

Interactive comment on “Depositional ice nucleation on solid ammonium sulfate and glutaric acid particles” by K. J. Baustian et al.

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Received and published: 1 December 2009

The authors would like to thank Referee #2 for his/her careful review and helpful comments. We provide a response to each of the points or questions raised:

1) This study employs a commercially available Linkam cryo-stage which is purged by a humidified flow of N₂ (g) at 1 atm. Inside the sample compartment of this cryo-stage supply tubes for N₂ (l) are located to cool the silver block (sample area) to low temperatures. If water vapor is introduced to this compartment which contains the ammonium sulfate and glutaric acid particles water vapor will always condense at the coldest point in that system (i.e. supply tubes at liquid N₂ temperature) and, thus, leading to a water vapor gradient within that compartment (e. g. similar to the Bergeron-Findeisen effect). This can significantly affect the desired relative humidity (RH) above the investigated

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particles within the compartment. High flows of water vapor into the cell may help but this would also increase the ice buildup continuously affecting the dew point of the humidified flow.

The Referee's point is well taken and the authors agree, it would be a grievous oversight if the authors had used the Linkam cell for experimentation with no modification. Indeed, using the unmodified cell resulted in visible ice forming on the LN2 lines. The authors have taken great care to adequately insulate the LN2 supply lines to ensure that the silver block is the coldest point within the cell. These modifications were not obvious and an extensive period of trial and error testing was required before an adequate insulation solution was achieved. We have carefully wrapped the supply lines with several layers of polystyrene foam and covered the entire area in a thick coating of low vapor pressure putty to fill any small cracks in the insulation. Given the modifications described, the coldest point in our cell is the top of the silver block, on which the sample rests. After these modifications were made no ice was observed visibly condensing within the cell. To further test our insulation system we compared vapor pressure measurements at the inlet and outlet of the cell at 223 K. If a large water vapor sink did exist in our cell, such as ice forming on the LN2 pipes, we would expect to find a lower vapor pressure at the cell outlet when compared to the inlet side. During this experiment the cell was cooled to 223 K and water vapor was added until the vapor pressure was near ice saturation with respect to the temperature of the silver block. Thus, under these conditions, ice would not form on the silver block, but would form on the much colder liquid nitrogen lines if they were not properly insulated. The hygrometer was first used to measure the vapor pressure at the outlet of the cell. Next, all else remaining unchanged, a piece of stainless steel tubing was inserted to by-pass the cell, effectively allowing us to measure the amount of water that was being introduced at the cell inlet. When the inlet and outlet vapor pressures were compared, there was only a 0.39% difference in the two vapor pressure measurements. Thus, there could be no large water vapor sink in the cell. A similar description has been added to the experimental section of our final manuscript to clarify this point.

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2) Besides of this crucial issue, during the ice nucleation experiments not the entire particle sample is visible. If ice forms on particles outside the visible area, RH above the observed particles is most likely not the one adjusted for similar reasons given above. This may be indirectly corroborated by the ice nucleation experiments conducted on blank substrates. For temperatures between 214 and 235 K it is stated that ice nucleation occurred for saturation ratios between 2.33 and 1.6 which are significantly above water saturation at these temperatures. From this it can be concluded that water vapor was depleted by another sink within the Linkam cell and artificially high supersaturations were needed to induce ice nucleation. To circumvent these issues usually such “ice nucleation flow systems” (particles on cold surface and humidified flow above) possess very small sample areas to ensure complete visibility of the experiment and to ensure uniform RH fields (see e. g. Eastwood et al., JGR, 2008). Here, the deliquescence experiments of NaCl are successful since for temperatures above -30°C saturation with respect to ice is not achieved and thus water vapor condenses as liquid onto the hygroscopic particles. For these reason the presented deliquescence experiments cannot ascertain the correct RH fields within the Linkam cell at lower temperatures. Having said this, can the authors prove experimentally and/or theoretically the correct RH above the particles. E. g. by repeating these experiments with highly efficient ice nuclei such as mineral dust particles (e. g. kaolinite etc.) or by other means?

The Referee implies that ice saturation ratios above water saturation, such as those observed during experiments using blank substrates, are not possible and from this infers that we must have a sink for water vapor in our cell that is skewing our measurements. The authors do not believe that ice saturation ratios observed for blank substrates are erroneous for several reasons. First, as discussed at length in #1, we do not believe that there is a water vapor sink in the cell based on the insulation system we installed. Second, the authors agree that such high Sice values would not be possible in the ambient atmosphere where liquid water droplets are present. However, in the case of our experimental setup, ice saturation ratios well above water saturation

are possible as long as no liquid water is present to incite homogeneous ice formation. High ice saturation ratios, much higher than those needed for homogeneous nucleation of pure water, have been previously observed in Knudson cell experiments in the absence of liquid water (Trainer et al., J. Phys. Chem. C, 2009).

Instead we believe that ice formation on the blank hydrophobic substrates did not occur until high saturation ratios because no particles were available to catalyze ice formation. It is also significant to note that during ice nucleation experiments, in every case ice formation was observed to occur on a particle.

The authors chose to examine depositional ice nucleation on solid ammonium sulfate particles in order to validate our experimental technique. Ammonium sulfate was an ideal candidate because, as noted in our manuscript and acknowledged by both Referees', several groups have previously performed ice nucleation experiments on solid ammonium sulfate particles. Our results are in good agreement with all other available studies and expand the temperature range of data available. Thus, the authors feel that the ammonium sulfate results validate this technique.

3) Page 20953, line 18: Within the manuscript it is not mentioned when lasers with wavelength of 532 nm or 780 nm have been employed. Please indicate the excitation wavelength used.

For these experiments only the laser of wavelength 532nm was employed. This has been clarified in the final version of our manuscript.

4) Page 20955, line 19, 20: Hung et al. used FTIR for detection of the ferroelectric phase transition of ammonium sulfate. Knopf and Koop used a Raman microscope to detect the ferroelectric phase transition in ammonium sulfate particles applying it as a calibration point in their heterogeneous ice nucleation study similar to this study.

The authors thank the Referee for pointing out this reference that was overlooked. It has been added to the final manuscript.

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5) Page 20957, line 2-4: Later in the manuscript it is mentioned that there are mixed particles, i.e. ammonium sulfate containing glutaric acid. 1. Please explain how those mixed particles formed? 2. Can you distinguish between particles which may lie on top of each other, e. g. a 300 nm ammonium sulfate particle on top of a 10 micrometer glutaric acid particle or vice versa?

Point 1. During experiments involving external mixtures of ammonium sulfate and glutaric acid, the majority of particles present are pure ammonium sulfate or glutaric acid particles. However, as mentioned, in several cases we observed particles of ammonium sulfate containing a small amount of glutaric acid as well. The authors can only speculate on the presence of these internally mixed or coated particles. Glutaric acid particles are dried at $\sim 0\%$ RH for a substantial amount of time before ammonium sulfate particles are impacted onto the same substrate. However, it seems possible that some of the time this process results in the impaction of an ammonium sulfate particle inside of a glutaric acid particle, which would look like an internally mixed particle.

Point 2. Using the experimental methods employed in this study we should be able to tell the difference between two particles of average size that are lying on top of one another. The focal point of the laser beam determines the spectrum you obtain from a particle. Therefore, as you adjust the focus you would expect to see spectra of both glutaric acid and ammonium sulfate, but at different places in the z-focus. In the specific example the referee gives (A 10 micron glutaric acid particle with a 300 nm ammonium sulfate particle inside) we would not expect to detect scattering from the ammonium sulfate particle. At 0.3 microns the ammonium sulfate particle would be below our limit of detection even if it was not encased in glutaric acid.

6) Page 20957, line 13: The dew point is changed by up to 2 degrees C per min. How does this compare to atmospheric conditions?

The authors have decided to omit this reference to dew point ramp rate in the final manuscript. This rate is not very relevant because we increase water vapor levels in a

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step-wise manner. After each time the RH is increased the dew point is allowed to rise and then settle before adding more water vapor.

7) Page 20957, last line: a reference for pre-activation is missing (e. g. Knopf and Koop, Wallace and Hobbs, or older studies)

Thank you for the suggestion, a reference has been added.

8) Page 20963, line 1: The ice nucleation experiments in which Abbatt and coworkers were involved applied an IR flow tube to study ice nucleation on ammonium sulfate. Only few experiments referred to in Abbatt et al. 2006 were conducted in a cloud chamber.

The authors appreciate this comment and have clarified this explanation in the final manuscript.

9) Page 20964, line 13: 1. What is the atmospheric significance of perchlorate? 2. How do you know that its deliquescence point will be reached before ice nucleation occurs at such low temperatures? Please give a reference for this case.

1. Perchlorate salts occur naturally in our environment and are also produced through manufacturing. They are injected directly into the atmosphere from sources such as rocket exhaust and fireworks and there is new evidence that there may be additional atmospheric source(s) related to nitrate and ozone chemistry. Because of their high solubility perchlorate salts are efficiently scavenged in precipitation and are therefore found in high concentrations in soil and groundwater.

2. In preliminary water uptake studies performed using the Raman setup we have observed deliquescence of sodium and magnesium perchlorate particles and no ice formation at temperatures between 263 K and 223 K (R. Gough, Investigating the Deliquescence Relative Humidity of Perchlorate Salts as a Function of Temperature: Implications for Mars, In prep). There are currently no published low-temperature water uptake studies similar to this, however, the deliquescence and efflorescence RH's

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we observe at cold temperature are similar to those observed by Zhao et al, PCCP, 2005 and Zhang et al., CSB, 2005 at room temperature. Preliminary results suggest the water uptake properties of perchlorate salts are independent of temperature, and can therefore be used as further evidence supporting the accuracy of our temperature calibration and RH measurements at low temperatures.

10) Figure caption of fig. 5: Does the illumination of the particles with laser light during the ice nucleation studies affect the particle temperature due to absorption of the rather dark particles?

What is perceived as a dark color in the microscope images is an artifact that comes from observing the particles through a bright-light microscope. In reality these ammonium sulfate crystals are pure white and not absorbing, but highly reflective. Particles are inspected using the optical microscope before and after being probed with the laser in order to identify any damage or changes that occur. No changes or damage have been observed. Further, we observe no changes in the Raman spectra for repeated measurements of the same particle. We do note, however, that for strongly absorbing particles not discussed here, the Raman laser can lead to damage. For these cases, damage is usually apparent in both the optical images and in the Raman spectra. The lack of changes in the optical images or Raman spectra of ammonium sulfate or glutaric acid gives us confidence that we are not damaging the particles discussed. In any case, the laser would not affect the results of our ice nucleation studies because the laser is not used until the end of each experiment when we probe the IN particle after ice sublimation.

Technical Corrections:

11) Page 20950, line 111: Change “that” to “than”

12) Page 20963: line 28: missing comma after “glutaric acid”

13) Figure 3: Please indicate the vibration bands of the Raman spectrum. Also, which

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vibration bands indicate the para- to ferroelectric phase transition? Please make a mark and give corresponding wave number.

14) Figure 5: Please add Raman vibration bands for both ammonium sulfate, glutaric acid, and ice. 218.08 K can be rounded to first digit after comma.

All of the technical corrections have been changed in the final manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 20949, 2009.

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