Review of: “On the composition of ammonia-sulfuric acid clusters during aerosol particle formation”
by Schobesberger et al., *Atmospheric Chemistry and Physics Discussions*, **2014**, *14*, 13413-13464

This manuscript presents results concerning ammonia-sulfuric acid nucleation experiments in the CLOUD chamber along with some comparisons to ambient measurements in Hyytiälä, Finland, and to computational modeling by the ACDC model. Cluster composition measurements were accomplished using the APi-TOF instrument. The main contribution of this manuscript to our understanding of new particle formation is that the composition of ammonia-sulfuric acid clusters depends primarily on the ratio of gas phase ammonia and sulfuric acid concentrations. A secondary dependence relates to temperature. This manuscript is within the scope of *Atmospheric Chemistry and Physics* and may eventually be publishable. However, several areas must first be addressed.

Major Comments

1. One area where this manuscript falls short relates to putting the measurements into a broader context with respect to existing literature. Several studies have examined the composition, structure, and reactivity of these clusters, and the authors need to do a better job of relating their work to previous work by others. A few areas where this was most evident are:
    a. Page 13417, lines 26-28: Computational modeling on charged clusters has addressed clusters up to 11 sulfuric acids, not simply eight molecules.[1] Additionally, a computational paper addressing uncharged clusters was just published and may be useful to the authors in the discussion of charged vs. uncharged clusters.[2] Moreover, several other experimental manuscripts address the structure of clusters that may be relevant to this work.[3-9] The authors need to better relate their measurements to these manuscripts. Note in particular that negatively charged clusters would be expected to have less ammonia because most sulfuric acid-bisulfate ion protons are tied up in hydrogen bonding with each other.
    b. Page 13418, lines 20-22: The authors should also reference ambient measurements by the cluster Chemical Ionization Mass Spectrometer (cluster CIMS).[10]
    c. Page 13432, lines 12-16: The observation that amines incorporate into these clusters despite concentrations below instrumental detection limits is remarkable. This observation is also explained by the kinetics of amine-ammonia exchange, which has been reported extensively.[11-14] The authors should place these observations from CLOUD into context based upon the existing literature. This comment is also relevant to discussions on page 13434, lines 11-14, and page 13434, lines 24-26.
2. The APi-TOF mass spectra are taken every 5 sec (page 13423, line 5). What is the timescale for ion-molecule collisions in the chamber? This would be important to know. If the measured mass spectrum is the result of a large number of collisions between charged and uncharged clusters, the measured composition could be impacted by charge transfer from one population to

the other. Therefore, the measured composition probably better represents the thermodynamic end state rather than any dynamic process along specific growth pathways (e.g. for positively charged or negatively charged clusters only). If the cluster distribution is impacted by conversion from charged to uncharged clusters, this might impact the interpretation, since growth pathways for positively, negatively, and uncharged clusters may be energetically different, even if they are growing by 1:1 addition of ammonia and sulfuric acid.

3. The reported $\Delta m/\Delta n$ values are averages over the entire mass spectrum. Have the authors done any analysis regarding how $\Delta m/\Delta n$ may change as a function of cluster size in one particular spectrum or how $\Delta m/\Delta n$ may change for a particular cluster as $[NH_3]/[H_2SO_4]$ or temperature are varied? Not addressing this on a single-cluster basis seems like a missed opportunity in this manuscript, since the APi-TOF provides highly resolved chemical composition information for each cluster. Averaging over an entire spectrum reduces the chemical information that can be extracted. For example, Fig. 7A and 7B show mass defect plots for positive and negative ions, respectively. Examination of each plot shows that cluster acidity changes substantially with cluster size. In both cases, larger clusters are more neutralized (contain more base) than smaller clusters. Can the authors provide any insight into this observation based on their measurements? Do these observations provide any insight as to where ammonium sulfate may become the favored composition over ammonium bisulfate? How do these trends change with gas phase composition and temperature? It appears much more could be gained through examination of the $[NH_3]/[H_2SO_4]$ and temperature dependencies on a single cluster level than through an averaged description over several tens of clusters that are already resolved by the APi-TOF instrument.

4. In the comparison of the CLOUD data to the ACDC modeling (page 13439, lines 7-29) the authors state that the model does a good job of predicting measured composition trends. However, in Fig. 5A, the model (of neutral clusters) is clearly overpredicting $\Delta m/\Delta n$ relative to the measurement (charged clusters). Wouldn’t this suggest that neutrals are growing differently than charged clusters?

5. The authors postulate about the effect of water, which was not measured and was not included in the ACDC model. In particular, they postulate on page 13439, lines 25-29, that water molecules may be able to compete with ammonia to serve as the critical base stabilizing sulfuric acid. Where is the justification for this argument? How is this reconciled with computational and ion spectroscopy measurements which indicate that interactions between water and ammonia or water and sulfuric acid are substantially weaker than interactions between ammonia and sulfuric acid?[2-9] The authors need to better address this area.

Minor Comments

1. The title implies that the study of uncharged clusters constitutes a major component of the manuscript. However, this manuscript mainly addresses charged clusters. The title should be revised to indicate that charged clusters are the main topic.

2. The authors frequently use both pptv and molecules/cm^3 to describe gas phase concentrations. For example, on page 13415, line 11, and on 13441, lines 17-18, both units are used. It would be helpful to the reader if the same units for both sulfuric acid and ammonia concentrations were used, especially since a main goal of this paper is explore the dependence of cluster composition on the ratio of the two gas phase compounds. There are benefits to using both units, so perhaps the authors could provide concentrations using both units.

3. Figure 1 does not appear to add anything substantial to the manuscript. Is there anything particularly important about how sampling from the chamber was accomplished that merits inclusion of this figure?

4. Page 14323, lines 26-27: LOPAP and PTR-MS are not defined in the text. The authors should confirm that all acronyms are defined somewhere in the text of the manuscript.

5. Section 3.1: Begin this section with a discussion of the reaction conditions. In general, the authors tended not to state up front for a given experiment what the reaction conditions were (temperature, relative humidity, gas phase concentrations, etc.).

6. Page 13430, lines 11-19: Based on the discussion here, the authors appear to suggest that an activation barrier may exist for uptake of ammonia to the clusters. Indeed, later on in the text (page 13436, lines 20-28) the authors discuss this in more detail. However, this discussion of the temperature dependence of cluster composition might merit more discussion.

References

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