

Response to Anonymous Referee #1

We thank the reviewer for providing helpful comments. Our responses to these comments are given in **bold** below. Changes we will make to the manuscript are discussed at the end of these comments.

Major Comments:

1. Although electrospray ionization produces cluster distributions far from equilibrium, the ions will quickly (milliseconds or less) revert to a distribution with only semi-stable clusters present, mainly due to collisions and charge transfer with other molecules. At reasonable temperature and RH the resulting cluster distribution should be close to the one expected in the atmosphere. On the other hand, measurements made in vacuum, may be distorted in comparison with ambient cluster formation. RH will be practically zero and the temperature is not very well-defined. As the authors point out the atmospheric implications as one of the major results of the paper, I feel more discussion is needed on the representativeness of these measurements, at least in chapter 4: Atmospheric implications. Naturally, clusters cannot be measured by any other means than mass spectrometry, which requires vacuum, and the possible perturbations caused by this should always be kept in mind. This paper discusses reactions occurring over time periods up to 40s in vacuum, and the authors should therefore be extra careful in the interpretation.

The reviewer is correct in noting that temperature is not well-defined in this experiment and RH is zero. However, we feel the presence of vacuum does not significantly alter our conclusions. With regard to temperature / internal energy, we performed an experiment in our previous work where we held positively-charged ions in the ion cyclotron resonance (ICR) cell and exposed them to a low pressure of unreactive argon gas or to no gas whatsoever [Bzdek et al., 2010a]. Exposure time was varied in order to investigate the time-dependent stability of these clusters. Cluster distributions did not change with increasing residence time in the ICR cell, indicating that the ions initially trapped in the ICR cell are sufficiently stable that they do not undergo ancillary reactions in addition to those due to exposure to a reactive gas. With regard to the role of RH, the reviewer is correct that by this method the role of water is not investigated. However, amine substitution for ammonia in these clusters is driven by the large difference in gas phase basicity between the two molecules. Solvation and cation-anion binding effects also play a role but the magnitude is much smaller. Therefore, it is unlikely that the presence of water in the cluster will make substitution less efficient.

2. One specific point that is mentioned in the paper is the instability of dimethylammonium sulfate clusters upon mass selection, but this is not discussed any further. If the substitution of DMA for NH₃ in the clusters is so highly favorable, why are the DMA clusters not more stable than the ones with NH₃? I feel this should be discussed in a bit more detail, as it may relate directly to the conclusions of the paper.

The ions that are ultimately trapped in the ICR cell result from larger, metastable charged clusters produced by electrospray that dissociate as they travel into and through the mass spectrometer. We know this because the m/z we select with the quadrupole does not always correspond to the ion that is ultimately trapped in the ICR cell. When this happens, the selected m/z is always greater than the detected m/z , which means metastable cluster dissociation has occurred [Bzdek *et al.*, 2010b]. The identity of the cluster that is ultimately trapped in the cell depends on the pathways and energetics of dissociation, which are not well understood at this point in time. The end result is that not all ions observed in a broadband mass spectrum can be efficiently isolated for reactivity studies.

3. Possibly relating the above point, figure 1b shows a similar amount of the sulfuric acid tetramer as of the dimer, but no data is presented on the DMA or NH₃ addition to the tetramer. This might have been a very interesting cluster as DMA substitutes NH₃ and adds 3 additional molecules onto the pentamer, but does not react at all with the trimer. Was the tetramer also not stable upon mass selection, just as the DMA sulfate clusters? And again, what does that mean?

We were unable to efficiently isolate this cluster in the ICR cell. See response to #2, above.

4. Page 10, line 17-18. The authors state that NH₃ did not add onto the (H₂SO₄)₅(NH₃)₁ cluster, but in figure 1b (H₂SO₄)₅(NH₃)₂ is of the same order as (H₂SO₄)₆(NH₃)₂. Can the authors comment on this? Is this perhaps due to the difference between ambient and vacuum conditions, or do the authors have some other explanation?

As discussed above (see response to #2), the clusters ultimately trapped in the ICR cell are the decay products of metastable ions produced by electrospray. It is not surprising that a small amount of this product is produced. However, the signal intensity for (H₂SO₄)₅(NH₃)₂ (by our notation: [(NH₄)₂(HSO₄)₃(H₂SO₄)₂]⁺ at m/z 521) is much lower than that for (H₂SO₄)₆(NH₃)₂ (by our notation: [(NH₄)₂(HSO₄)₃(H₂SO₄)₃]⁺ at m/z 619), suggesting that the ion at m/z 521 is less favored.

Minor Comments:

1. Where does the sodium contamination come from? Is the sodium source also present during the ammonium sulfate production? If it is, then what is the reason for sodium not substituting NH_3 ? A benefit of all the recently developed MS techniques to measure small clusters is that it has become evident that contaminations of some sort are almost always present, although most earlier studies have assumed them to be zero. It is understandable that the authors do not wish to have an extensive discussion on the contaminations of their experiment, but I would like to believe that this community has come far enough to understand that contaminations are practically always present in one form or another, and it is better to discuss them openly (and perhaps even learn from them) than to sweep them under the rug or just ignore them (to make it clear, I am not suggesting this was done in this paper). In this case, if sodium substitutes DMA in the clusters, does that suggest that sodium, although not atmospherically relevant in this context, would enhance cluster stabilization of H_2SO_4 even better than DMA?

Sodium is a ubiquitous contaminant and can arise from many sources, including glassware. It is not unusual to observe sodium adducts in electrospray ionization mass spectra. We do observe some sodium-substituted clusters upon electrospray of an ammonium sulfate solution, although they are much less intense. The benefit of our experimental method is that we can usually isolate a specific ion for reaction. Since we isolate sodium-free clusters for study, the presence of sodium in the broadband spectrum does not influence the results. We did not investigate reactions of sodium-containing clusters because they are not atmospherically relevant, at least with regard to new particle formation.

2. Why does DMA never add to a cluster with NH_3 , but always starts by substituting all NH_3 and then adding to the DMA cluster? Do the authors have any ideas on this?

With regard to kinetics, the rate for substitution is always faster than the rate for addition. However, the thermodynamics have not been investigated thoroughly. One would expect, however, that substitution would be more entropically favorable than addition, which may result in a more negative Gibbs free energy change for the reaction.

3. Could the residence time between the ESI and MS be varied? Did/would this change the measured distribution presented in figures 1 and 2, or are they already “close enough” to equilibrium and thus not changed remarkably?

Residence time between ESI and MS could not be varied. However, adjusting the length of time ions were held in the cell without undergoing any reaction did not change the cluster distribution, suggesting that the ions trapped in the ICR cell are “close enough” to their steady-state distribution.

4. Page 10 line 14. This should be Table 2.

We will adjust the revised manuscript accordingly.

5. Page 11, lines 8-13. Please move the Junninen reference earlier in the sentence, and possibly add “in this work” to the end. The sentence now suggests that Junninen et al made the electrospray of ammonium sulfate, but I assume the authors are referring to their own data?

We agree and will adjust the revised manuscript accordingly.

6. Without taking a stand in the debate of the importance of ion-induced nucleation, somewhere in chapter 4 I feel there should be a sentence or two also on the implications of these results on the neutral clusters (if any). As it is, nucleation is discussed, as are ion clusters, but neutral clusters are not mentioned at all, even though they might be much more important. This should at least be acknowledged somewhere. The major nucleating compound is commonly believed to be H_2SO_4 , with some stabilization needed from base compounds. How does the fact that amines seem to produce more stable clusters impact on the further growth of the particles? Is the more stable DMA cluster more likely to grow further by H_2SO_4 addition than the one with NH_3 , or has the cluster become so stable that H_2SO_4 no longer attaches as readily to it as to a NH_3 cluster? In the latter case amines would thus inhibit particle formation. Could the experimental setup be used to study also growth by H_2SO_4 to different clusters by bleeding in H_2SO_4 ? I do not suggest that the authors do this for this paper, only state that these results might also be interesting.

Positive ions are quite different from negative ions in both composition and reaction pathways. Whether neutral cluster composition is more similar to positive ion composition, negative ion composition, or neither is an area that requires further investigation with different experimental methods. With regard to the addition of H_2SO_4 , this experiment was not feasible in our setup. However, understanding the kinetics and thermodynamics of H_2SO_4 addition to clusters in this size range would be quite interesting.

Changes the authors will make to the manuscript:

In the revised manuscript, we will add additional paragraphs at the end of Section 3.1 (Electrospray of ammonium sulfate and dimethylammonium sulfate solutions) and at the end of Section 4 (Atmospheric implications) to address the concerns of the reviewer. Specifically, we address the role of vacuum and RH (major comment #1), cluster stability (major comments #1, 2, 3, and 4), sodium contamination (minor comment #1), and the

neutral cluster composition (minor comment #6). Additionally, we will correct the typographical errors noted by the reviewer (minor comments #4 and 5).

References:

Bzdek, B. R., et al. (2010a), Amine exchange into ammonium bisulfate and ammonium nitrate nuclei, *Atmos. Chem. Phys.*, *10*(8), 3495-3503.

Bzdek, B. R., et al. (2010b), Size-dependent reactions of ammonium bisulfate clusters with dimethylamine, *J. Phys. Chem. A*, *114*(43), 11638-11644.