 2F_2$, T_d is tetrahedral point group. A, E, and F are Mulliken symbols, stand for singly, doubly, and thirdly degenerate, separately). By means of optical levitation and Raman spectroscopy, Jordanov and Zellner⁷ observed four modes: the totally symmetric stretching mode ν_1 (A_1) at 3061 cm^{-1} , the anti-symmetric stretching mode ν_3 (F_2) at 3131 cm^{-1} , the bending mode ν_2 (E) at 1661 cm^{-1} , and ν_4 (F_2) at 1461 cm^{-1} . The Raman spectra of NH_4NO_3 droplet in 2500 to 4000 cm^{-1} region can be considered to arise from the contribution of NH_4^+ and H_2O . In order to understand the interactions between NH_4^+ , NO_3^- , and H_2O , a fitting process was applied to the spectra in this region as described in the experimental section. The operation is based on six component bands which are shown in Table 1.

The 2890 cm^{-1} band which is twice the frequency of the $\nu_2\text{-NH}_4^+$ bands can be used to explain this asymmetry with the component band attributed to the overtone of the NH_4^+ umbrella bending vibration. The 3090 cm^{-1} peak is attributed to the combination band of NH_4^+ umbrella bending and rocking vibrations. The peak at 3140 cm^{-1} is assigned to the NH_4^+ symmetric stretching vibration, and the one at 3220 cm^{-1} arises from NH_4^+ asymmetry stretching vibration. The peak at 3402 cm^{-1} arises from the strongly hydrogen-bonded components and the one at 3507 cm^{-1} is attributed to weakly hydrogen-bonded components.

Spinner²⁹ successfully used these vibration modes to fit the appreciably intense and broad combination and overtone bands

Table 1 Peak positions and vibration modes of NH_4^+ and H_2O in the range of $2500\text{--}4000\text{ cm}^{-1}$ in previous literature^{29–31}

	Peak position/ cm^{-1}	Assignment
NH_4^+	2890	the second overtone of NH_4^+ umbrella bending
	3090	the combination band of NH_4^+ umbrella bending and rocking vibrations
	3140	the NH_4^+ symmetric stretching vibration
	3220	the NH_4^+ antisymmetric stretching vibration
H_2O	3402	strongly hydrogen-bonded components
	3507	weakly hydrogen-bonded components

in the range $2700\text{--}3800\text{ cm}^{-1}$ of Raman spectra of $(\text{NH}_4)_2\text{SO}_4$. Here, same vibration modes were applied in Fig.5 as well, but the peak positions of these vibration modes were obtained from references.^{30–32}

3.4 Interactions between NH_4^+ , NO_3^- , and H_2O

There are complex interactions between ions and water molecules in NH_4NO_3 droplets, especially in supersaturated states on a molecular level, and these interactions have shown influence over hydrogen-bonding structures of water molecules as well.

NH_4^+ exerted hardly any influences on the structure of water molecules, and hydrogen bonds formed by H_2O and by NH_4^+ are similar in strength. These conclusions were supported by considerable number of studies. In the previous literature on the studies of NH_4NO_3 solution, it was concluded that NH_4^+ conspicuously resembles H_2O in several respects, including molar masses, bond angles, interatomic distances and partial molar volumes.²⁸ On the structural viewpoint of NH_4^+ in aqueous solution, the most representative picture of the coordination to emerge is of two hydration layers of water molecules. There is

a first hydration layer of four, which is strongly oriented so as to create nearly linear $\text{N} - \text{O} \cdots \text{H}$ interactions. This structural aspect is supported by the experimental X-ray and neutron diffraction studies.^{11,12} The second hydration layer of water molecules is much less oriented than the first. For the first hydration layer, NH_4^+ ions were confirmed to participate in five strong hydrogen bonds with water molecules through the optimized potentials for liquid simulations set of intermolecular potential functions.³³

NO_3^- is considered to be a “structure breaker”, for NO_3^- anion with a plane structure has a strict requirement for the orientation of water molecules associated with it. Consequently, the ionic hydration of NO_3^- will strongly destroy the three-dimensional network structures of water molecules. The bonding energy of $\text{HOH} \cdots \text{OH}_2$ ($\sim 13.8\text{ kJ} \cdot \text{mol}^{-1}$) is higher than that of $\text{HOH} \cdots \text{ONO}_2$. Because the atomic weight of hydrogen is much less than that of oxygen, hydrogen bonding can effectively decrease the $\text{O} - \text{H}$ stretching frequency of water molecules as hydrogen atom donors.^{34,35}

For the water $\text{O} - \text{H}$ stretching envelope, two components

Fig.5 Fitted band contours for droplets in the region of $2500\text{--}4000\text{ cm}^{-1}$

squares dot: the experimental Raman spectra. short dot lines: six fitted spectral bands. solid lines: the sum spectra of the six fitted spectral components.

R^2 : the coefficient of determination

can be resolved by curve fittings, which are the strongly (C_1) and weakly (C_2) hydrogen-bonded components. The intensities of these two components reduce with a decrease of the RH as shown in Fig. 6. It is easy to be understood as the water evaporation process following the RH decrease.

In order to illustrate how the proportions of different hydrogen-bonded components change with RH, the integrated intensity proportions of each component in RH are reported in Fig. 7. The signature of the strongly hydrogen-bonded components was observed to decrease in intensity with the decrease in RH, but the intensity of signatures from weakly hydrogen-bonded components were observed to increase on the other hand.

It has been well known that the hydrogen-bonds in the five-molecule tetrahedral structure are strong, while those in other structures are weak.³⁶ Therefore, at RH 70%, strongly hydrogen-bonded components should mainly come from the five-molecule tetrahedral structure of water and the water in the first shell of NH_4^+ . With the evaporation of water, probability of collision of H_2O with NH_4^+ and NO_3^- increases, while the same phenomenon between the water molecules decreases resulting in a decreasing proportion of strongly hydrogen-bonded components and an increasing proportion of weak ones. By further decreasing the RH, water molecule is likely to fit into the framework formed by the NH_4^+ and NO_3^- through hydrogen bonds, i.e., its two H atoms bonded with two O atoms of NO_3^-

and its O atoms bonded with H atoms of NH_4^+ . The hydrogen bonds formed in this structure should be weak, which accounts for the further increase of proportion of weakly hydrogen-bonded components.

4 Conclusions

By using *in-situ* micro-Raman spectroscopy, we obtained high S/N spectra of the NH_4NO_3 droplets in highly concentrated states without morphology-dependent resonances (MDRs) disturbance, which were frequently encountered in EDB measurements. With the decrease of RH, there is no shift in peak position and the similar FWHM for the $\nu_1\text{-NO}_3^-$ band in NH_4NO_3 droplets. Therefore, we concluded that the formation of the ion pairs between NH_4^+ and NO_3^- has little effect on the spectra features of NO_3^- . The O—H stretching region of water was fitted by six components to reveal the interactions between ions and water molecules. From the results of fittings, we can describe the change of various water components in NH_4NO_3 droplets ranging from dilute to supersaturated states. The proportion of the strongly hydrogen-bonded components was found to decrease at the expense of weak ones by increasing the RH.

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Fig.6 Areas of two fitted band components for hydrogen bonds at various RHs

Fig.7 Proportions of two fitted band components for hydrogen bonds at various RHs

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