Response to reviewers' comments (received 17 June and 2 July 2014)

20 September 2014

Journal: ACP
Title: "On the composition of ammonia-sulfuric acid clusters during aerosol particle formation"
MS No.: acp-2014-353
MS Type: Research Article
Authors: S. Schobesberger et al.

We thank the reviewers for their comments.
We have substantially revised the manuscript, in many parts extended, and we think that all referee comments have been covered adequately. As a result, the paper has gained in quality and in completeness, in particular as much of what has been added includes comparisons of our results with previously published studies, which we had previously somewhat neglected.
Our point-by-point replies are given below (blue Times New Roman font) following each of the reviewers' comments, which are repeated in full (black Arial font). Reproduced text from the revised manuscript is set in black and green bold Calibri font, green marking changes or additions.

****

Anonymous referee #1:

Schobesberger and authors have written a paper detailing their findings on the composition of ion clusters in a sulfuric acid/water/ammonia environment. The authors describe the key instrument (APi-ToF) used to measure the composition of cluster and particle ions formed by ion-induced nucleation. The main conclusion of the paper is that composition of these ions is dependent on the [NH3]/[H2SO4]. At high ratios above 10, the number of NH3 molecules added for each H2SO4 was between 1 and 1.4. They go on and compare these experimental results to computational chemistry and cluster modeling to conclude that neutral clusters are formed in a similar sequence of acid-base reactions. The conclusions of this paper fall within the scope of ACP and do contribute to knowledge; however, their overall conclusion is a bit far reaching as they extrapolate their ion measurements to neutral cluster dynamics. Furthermore, they do not compare their conclusions about neutral cluster dynamics to conclusions of previously measured neutral clusters of sulfuric acid and ammonia. Work needs to be done to address the comments below before it can be considered for publication.

Main Comments:

Ion vs. Neutral Clusters

Title: "On the composition of ammonia-sulfuric acid clusters during aerosol particle formation" This title is a bit misleading. The clusters that were observed in this study are ions and not electrically neutral clusters. Consider adding the word "ions" in the title to remove confusion.

The experimental observations of clusters in this study were indeed ions. Modeling results were obtained also for electrically neutral clusters, but we acknowledge that those are only secondary in importance here. As the referee suggests, we will add the word "ion" in the title to remove confusion:

"On the composition of ammonia-sulfuric acid ion clusters during aerosol particle formation".

Related to that and the further comments below, we also formulated a part of the 3rd paragraph in section 5 (conclusions) still more carefully:

The model simulations of neutral clusters and APi-TOF measurements of charged clusters are consistent and in good agreement with each other for cases of $[NH_3]/[H_2SO_4] > 10$. Under these conditions, also electrically neutral NH_3-H_2SO_4 clusters are likely to grow principally by adding, on average, 1 to 1.4 NH_3 molecules for each added H_2SO_4 molecule.

Correspondingly, a sentence in the abstract was softened:

Our results also suggest that ~~yet unobservable~~ electrically neutral NH_3-H_2SO_4 clusters, unobservable in this study, ~~grow~~ have generally the same ~~mechanism~~ composition as ionic clusters~~, particularly~~ for [NH3]/[H2SO4] > 10.

Line 15 pg 13417: Ammonia in neutral clusters was measured in Hanson and Eisele (2002). Their work is closely related to the work presented in this paper. Including a more detailed discussion between this work and theirs would the help the reader understand how this work relates to previous work.

We acknowledge that, in the strive for clarity and brevity, we had indeed neglected the comparison of our results with a number of closely related previous works. We aimed at extending our manuscript accordingly in the revised version. For the introduction, the corresponding additions were made mainly in the 3rd paragraph:

[…] The addition of NH3 vapor to the system of H_2O and H_2SO_4 vapors leads to a large enhancement of the rates of aerosol particle formation (Ball et al., 1999; Kirkby et al., 2011). On the molecular scale, investigations of negatively charged H_2SO_4 and NH_3-H_2SO_4 clusters obtained by ionizing neutral clusters showed that the NH_3-containing clusters can form more readily (specifically at warmer temperatures) than pure H_2SO_4 clusters (Eisele and Hanson, 2000; Hanson and Eisele, 2002). Theoretical ab-initio studies […]

More detailed discussion of how our work compares to the closely related earlier works by Hanson and Eisele was added in the discussion section (see replies below for details).

Line 1-5, pg 13420: The effects of various amine stabilization on neutral sulfuric acid dimers are shown in Jen et al. (2014) (recently published in JGR). This study looks at how hundreds pptv of ammonia and a few pptv of amines affect the observed sulfuric acid dimer concentration. This paper and Chen et al. (2012) both describe the acidbase reactions that are concluded upon in this paper. It seems appropriate that these papers should be compared to this work in order to determine if neutral clusters behave similarly to ion clusters.

We thank the referee for making us aware of the recent publication by Jen et al. (2014). That paper and Chen et al. (2012) conclude that neutral sulfuric acid dimer clusters can be stabilized by NH_3 as well as by amines. Also in our study, the neutral dimers from the ACDC simulation are stabilized mostly by one NH_3 molecule, i.e. $NH_3 \bullet (H_2SO_4)_2$ (as shown now in the new Fig. 4). The situation appears different for the measured ion clusters: The cation dimers mostly contain two NH_3 ligands, i.e. $(NH_3)_2 \bullet (H_2SO_4)_2 \bullet NH_4^+$, whereas the anion dimer and trimer contain no NH_3 at all, i.e. $H_2SO_4 \bullet HSO_4^-$ and $(H_2SO_4)_2 \bullet HSO_4^-$. However, all these dimers are consistent with the maintained conclusion that acid-base reactions are the binding mechanism: The cation dimer takes on one additional NH_3 more easily than the neutral dimer due to the presence of the ammonium ion NH_4^+, i.e. the conjugate acid of ammonia, which, for this purpose, acts as a weak acid. On the other hand, the anion dimer and trimer cannot take on any NH_3 due to the presence of the bisulfate ion HSO_4^-, i.e. the conjugate base of sulfuric acid, which acts as a stronger base than NH_3 (see e.g. Ortega et al., 2014).

To improve how this conclusion is presented, in particular to also refer previous works (and using the new Fig. 4 in the process – this new figure is discussed separately below), we modified the 2nd paragraph of section 4.5, split it and add to the new 2nd paragraph:

The resulting simulated neutral clusters at steady-state had an average NH_3 content of up to $m = n$, dependent on $[NH_3]/[H_2SO_4]$ (Fig. 4). Note here certain differences in the composition when comparing the combined results for neutral, positive and negative clusters, in particular for of the smallest ones. E.g., the neutral dimers ($n = 2$) are stabilized mostly by one NH_3 ligand, i.e. $NH_3 \bullet (H_2SO_4)_2$, which agrees with previous experimental and theoretical findings on the stabilization of the neutral dimer by NH_3 or other bases (e.g., Ortega et al., 2014; Jen et al., 2014). On the other hand, the positive dimers mostly contain two NH_3 ligands, i.e. $(NH_3)_2 \bullet (H_2SO_4)_2 \bullet NH_4^+$, whereas the anion dimer and trimer ($n = 1, 2$), on the other hand, contain no NH_3 at all, i.e. $H_2SO_4 \bullet HSO_4^-$ and $(H_2SO_4)_2 \bullet HSO_4^-$. Still, all these compositions are consistent with our assertion that acid-base reactions are the underlying binding mechanism: The ammonium ion NH_4^+ (the conjugate acid of ammonia) acts as a weak acid, accommodating one additional NH_3 compared to the neutral dimer. On the other hand, the anion dimer and trimer cannot accommodate any NH_3 due to the presence of the bisulfate ion HSO_4^-, the conjugate base of sulfuric acid, which acts as a stronger base than NH_3, as described above. However, we expect the addition of more ligands, described by the ratio $\Delta m/\Delta n$, to be independent of the electric charge for cluster sizes large enough that the acid or base effect of NH_4^+ or in particular HSO_4^- is neutralized.

Line 27-28, pg 13438 (onto the next page). The authors hypothesize that since at high [NH3], ion clusters grow by NH3 and H2SO4 in a 1:1 ratio, that neutral clusters must do the same. It would be a useful at this point to compare the detected ion clusters from this study to the neutral clusters detected in Hanson and Eisele (2002). Hanson and Eisele prepared neutral sulfuric acid clusters 2-7 with NH3 content between 0-7. Once these neutral clusters were charged via chemical ionization, the compositions of most ions quickly changed at T=275 K. This seems to indicate that the ion cluster's growth dynamics, or thermodynamics, in this study do not follow that of neutral clusters.

We agree that the opportunity of a comparison with the earlier work by Hanson and Eisele had been missed in the original manuscript, in particular where we discuss about the electrically neutral clusters, which we could not experimentally access in our study.

We added such a discussion now as a new 4th paragraph in section 4.5:

(Note that this addition refers to the new Fig. 4. Correspondingly, the figure numbering beyond the new Fig. 4 has changed by plus one.)

Neutral NH_3-H_2SO_4 clusters were previously investigated experimentally by Hanson and Eisele (2002), in conditions close to those in this study, with $[NH_3]$ between 100 and 800 pptv, $[H_2SO_4]$ between 1 and 3 10^9 cm^{-3} (40 to 110 pptv), at temperatures from −8 to +12 °C. The resulting $[NH_3]/[H_2SO_4]$ ranged from about 2 to 13, notably a range where we obtained few data. In that work, neutral clusters $(NH_3)_m \bullet (H_2SO_4)_n$, up to $n = 6$, were ionized by proton transfer to nitrate ions, yielding anion clusters $(NH_3)_m \bullet (H_2SO_4)_{n-1} \bullet HSO_4^-$, which were identified and counted using mass spectrometry. The NH_3-content in their ion clusters ranged from $m = 0$ to $n-1$, and was unaffected

by changes in gas-phase [NH_3]. The authors of that work could conclude that the ionization process may be ineffective for neutral clusters with an NH_3 content of $m \geq n$, and also that it may lead to a loss ligands, in particular of NH_3. The former conclusion agrees with our simulation results of an NH_3 content of small neutral clusters up to $m = n$ (Fig. 4) and it is roughly in line with our observation of anions with $m \geq n$ only starting from about $n \geq 6$ (Fig. 8B). The latter conclusion agrees qualitatively with the experimental and theoretical result in this study that the most prevalent (simulated) neutral cluster containing n H_2SO_4 contains one to three more NH_3 ligands than the most prevalent corresponding (measured) anion cluster, containing n–1 H_2SO_4 (Fig. 4B). Interestingly, Hanson and Eisele (2002) also detected trimer anions ($n = 3$) including up to two NH_3 ligands, whereas no trimer anions containing NH_3 were found in our study (cf. section 4.1). This difference is likely due the different production mechanism for their ion clusters, i.e. ionization of neutral clusters as opposed to growth of smaller already-charged clusters.

In sum, we believe that there are no contradictions between our experimental findings and those of Hanson & Eisele (2002). We also simulated steady-state neutral cluster distributions, using ACDC. Also those results do not appear to stand in a contradiction with the neutral clusters investigated by Hanson & Eisele (2002), as they were detected only after deprotonating them into anion clusters, and our understanding of how these formerly neutral clusters fragment upon their ionization is limited. So the composition of the neutral NH_3-H_2SO_4 clusters has not been determined in all details. But the constraints on their composition given first by the experiments by Hanson & Eisele (2002), the suggested conclusions from our measurements, and the results from the ACDC simulations, all appear to be in agreement within our current understanding.
We go into a bit more details on how the growth dynamics of ion clusters and neutral clusters relate to each other in the subsequent new last paragraph in section 4.5 (see also reply to comment 2 of referee 2). That paragraph also serves to justify the last statement in preceding paragraph.

Figure 3, pg 13458: cluster size 4 sulfuric acids seems to be a special cluster size as there is a mixture of pure sulfuric acid clusters, ammonia+sulfuric acid clusters, and various aminated sulfuric acid clusters. Any explanation for why n=4 is special? This is a place to compare the findings of Chen et al. (2012) who identified n=4 as the first neutral cluster size that does not undergo sulfuric acid evaporation.

For negatively charged clusters $(NH_3)_m \bullet (H_2SO_4)_{n-1} \bullet HSO_4^-$, the underlying reason behind the specialty of n = 4 is the base competition between the bisulfate ion and the ammonia or amines. The bisulfate ion (HSO_4^-) is a Lewis base, and forms very stable clusters with one and two sulfuric acid molecules (n = 2 and n = 3), so other bases cannot join these anion clusters. But (as for other bases), HSO_4^- is only able to stabilize up to 2 or 3 sulfuric acid molecules in the cluster. For larger clusters, a second base molecule can substantially increase the clusters' stability if it joins. Electrostatic repulsion obviously forbids the addition of another HSO_4^- here, so that in our case here, the second base joining in is ammonia (effective from n = 4 onwards) or an amine (mostly dimethylamine; effective from already from n = 3 onwards, but more so for n = 4).
A condensed form of that reasoning is found in sections 4.1 and 4.3. Details are found in Ortega et al. (2014; in particular Fig. 2 therein).
We added a sentence in section 4.1 for additional clarity:

Only when *n* > 2, the cluster is acidic enough to accept NH_3 molecules. If NH_3 or amines are available, their inclusion into larger clusters (*n* > 2) substantially enhances the clusters' stability, leading to a higher abundance as well as detectability in our measurements, compared to the pure sulfuric acid cluster (Ortega et al., 2014).

The above is also a formulation of the reason for which base ligands, if present, are lost from small electrically neutral clusters upon their ionization by removal of a proton (= creation of a bisulfate ion). Chen et al. (2012) employed such chemical ionization to obtain anion clusters $(H_2SO_4)_{n-1} \bullet HSO_4^-$ up to n = 4 from neutral clusters that are likely of the form $x \bullet (H_2SO_4)_n$, where x is probably amines or ammonia. They concluded from their ambient measurements that those neutral clusters have negligible H_2SO_4 evaporation rates for $n \geq 4$.
So under these points of view, there actually does not seem to be a direct connection between the negatively charged "special" n=4-clusters in our study, $(\text{base})_m \bullet (H_2SO_4)_3 \bullet HSO_4^-$, and the electrically neutral "special" n=4-clusters in Chen et al. (2012), $x \bullet (H_2SO_4)_4$. To our knowledge, the resolution as for why n = 4 is special in the latter case remains a task for future research. Therefore, and to try to keep the already long manuscript in a reasonable scale, we decided not to include a more detailed discussion of how our results compare to Chen et al. (2012) at this time.

APi-TOF vs ACDC

Page 13439: In general, how do the cluster compositions predicted by ACDC actually compare to APi-TOF ion cluster measurements? On pg 13429, the number of sulfuric acids n is between 4 and 18, which is higher than what is simulated in ACDC (n=1-5). The good agreement between ACDC and the measurements is strange as the measurements are comparing larger clusters ions to the simulation of small clusters.

The revised manuscript includes a new Fig. 4 that shows our APi-TOF measurement results in a step more detail. Shown are the average number of clustered NH_3 molecules (*m*) for each $(H_2SO_4)_n$ umbrella for each experiment at the mainly investigated chamber temperatures. Both positive and negative clusters are included, as well as the neutral clusters from the ACDC simulations, and negative clusters from ambient measurements. Amongst other benefits, this new figure shows more clearly how the ACDC results for neutral clusters compare to the APi-TOF measurements of charged clusters. (See also our reply to referee 2's comment 3 below.)
Correspondingly, section 4.5 saw substantial additions. (For details, see reply to comment above on the comparison to Hansele & Eisele, 2002, and replies to referee 2's comments 2, 4 and 5 below.) Among these are the additions to the 2nd paragraph discussed above in the reply to the comment on *Line 1-5, pg 13420*), and thereafter:
[…]
We calculated the Δ*m*/Δ*n* ratio for the simulated neutral clusters in the same way as for the measured data. However, a single neutral H_2SO_4 molecule was taken as the starting point for the simulated neutral clusters, due to the absence of the HSO_4^- base. […]
This is to reinforce our hypothesis, as described in the 1st paragraph of section 4.5, that the chief difference in the compositions of neutral and charged clusters is due to the basic (or acidic) effect of the ion (mainly the basicity of HSO_4^-). This effect reduces with size (see e.g. Fig. 4), in particular the slope when plotting *m*-vs-*n* (Fig. 4). The slopes from fitting those

data, $\Delta m/\Delta n$, are plotted in Fig. 6A. So only anion clusters $(NH_3)_m \bullet (H_2SO_4)_n \bullet HSO_4^-$ with n ≥ 4 were used for obtaining $\Delta m/\Delta n$, but all available neutral clusters $(NH_3)_m \bullet (H_2SO_4)_n$.

Figure 5, pg 13460: ACDC model does not seem to capture the temperature dependence that is seen in the measurements. Is there any explanation for this?

Note that there are a couple of discrepancies between the ACDC model and our observation, which we hope are now discussed more clearly, in particular in section 4.5. For details, please see replies to referee 2's comments 2, 4 and 5.

Specifically for temperature effects, we observed a slightly higher NH_3-content of the clusters at saturation for lower temperatures. Qualitatively, such a behavior is reproduced by ACDC and the included cluster stability calculations, as described in the now 7th paragraph in section 4.4, which also saw some additions:

Note that the anion clusters tended to feature slightly higher saturation values of $\Delta m/\Delta n$ at lower temperatures. This feature could be an indication of the enhanced evaporation of NH_3 molecules from the clusters at higher temperatures, both before and after the sampling. Indeed, results of computer simulations using the atmospheric cluster dynamics code (ACDC) suggest that there may be a systematic slight underestimation of the NH_3 content of the experimentally observed clusters in these conditions of relatively abundant gas-phase NH_3 that we cannot exclude (Olenius et al., 2013b; Olenius et al., 2013a). Those as well as earlier studies (e.g., Kurtén et al., 2007) have demonstrated how at least small NH_3-H_2SO_4 clusters are expected to hold onto a higher number of NH_3 molecules at lower temperatures.

As the referee correctly states, the observed temperature dependence for low $[NH_3]/[H_2SO_4]$ is *not* captured by ACDC. Also the model substantially overestimates $\Delta m/\Delta n$ in this regime. The latter discrepancy two possible explanations are suggested in the manuscript (section 4.5; see also our reply to referee 2's comment 5 for more detail), but no explanation specifically for the former discrepancy is given. We argue in section 4.4 (6th paragraph of the revised manuscript) that the *observed* temperature dependence is consistent with a barrier for the uptake of NH_3. ACDC does not include any barriers for any cluster formation: It assumes that all partners of a collision instantaneously arrange to their minimum energy configuration. The consistency with an effective barrier for NH_3 uptake is maintained. Such a barrier has also been previously concluded on in an independent experiment/model study (Bzdek et al., 2013). The overall substantial overestimation of $\Delta m/\Delta n$, when compared to experimental results, may be due to the very same reason. In our paper, we only use existing ACDC code, so a deeper explorations of possible modifications to ACDC (e.g. to investigate how modeled results would change with inclusion of uptake barriers) go beyond the scope here. We modified and extended paragraph 3 in section 4.5, to address this possible oversimplification of ACDC:

[…] This discrepancy may arise for at least three reasons: 1) H_2O molecules were not included in the model simulations, though they are abundant at RH = 40% and may play a more important role at relatively low $[NH_3]$; 2) small neutral clusters may indeed contain more NH_3 than their negatively charged counterparts; 3) there is a barrier for the uptake of NH_3 that is not modeled by ACDC. […] Reason 3 implicates a barrier for the uptake of NH_3, but barrierless addition of of H_2SO_4. The same conclusion was suggested above (section 4.4) and by an independent study (Bzdek et al., 2013). ACDC assumes that collision partners instantly arrange to their minimum energy configuration, from which the new cluster may subsequently break apart. This assumption may be too simple for conditions of low $[NH_3]/[H_2SO_4]$.

Minor Comments:

Line 2, pg 13417: ". . .practically omnipresent..." is an awkward phrase.

Agreed. Changed to the slightly less awkward "ubiquitous".

Line 28, pg 13418: ". . .such as amines, suffer from similar problems." What are the problems? Similar to the problems of detecting ammonia, but the problems were never stated.

A discussion of the challenges of those measurements probably goes beyond the scope of our paper, so changed as follows (including more references also):

In particular low concentrations of NH_3 or other bases, such as amines, remain challenging to measure accurately in the atmosphere (e.g., Chang et al., 2003; Huang et al., 2009; von Bobrutzki et al., 2010; VandenBoer et al., 2011). ~~Atmospheric measurements of other bases, such as amines, suffer from similar problems.~~

Line 20-21, pg 13420: "The trace gases sulfur dioxide and NH3 can be added on demand via individual independent lines." Were the two gases injected continuously throughout the experiment? If not, does a small aliquot of NH3 get consumed with time?

Yes, all gases had to be injected continuously to maintain a the desired levels of concentration. Tried to clarify by the following addition in section 2.1:

[…] Fresh humidified air and trace gases are fed into the chamber continuously at a total rate of 85 L min^{-1}, while air is extracted by the measuring instruments. The desired concentration of each gas is achieved by continuous constant injection at the according flow rate. […]

Figure 1, pg 13455: "1.02 m sampling probe. . ." the text says 1.2 m sampling probe. Which is correct? There is a diameter decrease in APi-TOF sampling probe. Have the losses been quantified as a result of the ions passing through this reducer?

Thanks for spotting the mistake. The sampling probe was 1.2 m long during the CLOUD 2 and 3 campaigns; we corrected Fig. 1.

The 1-inch tubing was reduced to 10-mm for connection to the APi-TOF inlet. We aimed at keeping the flows sufficiently small for a laminar flow profile. In this respect, the increase in flow velocity resulting from the reduction was taken into consideration. Ion losses due to the reducer, however, were not quantified. More on ion losses during sampling in the replies below.

Line 2, pg 13422: The sampling probe was 1.2 m long with 0.5 m inside the chamber. How do the diffusion losses in the sampling lines compare between the NAIS and the APi-TOF? Figure 1 shows the length of the sampling tube to the NAIS to be half the length of the APi-TOF. Would differences in diffusion losses complicate the conclusion stated in Line 14, pg 13423 ("Comparison between the APi-TOF and the NAIS for our measurements produce similar agreement")? […]

The sampling tube length from the split to the NAIS was about 0.3 m, i.e. shorter compared to the ~0.5 m to the APi-TOF. The volume flow rate to the NAIS was about double the flow rate to the APi-TOF. All in all therefore, the NAIS was at an "advantage" regarding diffusion losses. The situation is further complicated by the NAIS being equipped with a dilution system. (The NAIS's native sampling rate is >50 L/min, so part of its exhaust was filtered and added to the sample flow from the chamber of <24 L/min. This was just before the instrument's inlet, and is not shown in Fig. 1.) Details of the NAIS setup will be described in a manuscript that is currently in preparation (Franchin et al., 2014).

Nonetheless, the NAIS provided the only direct quantitative ion measurements during the CLOUD 2 and 3 campaigns. The whole sampling setup for the NAIS was carefully characterized in separate laboratory experiments, in particular for size-dependent ion losses (mostly due to the dilution system and diffusional losses). As a result we got corrected number size distributions for ions in the range 0.8-40 nm.

For the APi-TOF on the other hand, the quantification of ion losses from sampling to detection is more complicated, in particular due to mass-dependent ion transmission in the APi (as described in the manuscript). For comparing with the NAIS, we did characterize this transmission efficiency, but the results thereof have a relatively high uncertainty attached to them (cf., e.g., Ehn et al., 2011). Diffusion losses along the sampling line were crudely calculated assuming laminar flows in a tube (Gormley and Kennedy, 1949), not taking into account complicating factors such as the Y-split and the reducer (see reply above). The comparison with the NAIS was therefore mostly qualitative, i.e. comparing the shapes of the ion size distributions, and only roughly the ion concentrations. We think that details on these comparisons are beyond the scope of this paper, as the focus is on the composition of the ions and ion number concentrations are never discussed.

As a support of our argument in the manuscript, we present some of these comparison results here, in Fig. R1. The figure shows the relevant parts of the corrected ion number size distributions from the NAIS, together with APi-TOF results. For this purpose, the APi-TOF results have been converted from ion mass to ion mobility diameter (using bulk densities) and from ion counts to ion number concentrations, taking into account the measured and roughly calculated corrections described above, and then grouped into corresponding NAIS channels, using NAIS transfer functions (Gagné et al., 2011; Ehn et al., 2011; idealized to isosceles triangles in $\log_{10}$(diameter) space).

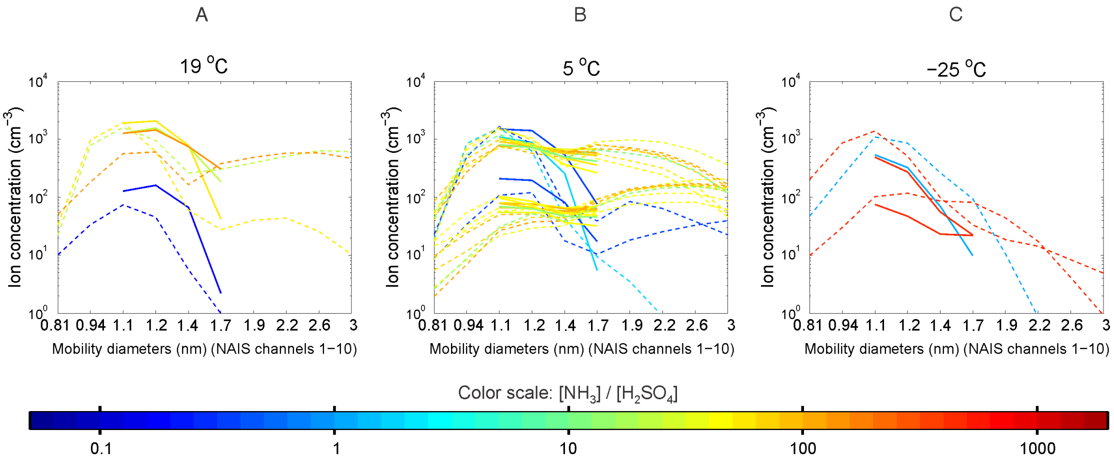

Fig. R1. Corrected ion number size distributions from the NAIS measurements (dashed lines), and the corresponding results from the APi-TOF measurements (solid lines in corresponding colors), following conversion as described in the text, for particle formation experiments at chamber temperatures of 19 °C (**A**), 5 °C (**B**), and –25 °C (**C**). For not overcrowding the figures, only selected experiments are shown, namely those where the APi-TOF obtained signal up to the upper limit of the 6th NAIS channel's transfer function (nominal size for 6th channel = 1.7 nm; transfer function >0 from 1.16 to 2.06 nm).

Fig. R1 shows some qualitative agreement between the ion distributions obtained from the NAIS and the APi-TOF, despite the relatively poor resolution of the NAIS and the several crude simplifications and assumptions made to obtain the comparisons. Most importantly, the instruments agree roughly on the shape of the ion size distributions, giving us confidence that the APi-TOF ion cluster spectra indeed reflect the ion clusters in the corresponding mobility size range, i.e. that they are not merely fragments of much larger ions.

However, there are substantial deviations and variations in the number concentrations obtained from the NAIS or the APi-TOF (note the logarithmic scaling). For that we may partly blame the multitude of assumptions and simplifying estimations described above, which also involve difficult-to-quantify uncertainties, as well as the NAIS' orders of magnitude poorer resolution.

We softened statement in section 2.3 somewhat:

Comparisons between the APi-TOF and the NAIS for our measurements produced a ~~similar~~ fair agreement as well, so the ion mass spectra obtained by the APi-TOF are, in general, representative of the actual population of small ions and ion clusters.

[…] In addition, the sampling line was quite long and went from the chamber at a temperature between -25 and 20 C to the temperature near instruments (which can get quite warm). It is possible that the sample flow and ions were heated before measurement. The authors have commented that temperature affects the composition of cluster ions. Is it possible that the ion clusters sampled are different than what was present in the chamber?

Heating of the sample from the chamber to the instruments is indeed a potential problem, as part of the sampling lines were at room temperature (which could vary between 5 °C in late fall to >25 °C in summer).

We tried to mitigate the problem by carefully insulating the (sometimes fairly long) sampling lines from the chamber's thermal insulation all the way to the instruments' inlet, using Armaflex and aluminum tape on the outside. Further *de facto* insulation is provided by the air flow itself, as only 0.8 out of ~10 L/min are actually sucked into the APi-TOF from the center of the flow. We did not measure the effectiveness of these efforts, but estimative heat flux simulations suggest that at a room temperature of 20 °C, air sampled from the chamber at –25 or at 5 °C is warmed up to –16.5 ± 2 °C or 8.5 ± 2 °C, respectively, at the center of the flow. Such heating would not influence the primarily qualitative conclusions made in our paper regarding temperature effects. In fact it would act in reducing the magnitude of observed temperature effects. We also did not observe any effects of room temperature variations on the APi-TOF results. In conclusion, we think that ambient heating of the sample lines does not cause a problem here, but it should be mentioned in the paper. We thus added a paragraph in section 2.2:

Fig. 1 shows that much of the sampling line was exposed to room temperature (>5 °C). We thermally insulated the lines using Armaflex pipe insulation with aluminum tape on the outside, to minimize unwanted heating of the air taken from the chamber. The 0.8 L min^{-1} sample drawn into the APi-TOF was taken from the center of a ~10 L min^{-1} flow, further mitigating heating of the sample. Simulations of the heat flux from warm ambient air into cool air flowing in a tube, insulated by a jacket of air, indicate that the APi-TOF sample may be heated up to several degrees before reaching the APi-TOF (e.g., from –25 to –16.5 °C or from 5 to 8.5 °C, ± 2 °C, at a room temperature of 20 °C). However, such heating would not qualitatively influence the conclusions regarding temperature effects in this study. In fact, it would only reduce the magnitude of the observed temperature effects.

Also added a reminding sentence at the new 1st paragraph in section 3.4.

Line 14-16, pg 13423: The authors comment that fragmentation in the APi-TOF is possible however good agreement with the NAIS indicates otherwise. It would be useful to see this direct comparison as the NAIS might not have high enough resolution to be directly compared to the APi-TOF measurements. Since this paper is focused on cluster ion composition, making a strong argument that measured ion cluster represent ion-induced formed ion clusters, instead of fragments, in the chamber is essential.

Please see Fig. R1 and the associated reply above (to comment on line 2, page 13422).

Line 17-19, pg 13423: The authors go on to indicate that molecules from the ions may be lost during sampling. Which molecules are lost, as applied to these experimental conditions? Would these evaporated molecules from ion clusters affect the smaller or larger ion clusters more?

If molecules are lost from an ion, it will be those that are bound most weakly. I.e. the answer is specific to each ion cluster. The APi-TOF results alone do not allow us to make conclusions on which molecules may be lost from which specific cluster. However, we conclude here, supported by the results of previous works, that bases (NH_3 and HSO_4^-) and acids (H_2SO_4 and NH_4^+) bind to each other via acid-base reactions. So for clusters containing "excess" H_2SO_4 ($m < n$ for cations, $m < n-1$ or $n-2$ for anions), for instance, it is plausible that the NH_3 molecules are more strongly bound than the excess H_2SO_4 molecules, and H_2SO_4 will be lost preferentially.

For the smaller ions in particular, the answer is best found from results from other works, e.g. quantum chemical calculations on these clusters' stabilities (Ortega et al., 2014). Also see the table of evaporation rates now included in the revised manuscript (Tables 1-3).

In general, larger ion clusters are expected to be less vulnerable to evaporation than smaller clusters. However, most small charged clusters (ca. $n < 4$) are more stable if they are smaller, probably due to the additionally stabilizing electrostatic effect (see, e.g., Ortega et al., 2014, in particular Figs. 2-6).

Line 19, pg 13429: The description of _m/_n is confusing. The number of NH3 added for each H2SO4 was determined how? Was this determined by looking at the mass spectra as it depended on time? Or was this determined by looking at specific cluster ion mass and calculating the ratio of NH3/H2SO4 molecules in the cluster ion? The authors should mention how this was calculated and at what point in the experiment they analyzed the data (i.e. was it at steady state of sulfuric acid? Steady state of APi-TOF signals?)

The description was indeed lacking some needed explanations in the main text. We added a new 4th paragraph in section 3.1:

Note that the APi-TOF spectra shown and analyzed in this study are averages over the duration of the steady-state conditions during a new-particle formation experiment (illustrated in Fig. 2). The steady-state periods were defined as the period during which no change in the APi-TOF ion spectrum occurred. Their duration ranged from 200 seconds to over six hours.

We also revised the beginning of section 3.4 (introducing also the new Fig. 4):

For all experimental conditions, negative ion clusters with more than 4 or 5 sulfur atoms grew by the accretion of NH_3 and H_2SO_4 molecules, forming progressively larger $(NH_3)_m \bullet (H_2SO_4)_n \bullet HSO_4^-$ clusters. The number of ~~added~~ NH_3 molecules added on average per added H_2SO_4 molecule remained near constant from 4 or 5 sulfur atoms up to the upper detection limit of about 27 sulfur

atoms, within the measurement uncertainties. These findings are illustrated in Fig. 4, which shows the average number of NH_3 molecules (m) in clusters containing a certain amount of H_2SO_4 molecules (n), for each experiment and grouped by temperature.

We define the average number of added NH_3 molecules per added H_2SO_4 molecule as $\Delta m/\Delta n$. This ratio corresponds to the slope of linear fits in m-vs.-n plots as in Fig. 4. For anions, we calculated values of $\Delta m/\Delta n$ for $n \geq 4$, and found that $\Delta m/\Delta n$ is well suited to describe the whole anion spectra during new-particle formation events in the NH_3-H_2SO_4-system: two spectra with the same $\Delta m/\Delta n$ were practically identical (unless $\Delta m/\Delta n$ was close to zero, see section 3.5), and, for a given temperature and RH, $\Delta m/\Delta n$ was only dependent on the ratio between the NH_3 and H_2SO_4 gas-phase concentrations, i.e. on $[NH_3]/[H_2SO_4]$ (color scale in Fig. 4, horizontal axis in Fig. 5). In our ~~later~~ analysis for this study, values of $\Delta m/\Delta n$ ~~will be~~ were calculated over the range $4 \leq n \leq 18$ in the case of anion clusters, because $\Delta m/\Delta n$ was approximately constant for $n \geq 4$ and we obtained a signal from clusters up to at least $n = 18$ in most of the experiments.

[…]

Line 7-8, pg 13439 ". . .difficulties in measuring neutral clusters do not concern computer simulations." Awkward sentence and not scientifically relevant.

Agreed that the sentence is not suitable, as details on measurements of electrically neutral compounds are not discussed. Changed to:

However, we studied their composition using ACDC computer simulations.

Line 13-14, pg 13439: The evaporation rates are very important for modeling cluster dynamics and can be easily manipulated (set to nonsensical numbers) to get the model to fit observed results. Please include a table with evaporation rates used as this is the most accessible way for readers to conceptualize the most relevant contributions of each cluster type in the cluster balance equations.

We added three tables, showing the used evaporation rates (Tables 1-3). Reference to the tables is added in section 4.5:

[…] Cluster evaporation rates were calculated from quantum chemical Gibbs free energies of formation of the clusters (Tables 1-3). […]

Line 22, pg 13440: The authors write the ammonia concentration in the boreal forest (is this Hyytiala forest?). What is the estimate of the amine concentration, specifically dimethylamine?

We had to be rather conservative with this estimate as we lack direct amine measurements at our measurement site in Hyytiälä (located inside a boreal forest) at that time, and direct amine measurements at CLOUD were only available during later measurement campaigns. But judging from all APi-TOF data, plus amine measurements in subsequent campaigns at CLOUD, we estimate the dimethylamine concentrations in Hyytiälä to be less than 1 pptv (see section 5).

A few small changes were made to the manuscript to clarify that our results from boreal forest environments originate from the measurement site in Hyytiälä in southern Finland.

Line 15, pg 13443: "measurements in the boreal forest have shown that large NH3-H2SO4 clusters do not usually contain any amines." Are these "measurements" from this work or cited elsewhere? Also, please specify that the clusters are ion clusters. It is possible neutral ambient clusters might contain amines but no ammonia.

Agreed, added “ion”. The statement refers to previously published results in Schobesberger et al. (2013a). We moved the corresponding citation from the end of the subsequent sentence to the end of this sentence.

Line 19-20, pg 13443: The authors conclude that their CLOUD measurements agree with their ambient measurements, thus the ambient amine concentration must be <1 pptv. This is an overreaching statement. Not all amines behave like dimethylamine. Furthermore, as the authors have stated, temperature plays a key role in what ions are detected by the APi-TOF. Are the temperatures of inlets identical between the CLOUD experiments and in the field? Consider rewriting the section to avoid vagueness.

Corrected by replacing “ambient amine concentrations” with “ambient dimethylamine concentrations”.
Regarding temperature effects in connection with heating at the inlet, please see the comment above (starting “[…] In addition,”). In the field, the inlet stuck through the wall of the container that housed the APi-TOF with its inlet at the wall. The residence time of the sample inside the container was thus minimal, and effects on its temperature are negligible, i.e. it entered the APi-TOF at the ambient temperature. Details on the APi-TOF’s sampling setup in the field are found in the Supporting Information of Schobesberger S., et al. (2013a).
The temperature at the field site was usually around 5 °C, i.e. very similar to many experiments made in the CLOUD chamber at 5 °C. Specific actual temperatures are color-coded in Fig. 6A and given in the caption of Fig. 8C (formerly Figs. 5A and 7C).

Figure 4, pg 13459: what do the colored green and red sections indicate?

Cyan- and orange-colored markers refer to non-standard RH, as indicated. We corrected the figure caption to state that the red-shaded section indicates conditions for which we observed positively charged clusters. (Before, the caption mistakenly referred to a “grey area”.)

Figure 5, pg 13460: The color bar scale reaches down to -30 C (dark blue). According to the text, the lowest temperature was -25 C. As it is difficult to distinguish between darker blue and dark blue, please truncate the scale -25 C.

Done. (This color scale was deliberately adjusted to reach down to –30 °C, in order to obtain an orange color for the data for 5 °C, as before their color had been close to a harder-to-spot yellow. As correctly noted, the only dark blue in effect is for the measurements at –25 °C.)

****

Anonymous referee #2:

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:

We thank also referee #2 for making us aware of our negligence in relating our work properly to previous work by others. We believe that the revised manuscript is substantially improved in this respect. More detailed replies below, as well as in the corresponding replies to referee #1.

> 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.
>
> Acknowledging reference 1, we enhanced our introduction accordingly (within the 3rd paragraph):
>
> **[…] Theoretical ab-initio studies show that NH_3 forms strong bonds with H_2SO_4, greatly enhancing the stability of H_2SO_4-containing clusters, for both electrically neutral and charged clusters (e.g., Kurtén et al., 2007b; Ortega et al., 2008; DePalma et al., 2012; Ortega et al., 2012). Generally, these studies predict a maximum base:acid ratio of 1:1, however the maximum cluster size is usually computationally limited, e.g. to up to about 8 molecules in Ortega et al. (2014) or to about 20 molecules in DePalma et al. (2012). […]**
>
> We appreciate also having reference 2 pointed out to us, as it has only been published this June. It is in particular interesting for its results on the effect of water molecules on NH_3-H_2SO_4 (and on amine-H_2SO_4) clusters, which we discuss below in our reply to comment 5. We also want to thank the referee for pointing out a number of interesting IR spectroscopy studies that we had neglected. Those studies investigated the structure of the bonds within NH_3-H_2SO_4 clusters. We include now a discussion of how the most relevant of these studies (and related theoretical studies) agree with our findings in a new 3rd paragraph in section 4.4:
>
> **These findings are in agreement with previous studies that investigated the structure of the bonds in electrically charged or neutral NH_3-H_2SO_4 clusters: Both theoretical (e.g., Ortega et al., 2012; DePalma et al., 2012) and experimental studies (e.g., Rozenberg et al., 2011; Froyd and Lovejoy, 2012; Johnson and Johnson, 2013) have shown that NH_3 molecules are bound to H_2SO_4 molecules via the transfer of a proton from the acid to the base (acid-base reaction) in all but the smallest of these clusters. Note that for simplicity, the chemical formulas used in this paper disregard these reactions.**

Regarding amine-sulfuric acid clusters, we decided not to go into details of the bindings therein that several works (including some of the mentioned references) have investigated, to keep the already-long manuscript focused on ammonia-sulfuric acid clusters instead. (However, some revisions in the corresponding section 4.3 were anyway done, as discussed below.)

Note also that our measurements for this study cannot directly address the detailed structure of the NH_3-H_2SO_4 clusters. The focus of the paper is instead on the general composition of these clusters, and how this composition changes with cluster size and how it relates to different experimental and ambient conditions.

b. Page 13418, lines 20-22: The authors should also reference ambient measurements by the cluster Chemical Ionization Mass Spectrometer (cluster CIMS).[10]

Indeed. We reference these measurements now in the introduction.

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.

While some of the works by Bzdek et al. are already referenced, we agree that their studies may deserve a more detailed consideration also where we discuss the uptake of very low (contaminant) concentrations of ammonia and especially amines. We still decided to keep such discussion relatively short, as the main messages of our study concerns ammonia-sulfuric acid clusters specifically. The according additions went into section 4.3 of our manuscript:

[…] The resultant dominant role of NH_3 in the growth of the clusters, as opposed to organic bases (amines or amides), is most likely due to the differences in respective contaminant-level concentrations ([NH_3] about 2 to 4 pptv, [C_2H_7N] < 1 pptv). Indeed, previous experimental studies on both positively and negatively charged dimethylamine-NH_3-H_2SO_4 clusters showed that dimethylamine molecules would quickly displace NH_3 molecules in these clusters already at low pptv level amine concentrations, whereas the opposite (displacement of dimethylamine by NH_3 molecules) does not occur even at much higher gas-phase NH_3 concentrations (Bzdek et al., 2010; Bzdek et al., 2011).

The effect of higher than contaminant gas-phase concentrations of amines, in particular of dimethylamine, on the composition of growing clusters and on particle formation rates was thoroughly investigated in subsequent CLOUD campaigns (Almeida et al., 2013). A large influence on cluster formation and particle formation rates was found at dimethylamine concentrations as low as 3 pptv. Specifically, growing ion clusters consisted of practically only dimethylamine and H_2SO_4, and particle formation rates were significantly enhanced. The enhancement of particle formation rates in those experiments was due to dimethylamine being a stronger base than NH_3 and consequently forming more stable bonds with H_2SO_4 molecules, as has been shown both theoretically (e.g., Bzdek et al., 2010) and experimentally (e.g., Kurtén et al., 2008). […]

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.

Yes, the spectra were taken every 5 s, but the spectra presented in this study are averages over much larger time periods, spanning from 3 minutes to even 6 hours. These averages were taken over the duration of steady-state APi-TOF ion spectra during new particle formation at steady conditions. In the manuscript, this was explicitly stated only in Fig. 2, so we now added a sentence as new third paragraph in section 3.1:

Note that the APi-TOF spectra shown and analyzed in this study are averages over the duration of the steady-state conditions during a new-particle formation experiment (illustrated in Fig. 2). The steady-state periods were defined as the period during which no change in the APi-TOF ion spectrum occurred. Their duration ranged from 200 seconds to over six hours.

We agree with the referee that collisions between charged and uncharged clusters occur, as well as collisions between charged clusters. As the referee states, the steady-state APi-TOF ion spectra that form the backbone of the studied data cannot be directly used for assessing dynamic processes, such as the actual growth pathways.

However, the ACDC simulations do take all these collisions into account. In our study here, only the compositions of the neutral clusters ($(NH_3)_m(H_2SO_4)_n$ up to $m = n = 5$) in steady-state conditions are shown, as the goal was the comparison with experimental results from the APi-TOF measurements. Details on the simulations are found in earlier publications (Olenius et al., 2013a, b). In these simulations, >99% of the charged clusters grow by the step-wise addition of H_2SO_4 and NH_3 molecules, unaffected by neutral clusters, due to the small concentration of clusters involved. However, it was also found that a major fraction of electrically neutral clusters will in fact form by the recombination of charged clusters, if sulfuric acid concentration is low and temperature high (e.g., $[H_2SO_4] \leq 10^6$ cm^{-3} at 5 °C).

In any event, these considerations were not discussed in our original manuscript, so we added the following paragraph at the end of section 4.5:

Note that the data presented in this work do not in fact allow conclusions on the details of the actual growth process of the clusters, but our discussion of the measured cluster size distributions here may have implied the assumption of a step-wise addition of single H_2SO_4 and NH_3 molecules. In the ACDC simulations, >99% of the modeled charged clusters indeed grow by the step-wise addition of single molecules, due to the small concentrations of the involved clusters. However, a major fraction of the modeled electrically neutral clusters form by the recombination of charged clusters, if $[H_2SO_4]$ is low and temperature high (e.g., $[H_2SO_4] \leq 10^6$ cm^{-3} at 5 °C) (details in Olenius et al., 2013a).

We also correspondingly corrected statements that may imply a specific growth pathway without given corresponding evidence:

Abstract:

Our results also suggest that ~~yet unobservable~~ electrically neutral NH_3-H_2SO_4 clusters, unobservable in this study, ~~grow~~ have generally the same ~~mechanism~~ composition as ionic clusters~~, particularly~~ for [NH3]/[H2SO4] > 10.

Section 4.4:

The APi-TOF measurements of NH_3-H_2SO_4 clusters during particle formation experiments at the CLOUD chamber revealed ~~how~~ that these clusters grow by the accretion of certain numbers of NH_3 and H_2SO_4 molecules.

[…]

From the tetramer onwards (#S ≥ 4; see section 4.2 for exceptions), the anions became chemically (not electrically) neutralized, as the clusters grew by the addition of slightly more than one base per acid in average (Fig. 7B).

Section 4.5:

Therefore we would expect electrically neutral clusters to grow by the same ~~mechanism~~ ratio $\Delta m/\Delta n$ already from the first bond-formation onwards.

[…]

At low values $[NH_3]/[H_2SO_4]$, however, the simulated neutral clusters ~~took up much more NH3 as they grew~~ gained NH_3 at a much higher rate than the measured negatively charged clusters.

3. The reported Δm/Δn values are averages over the entire mass spectrum. Have the authors done any analysis regarding how Δm/Δn may change as a function of cluster size in one particular spectrum or how Δm/Δn may change for a particular cluster as [NH3]/[H2SO4] 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 [NH3]/[H2SO4] 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.

We did present mostly averages over large parts of our ion spectra in order to reduce the amount of presented information. Each spectrum was, however, analyzed in more detail than shown. Therefore, prompted by the referees comment, we think now that the provision of more information is anyway useful, as it visualizes some details of our results that had previously only been described by the text, and it may also make the paper easier for the reader to follow through.

Therefore the revised manuscript goes one step further in the detail of results shown with the new Figure 4, showing the average number of clustered NH_3 molecules (m) for each cluster size (roughly equal to the number of clustered H_2SO_4 molecules, n)) for each experiment at the mainly investigated chamber temperatures, for both positive and negative clusters. Neutral clusters from the ACDC simulations are show as well as, as are negative clusters from ambient measurements with a suitable mean temperature. This figure also visualizes well that from about n = 4 onwards, $\Delta m/\Delta n$ stays about constant for negatively charged clusters, as described in sections 3.4 and 4.4, therefore answering the referees questions above, on how $\Delta m/\Delta n$ changes with cluster size and with temperature. The new figure also serves as an introduction to the following figures. Note that not shown are ranges and uncertainties in m, as well as data from even larger negative clusters that were measured during some experiments at CLOUD ($18 > n > 28$; e.g. as in Fig. 8B), in order to improve the clarity of the figure. $\Delta m/\Delta n$ has not seen to change in that range within uncertainties.

Also note that a closer look here reveals that m vs. n is in fact not as linear for the positive clusters at the highest $[NH_3]/[H_2SO_4]$ as for the negative clusters: There is a kink at $m = n = 10$, where the slope $\Delta m/\Delta n$ increases from 1.0 to about 1.3. For simplicity this finding is omitted in Fig. 6A (i.e. the previous Fig. 5A), but it is now mentioned in the discussion of the related new Fig. 9 (see below.)

To introduce the new Fig. 4, a sentence was added to the 1st paragraph in section 3.4:

The number of added NH_3 molecules per added H_2SO_4 molecule remained nearly constant from 4 or 5 sulfur atoms up to the upper detection limit of about 27 sulfur atoms, within the measurement uncertainties. These findings are illustrated in Fig. 4, which shows the average number of NH_3 molecules (m) in clusters containing a certain amount of H_2SO_4 molecules (n), for each experiment and grouped by temperature.

The subsequent text saw minor changes as well to take into account the new Fig. 4.

Our manuscript describes how the acids in the clusters get more and more neutralized, as they grow, if $[NH_3]/[H_2SO_4]$ is sufficiently high. The composition is close to a molar ratio $NH_3/H_2SO_4 = 1$, i.e. that of ammonium bisulfate. If $\Delta m/\Delta n > 1$, further neutralization may lead to the partial formation of ammonium sulfate (molar ratio $NH_3/H_2SO_4 = 2$). However, the maximum $\Delta m/\Delta n$ we observed was about 1.4. If such a ratio were constant up to larger cluster sizes, the molar ratio $NH_3/H_2SO_4 = 1.4$ would be approached (fairly quickly: closer than 4% at $\#(H_2SO_4)=80$, ~ 3 nm mobility size). As described in the paper, we did not find conditions for which a higher $\Delta m/\Delta n$ would be obtained, i.e. where ammonium sulfate would be the favored composition. To illustrate the above, we include a new Figure 9 that shows specifically the molar ratio NH_3/H_2SO_4 (i.e. to which degree H_2SO_4 in the clusters is neutralized) as a function of cluster size, for the experiments yielding the highest $\Delta m/\Delta n$, and for each of the three mainly investigated temperatures (–25 °C, 5°C, 19 °C). Note that fragmentation in the instrument may have decreased the observed $\Delta m/\Delta n$ somewhat, as discussed in section 4.4 and in Olenius et al. (2013b). Fig. 9 also shows how the NH_3/H_2SO_4 would develop if the clusters continued to grow at a constant $\Delta m/\Delta n$. Only if $\Delta m/\Delta n$ increased for larger (unobserved) clusters, would ammonium sulfate become the favored composition. This is also for the most "NH_3-favoring" conditions examined; namely, for anions and –25 °C, $[NH_3]$ = 100 ppt, $[NH_3]/[H_2SO_4] = 400$; for 5 °C, $[NH_3]$ = 150 ppt, $[NH_3]/[H_2SO_4] = 120$; for 19 °C, $[NH_3]$ = 1100 ppt, $[NH_3]/[H_2SO_4] = 600$.

For including Fig. 9, the text has seen the following main changes:

In 2nd paragraph in section 4.4:

Note that a ratio of $\Delta m/\Delta n = 1$ corresponds to the stabilization of each H_2SO_4 molecule by an NH_3 molecule, as in ammonium bisulfate (whereas $\Delta m/\Delta n = 2$ would correspond to the full neutralization of each H_2SO_4 molecule by two NH_3 molecules, as in ammonium sulfate).

Added to 8th paragraph in section 4.4:

The maximum observed $\Delta m/\Delta n$ ratios were about 1.4 for anion clusters and 1.1 for cation clusters. Therefore the NH_3-H_2SO_4 molar ratio (m/n) exceeded unity beyond a certain cluster size, as illustrated in Fig. 9. Note that if the clusters' growth continued to adhere to the observed $\Delta m/\Delta n$ ratios also beyond a mobility size of 2 nm, m/n would approach these values (grey curves in Fig. 9).

And if $\Delta m/\Delta n$ stayed below 1.5, as observed, also for larger clusters, ammonium bisulfate would remain the favored composition (as opposed to ammonium sulfate). However, it should also be noted here that for the positively charged clusters both Fig. 4 and, more clearly, Fig. 9 reveal an apparent discontinuity at $m = n = 10$, with an increase of the slopes, specifically an increase of $\Delta m/\Delta n$ from 1.0 to about 1.3 for the larger positively charged clusters.

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 Δm/Δn relative to the measurement (charged clusters). Wouldn't this suggest that neutrals are growing differently than charged clusters?

We state in this section (4.5) that the model agrees with the measured compositions in some respects, but not all, namely (as the referee correctly remarks) in that the simulated neutral clusters exhibit a much higher $\Delta m/\Delta n$ relative to the measured charged clusters. The following change was implemented to better prepare the reader for the subsequent "but":

The results from the simulations of neutral clusters agreed with the measurements of charged clusters in ~~several~~ some respects:

Indeed, the second of the two suggested explanations for that over-prediction is that neutral NH_3-H_2SO_4 clusters do grow differently than their charged counterparts.

We hope that the manuscript is generally clearer now in the discussion of the ACDC results, as the 2nd paragraph (now 2nd and 3rd paragraph) in section 4.5 was revised (see also reply to comment 5 below), and a new last paragraph was added to the section, describing our findings on the detailed growth mechanism of charged vs. neutral clusters (see reply to comment 2).

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.

It is indeed well known that interactions with water (H_2O) and NH_3, and H_2O and H_2SO_4 are much weaker than those between NH_3 and H_2SO_4. We tried to reinforce that in this place in the revised manuscript.

However, our measurements show that the role of NH_3 in building growing anion clusters, generally observed as $(NH_3)_m(H_2SO_4)_nHSO_4^-$, decreases markedly at conditions of relatively low $[NH_3]$. $\Delta m/\Delta n$ as well as m/n decreases with decreasing $[NH_3]/[H_2SO_4]$, until m = 0 and anion clusters grow by the clustering of only H_2O and H_2SO_4 molecules. (It may in any case be misleading to call H_2O a "stabilizing base", so we omit that in the revised manuscript.) Although NH_3 interacts much more strongly with H_2SO_4, it is not included in the clusters, whereas H_2O is. The simplest reason is merely the low gas-phase concentrations of NH_3 (< 5 pptv) in those conditions. In the practical absence of NH_3 therefore, the interactions between H_2O and H_2SO_4 are critical for forming these clusters, relatively weak as they are. Note that the participating H_2O are usually not observed, though studies on the enhancing effect of H_2O

on vapor pressure suppression of and particle formation by H_2SO_4 imply their participation (e.g., Vehkamäki et al., 2002; Lovejoy et al., 2004). In addition, computational chemistry studies show that hydrated NH_3-H_2SO_4 clusters contain less H_2O than hydrated H_2SO_4 clusters (Henschel et al., 2014).

In sum, the role of H_2O in the formation of (NH_3-)H_2SO_4 clusters is expected to increase with a decreasing role of NH_3. This expectation is consistent with our measurement results here, but H_2O is not considered in the ACDC model, so the simulated (NH_3-)H_2SO_4 clusters can only be stabilized by NH_3 (or charge), even in low-[NH_3] conditions. Qualitatively therefore, the absence of H_2O in the model could lead to the observed over-prediction of the clusters' NH_3 content and hence $\Delta m/\Delta n$ by the ACDC model (Fig. 6A). Admittedly, a study of estimating such an overestimation is missing from our manuscript, and it remains a topic for future research.

We try to better address this issue now by the following changes.

New 4th paragraph in section 4.4:

Note also that all of the observed clusters were probably hydrated before their H_2O molecules were lost in the sampling process, due to the abundance of H_2O at the conditions in the CLOUD chamber (e.g., Henschel et al., 2014). The stabilizing effect of H_2O on H_2SO_4 is much smaller than that of NH_3 (e.g., Kurtén et al., 2007a; DePalma et al., 2014), but at least in the absence of NH_3, the contribution of H_2O is important (e.g., Vehkamäki et al., 2002).

Specific modifications in the now 3rd paragraph of section 4.5 (amongst others in the same paragraph):

This discrepancy may arise for at least three reasons: 1) H_2O molecules were not included in the model simulations, though they are abundant at RH = 40% and may play a more important role at relatively low [NH_3]; 2) small neutral clusters may indeed contain more NH_3 than their negatively charged counterparts; 3) […] Reason 1 would imply that H_2O molecules partially take over the role of stabilizing sulfuric acid clusters from NH_3 at relatively low [NH_3] ~~for acting as the critical bases that stabilize sulfuric acid clusters~~. Qualitatively, this suggestion agrees with the expectation of H_2O contributing to stabilization of sulfuric acid clusters, especially in the absence of NH_3, (e.g., Vehkamäki et al., 2002), and of these clusters containing more H2O with less NH3 (Henschel et al., 2014). As H_2O was absent in the ACDC simulations, the clusters' NH_3 content may thus be over-predicted. Reason 2 (more NH_3 in neutral than in anion clusters) appears plausible on its own, as it would put the reliance on NH_3 of neutral clusters between that of anion clusters (no NH_3 required) and cation clusters (relatively much NH_3 required). […]

In addition, we extended this paragraph for a 3rd possible reason, in reaction to referee 1's related comment 5 (see above).

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.

Added the word "ion" in the title:

"On the composition of ammonia-sulfuric acid ion clusters during aerosol particle formation".

2. The authors frequently use both pptv and molecules/cm3 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.

Good idea. Including now both units for either [NH_3] or [H_2SO_4] (i.e. pptv as well as cm^{-3}) in many important places, including those mentioned.

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?

Figure 1 is probably the least important one in this manuscript, but we feel that the sampling setup should be described for completeness, in particular for the revised manuscript. It also aids in understanding the description in section 2.2. Furthermore, it gave rise to specific and important questions by referee 1, and replies (see above).

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.

They are actually defined in section 2.1 (page 13421, lines 27-28).

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.).

We agree that we were somewhat negligent in providing the measurement conditions. We corrected for this, by giving an overview in section 3.1 (as suggested) in the form of a new 1st paragraph and an additional sentence at the start of the now 5th paragraph. Further, slightly clarified the first sentence in section 3.3:

No amines were deliberately added into the chamber for the experiments discussed here, i.e. ~~during~~ throughout the CLOUD 2 and CLOUD 3 campaigns.

We also added a short introductory paragraph to section 3.4.

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.

A somewhat more detailed discussion of such a barrier is now included related to the comparison with ACDC (section 4.5; see answer to referee 1's comment 5 for details).

Additional evidence for such a barrier from comparison with ACDC is now discussed in section 4.5 (paragraph 3). The analysis of time series may add some insights here, but noise levels are becoming an issue when looking at the signal of *individual ion clusters* at time steps (thus averaging times) of one minute or less. We believe the analysis of time series to add too much complexity to this paper and leave it for more detailed future studies. Unfortunately, we anyway fear that our data will remain too noisy at the needed time resolution to yield insightful details of the step-by-step clustering process on the level of individual ions.

References

1. DePalma, J. W.; Bzdek, B. R.; Doren, D. J.; Johnston, M. V., Structure and energetics of nanometer size clusters of sulfuric acid with ammonia and dimethylamine. *J. Phys. Chem. A* **2012,** *116* (3), 1030-1040.
2. DePalma, J. W.; Doren, D. J.; Johnston, M. V., Formation and growth of molecular clusters containing sulfuric acid, water, ammonia and dimethylamine. *J. Phys. Chem. A* **2014,** doi: 10.1021/jp503348b.
3. Jiang, L.; Wende, T.; Bergmann, R.; Meijer, G.; Asmis, K. R., Gas-phase vibrational spectroscopy of microhydrated magnesium nitrate ions MgNO3(H2O)1-4. *J. Am. Chem. Soc.* **2010,** *132* (21), 7398-7404.
4. Johnson, C. J.; Johnson, M. A., Vibrational spectra and fragmentation pathways of size-selected, D2-tagged ammonium/methylammonium bisulfate clusters. *J. Phys. Chem. A* **2013,** *117* (50), 13265-13274.
5. Rozenberg, M.; Loewenschuss, A., Matrix isolation infrared spectrum of the sulfuric acid-monohydrate complex: New assignments and resolution of the "missing H-bonded v(OH) band" issue. *J. Phys. Chem. A* **2009,** *113* (17), 4963-4971.
6. Rozenberg, M.; Loewenschuss, A.; Nielsen, C. J., Complexes of molecular and ionic character in the same matrix layer: Infrared studies of the sulfuric acid/ammonia system. *J. Phys. Chem. A* **2011,** *115* (23), 5759-5766.
7. Rozenberg, M.; Loewenschuss, A.; Nielsen, C. J., Trimethylamine/sulfuric acid/water clusters: A matrix isolation infrared study. *J. Phys. Chem. A* **2014,** *118* (6), 1004-1011.
8. Yacovitch, T. I.; Heine, N.; Brieger, C.; Wende, T.; Hock, C.; Neumark, D. M.; Asmis, K. R., Communication: Vibrational spectroscopy of atmospherically relevant acid cluster anions: Bisulfate versus nitrate core structures. *J. Chem. Phys.* **2012,** *136* (24), doi: 10.1063/1.4732148.
9. Yacovitch, T. I.; Wende, T.; Jiang, L.; Heine, N.; Meijer, G.; Neumark, D. M.; Asmis, K. R., Infrared spectroscopy of hydrated bisulfate anion clusters: HSO4-(H2O)1-16. *J. Phys. Chem. Lett.* **2011,** *2* (17), 2135-2140.
10. Zhao, J.; Smith, J. N.; Eisele, F. L.; Chen, M.; Kuang, C.; McMurry, P. H., Observation of neutral sulfuric acid-amine containing clusters in laboratory and ambient measurements. *Atmos. Chem. Phys.* **2011,** *11* (21), 10823-10836, doi: 10.5194/acp-11-10823-2011.
11. Bzdek, B. R.; Ridge, D. P.; Johnston, M. V., Amine exchange into ammonium bisulfate and ammonium nitrate nuclei. *Atmos. Chem. Phys.* **2010,** *10* (8), 3495-3503.
12. Bzdek, B. R.; Ridge, D. P.; Johnston, M. V., Size-dependent reactions of ammonium bisulfate clusters with dimethylamine. *J. Phys. Chem. A* **2010,** *114* (43), 11638-11644, doi: 10.1021/jp106363m.
13. Bzdek, B. R.; Ridge, D. P.; Johnston, M. V., Amine reactivity with charged sulfuric acid clusters. *Atmos. Chem. Phys.* **2011,** *11* (16), 8735-8743, doi: 10.5194/acp-11-8735-2011.
14. Bzdek, B. R.; Ridge, D. P.; Johnston, M. V., Reactivity of methanesulfonic acid salt clusters relevant to marine air. *J. Geophys. Res.-Atmos.* **2011,** *116* (D3), D03301, doi: 10.1029/2010JD015217.

****

Other minor revisions not mentioned previously:

Softened a sentence in the first paragraph in section 3.4:

The number of added NH_3 molecules per added H_2SO_4 molecule remained near constant from 4 or 5 sulfur atoms up to the upper detection limit of about 27 sulfur atoms, within the measurement uncertainties.

Updated references to: Schnitzhofer et al. (AMTD → AMT, 2014), Ortega et al. (ACPD → ACP, 2014), Lehtipalo et al. (2014, volume & pages), Makkonen et al. (2014, volume & pages).

Some minor corrections, small clarifying modifications to sentences, and typos.

****

References:

Bzdek B. R., et al., *J. Am. Chem. Soc.*, 135, 3276-3285 (2013).
Chen M., et al., *Proc. Natl. Acad. Sci. USA*, 109, 18713-18718 (2012).
Ehn M., et al., *Aerosol Sci. Tech.*, 45, 522-532 (2011).
Eisele F. L., Hanson D. R., *J. Phys. Chem. A*, 104, 830-836 (2000).
Franchin A., et al., in preparation for *Atmos. Chem. Phys. Discuss.* (2014).
Gagné S., et al, *Atmos. Meas. Tech.*, 4, 805-822 (2011).
Hanson D. R., Eisele F. L., *J. Geophys. Res.*, 107, AAC 10-11-AAC 10-18 (2002).
Henschel H., et al., *J. Phys. Chem. A*, 118, 2599-2611 (2014).
Jen C. N., McMurry P. H., Hanson D. R., *J. Geophys. Res. Atmos.*, 119, 7502–7514 (2014).
Lehtipalo K., et al., *Boreal Env. Res.*, 19 (suppl. B), 215-236, 2014.
Makkonen U., et al., *Boreal Env. Res.*, 19 (suppl. B), 311-328, 2014.
Lovejoy E. R., Curtius J., Froyd K. D., *J. Geophys. Res.*, 109, D08204 (2004).
Olenius T., et al., *J. Chem. Phys.*, 139, 084312 (2013a).
Olenius T., et al., *Farad. Discuss.*, 165, 75-89 (2013b).
Ortega I. K., et al., *Atmos. Chem. Phys.*, 14, 7995-8007.
Schnitzhofer R., et al., *Atmos. Meas. Tech.*, 7, 2159-2168 (2014).
Schobesberger S., et al., *Proc. Natl. Acad. Sci. USA*, 110, 17223-17228 (2013a).
Vehkamäki H., et al., *J. Geophys. Res.*, 107, AAC 3-1–AAC 3-10 (2002).