

Investigation of the hygroscopic properties of $\text{Ca}(\text{NO}_3)_2$ and internally mixed $\text{Ca}(\text{NO}_3)_2/\text{CaCO}_3$ particles by micro-Raman spectrometry

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Received: 9 April 2008 – Published in Atmos. Chem. Phys. Discuss.: 3 June 2008

Revised: 7 October 2008 – Accepted: 17 October 2008 – Published: 9 December 2008

Abstract. To understand and predict the role of mineral aerosol particles processed by reactive nitrogen species in the atmosphere, the hygroscopic properties of both $\text{Ca}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2$ -containing mineral particles must be well understood. Using a micro-Raman system, the hygroscopic behaviors of micro-sized individual $\text{Ca}(\text{NO}_3)_2$ and internally mixed $\text{Ca}(\text{NO}_3)_2/\text{CaCO}_3$ particles in both dehumidifying and humidifying processes were investigated systematically. In addition to accurate quantification of the dependence of water content on relative humidity (RH), significant new spectroscopic evidence related to chemical structure was also obtained to confirm the occurrence of amorphous solid state and to better understand the phase transition process. The $\text{Ca}(\text{NO}_3)_2$ particles exhibit reversible behavior in the dehumidifying and humidifying processes; they are in the state of solution droplets above 10% RH and amorphous hydrates below 7% RH, and phase transition occurs at 7–10% RH. The hygroscopic behavior of $\text{Ca}(\text{NO}_3)_2/\text{CaCO}_3$ particles is identical to that of pure $\text{Ca}(\text{NO}_3)_2$ particles, suggesting a negligible effect of the slightly soluble CaCO_3 inclusion on the hygroscopic behavior of $\text{Ca}(\text{NO}_3)_2/\text{CaCO}_3$ particles.

global scales (Dentener et al., 1996; Seinfeld et al., 2004; Tang et al., 2004). When transported through a polluted atmosphere, reactive components of mineral aerosols such as calcite and dolomite can react readily with reactive nitrogen species to yield nitrate salt products (Song and Carmichael, 2001; Krueger et al., 2003, 2004). The presence of $\text{Ca}(\text{NO}_3)_2$ in aged mineral aerosols has been verified by single-particle analysis in different areas of the world (Lee et al., 2002; Mamane and Gottlieb, 1992; Ro et al., 2005). Recently, it has been confirmed that CaCO_3 dust particles in the atmosphere can be converted completely to $\text{Ca}(\text{NO}_3)_2$ (Laskin et al., 2005a; Sullivan et al., 2007). In comparison to carbonate minerals, the $\text{Ca}(\text{NO}_3)_2$ product is very soluble and should have very different hygroscopic behavior. Because phase and water content govern the shape, size, refractive index, and reactivity of aerosol particles, the hygroscopic properties of both $\text{Ca}(\text{NO}_3)_2$ particles and $\text{Ca}(\text{NO}_3)_2$ -containing mineral particles should be investigated in detail before evaluating the effect of mineral dust particles on climate and atmospheric chemistry.

The hygroscopic behavior of $\text{Ca}(\text{NO}_3)_2$ particles has been investigated in laboratory studies using the electrodynamic balance (EDB; Tang and Fung, 1997), environmental scanning electron microscope (ESEM; Laskin et al., 2005b), and tandem differential mobility analyzer (TDMA; Gibson et al., 2006b). Whereas the EDB measurements covered both dehumidifying and humidifying processes, the other two studies focused only on the humidifying process. Although all three studies agreed that deliquescence transition of $\text{Ca}(\text{NO}_3)_2$ particles occurred between solution phase and amorphous solid phase, which has not been observed previously in bulk samples, only Tang and Fung attempted to describe the amorphous phase in terms of water content

1 Introduction

Large quantities of mineral dust particles are emitted from desert and arid regions on the earth every year (Tegen et al., 1996) and transported over long distances, influencing the climate and atmospheric chemistry on both regional and



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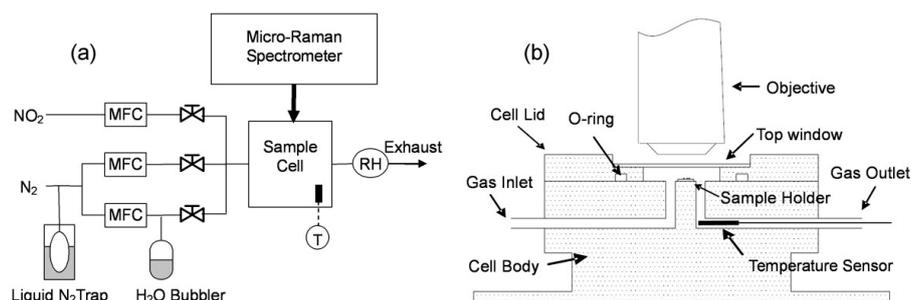


Fig. 1. Schematic diagram of the (a) experimental setup and (b) sample cell.

and morphological features. Moreover, the deliquescence transition process did not show good agreement among the three studies. EDB measurements indicated that the particle water content increased from 10% relative humidity (RH) and reached that of the corresponding supersaturated droplets at 15% RH. Using ESEM, Laskin et al. (2005b) observed initial morphological changes at 8% RH, a further volume increase at 9–10% RH, and fully developed droplet formation at 11% RH. Because only a very small change in size was measured, the TDMA study concluded that the transition occurred close to 10% RH.

The investigation of the hygroscopic properties of $\text{Ca}(\text{NO}_3)_2$ -containing mineral particles has been limited to ESEM observations. Laksin et al. (2005b) reported that individual $\text{Ca}(\text{NO}_3)_2$ particles and internally mixed $\text{Ca}(\text{NO}_3)_2/\text{CaCO}_3$ particles showed identical morphological changes from 7 to 11% RH, suggesting similar deliquescence processes. Shi et al. (2008) observed $\text{Ca}(\text{NO}_3)_2$ -containing dust particles in the aqueous phase at 15% RH, which increased in size with increasing humidity. There have been no more systematic investigations of the hygroscopic behavior of $\text{Ca}(\text{NO}_3)_2$ -containing mineral dust particles, including both phase transition and the RH dependence of the water content.

Micro-Raman spectroscopy allows in situ analyses of the dynamic processes of micro-sized individual aerosol particles and has unexplored potential in characterizing aerosol hygroscopic behavior. The concentration dependence of spontaneous Raman scattering allows the quantitative analysis of the water-to-solute molar ratio (WSR) of liquid droplets (Reid et al., 2007), at the same time, peak position of the anion Raman band is a sensitive indicator of the chemical structure of particles and hence phase transition (Widmann et al., 1998; Musick et al., 2000; Lee et al., 2008; Ling and Chan, 2008). Moreover, morphological changes can also be observed with microscope equipped with Raman spectrometer. It should be noted that micro-Raman spectrometry was combined with EDB in Tang and Fung's (1997) study of $\text{Ca}(\text{NO}_3)_2$ particles, but has been used mainly to study ion associations and hydrogen bonds in concentrated solution, rather than to characterize phase transition and hygroscopic

growth.

We used micro-Raman spectrometry as a standalone technique to investigate the hygroscopic behavior of micro-sized particles deposited on fluorinated ethylene propylene (FEP) substrate. Both pure $\text{Ca}(\text{NO}_3)_2$ particles and internally mixed $\text{Ca}(\text{NO}_3)_2/\text{CaCO}_3$ particles were studied. The particle WSR was quantified using the intensity ratio of the water band to the solute band, and new spectroscopic evidences related to structural changes were provided for phase transition and phase determination. We present the hygroscopic behavior measurements and compare them with those of previous studies and bulk thermodynamic predictions.

2 Experimental

2.1 Apparatus and procedures

The experimental setup and sample cell are illustrated in Fig. 1. The sample cell was designed with reference to the reaction cell used to study the heterogeneous reactions of individual particles by Raman spectrometry (Chen et al., 2005) and the flow cell used to study the deliquescence of organic acid particles by optical microscopy (Parsons et al., 2004). The lid and body of the cell were constructed of stainless steel. A piece of round cover glass (25 mm in diameter, 0.15 mm thick) was used as the top window and was sealed to the cell lid with high vacuum grease. The cell lid was sealed to the cell body using a fluororubber O-ring. Substrate carrying individual particles was fixed on the sample holder.

An ideal substrate for the characterization of individual aerosol particles by micro-Raman spectrometry was considered to have a flat stable surface, lack of Raman response, tolerance for high laser densities, and ease of particle recognition (Godoi et al., 2006). For the investigation of particle hygroscopic behavior, the substrate should also be strongly hydrophobic so that heterogeneous nucleation of the droplets on the substrate can be suppressed. Thus, we used 0.1 mm thick Teflon[®] FEP film (DuPont) as the substrate. Its strengths include: (1) high chemical inertness and stability to laser radiation; (2) strong hydrophobic properties and a very flat surface after annealing; (3) relatively low Raman signals, no

overlap with the strong $\nu_1\text{-NO}_3^-$ band and the OH stretching vibration envelope; (4) many sharp Raman lines providing good internal standards for the spectra calibration of aerosol particles; and (5) high contrast to particles on it as a substrate, thus facilitating microscopic observation. Of course, the FEP film has some limitations: its $\nu_1(\text{CF}_2)$ band at 734 cm^{-1} overlaps with some weak bands of salts of interest such as $\nu_4\text{-NO}_3^-$, which is sensitive to contact ion pairs in supersaturated droplets. Before use, the FEP film was annealed to a silicon wafer for ease of manipulation with reference to the method of Parsons et al. (2004). The annealing process can significantly reduce the number of defects on the surface of the FEP film.

The relative humidity in the cell was regulated by the continuous flow of a mixture of dry and humidified N₂. Ultra-high-purity nitrogen (99.999%, Beijing Huilong Changhai) was first passed through a liquid N₂ trap to remove impurities such as hydrocarbons and water vapor and was then split into two streams; one stream was humidified by bubbling through deionized water (18.2 MΩ·cm, Milli-Q, Millipore) and was then mixed with the other stream. The relative humidity in the sample cell was varied by adjusting the ratio of the flow rates of dry and humidified N₂ using mass flow controllers while maintaining a total flow rate of 200 ml/min. Internally mixed Ca(NO₃)₂/CaCO₃ particles was prepared by exposing individual CaCO₃ particles to NO₂/H₂O/N₂ mixture, which was generated by adding the third stream of NO₂ (2000 ppm; Messer) at a controlled flow rate. The relative humidity and temperature of the outflow from the sample cell were measured using a hygrometer (HMT 100; Vaisala) that had a measurement accuracy of $\pm 1.7\%$ RH and $\pm 0.2^\circ\text{C}$. Because a temperature difference between the humidity sensor and the zone of interest will cause considerable error in RH measurement, the sample cell was equipped with another small temperature sensor (Pt 100, 1/3 DIN B; Heraeus) that had an accuracy of $\pm 0.2^\circ\text{C}$. The distance from the temperature sensor to the substrate was $< 10\text{ mm}$; thus, it was safe to take the measured value as the local temperature over the substrate. Because the absolute humidity of the gas stream was constant at equilibrium, the local RH over the substrate could be calculated using the known local temperature, outflow RH, and outflow temperature.

A commercially available micro-Raman spectrometer (LabRam HR 800; Horiba Jobin Yvon) was used. This spectrometer is equipped with a microscope (Olympus BX40), a motorized x,y-stage, and a charge-coupled device (CCD) detector. The sample cell was mounted on the x,y-stage. The excitation source was an argon ion laser (Spectra Physics) operating at 514.5 nm with an output power of 25 mW. A 50×/NA0.5 long working distance objective was used. The excitation laser was focused through the top window of the sample cell onto the particle of interest. The backscattering signal, after passing through 600 g/mm grating, was detected by the CCD. Raman spectra in the range of 100–4000 cm^{-1} were obtained using an exposure time of 10 s.

The microscopic images of the particle of interest were also recorded to observe phase transition and morphological change. For NO₂-treated CaCO₃ particles, data for Raman mapping were collected over a $12\ \mu\text{m} \times 12\ \mu\text{m}$ area using a step of $2\ \mu\text{m}$ and an exposure time of 5 s. The intensity of Raman bands at $\sim 1050\ \text{cm}^{-1}$ ($\nu_1\text{-NO}_3^-$) and $\sim 1085\ \text{cm}^{-1}$ ($\nu_1\text{-CO}_3^{2-}$) were mapped to investigate the relative amount of each component.

The (NH₄)₂SO₄ (99.999%; Alfa Aesar), Ca(NO₃)₂·4H₂O (ACS, 99–103%; Riedel-de Haën), and CaCO₃ (99.999%; Alfa Aesar) were used without further purification. All of the salts were ground and then dispersed on the substrate. Three to six individual particles with diameters of 5–10 μm were selected for investigation in each experiment. During a typical experiment, the relative humidity was increased or decreased in steps of 1–10% RH. Smaller steps were used around phase transition points. Pre-experiments with different equilibrium times were performed to ensure that the particles could achieve the equilibrium state at each RH. All of the measurements were made at ambient temperatures of $25 \pm 0.5^\circ\text{C}$.

2.2 Quantification of particle WSR

The concentration dependence of spontaneous Raman scattering allows the quantitative analysis of the WSR of liquid droplets (Reid et al., 2007). Jordanov and Zellner (2006) attempted to quantify the RH dependence of WSR in levitated (NH₄)₂SO₄ particles with Raman spectroscopy, but were unsuccessful because of strong band distortion of NH₄⁺ and H₂O caused by the morphology-dependent resonances of spherical droplets. In contrast, the disturbance of morphology-dependent resonances was successfully excluded from our experiment by depositing particles on the substrate, rather than levitating them.

We quantified the WSR of Ca(NO₃)₂ droplets using the ratio of the integrated intensity of the H₂O stretching envelope (2900–3800 cm^{-1}) to that of $\nu_1\text{-NO}_3^-$ over 1010–1090 cm^{-1} . For (NH₄)₂SO₄ droplets, the stretching envelope of NH₄⁺ overlapped with that of H₂O; hence, the total intensities of these two envelopes were integrated at first, then the WSR of (NH₄)₂SO₄ droplets can be calculated according to:

$$\frac{I_{\text{NH,OH}}}{I_{\text{Sulfate}}} = \frac{A \cdot n_{\text{H}_2\text{O}} + B \cdot n_{\text{NH}_4^+}}{C \cdot n_{\text{SO}_4^{2-}}} = \frac{A}{C} \cdot \frac{n_{\text{H}_2\text{O}}}{n_{\text{SO}_4^{2-}}} + \frac{2B}{C} \quad (1)$$

where $I_{\text{NH,OH}}$ is the integrated intensity of the NH and OH stretching envelope over 2680–3780 cm^{-1} ; I_{Sulfate} is the integrated intensity of $\nu_1\text{-SO}_4^{2-}$ over 940–1020 cm^{-1} ; $n_{\text{H}_2\text{O}}$, $n_{\text{NH}_4^+}$, and $n_{\text{SO}_4^{2-}}$ are the molecular numbers of H₂O, NH₄⁺, and SO₄²⁻ in the solution, respectively; and A , B , and C are constants.

A series of bulk solutions reaching the saturation point of each salt were prepared for calibration. Because the

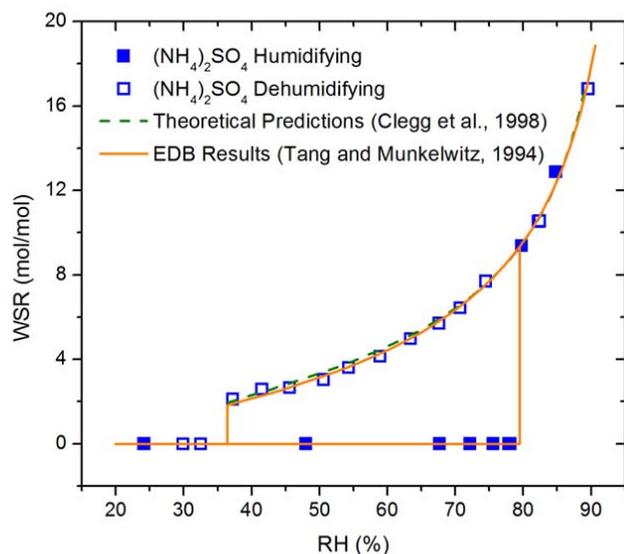


Fig. 2. Water-to-solute molar ratio (WSR) of $(\text{NH}_4)_2\text{SO}_4$ particles as a function of relative humidity (RH) in humidifying and dehumidifying processes.

$\text{Ca}(\text{NO}_3)_2$ solution can readily supersaturate even in the bulk phase (Stokes and Robinson, 1948), a supersaturated $\text{Ca}(\text{NO}_3)_2$ bulk solution with a 4:1 molar ratio of H_2O : solute was prepared by cooling the melted $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals. The calibration curves of $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{SO}_4$ were extrapolated linearly to supersaturated concentrations (as shown in Fig. A1).

2.3 Raman spectra treatment

The obtained Raman spectra were analyzed using Labspec 5 software. The $\nu_1\text{-SO}_4^{2-}$ Raman band centered at $\sim 978\text{ cm}^{-1}$ and the $\nu_1\text{-NO}_3^-$ Raman band centered at $\sim 1055\text{ cm}^{-1}$ were fit to the Gaussian-Lorentz function to obtain precise values of peak position and full width at half-maximum (FWHM). CF_2 bend vibration of the FEP substrate at 383 cm^{-1} (Hannon et al., 1969) was also fit and taken as an internal calibrator of peak position.

3 Results

3.1 Hygroscopic properties of $(\text{NH}_4)_2\text{SO}_4$ particles

The hygroscopic properties of $(\text{NH}_4)_2\text{SO}_4$ have been studied extensively and are well understood. To evaluate the performance of our experimental apparatus and approach, we first studied $(\text{NH}_4)_2\text{SO}_4$ particles. Figure 2 shows the RH dependence of the WSR of $(\text{NH}_4)_2\text{SO}_4$ in humidifying and dehumidifying processes. The quantified WSR of $(\text{NH}_4)_2\text{SO}_4$ particles droplets showed excellent agreement with that measured by Tang and Munkelwitz (1994) using EDB and that

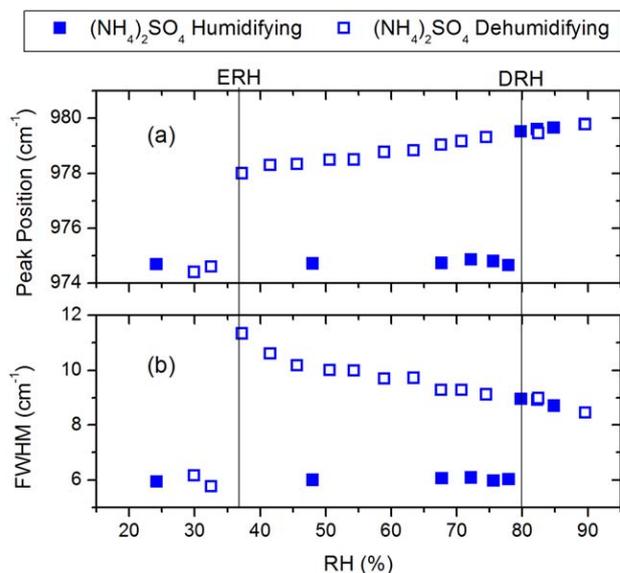


Fig. 3. The relative humidity (RH) dependence of (a) position and (b) full-width at half-maximum (FWHM) of the $\nu_1\text{-SO}_4^{2-}$ band in humidifying and dehumidifying process.

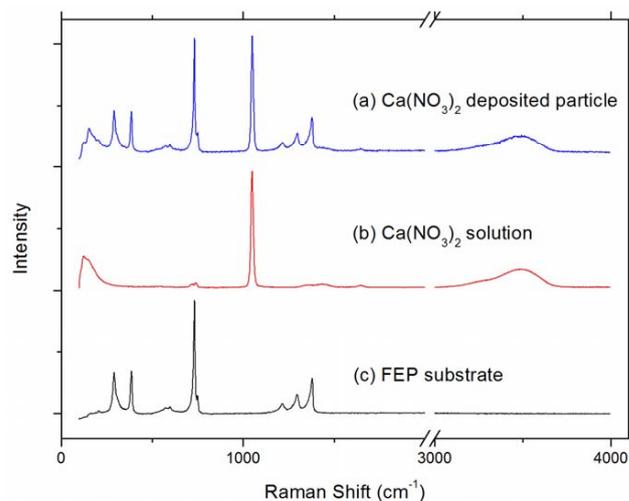


Fig. 4. Raman spectra of (a) $\text{Ca}(\text{NO}_3)_2$ particle deposited on FEP substrate, (b) $\text{Ca}(\text{NO}_3)_2$ solution and (c) FEP substrate.

predicted from thermodynamics (Clegg et al., 1998). Deliquescence and efflorescence transitions were observed at 80% RH and 37–41% RH, respectively, in good agreement with previous studies (Martin, 2000).

Figure 3 shows the changes in (a) peak position and (b) FWHM of $\nu_1\text{-SO}_4^{2-}$ band in dehumidifying and humidifying processes. In the dehumidifying process, there was only a slight red shift and broadening of $\nu_1\text{-SO}_4^{2-}$ until 37% RH, at which point $\nu_1\text{-SO}_4^{2-}$ shifted sharply from 978 cm^{-1} to 975 cm^{-1} , and its FWHM suddenly decreased from 11 cm^{-1}

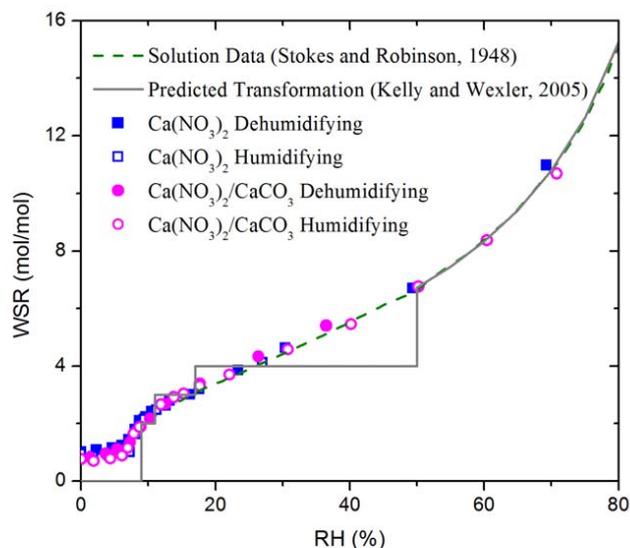


Fig. 5. Water-to-solute molar ratio (WSR) of $\text{Ca}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2/\text{CaCO}_3$ particles as a function of relative humidity (RH) in dehumidifying and humidifying processes.

to 6 cm^{-1} , corresponding to the efflorescence transition. In the humidifying process, an abrupt blue shift and broadening of the $\nu_1\text{-SO}_4^{2-}$ band were evident at 80% RH, corresponding to the deliquescence transition. The concurrence of phase transitions and distinct changes in the peak position and FWHM of $\nu_1\text{-SO}_4^{2-}$ at the same RH indicate that the phase transition can also be identified from the sharp shift of peak position and FWHM of the anion band using Raman spectra. Apparently, the sharp shift of peak position and the sudden change in FWHM of Raman spectra provide a very clear identification of the phase transition.

3.2 The hygroscopic properties of $\text{Ca}(\text{NO}_3)_2$ particles

A free NO_3^- ion has a plane structure with D_{3h} symmetry and has three fundamental Raman active vibration bands at 1049, ~ 1370 , and 718 cm^{-1} , corresponding to the in-phase symmetric stretching mode ($\nu_1\text{-NO}_3^-$), the out-of-phase stretching mode ($\nu_3\text{-NO}_3^-$), and the in-plane bending mode ($\nu_4\text{-NO}_3^-$), respectively (Nakamoto, 1986; Zhang et al., 2004). Figure 4 shows the Raman spectra of $\text{Ca}(\text{NO}_3)_2$ droplet deposited on FEP substrate, $\text{Ca}(\text{NO}_3)_2$ solution and FEP substrate. The observed Raman spectrum of deposited $\text{Ca}(\text{NO}_3)_2$ droplet is superimposition of the Raman spectrum of $\text{Ca}(\text{NO}_3)_2$ solution and that of FEP substrate, showing no MDR disturbance. Although the Raman bands of FEP substrate overlapped with $\nu_3\text{-NO}_3^-$ and $\nu_4\text{-NO}_3^-$ bands, they have no intervene to the strong $\nu_1\text{-NO}_3^-$ band and the OH stretching vibration envelope at $2900\text{--}3800\text{ cm}^{-1}$, which are necessary in the following quantitative analysis.

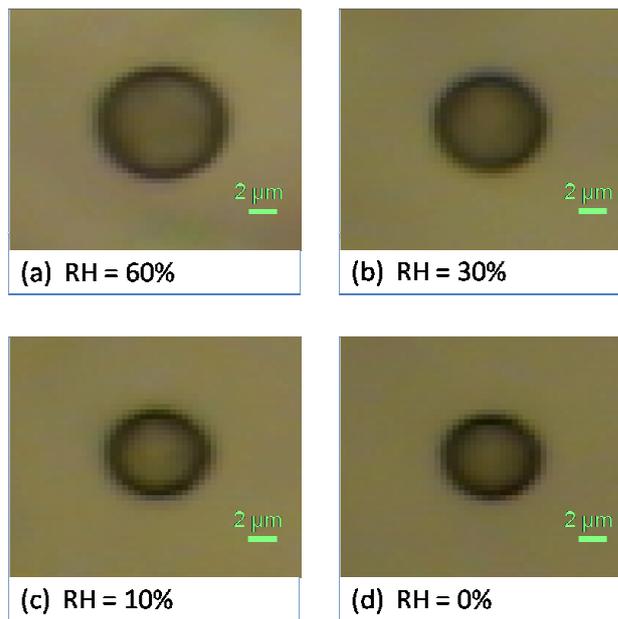


Fig. 6. Microscopic images of a typical $\text{Ca}(\text{NO}_3)_2$ particle in dehumidifying process.

Figure 5 shows the WSR of $\text{Ca}(\text{NO}_3)_2$ particles and $\text{Ca}(\text{NO}_3)_2/\text{CaCO}_3$ particles quantified by Raman spectrometry as a function of RH during dehumidifying and humidifying process. In dehumidifying process the $\text{Ca}(\text{NO}_3)_2$ droplets evaporated following the predicted curve derived from isopiestic measurements with bulk solution (Stokes and Robinson, 1948) above 11% RH. Greater decreases in WSR were observed when RH was decreased from 11% to 7%. Below 7% RH, the WSR was stable at ~ 1 without further significant changes. It indicated that phase transition occurred at 11–7% RH. Nevertheless, calcium nitrate particles have very low WSR under conditions of low humidity and hence low signal-to-noise ratio of the water envelope in Raman spectra. In addition, the calibration curve is extrapolated to high concentration. Thus, the sensitivity and accuracy of the calculated WSR under conditions of low humidity are limited. Therefore, it is impossible to conclude whether a phase transition occurs based solely on changes in WSR.

Figure 6 presents microscopic images of a typical calcium nitrate particle in dehumidifying process. As shown in Fig. 6, the $\text{Ca}(\text{NO}_3)_2$ droplets changed in size with decreasing RH, but kept spherical shape during the whole dehumidifying process, even at a RH near to zero. No crystallization was observed, this could be due to the reason that phase transition was not occurred and $\text{Ca}(\text{NO}_3)_2$ particles were in a state of highly supersaturated solutions at RH lower than 7%; or a phase transition occurs, e.g. the $\text{Ca}(\text{NO}_3)_2$ droplets had transformed to amorphous solid particles, which have a spherical shape like supersaturated droplets.

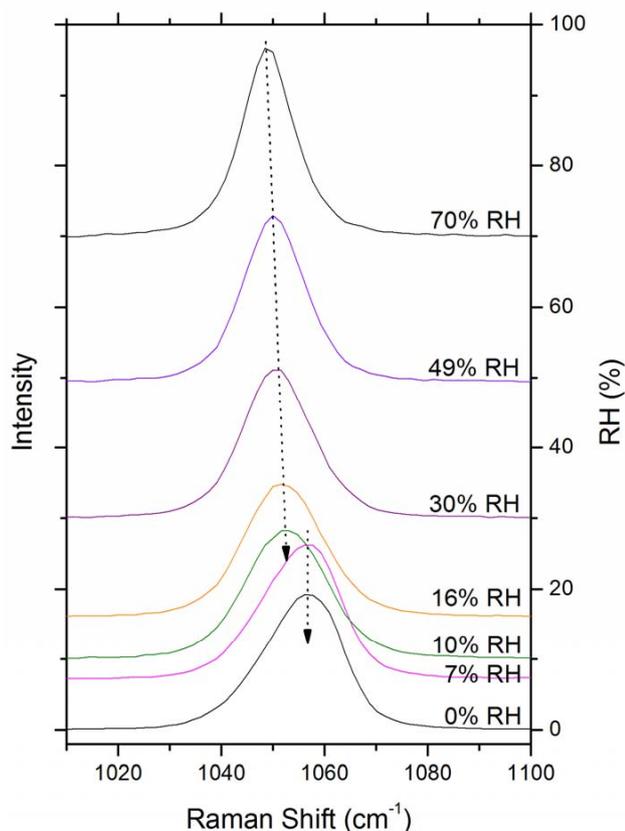


Fig. 7. $\nu_1\text{-NO}_3^-$ Raman peak of $\text{Ca}(\text{NO}_3)_2$ particles at various RH in dehumidifying process.

To find out what happened to $\text{Ca}(\text{NO}_3)_2$ droplets during the dehumidifying process, especially at RH lower than that of the likely phase transition point, we investigated the changes in position and FWHM of the $\nu_1\text{-NO}_3^-$ band in the dehumidifying process, because the symmetric stretching vibration band $\nu_1\text{-NO}_3^-$ is sensitive to structural changes in nitrate solution (Frost and James, 1982; James et al., 1982; Koussinsa and Bertin, 1991). Figure 7 shows the $\nu_1\text{-NO}_3^-$ Raman band evolution in dehumidifying process. Above 10% RH, $\nu_1\text{-NO}_3^-$ band gradually broadened and shifted to a higher frequency with decreasing RH, from 1049 cm^{-1} at 70% RH to 1053 cm^{-1} at 10% RH. From 10% RH to 7% RH, $\nu_1\text{-NO}_3^-$ band showed a much more marked shift to a higher frequency, from 1053 cm^{-1} to 1056 cm^{-1} . At the same time, its shape became a little narrower and asymmetric. Below 7% RH, both position and shape of $\nu_1\text{-NO}_3^-$ band had no further change. These band characteristics changes in dehumidifying process are more clearly shown in the curves of $\nu_1\text{-NO}_3^-$ peak position and FWHM vs. RH in Fig. 8. Concomitant with WSR evolution in the dehumidifying process, the jump in the $\nu_1\text{-NO}_3^-$ band position and FWHM at 10–7% RH and lack of further changes below 7% RH provided strong evidence that a different phase occurred below 7% RH

and that the transition from solution to this phase occurred at 10–7% RH.

After knowing that a phase transition occurred at 10–7% RH, the next step is to identify the phase of calcium nitrate particles below 7% RH. As shown in Fig. 6, calcium nitrate particles kept spherical shape in the whole dehumidifying process and did not have crystal morphology even when RH was nearly 0.0%. Besides, the hydration number of calcium nitrate particles below 7% RH was determined as one, while $\text{Ca}(\text{NO}_3)_2\cdot\text{H}_2\text{O}$ is not a stable crystal hydrate of $\text{Ca}(\text{NO}_3)_2$ (Frazier et al., 1964). Therefore, we concluded that calcium nitrate particles below 7% RH should be in amorphous solid state, rather than crystal solid state. In the following discussion, we will use dehydration to describe the phase transition of calcium nitrate from droplet to amorphous solid state.

According to band component analysis (Koussinsa and Bertin, 1991), four solvated species were resolved in the $\nu_1\text{-NO}_3^-$ of $\text{Ca}(\text{NO}_3)_2$ solution and assigned as free aquated ions NO_3^- (aq) at 1047.6 cm^{-1} , solvent-separated ion pairs $\text{NO}_3^-\cdot\text{H}_2\text{O}\cdot\text{Ca}^{2+}$ at 1050 cm^{-1} , contact ion pairs $\text{NO}_3^-\cdot\text{Ca}^{2+}$ at 1053 cm^{-1} , and ion aggregates $(\text{NO}_3^-\cdot\text{Ca}^{2+})_x$ at 1055 cm^{-1} . The gradual blue shift of $\nu_1\text{-NO}_3^-$ from 1049 cm^{-1} at 80% RH to 1053 cm^{-1} at 10% RH (Fig. 8a) corresponds to an increasing proportion of more ordered species such as contact ion pairs and ion aggregates in supersaturated solutions. Because the most ordered species $(\text{NO}_3^-\cdot\text{Ca}^{2+})_x$ in calcium nitrate solution appeared at 1055 cm^{-1} , whereas that of anhydrate nitrate appeared at 1067 cm^{-1} (Tang and Fung, 1997), the band maximized at 1056 cm^{-1} below 7% RH is indicative of a phase between these species. In addition, the narrower band width below 10% RH is an indication of nitrate ions with more fixed orientations in microenvironments than in corresponding supersaturated solution (Zhang et al., 2004). These Raman spectroscopic signatures also provides an evidence that during the dehumidifying process, $\text{Ca}(\text{NO}_3)_2$ droplets had transformed to amorphous hydrate particles at 10–7% RH.

In the humidifying process, the amorphous $\text{Ca}(\text{NO}_3)_2$ remained unchanged until $\sim 7\%$ RH, at which point its WSR began to increase and the $\nu_1\text{-NO}_3^-$ shifted to a lower frequency with increasing FWHM. Above 10% RH, both the growth of the WSR and the red shift of the $\nu_1\text{-NO}_3^-$ slowed down, and remarkably, the FWHM of the $\nu_1\text{-NO}_3^-$ begin to decrease. These observations indicate that deliquescence of amorphous $\text{Ca}(\text{NO}_3)_2$ began at $\sim 7\%$ RH and transformed to solution droplets above 10% RH. Both the curve of WSR vs. RH (Fig. 5) and the curves of peak position and FWHM of $\nu_1\text{-NO}_3^-$ vs. RH (Fig. 8) in the humidifying process showed excellent agreement to those in the dehumidifying process, indicating that the deliquescence and dehydration of calcium nitrate particles are reversible processes.

3.3 Hygroscopic properties of internally mixed $\text{Ca}(\text{NO}_3)_2/\text{CaCO}_3$ particles

Although field results of completely processed CaCO_3 particles to $\text{Ca}(\text{NO}_3)_2$ particles have been reported, in most cases $\text{Ca}(\text{NO}_3)_2$ and carbonate mineral components are internally mixed (Mamane and Gottlieb, 1992; Ro et al., 2002, 2005; Shi et al., 2008). To understand the hygroscopicity of $\text{Ca}(\text{NO}_3)_2$ -containing mineral dust particles, internally mixed $\text{Ca}(\text{NO}_3)_2/\text{CaCO}_3$ particles were prepared by exposing individual CaCO_3 particles to 100 ppm NO_2 gases for 50 min at 37% RH, and their hygroscopic behavior was studied. The CaCO_3 particle was present in irregular crystalline form before the exposure to $\text{NO}_2/\text{H}_2\text{O}/\text{N}_2$ mixture (Fig. 9a). The reacted CaCO_3 particle clearly increased in size and become round, with two distinctly different parts (Fig. 9b). Raman mapping results further confirmed that they are $\text{Ca}(\text{NO}_3)_2$ solution and CaCO_3 crystalline core (Fig. 9c).

Changes in the WSR of the internally mixed $\text{Ca}(\text{NO}_3)_2/\text{CaCO}_3$ particles in humidifying and dehumidifying processes are presented in Fig. 5. The particle WSR was quantified using a method identical to that used for pure $\text{Ca}(\text{NO}_3)_2$ particles, denoted as the water-to- $\text{Ca}(\text{NO}_3)_2$ molar ratio. The corresponding evolution of $\nu_1\text{-NO}_3^-$ band position and FWHM is also illustrated in Fig. 8a and b. From Figs. 5 and 8, we can easily see that the internally mixed $\text{Ca}(\text{NO}_3)_2/\text{CaCO}_3$ particles exhibit hygroscopic behavior identical to that of pure $\text{Ca}(\text{NO}_3)_2$ particles in both humidifying and dehumidifying processes. Their $\text{Ca}(\text{NO}_3)_2$ part is in the amorphous hydrate state below 7% RH, and both deliquescence and dehydration occur at 7–10% RH. Once in solution, the particles grow and evaporate following the curve derived from isopiestic measurements with bulk solution of calcium nitrate. In conclusion, the hygroscopic behavior of internally mixed $\text{Ca}(\text{NO}_3)_2/\text{CaCO}_3$ particles is determined by the $\text{Ca}(\text{NO}_3)_2$. The slightly soluble CaCO_3 core has a negligible effect on the phase transition and RH dependence of the particle WSR.

4 Discussion

Compared with EDB, ESEM, and TDMA, micro-Raman spectrometry provides more than one way to investigate the hygroscopic behavior of calcium nitrate particles. The WSR can be quantified by the relative intensity of Raman bands, the morphological changes can be observed with microscope equipped with Raman spectrometer, and at the same time, the $\nu_1\text{-NO}_3^-$ band position and FWHM are sensitive to structural changes. Although the RH dependence of particle WSR and morphological changes are expressions of hygroscopic properties, chemical structural changes are actually the determining factor. This factor is complementary and can help to gain a more complete understanding of the hygroscopic process. As described in Sect. 3, evidence of a phase transition was

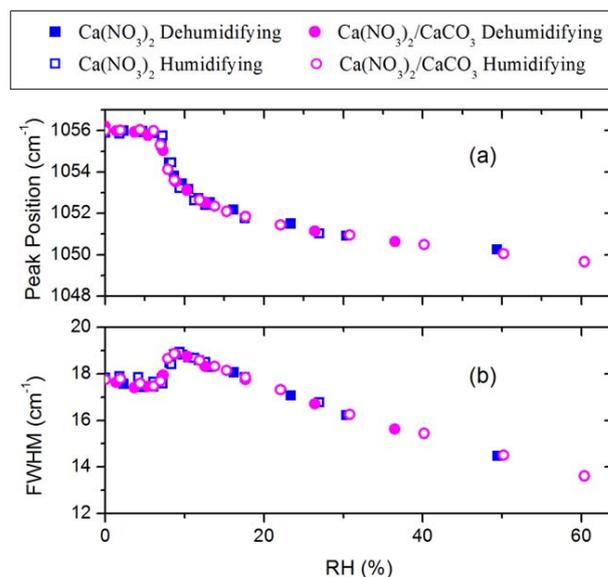


Fig. 8. Relative humidity (RH) dependence of (a) peak position and (b) full width at half-maximum (FWHM) of the $\nu_1\text{-NO}_3^-$ band of $\text{Ca}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2/\text{CaCO}_3$ particles in dehumidifying and humidifying processes.

found in the curve of WSR vs. RH at 11–7% and, more importantly and obviously, in the curve of the $\nu_1\text{-NO}_3^-$ band position and width vs. RH.

Raman spectrometry is a promising technique for quantifying the WSR of droplets that have insoluble inclusions. The most commonly used techniques to measure particle water content are EDB and TDMA, which measure the total mass and size of particles, respectively. However, if insoluble inclusions are present in a droplet, the WSR or concentration of the droplet cannot be determined by EDB or TDMA if the precise mass or size of the inclusion is unknown. In contrast, the presence of inclusions will not affect the quantification of droplet concentration with Raman spectrometry because the WSR is determined directly using the relative intensity of the solute Raman band to water Raman band. In the case of internally mixed $\text{Ca}(\text{NO}_3)_2/\text{CaCO}_3$ particles, the WSR was quantified accurately even when the ratio of $\text{Ca}(\text{NO}_3)_2$ to CaCO_3 was unknown. In the atmosphere, soluble salts or organic components are often internally mixed with insoluble soot or mineral components (Posfai et al., 1999; Vogt et al., 2003; Ro et al., 2002, 2005). Our knowledge of the physicochemical properties of these complicated aerosol particles is far from complete. Raman spectrometry may be a very useful tool with which to investigate the hygroscopic behaviors of these complicated aerosol particles.

The deliquescence process of amorphous $\text{Ca}(\text{NO}_3)_2$ particles demonstrated here can explain the morphological changes observed by ESEM (Laskin et al., 2005b) and agree with the deliquescence transition point identified by TDMA (Gibson et al., 2006b). However, our findings differ

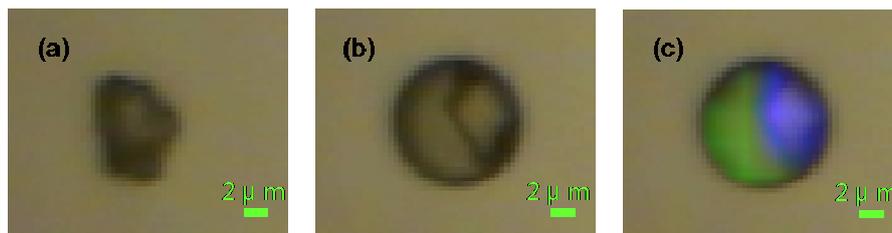


Fig. 9. Microscopic images of a typical CaCO_3 particle (a) before and (b) after exposure to NO_2 and (c) Raman mapping image after exposure to NO_2 . The green image represents the average intensity at $1020\text{--}1075\text{ cm}^{-1}$, corresponding to $\nu_1\text{-NO}_3^-$, whereas the blue image represents the average intensity at $1075\text{--}1100\text{ cm}^{-1}$, corresponding to $\nu_1\text{-CO}_3^{2-}$.

from those obtained by EDB (Tang and Fung, 1997), which showed a higher deliquescence RH of $\sim 13\%$ RH. The EDB results also indicated a different behavior in dehumidifying process that $\text{Ca}(\text{NO}_3)_2$ droplets continued to lose water upon system evacuation until in vacuum (0% RH) they turned into amorphous solid particles with a WSR of 1:1. In contrast, in our study the changes in WSR and in $\nu_1\text{-NO}_3^-$ band position and FWHM both indicated that dehydration occurred at 10–7% RH. Although there have been no other reports regarding the hygroscopic behavior of calcium nitrate particles in dehumidifying process, Gibson et al. (2006b) prepared amorphous calcium nitrate for hydration experiments by evaporating droplets in a diffusion dryer in which the RH can be reduced to only several percent; their findings support our observation that dehydration occurs above 0% RH.

The disagreement between our results and those reported by Tang and Fung (1997) may have been because of the different equilibrium time used. The gas transport in very viscous particles can hinder gas–particle equilibrium. For example, Chan et al. (2000) reported significant retardation of the water evaporation rate of highly concentrated $\text{Mg}(\text{SO}_4)_2$ droplets. We performed pre-experiments to ensure that equilibrium could be reached at each RH. It took approximately 15 min for a $\text{Ca}(\text{NO}_3)_2$ particle with several micrometers in diameter to attain an equilibrium state at 7–10% RH. However, the equilibrium time that is normally used in hygroscopic experiments is on the order of a few seconds (Chan and Chan, 2005), which is too short for sufficient mass transfer for viscous supersaturated $\text{Ca}(\text{NO}_3)_2$ droplets. The equilibrium time was not explicitly stated by Tang and Fung’s paper, if inadequate equilibrium time was used in their experiment, the observed RHs of dehydration and deliquescence would have been underestimated and overestimated, respectively.

Crystallographic studies indicate that anhydrate calcium nitrate and its di-, tri-, and tetrahydrates occur as solid phases (Frazier et al., 1964). The corresponding stable form in different ranges of RH has been predicted by bulk thermodynamics (Kelly and Wexler, 2005). The tetrahydrate is expected to be in the solid phase in equilibrium with the $\text{Ca}(\text{NO}_3)_2$ saturated solution with a transition point at

50% RH (Fig. 5). Solid–solid phase transitions are expected below 50% RH, including transformation from tetrahydrate to trihydrate at 17% RH, from trihydrate to dehydrate at 11% RH, and from dehydrate to anhydrate at 9% RH. However, instead of transforming into the tetrahydrate at 50% RH as expected, $\text{Ca}(\text{NO}_3)_2$ droplets continuously lost water until they were highly supersaturated at 10% RH, after which they began to convert to a solid metastable phase, i.e. amorphous hydrate, which was not predicted by bulk thermodynamics. Hysteresis of efflorescence is very common for microparticles and is usually explained by the absence of heterogeneous nucleation (Martin, 2000). However, kinetic limitations cannot explain these observations completely. As shown in Sect. 3, the internally mixed $\text{Ca}(\text{NO}_3)_2/\text{CaCO}_3$ droplets transformed to amorphous particles at the same relative humidity as pure $\text{Ca}(\text{NO}_3)_2$ particles, although there are large CaCO_3 nuclei in these particles that can invariably induce heterogeneous nucleation. Further investigations are required to determine why the calcium nitrate solution on dust particles does not transform to its stable tetrahydrate. Nevertheless, these observations indicate the very different behavior and mechanism of phase transition in microparticles than those in bulk samples. Thus, it is inappropriate to infer the phase transition behavior of $\text{Ca}(\text{NO}_3)_2$ microparticles from their bulk properties. In fact, in addition to the very different properties of calcium nitrate particles as compared with bulk samples, Tang et al. (1995) also reported discrepancies between microparticle hygroscopic behavior and bulk thermodynamic predictions for some other salts. The role of atmospheric aerosol particles, therefore, cannot always be assessed solely based on bulk properties. Care should be taken when using bulk thermodynamic calculations to infer aerosol properties; some experiments for the study of aerosol properties using bulk samples may lead to erroneous results.

It’s interesting to note that the dehydration process of $\text{Ca}(\text{NO}_3)_2$ microparticles showed no hysteresis effect when compared to the deliquescence process, while the efflorescence process of microparticles in general had hysteresis effect when compared to the deliquescence process. The hysteresis effect between deliquescence and efflorescence processes is usually explained by kinetic inhibition of crit-

ical germ nucleation in efflorescence process. However, when phase transition experiences gentler rearrangement of atoms, e.g. displacive transformation (Martin, 2000), it does not require the formation of a critical germ, and hence is not kinetically inhibited. The Raman spectrum of amorphous $\text{Ca}(\text{NO}_3)_2$ particles is only slightly different to that of $\text{Ca}(\text{NO}_3)_2$ supersaturated droplets, suggesting they may have similar chemical properties. Thus, the phase transition from $\text{Ca}(\text{NO}_3)_2$ solution droplets to amorphous particles is probably not kinetically inhibited and it may explain the absence of hysteresis effect between the dehydration and deliquescence processes of $\text{Ca}(\text{NO}_3)_2$ microparticles.

5 Conclusions and atmospheric implications

Our results indicate that the micro-Raman technique is a powerful tool with which to investigate the hygroscopic behavior of individual $\text{Ca}(\text{NO}_3)_2$ and internally mixed $\text{Ca}(\text{NO}_3)_2/\text{CaCO}_3$ particles. The RH dependence of the WSR was quantified accurately for $\text{Ca}(\text{NO}_3)_2$ particles with and without CaCO_3 inclusion. Significant new spectroscopic evidence related to chemical structure was provided to identify phase transition. Thus, the hygroscopic behavior of $\text{Ca}(\text{NO}_3)_2$ particles was characterized in more detail and more reliably than had been possible previously, and the hygroscopic properties of internally mixed $\text{Ca}(\text{NO}_3)_2/\text{CaCO}_3$ particles were investigated systematically for the first time.

Individual $\text{Ca}(\text{NO}_3)_2$ particles showed reversible behaviors in humidifying and dehumidifying process. The $\text{Ca}(\text{NO}_3)_2$ particles were in the form of solution droplets above 10% RH and amorphous hydrates below 7% RH; phase transitions occurred between 7–10% RH. The hygroscopic behavior of internally mixed $\text{Ca}(\text{NO}_3)_2/\text{CaCO}_3$ particles was fully controlled by the $\text{Ca}(\text{NO}_3)_2$ and was identical to that of pure $\text{Ca}(\text{NO}_3)_2$ particles. That is, the slightly soluble CaCO_3 core has a negligible effect on phase transition and the RH dependence of the particle water content.

Typical ambient relative humidity is in the range of 20–90%; thus, calcium nitrate particles or calcium nitrate products on mineral dust particles are usually in the solution state in the atmosphere, whereas the original mineral particles are normally insoluble. In another word, when dust particles transported in the atmosphere were aged by reactive nitrogen species, their water content and hygroscopic properties would be significantly increased. Possible impacts of the enhanced hygroscopicity on the optical properties of mineral particles, including single scattering albedo, CCN activities, etc., have been discussed in related papers (Vlasenko et al., 2006; Gibson et al., 2006a, b). While these studies provided a preliminary understanding on how atmospheric aging of mineral dust may impact climate, a more comprehensive and quantitative assessment of the impact is necessary. Besides, the hygroscopic nature of calcium nitrate product can also affect the reaction extent and mechanism of mineral particles

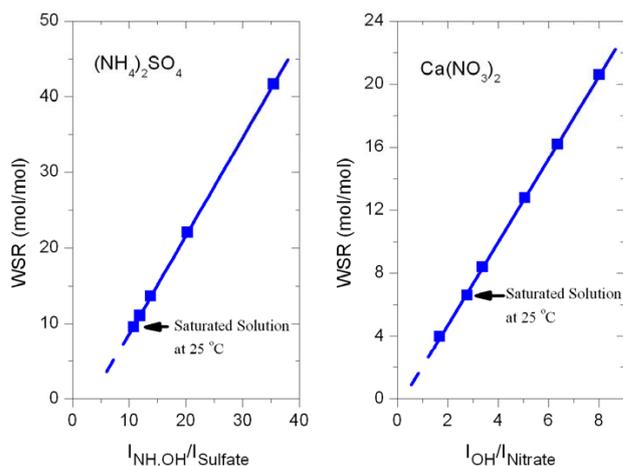


Fig. A1. Calibration curves of $(\text{NH}_4)_2\text{SO}_4$ and $\text{Ca}(\text{NO}_3)_2$.

Calibration curves for the water-to-solute molar ratio (WSR) of $(\text{NH}_4)_2\text{SO}_4$ and $\text{Ca}(\text{NO}_3)_2$ droplets. The solid line shows the linear fit of the experimental data; the broken line shows the extrapolation to supersaturated concentration.

with reactive nitrogen species. A number of laboratory studies have confirmed that the heterogeneous reaction of calcite and HNO_3 is not limited to the particle surface above the deliquesce RH of amorphous $\text{Ca}(\text{NO}_3)_2$, and that its uptake coefficient is dependent on relative humidity (Laskin et al., 2005b; Vlasenko et al., 2006; Prince et al., 2007). When a calcium nitrate solution film forms, the interface where the heterogeneous reaction takes place should change from gas-solid to gas-solution-solid. However, detailed reaction mechanism and related kinetic parameters are not reported in literatures. Thus, systematical investigation of the reaction mechanisms should be carried out in the future research.

Acknowledgements. This work was supported by the National Basic Research Priorities Program (Grant No. 2002CB410802) and National Natural Science Foundation of China (Grant No. 40490265, 20637020).

Edited by: S. Martin

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