Atmospheric
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Discussions

Interactive comment on "On the composition of ammonia-sulfuric acid clusters during aerosol particle formation" *by* S. Schobesberger et al.

Anonymous Referee #1

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

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.

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.

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 acid-base 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.

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.

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.

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.

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?

Minor Comments:

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

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.

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?

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")?

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?

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.

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?

Line 19, pg 13429: The description of $\Delta m/\Delta n$ 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?)

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

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.

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?

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.

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.

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?

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

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.

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