Atmos. Chem. Phys. Discuss., 8, S6310–S6319, 2008
www.atmos-chem-phys-discuss.net/8/S6310/2008/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Investigation of the hygroscopic properties of Ca$(NO_3)_2$ and internally mixed Ca$(NO_3)_2$/CaCO_3 particles by micro-Raman spectrometry" *by* Y. J. Liu et al.

Y. J. Liu et al.

Received and published: 25 August 2008

1. Comparison of spectra obtained from bulk samples and deposited particles (seen in the 2nd comment) and spectra showing the changes of v1-NO3- Raman band with RH are included in the revised manuscript.

2. We agree that it would be better to do the calibration using particles directly. However, due to fast mass transfer of micro-sized droplets used in our experiments with ambient water vapor, it is difficult to prepare and maintain a deposited particle with controlled water content. The comparison of bulk phase and micro-sized droplet spectra have been made using both single droplet and bulk sample measurements in many studies (Fung and Tang, 1992; Vehring and Schweiger, 1992; Reid et al., 2007), these

studies all found that droplet and bulk samples of the same chemical composition gave equivalent Raman spectra.

Our results showed that the spectra of calcium nitrate particle is very similar to that of calcium nitrate bulk solution, and FEP substrate had no interference to v1-NO3- Raman band and OH stretching envelope. Therefore, the calibration of droplets concentration can be done based on bulk samples, and it is much easier to prepare bulk solutions of certain concentrations. In our manuscript, we reported that we were able to accurately quantify the water content of ammonium sulfate particle. This further proves that calibration of droplet concentration based on bulk results is suitable method.

3. The spectra resolution of our spectrometer is 1.5 cm-1 using the 600g/mm grating, obtained from the FWHM of the Neon light line. The peaks were fitted using the Gaussian-Lorentzian function, and reproducible results were obtained using the same curve fit parameters on a given curve. We made 20 trial runs and found the standard deviation of Raman band position was less than 0.1 cm-1, this suggests the precision of the band positions of our instrument is about 0.1 cm-1.

Similar methods can be found in many references which studied the stress of semiconductor material by the Raman peaks changes (De Wolf, 1996a, b; Gogotsi et al., 1999). Besides, CF2 bend vibration of the FEP substrate at 383 cm-1 was used as an internal calibrator of peak position in the present work, this helped to further improve the measurement accuracy (P10604, line 20).

4. As described in Line 14, P10603, we have examined the equilibrium time of Ca(NO3)2 particles under different RH. A particle was first kept at a RH for a time long enough to reach equilibrium, its Raman spectra was recorded every 5 minutes to check if the WSR has reached to a constant. And then RH was changed by adjusting the flow rates of water vapor and N2 in the system, the RH and Raman spectra of the particle were recorded every few minutes. The equilibrium time can be roughly estimated based on how the curve of the water-to-solute band intensity ratio followed the

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change of the RH curve.

Our results showed, when the RH of sample cell changed from 22 to 18 percent in 2 min, the intensity ratio also reached to a constant in 2 min, this suggests a short equilibrium time, i.e., once the RH of sample cell reached to a constant, the water content of the particle reached to a constant almost at the same time. The same behavior has been observed at RH higher final 18 percent. This can be explained by the fact that, in our study, the particles were small, about 5-10 um, and hence mass transfer is fast. However, at low RH, when the RH of the sample cell was adjusted from 11 to 9 percent in 3 min, the intensity ratio took 10-15 min to reach equilibrium. The same behavior has been observed at final RH lower than 15 percent. Therefore, in our study, when the final RH in the sample cell was higher than 15 percent, we recorded Raman spectra 5 min after RH was stabilized; when the final RH in the sample cell was lower than 15 percent, we recorded Raman spectra 15 min after RH was stabilized.

5. The work of Jordanov and Zellner (2006) was unsuccessful for hygroscopic measurements, due to the influence of morphological dependence resonance on WSR measurement. Their work was cited when we introduced particle-water-content quantification method with Raman spectrometry (P10603, line 20).

In Chan's papers (Zhang and Chan, 2002; Zhang et al., 2004), WSR was measured with EDB, instead of using Raman spectrometry, and their works will be cited in our revised manuscript. In our study, we establish a method to quantify WSR of a particle solely based Raman intensity and its correlation with WSR, this is different from method measuring WSR with EDB, as reported in Chan's papers. We agreed with C. Chan that MDR were minimal when particle size was sufficiently large. However, MDR can not be ignored in our study, where 5-10 um particles was studied, this is the same size range of the mineral particles in the atmosphere.

6. The use of peak shifts and FWHM in Raman spectra of aerosol particles for investigation of phase transformation (Lee et al., 2008; Ling and Chan, 2008) is cited in the

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revised manuscript. Many thanks for providing the information.

7. The hydration number of amorphous hydrate is 1, as shown in Fig. 4.

8. In our study, there are a number of particles exhibiting very clear shell-core structure; to avoid confusion, we will delete the shell description of the particles in the revised manuscript.

Reaction conditions: internally mixed Ca(NO3)2/CaCO3 particles were prepared by exposing individual CaCO3 particles to 100 ppm NO2 gases at 37 percent RH for 50 min. It will be specified in the revised manuscript.

Raman Mapping Condition: Raman spectra were collected over a 12 um x 12 um area using a step of 2 um and an exposure time of 5 s. The intensity of Raman bands at 1050 cm-1 (v1-NO3-) and 1085 cm-1 (v1-CO32-) were mapped to investigate the relative amount of each component. (as written in P10603, line 5)

9. The WSR of calcium nitrate/carbonate mixed particle is obtained using the ratio of the integrated intensity of the H2O stretching envelope (2900-3800 cm-1) to that of v1-NO3- , namely water-to-Ca(NO3)2 Raman band intensity ratio. Using the calibration based on bulk sample of calcium nitrate, we can get the water-to-Ca(NO3)2 molar ratio. As shown in Fig. 4, when RH is the same, the water-to-Ca(NO3)2 molar ratio of calcium nitrate/carbonate mixed particle is identical to that of pure calcium nitrate particle. Therefore, we concluded that the hygroscopic behavior of internally mixed Ca(NO3)2/CaCO3 particles was determined by solely Ca(NO3)2. Onasch et al. (2000) have studied the hygroscopic properties of mixed (NH4)2SO4/CaCO3 particles. They also found the slight soluble CaCO3 had a negligible effect on the concentration dependent water activities.

10. We agreed that the wording on P10609 was not clear with respect to what we wanted to express. For the dehydration process of Ca(NO3)2 particles, there are two questions: if phase transition does occur, and if it does, what the new phase is.

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To find the answer for the first question, we used evidences from WSR variation, microscopic images, and v1-NO3- spectra changes. What finally convinced us that a phase transition had occurred at 7-10 percent RH is the changes of band position and FWHM of v1-NO3-. v1-NO3- is sensitive to structural changes in nitrate solution; the discontinuous changes of v1-NO3- band position and width are indicative of chemical structural changes.

If the particles kept in supersaturated solution states below 10 percent RH, as suggested by C. Chan, we should observe a steady and continuous change of v1-NO3- band position and FWHM, with the decrease of RH. However, in our study we found a discontinuity of the change of v1-NO3- band position, when RH was lower than 10 percent, as shown Fig. 6 in the manuscript. When RH was higher than 10 percent, v1-NO3- gradually became broader with decreasing RH and shifted to a higher frequency, from 1049 cm-1 at 70 percent RH to 1053 cm-1 at 10 percent RH. From 10 to 7 percent RH, v1-NO3- showed a much more significant shift to a higher frequency, from 1053 cm-1 to 1056 cm-1. At the same time, its FWHM showed a slight reduction instead of further increasing (Fig. 6b). Below 7 percent RH, both the position and FWHM of the v1-NO3- band remained unchanged. The discontinuity of v1-NO3- band position and FWHM vs. RH at 10-7 percent RH and lack of further changes below 7 percent RH provided strong evidence that a different phase occurred below 7 percent RH and that the transition from solution to this phase occurred at 10-7 percent RH.

The second question is what the new phase is. We agree with C. Chen that the peak position analysis alone could not provide a solid evidence for new phase identification, evidences from other methods, such as morphological observation with microscopic image, WSR measurements, and XRD observation of the particles are necessary. From Fig. 5 in the present manuscript, we could see that calcium nitrate particles below 7 percent RH kept spherical shape, and did not have crystal morphology. Besides, the hydration number of the new phase is 1, and Ca(NO3)2.H2O is not one of the stable crystal hydrates of Ca(NO3)2 (Frazier et al., 1964). Therefore, we believed

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that calcium nitrate particles below 7 percent RH were in amorphous solid state. Tang and Fung also gave similar conclusion (Tang and Fung, 1997). Of course, to fully understand the structure of the new phase, more information from XRD is needed.

11. We think that the phrase "water content" used in the text caused this confusion. We intended to say that micro-Raman analysis can determine water-to-solute ratio (WSR) of a particle by just measuring the intensity of the solute Raman band and that of water Raman band without knowing the mass or size of insoluble inclusion in the droplets. We have changed the "water content" to "WSR" in the revised manuscript.

EDB/TDMA measurements determine the changes in mass/size of particles. To determine the WSR of a droplet, one has to know the mass/size of the insoluble inclusion. For example, in the study of Onasch et al. (2000), CaCO3 was the insoluble inclusion of the mixed (NH4)2SO4/CaCO3 particles. To determine the mass of CaCO3, they have to dissolve (NH4)2SO4 into a water solution saturated with calcium carbonate, at first. A supermicron dilute droplet from the solution was then trapped by EDB. Volume of the droplet was measured with a microscope. The mass of calcium carbonate in the droplet is then determined from the solubility of calcium carbonate in the mixed salt solution and the volume of the trapped particle. Through droplet evaporation in dry N2 environment, a micro-sized (NH4)2SO4/CaCO3 crystalline particle was finally prepared.

12. In our paper, we did not report the results of Ca(NO3)2 tetrahydrate solid. The grounded calcium nitrate tetrahydrate particles were used to prepare micro-sized calcium nitrate droplets by increasing the RH to high value. Our focus was the dehydration process of calcium nitrate droplets and the following hydration process. The hydration of calcium nitrate tetrahydrate particles was not discussed.

13. Our description of calcium nitrate solution as viscous at low RH is based on two facts: The first is the chemical structure of Ca(NO3)2 droplets based on NO3- Raman spectra, which is similar to C. Chan's work. According to band component analysis

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(Koussinsa and Bertin, 1991), four solvated species were resolved in the v1-NO3- of Ca(NO3)2 solution and assigned as free aquated ions NO3- (aq) at 1047.6 cm-1, solvent-separated ion pairs NO3-.H2O.Ca2+ at 1050 cm-1, contact ion pairs NO3-.Ca2+ at 1053 cm-1, and ion aggregates (NO3-.Ca2+)x at 1055 cm-1. The gradual blue shift of v1-NO3- from 1049 cm-1 at 80 percent RH to 1053 cm-1 at 10 percent RH (Fig. 6a) corresponds to an increasing proportion of more ordered species such as contact ion pairs and ion aggregates in supersaturated solutions (P10607, line 6).

The second is the equilibrium time at different RH range for calcium nitrate particles, as explained in the response to question 4. For calcium nitrate particles above 15percent RH and ammonium sulfate particles in the whole RH range, we found almost no time lag between the curves of sample cell RH and the curves of water-to-solute Raman intensity ratio of the particles, when the RH was adjusted. However, for calcium nitrate particles below 15 percent RH, when the ratio of water-to-solute intensity of the particles reached to a constant, it was about 10 min behind sample cell RH stabilized. This is a very clear evidence that there is mass transfer limitation for calcium nitrate particles at low RH, but no limitation for calcium nitrate particles at higher RH and for ammonium sulfate particles in the whole RH range. This is consistent with our suggestion that calcium nitrate solution was viscous at low RH.

14. It is interesting to note that the amorphous Ca(NO3)2 particles did not transform to more stable state at low RH, even if we kept them under RH near to zero for 24 hours. Tang and Fung (1997) had also reported that in vacuum Ca(NO3)2 droplets turned into an amorphous particle containing 1 H2O/solute, and that during evaporation most Sr(NO3)2 droplets also became amorphous solid that "consistently and tenaciously held about 1 H2O/solute even in vacuum".

15. We agree that reactive uptakes and reaction mechanisms of CaCO3 dust particles with other chemical species are possible, but formation of nitrate can significantly enhance its hygroscopicity and further change the reaction limit and mechanism, as discussed in the implication part.

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In the paper of Ro et al. (2005), four "Asian Dust" samples collected in Korea were characterized by single-particle technique. There were two samples containing reacted CaCO3 species. CaCO3 reacted with NOx and SO2 to a similar extent in the March-01 sample (6 vs. 7), and nitrate-containing particles outnumber sulfate-containing particles for the May-01 sample (128 vs. 36). However, in the paper of Ro et al. (2005), there is no statement nor evidence that "SO2 uptake by CaCO3 and seasalt particles were more significant than the NO2 uptake by CaCO3".

16. Many thanks for the suggestion. We included the relevant parts in the introduction section. We also improved the conclusions and implications by drawing conclusions more specifically from the results of the current manuscript.

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