Response to Interactive comment on “Electrical charging changes the composition of sulfuric acid-ammonia/dimethylamine clusters” by anonymous referee 1

We want to thank the referee for his or her useful comments that certainly have helped to improve the quality of our manuscript. The answers to the comments by the referee (reproduced in bold) can be found below.

The work presented in the paper is rather thin, amounting to calculating evaporation rates from already published calculations.

There needs to be an actual application and comparison to experiment (and here they should discuss what was already done in the Faraday transactions work.) They should apply their proposed methodology (as in the very last paragraph) to neutral cluster determinations in the literature, one possibility is the original cluster work from Eisele and Hanson. They should also compare and contrast with the Zhao et al. detection of neutral clusters in the atmosphere.

The aim of this study is to assess the effect of charging on the exact chemical composition of small sulfuric acid–base clusters via the cluster evaporation rates derived from the calculated free energies. This is now better explained in the Abstract and the Conclusions. While the free energies of the studied clusters have already been published, this is in itself already an important new application, which is also directly relevant to experiments being performed by multiple groups. To compare our results with observations as suggested by the referee, we have now included in the figures and discussion evaporation rates of charged clusters determined from semi-experimental formation free energies available in the literature (Froyd and Lovejoy, 2003; Froyd and Lovejoy, 2012). The relative cluster stabilities agree well with our theoretical results. Unfortunately, there are not yet many studies on the detection of neutral clusters by chemical ionization. Our results agree with the observations of Zhao et al. (2011), who found that clusters containing at least four sulfuric acid molecules may contain also amine or ammonia after being negatively charged (which is consistent with earlier work by Eisele and Hanson (2000) and Hanson and Eisele (2002). To experimentally verify our conclusions on the effect of charging, a sample of neutral clusters should be observed after charging it both positively and negatively. This type of experiment is now proposed in the Conclusions.

Clusters will be in the presence of relatively large amounts of water vapor. Neutrals will likely have several water molecules, and the authors could present calculations on the water content of ions and whether water has a stabilizing effect.

We agree that considering the effect of hydration would be interesting. Unfortunately, no extensive dataset including formation energies of both electrically charged and neutral hydrated clusters is yet available. We also argue that it is important to understand the effect of charging on cluster composition first in the more simple dry case before proceeding to study the effect of hydration. Moreover, hydration is unlikely to have a large qualitative effect on the relative stabilities of acid–base clusters.

The charging process itself. Common reagent ions for neutral cluster detection are HNO3.NO3- and H3O+.(H2O)_5,6. In the case of the former, charging may involve leaving behind an HNO3 ligand which may help to stabilize clusters. In either case, there is usually some heat from the reaction that will increase evaporation rates.

The nitrate ion is indeed capable of stabilizing the charged cluster and might prevent the evaporation of a base molecule (Kupiainen-Määttä et al., 2103). However, studying the effect of the ligand on the stabilities of the set of clusters included in this work is unfortunately not possible due to the excessive computational costs of sampling the configurations and performing the electronic structure calculations on the full set of NO_3^- -containing clusters. The actual ionization process involving the NO_3^- ion for clusters containing one or two sulfuric acid molecules has been studied in detail by Kupiainen-Määttä et al. (2013). We also note that Zhao et al. (2011) do not report observations of any clusters containing HNO_3 ligands - their negative cluster spectra were dominated by sulfuric acid – ammonia and sulfuric acid – amine clusters. Thus, while clustering with HNO_3 may certainly play some role in the final cluster distribution, it does not seem to have a large effect at least for the instrument settings and conditions used in the Zhao et al study.

The first paragraph of the results is actually a repeat of the methods ?...?

We have now modified the text and removed the repetitive sections.

Table 2a and b are not that helpful.

We have removed the tables from the text and included them in the supplementary material

Figures 5 and 6 are poorly discussed and the captions could be tightened up. I did not get much from these figures....

We have improved the quality of the figures and re-formulated the discussion related to them.

Figure 4 could have the protonated H2SO4 clusters included and of course water would be needed. In addition, Froyd and Lovejoy have benchmark data with which to compare that would really bolster that section of the paper.

Unfortunately there is no data available for H_3O^+ H_2SO_4 clusters at the B3RICC2 level. We have now used the available semi-experimental data from Froyd and Lovejoy (2012) to calculate the evaporation rates of positively charged sulfuric acid-ammonia clusters and included them in Figures 4 and 6.

Figure 3 should have the experimental evaporation rates of neutral H2SO4 clusters but in the presence of water vapor. H2SO4 evaporation rates will drop substantially.

The purpose of the figure is to compare the stabilizing effect of one base molecule, where the base is either ammonia, DMA or a bisulfate ion on sulfuric acid clusters to illustrate the base-competition that leads to the loss of ammonia and DMA molecules from the negatively charged clusters. Since water is also a base, the comparison must be done using unhydrated sulfuric acid clusters in order to study the effect of one base at a time.

References

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