

Interactive comment on “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” by Y. J. Liu et al.

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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 - Y. J. Liu, T. Zhu, D. F. Zhao, and Z. F. Zhang

This paper presents hygroscopic measurements of calcium nitrate and mixed calcium nitrate/calcium carbonate particles deposited on a substrate based on micro-Raman analysis. This technique combines the use of a hydrophobic substrate for studying supersaturated droplets (Parsons et al., cited in the manuscript) and the use of Micro-Raman spectroscopic characterization of deposited particles (e.g., Wu and Chan,

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2008). The results presented are interesting. However, there are a number of important issues in the discussion and the analysis of the results that need further work. A major revision is required.

1. It is rather unusual to have a paper based on spectroscopic analysis without showing a single spectrum. Spectra showing the changes of the peaks would be useful.

2. Figure A1: The calibration was done based on bulk samples for calcium nitrate. Should calibrations be performed using the actual calcium nitrate and calcium nitrate/carbonate particles like those examined for hygroscopic growth in the experiments? Comparisons of spectra obtained from bulk samples and deposited particles would be useful to show the equivalency.

3. P.10602: What was the spectral resolution in the measurements? In the peak position analysis of Figures 3 and 6, very high data resolution is required.

4. P.10603: It is not clear if sufficient time was allowed for equilibrium in the experiment. At the later discussion the authors stated that about 15 min was spent at low RH. How did the authors confirm that 15 min was enough to attain the equilibrium state, especially at higher RH?

5. P.10603: The discussion of the use of Raman spectroscopy for hygroscopic measurements citing the "unsuccessful attempts" by Jordanov and Zellner (2006) may not present the most accurate picture on the current state of research on the topic to the readers. In fact, we have correlated Raman peak intensities of levitated particles and WSR in a number of papers including some cited in the manuscript. The effects of morphological dependence resonance peaks are minimal when we used sufficiently large particles. See next comment.

6. P.10605: We have recently shown the use of peak shifts and FWHM in Raman spectra of aerosol particles for investigation of phase transformation of both inorganics and organics (Lee et al., 2008; Ling and Chan, 2007 and 2008). These can be useful

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references for introducing the approach.

7. P.10607: On the "amorphous hydrate particle", what is its number of hydration?

8. P.10608: I don't see a shell structure from Figure 7. Figure 7c shows that calcium nitrate (green) is in the left part and calcium carbonate (blue) is in the right part of the image, according to the color scale given. However, the evidence and explanation for the characterization was absent. Information on the reaction conditions and Raman mapping was also unclear.

9. P.10608: It is not clear how the WSR for the mixed particle is obtained. This is a critical issue that needs to be explicitly clarified, especially in light of the fact that the composition of the mixed particle is not known, which is also a point that the authors highlighted as novel. With the information presented in the manuscript, it is difficult for me to have an appreciation on the claim that the WSR of the mixed particles and pure calcium nitrate particles are similar. Intuitively, I would think they are different.

10. P.10609: I wish I can be as confident as the authors are on the formation of amorphous solid at low RH, without knowing its chemical identity of the particle at low RH or any info on its XRD pattern. The evidence provided in the paper is relatively weak: a. Hygroscopic measurement could not confirm the phase transition due to the limited sensitivity of water signal at low RH as mentioned in Section 3.2. b. Refer to the peak position analysis, the amorphous phase transformation was verified by considering the blue shift of nitrate stretching peak from 1049 cm^{-1} at 70%RH to 1056 cm^{-1} at 7% RH. However, the explanation of most ordered species in $\text{Ca}(\text{NO}_3)_2$ solution appeared at 1055 cm^{-1} , whereas that of anhydrate nitrate appeared at 1067 cm^{-1} , the band maximized at 1056 cm^{-1} below 7% is indicative of a phase between these species is confusing. It is hard to identify the amorphous solid transformation from supersaturated droplet by just a 1 cm^{-1} shifting. c. The FWHM analysis also cannot provide a strong evidence for the amorphous solid transformation. Together with the peak position, I can only confirm that the particle became more saturated upon evaporation and

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was in a supersaturated state at 7-10%RH and the state of particle remain unchanged even the RH was decreased to zero. d. Again, the particle images in figure 5 were actually in low quality that it is not possible to distinguish between supersaturated droplet and amorphous states.

11. P.10609: The statements between line 16 and 25 need to be clarified. The statements seem to suggest the micro-Raman analysis determines the absolute amount of water and it is definitely not true, as based on the results presented in this paper. EDB/TDMA measurements determine total mass/size but more precisely, it is often the changes in mass/size that are used in hygroscopic measurements. There are many EDB and TDMA hygroscopic measurements involving insoluble or less soluble species in which the particles contain a solid.

12. Tang and Fung (1997) have found different DRH values for anhydrous $\text{Ca}(\text{NO}_3)_2$ and amorphous form. The grounded $\text{Ca}(\text{NO}_3)_2$ tetrahydrate solid were used for investigation as mentioned in P.10603 but the deliquescence RH of the initial solid was not reported. The deliquescence RH of the solid is probably different from the amorphous $\text{Ca}(\text{NO}_3)_2$.

13. P.10610: Mass transfer limitation can be important and hinder the equilibrium water uptake measurements for some species such as MgSO_4 (as cited) but not for all salts including common salts such as NaCl or ammonium sulfate. Strong contact ion pairs of Mg and sulfate were found based on the spectral changes of the sulfate peak in concentrated MgSO_4 solutions. The authors described calcium nitrate solution as viscous. Any further information on the viscosity of the solution? Chan and Chan (2005) discussed TDMA measurements which have a short residence time (equilibration time). However, EDB measurements such as Tang and Fung (1997) do not have such limitations. The authors quote a number of 10-15 minutes for the calcium nitrate particles. It is useful to quote numbers for NaCl or AS for a direct comparison and evaluation of mass transfer limitations in their experiments.

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14. The current results do not provide information on the thermodynamic stability of the amorphous $\text{Ca}(\text{NO}_3)_2$. If amorphous $\text{Ca}(\text{NO}_3)_2$ exists, it would be in a metastable form. Transformation to the more stable solid phase should be considered and various deliquescence properties are expected.

15. P.10612: The authors emphasized the implication of $\text{Ca}(\text{NO}_3)_2$ formation on CaCO_3 dust which enhances the heterogeneous reaction due to its highly hygroscopic behavior. However, it should also be mentioned that reactive uptakes and reaction mechanisms with other chemical species are possible. Ro et al. (2005) have reported that the SO_2 uptake by CaCO_3 and seasalt particles were more significant than the NO_2 uptake than CaCO_3 .

16. Conclusions and Implications can be improved by drawing conclusions more specifically from the results of the current manuscript. Some information appears to be more appropriate to be put in the introduction. For example, it is well known that thermodynamic behaviors of aerosol particles undergoing supersaturated states are different from those predicted by bulk thermodynamics. Similarly, the role of heterogeneous reactions and subsequent water uptake of particles has been well documented in a number of papers, for example, by Laskin and co-workers.

References:

Wu, H. B.; Chan, C. K. Effects of potassium nitrate on the solid phase transitions of ammonium nitrate particles. *Atmospheric Environment*. 2008, 42(2), 313-322.

Lee, A. K. Y.; Ling, T. Y.; Chan, C. K. Understanding hygroscopic growth and phase transformation of aerosols using single particle Raman spectroscopy in an electrodynamic balance. *Faraday Discussions*. 2008, 137, 245-263.

Ling, T. Y.; Chan, C. K. Formation and Transformation of Metastable Double Salts from the Crystallization of Mixed Ammonium Nitrate and Ammonium Sulfate Particles. *Environmental Science & Technology*. 2007, 41(23), 8077-8083.

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Ling, T. Y.; Chan C. K. Partial crystallization and deliquescence of particles containing ammonium sulfate and dicarboxylic acids. *Journal of Geophysical Research*. 2008, 113, D14205, doi:10.1029/2008JD009779

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