Electrical charging changes the composition of sulfuric acid–ammonia/dimethylamine clusters

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Abstract. Sulfuric acid clusters stabilized by base molecules are likely to have a significant role in atmospheric new-particle formation. Recent advances in mass spectrometry techniques have permitted the detection of electrically charged clusters. However, direct measurement of electrically neutral clusters is not possible. Mass spectrometry instruments can be combined with a charger, but the possible effect of charging on the composition of neutral clusters must be addressed in order to interpret and understand the measured data. In the present work we have used formation free energies from quantum chemical methods to calculate the evaporation rates of electrically charged (both positive and negative) sulfuric acid–ammonia/dimethylamine clusters. To understand how charging will affect the composition of electrically neutral clusters, we have compared the evaporation rates of the most stable neutral clusters with those of the corresponding charged clusters. Based on the evaporation rates of different molecules from the charged clusters, we determined the most likely resulting cluster composition when a stable neutral cluster is charged and the molecules with the highest evaporation rates are lost from it. We found that all of the most stable neutral clusters will be altered by both positive and negative charging. In the case of charging clusters negatively, base molecules will completely evaporate from clusters with 1 to 3 sulfuric acid molecules in the case of ammonia, and from clusters with 1 or 2 sulfuric acid molecules in the case of dimethylamine. Larger clusters will maintain some base molecules, but the H_2SO_4 : base ratio will increase. In the case of positive charging, some of the acid molecules will evaporate, decreasing the H_2SO_4 : base ratio.

1 Introduction

Atmospheric aerosol particles affect climate both directly and indirectly (IPCC, 2007; Merikanto et al., 2009). One of the less understood aerosol related processes is the formation of new particles from condensable vapors in the atmosphere. The participation of sulfuric acid in this process is clear (see, for example, Sipilä et al., 2010), but sulfuric acid on its own cannot explain the new-particle formation rates observed during different field campaigns. It has long been known that sulfuric acid clusters need to be stabilized to be able to form aerosol particles. The identity of these stabilizing compounds has been the subject of several studies during the recent years. Ammonia has been one of the most studied candidates to stabilize sulfuric acid clusters (Weber et al., 1996, Merikanto et al., 2007; Benson et al., 2010). Recent results from the state-of-the-art Cosmics Leaving Outdoor Droplets (CLOUD) experiment at CERN (Kirkby et al., 2011) have shown that, although the presence of ammonia can enhance the observed particle formation rate, the rates measured in the experiment are still far from those observed in the atmosphere. Organic compounds, especially organic nitrogen bases such as amines, have become the strongest candidate to explain observed formation rates. Mäkelä et al. (2001) reported the presence of amines in particles during new-particle formation events. Different quantum chemical studies have shown that amines stabilize sulfuric acid clusters more efficiently than ammonia (Kurtén et al., 2008, Loukonen et al., 2010; Nadykto et al., 2011). This is supported

by atmospheric and laboratory measurements (Smith et al., 2010; Zhao et al., 2011; Almeida et al., 2013).

The main problem in understanding new-particle formation is that the key steps occur in small molecular clusters, below 1.5 nm in diameter (see, for example, Kulmala et al., 2013). Recent developments in cutting-edge high-resolution mass spectrometry have enabled the chemical characterization of charged clusters from the molecular scale upward (Junninen et al., 2010; Ehn et al., 2011; Kirkby et al., 2011; Kulmala et al., 2013). These measurements can only provide the elemental composition of the detected clusters, which makes it impossible to distinguish between different compounds with the same elemental formula. For example, the compound with the elemental formula C_3H_7N can be either dimethylamine $((CH_3)_2NH)$ or ethylamine $(CH_3CH_2NH_2)$. In addition, these measurements alone yield no information on the composition of neutral clusters. A charger can be included in front of the mass spectrometer (Jokinen et al., 2012), but depending on the charging mechanism used in the instruments, some cluster types may not be charged, others may be broken up and others may be chemically completely altered by the process (Kurtén et al., 2011; Kupiainen-Määttä et al., 2013). Furthermore, clusters sampled by the atmospheric pressure interface time-of-flight mass spectrometer (APi-TOF-MS) pass through a low-pressure interface, where loosely bound molecules can evaporate from the clusters. In addition, high-energy collisions with gas molecules inside the instrument can also affect the composition of the detected clusters.

In the present work, we have used the formation free energies from our previous quantum-chemistry-based works (Kupiainen et al., 2012; Olenius et al., 2013a, b) to calculate the evaporation rate of charged sulfuric acid–ammonia and sulfuric acid–dimethylamine (DMA) clusters. We present a detailed analysis of the stability of charged clusters with different compositions. In addition, we compare the evaporation rates of the most stable electrically neutral clusters (Ortega et al., 2012) to those of the corresponding charged clusters in order to determine how the charging process will affect the composition of the neutral clusters.

In the atmosphere, water vapor is always present and the clusters are likely to be hydrated to some extent. In this study, however, we focus on the more simple case of dry clusters to gain a general understanding on the dependence of the optimal acid : base ratio on charging state. As water can act both as a weak acid and a weak base, it may complicate matters slightly, but while it changes the effective evaporation rates of clusters (Paasonen et al., 2012; Almeida et al., 2013), it is unlikely to have a strong impact on the ratio of stronger acid and base molecules in the most stable clusters. Furthermore, one of the main goals of this study is to understand how the charging process affects cluster composition inside measurement instruments. Within these instruments, the clusters are almost always subjected to low-pressure environments, where the absolute water concentration is very low compared

to the ambient atmosphere. Thus, while water molecules continue evaporating from the clusters (the evaporation rate is independent of the vapor concentration), the collision rate of water molecules with the clusters drops dramatically. In other words, the atmospheric hydration equilibrium is not maintained, and the clusters rapidly lose water in the instruments. The timescale for this water loss corresponds to the inverse of the water evaporation rates, and is typically on the order of micro- or nanoseconds – much shorter than the typical total residence time in the instrument. For this reason, hydrated clusters are, except for a few very strongly bound cases such as $HSO_4^- \cdot H_2O$, seldom observed in mass spectrometric experiments at anywhere close to room temperature. Therefore, studying the dry clusters is appropriate for understanding the effect of charging on cluster composition inside measurement instruments, even when the clusters are extensively hydrated before entering the instruments.

2   Methodology

In this work we have used the formation free energies calculated in our previous works (Kupiainen et al., 2012; Olenius et al., 2013a, b) using a multistep quantum chemical method (Ortega et al., 2012). The geometry optimizations and frequency calculations were performed with the Gaussian09 program (Frisch et al., 2009) using the B3LYP hybrid functional (Becke, 1993) and a CBSB7 basis set (Montgomery et al., 1999), and a single-point electronic energy was then calculated with the TURBOMOLE program (Ahlrichs et al., 1989) using the RI-CC2 method (Hättig and Weigend, 2000) and an aug-cc-pV(T+d)Z basis set (Dunning et al., 2001). We will refer to this method as B3RICC2.

In a previous study (Ortega et al., 2012) we compared the results obtained with the B3RICC2 method with those of the high-level multistep method CBS-QB3 (Montgomery et al., 1999). The agreement between these two methods was very good (with an average difference of 0.74 kcal mol^{-1}). Later work by Leverenz et al. (2013) has shown that B3RICC2 somewhat overestimates the binding of sulfuric acid–DMA clusters compared to higher level methods. On the other hand, the experimental results of Almeida et al. (2013) confirm our finding that DMA stabilizes sulfuric acid dimers significantly more strongly than ammonia.

Unfortunately, the Gibbs formation free energies of the neutral clusters studied here have not been determined experimentally. Present experimental techniques to estimate the Gibbs formation free energies are based on mass spectrometry measurements, and thus only charged clusters can be studied. This leaves theoretical methods, of which quantum chemistry is currently the most accurate method, as the only way to determine Gibbs formation free energies of neutral clusters. Experimental Gibbs formation free energies exist for some of the charged clusters studied in this work (Froyd and Lovejoy, 2003, 2012). For these cases a direct

comparison between quantum chemical and experimental results is possible.

The evaporation rate of a certain molecule or cluster, $N_i(\gamma_i)$, from the cluster N_{i+j} is related to the Gibbs formation free energies through the equation (see, for example, Ortega et al., 2012, and references therein)

$$\gamma_i\left(N_{i+j}\right) = \beta_{ij}c_{\text{ref}}\exp?\left(\frac{\Delta G\left(N_{i+j}\right) - \Delta G\left(N_i\right) - \Delta G\left(N_j\right)}{kT}\right) \quad (1)$$

where β_{ij} is the collision rate of N_i with N_j; $\Delta G(N_{i+j})$, $\Delta G(N_i)$ and $\Delta G(N_j)$ are the Gibbs free energies of formation of clusters N_{i+j}: N_i and N_j from monomers at the reference vapor concentration c_{ref}; k is the Boltzmann constant and T is the temperature. It must be noted that in the case where N_i and/or N_j are/is monomers/a monomer, $\Delta G(N_i)$ and/or $\Delta G(N_j)$ are/is by definition zero.

The collision rate of a charged cluster with a neutral molecule or cluster was calculated according to the parameterization of Su and Chesnavich (1982) that takes into account the dipole moment and polarizability of the neutral species. This parameterization was chosen based on the work by Kupiainen-Määttä et al. (2013) and its good performance in reproducing observed experimental collision rates (Viggiano et al., 1997).

3 Clusters included in the study

We have included negatively and positively charged clusters containing up to four sulfuric acid and four DMA molecules and up to five sulfuric acid and five ammonia molecules. Some clusters with an unfavorable acid : base ratio have been left out due to their relatively low stability, as discussed by Olenius et al. (2013a). Tables S1a and S1b in the Supplement summarize the specific negative and positive clusters included in this study.

As a comparison, we have also used semi-experimental cluster energies for positively charged sulfuric acid–ammonia clusters from Froyd and Lovejoy (2012) and for negatively charged sulfuric acid clusters from Froyd and Lovejoy (2003). In both experimental studies the reaction enthalpies and entropies were determined by a Van't Hoff analysis of equilibrium constants. It has to be noted that in some cases, for example for negatively charged pure sulfuric acid clusters, a direct determination of entropy was not possible, and thus the reported entropies were calculated using ab initio methods. In the comparison we have also included theoretical cluster energies for negatively charged and electrically neutral sulfuric acid–ammonia clusters calculated by Herb et al. (2011, 2013) with the PW91PW91/6-311++G(3df,3pd) method.

4 Results

Figure 1 shows the structures of the most stable clusters with one to four (or five in the case of pure sulfuric acid and ammonia-containing clusters) sulfuric acid molecules for (a) negatively charged sulfuric acid clusters, (b) negatively charged ammonia-containing clusters, (c) negatively charged DMA-containing clusters, (d) positively charged ammonia-containing clusters and (e) positively charged DMA-containing clusters (xyz coordinates for all clusters included in the study are provided in the Supplement). Note that in the case of negatively charged base-containing clusters, the "most stable cluster" refers to the most stable cluster with at least one base molecule, not to the most stable negatively charged cluster overall. Negatively charged DMA-containing clusters must contain at least three sulfuric acid molecules (including the bisulfate ion) to have a low enough evaporation rate to be abundant under atmospheric conditions, while in the case of ammonia-containing clusters, four sulfuric acid molecules (including the bisulfate ion) are needed. For negative clusters containing four acids and either DMA or ammonia, the most stable clusters contain two base molecules. The second DMA molecule accepts a proton from the HSO_4^- ion, forming a sulfate ion (SO_4^{2-}). The sulfate ion is also formed in the $(H_2SO_4)_4 \cdot HSO_4^- \cdot (NH_3)_3$ cluster.

The general structures of the most stable positively charged clusters are similar for both the ammonia- and DMA-containing systems. All base molecules are found in their protonated form as long as the cluster contains enough sulfuric acid molecules to donate the protons. Unsurprisingly, the sulfate ion (SO_4^{2-}) is never formed in positively charged clusters. The composition of the most stable positively charged clusters can be summarized as $(HSO_4^-)_x \cdot (NH_4^+)_{x+1} // ((CH_3)_2NH_2^+)_{x+1}$.

In our previous work (Ortega et al., 2012) we showed that, based on the computed Gibbs formation energies alone, cluster-fission processes were expected to be more important than monomer evaporation for some neutral clusters. Thus, in the present work, we have calculated the monomer evaporation rates and all the possible cluster fission rates. In some cases two or more evaporation pathways have similar rates, so we have decided to use the sum of all possible evaporation pathways in the study. Tables 1 and 2 summarize the highest evaporation rate for each cluster, the molecule/cluster with the highest rate, and the total evaporation rate, which is the sum over all possible evaporation pathways. As in the neutral system, cluster fission is only relevant for DMA-containing clusters. The fragments leaving the cluster in the fission process are $(H_2SO_4)_2 \cdot (CH_3)_2NH$ and $(H_2SO_4)_2 \cdot ((CH_3)_2NH)_2$, which are extremely stable (Ortega et al., 2012).
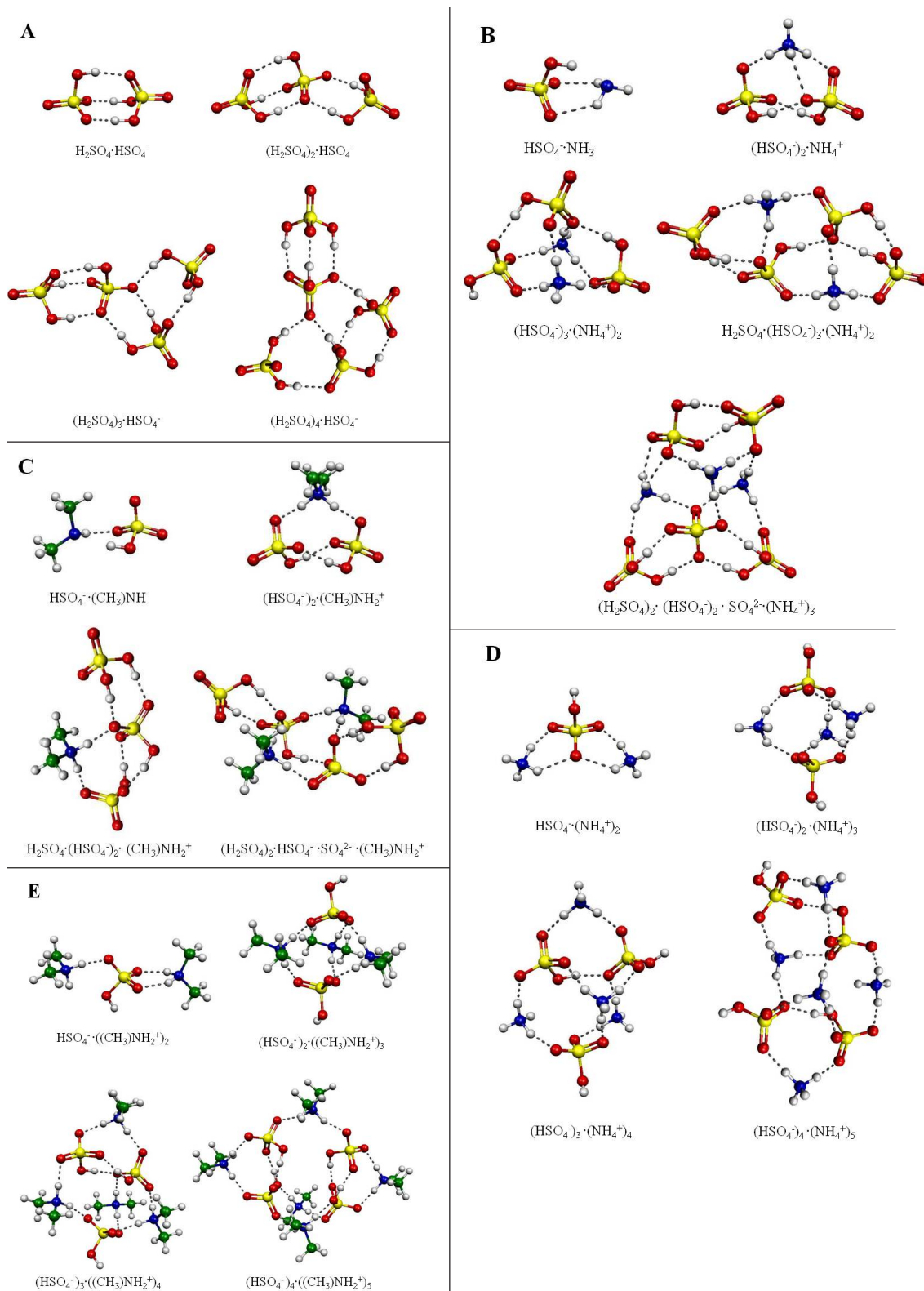
Figure 1. Structures of clusters with one to four/five sulfuric acid molecules and the most favorable number of base molecules (those with the lowest total evaporation rate) for **(A)** negatively charged sulfuric acid clusters, **(B)** negatively charged ammonia-containing clusters, **(C)** negatively charged DMA-containing clusters, **(D)** positively charged ammonia-containing clusters and **(E)** positively charged DMA-containing clusters. Red spheres represent oxygen atoms, yellow spheres represent sulfur atoms, blue spheres represent nitrogen atoms, white spheres represent hydrogen atoms and green spheres represent carbon atoms.

Table 1. Highest evaporation rate, corresponding evaporating molecule/cluster and total evaporation rate at 298.15 K for different negatively charged clusters studied.

Cluster	Highest evaporation rate (s^{-1})	Corresponding evaporating molecule/cluster	Total evaporation rate (s^{-1})
$H_2SO_4 \cdot HSO_4^-$	2.70×10^{-15}	H_2SO_4	2.70×10^{-15}
$(H_2SO_4)_2 \cdot HSO_4^-$	5.60×10^{-3}	H_2SO_4	5.60×10^{-3}
$(H_2SO_4)_3 \cdot HSO_4^-$	2.41×10^1	H_2SO_4	2.41×10^1
$(H_2SO_4)_4 \cdot HSO_4^-$	2.82×10^3	H_2SO_4	2.82×10^3
$HSO_4^- \cdot NH_3$	4.23×10^{11}	NH_3	4.23×10^{11}
$H_2SO_4 \cdot HSO_4^- \cdot NH_3$	2.00×10^{10}	NH_3	2.00×10^{10}
$(H_2SO_4)_2 \cdot HSO_4^- \cdot NH_3$	1.57×10^5	NH_3	1.57×10^5
$(H_2SO_4)_3 \cdot HSO_4^- \cdot NH_3$	2.74×10^1	NH_3	2.74×10^1
$(H_2SO_4)_4 \cdot HSO_4^- \cdot NH_3$	1.90	H_2SO_4	2.29
$(H_2SO_4)_2 \cdot HSO_4^- \cdot (NH_3)_2$	1.16×10^5	NH_3	1.16×10^5
$(H_2SO_4)_3 \cdot HSO_4^- \cdot (NH_3)_2$	1.09×10^1	NH_3	1.09×10^1
$(H_2SO_4)_4 \cdot HSO_4^- \cdot (NH_3)_2$	3.45×10^{-1}	NH_3	4.06×10^{-1}
$(H_2SO_4)_3 \cdot HSO_4^- \cdot (NH_3)_3$	2.19×10^3	NH_3	2.19×10^3
$(H_2SO_4)_4 \cdot HSO_4^- \cdot (NH_3)_3$	9.42×10^{-3}	NH_3	9.42×10^{-3}
$(H_2SO_4)_4 \cdot HSO_4^- \cdot (NH_3)_4$	3.14×10^9	NH_3	3.14×10^9
$HSO_4^- \cdot (CH_3)_2NH$	8.18×10^9	$(CH_3)_2NH$	8.18×10^9
$H_2SO_4 \cdot HSO_4^- \cdot (CH_3)_2NH$	5.23×10^2	$(CH_3)_2NH$	5.23×10^2
$(H_2SO_4)_2 \cdot HSO_4^- \cdot (CH_3)_2NH$	5.28×10^{-2}	$(CH_3)_2NH$	5.71×10^{-2}
$(H_2SO_4)_3 \cdot HSO_4^- \cdot (CH_3)_2NH$	1.89	$(H_2SO_4)_2 \cdot (CH_3)_2NH$	2.11
$H_2SO_4 \cdot HSO_4^- \cdot ((CH_3)_2NH)_2$	3.82×10^8	$(CH_3)_2NH$	3.82×10^8
$(H_2SO_4)_2 \cdot HSO_4^- \cdot ((CH_3)_2NH)_2$	2.67×10^{-1}	$(CH_3)_2NH$	2.67×10^{-1}
$(H_2SO_4)_3 \cdot HSO_4^- \cdot ((CH_3)_2NH)_2$	1.47×10^{-3}	$(H_2SO_4)_2 \cdot ((CH_3)_2NH)_2$	1.47×10^{-3}
$(H_2SO_4)_2 \cdot HSO_4^- \cdot ((CH_3)_2NH)_3$	2.46×10^4	$(CH_3)_2NH$	2.46×10^4
$(H_2SO_4)_3 \cdot HSO_4^- \cdot ((CH_3)_2NH)_3$	3.10×10^1	$(CH_3)_2NH$	3.10×10^1
$(H_2SO_4)_3 \cdot HSO_4^- \cdot ((CH_3)_2NH)_4$	7.70×10^1	$(CH_3)_2NH$	7.70×10^1

4.1 Negative clusters

Evaporation rates of pure sulfuric acid, sulfuric acid–ammonia and sulfuric acid–DMA clusters at 298.15 K are compared in Fig. 2. The negatively charged sulfuric acid dimer, $H_2SO_4 \cdot HSO_4^-$, is extremely stable, with an evaporation rate of practically zero. The negatively charged sulfuric acid trimer, $(H_2SO_4)_2 \cdot HSO_4^-$, is also stable, with an evaporation rate of $5.60 \times 10^{-3}\,s^{-1}$. The collision frequency of free sulfuric acid molecules with one charged trimer is around $1 \times 10^{-9}\,s^{-1}\,cm^{-3}$. Thus, if the concentration of sulfuric acid monomers is around 5×10^6 cm^{-3} or larger, the collisions of sulfuric acid monomers with the cluster will be faster than evaporation. In the case of the charged tetramer, $(H_2SO_4)_3 \cdot HSO_4^-$, the evaporation rate is already relatively high, requiring a higher concentration of sulfuric acid to allow for a collision before the cluster evaporates. The charged pure sulfuric acid pentamer, $(H_2SO_4)_4 \cdot HSO_4^-$, is not stable, with an evaporation rate of $2.82 \times 10^3\,s^{-1}$. Therefore, as in the neutral case (Ortega et al., 2012), additional stabilizing compounds are needed to allow for further additions of sulfuric acid molecules to the cluster. Similar results are ob-

tained using formation free energies from Froyd and Lovejoy (2003) and Herb et al. (2013) (Fig. 2).

Ammonia evaporation rates from $HSO_4^- \cdot NH_3$ and $H_2SO_4 \cdot HSO_4^- \cdot NH_3$ clusters are around 10^{10}–$10^{11}\,s^{-1}$. For the $(H_2SO_4)_2 \cdot HSO_4^- \cdot NH_3$ cluster, the ammonia evaporation rate is close to $10^5\,s^{-1}$, and thus the ammonia concentration needs to be on the order of 10^{14} cm^{-3} (around 4 ppm) for collisions to be frequent enough to retain ammonia in the cluster after charging. The $(H_2SO_4)_3 \cdot HSO_4^- \cdot NH_3$ cluster is as stable as the pure charged four sulfuric acid cluster $(H_2SO_4)_3 \cdot HSO_4^-$, and the $(H_2SO_4)_3 \cdot HSO_4^- \cdot (NH_3)_2$ is the most stable negatively charged cluster with four sulfuric acid molecules. Both the $(H_2SO_4)_4 \cdot HSO_4^- \cdot NH_3$ and $(H_2SO_4)_4 \cdot HSO_4^- \cdot (NH_3)_2$ clusters are more stable than the pure five sulfuric acid cluster, $(H_2SO_4)_4 \cdot HSO_4^-$. In the case of the $(H_2SO_4)_4 \cdot HSO_4^- \cdot NH_3$ cluster, H_2SO_4 will evaporate faster than ammonia from the cluster. The results obtained using formation free energies from Herb et al. (2013) show a similar trend. Nevertheless, it has to be noted that the data from Herb et al. (2013) are limited to clusters containing just one ammonia molecule, and thus the stability of negatively charged clusters with three and four sulfuric acid

Table 2. Highest evaporation rate, corresponding evaporating molecule/cluster and total evaporation rate at 298.15 K for different positively charged clusters studied.

Cluster	Highest evaporation rate (s^{-1})	Corresponding evaporating molecule/cluster	Total evaporation rate (s^{-1})
$H_2SO_4 \cdot NH_4^+$	3.53×10^{-1}	H_2SO_4	3.53×10^{-1}
$(H_2SO_4)_2 \cdot NH_4^+$	2.79×10^2	H_2SO_4	2.79×10^2
$NH_3 \cdot NH_4^+$	5.45×10^{-5}	NH_3	5.45×10^{-5}
$H_2SO_4 \cdot NH_3 \cdot NH_4^+$	2.76×10^{-2}	H_2SO_4	2.76×10^{-2}
$(H_2SO_4)_2 \cdot NH_3 \cdot NH_4^+$	1.22	H_2SO_4	1.22
$(H_2SO_4)_3 \cdot NH_3 \cdot NH_4^+$	4.16×10^2	H_2SO_4	4.16×10^2
$(NH_3)_2 \cdot NH_4^+$	2.13×10^4	NH_3	2.13×10^4
$H_2SO_4 \cdot (NH_3)_2 \cdot NH_4^+$	9.84×10^2	NH_3	9.84×10^2
$(H_2SO_4)_2 \times (NH_3)_2 \cdot NH_4^+$	2.31×10^{-5}	NH_3	2.31×10^{-5}
$(H_2SO_4)_3 \cdot (NH_3)_2 \cdot NH_4^+$	2.25×10^2	H_2SO_4	2.25×10^2
$(H_2SO_4)_4 \cdot (NH_3)_2 \cdot NH_4^+$	5.64×10^3	H_2SO_4	5.65×10^3
$(H_2SO_4)_2 \cdot (NH_3)_3 \cdot NH_4^+$	1.69×10^4	NH_3	1.69×10^4
$(H_2SO_4)_3 \cdot (NH_3)_3 \cdot NH_4^+$	5.75×10^{-4}	NH_3	5.85×10^{-4}
$(H_2SO_4)_4 \cdot (NH_3)_3 \cdot NH_4^+$	1.18×10^2	H_2SO_4	1.18×10^2
$(H_2SO_4)_3 \cdot (NH_3)_4 \cdot NH_4^+$	2.28×10^4	NH_3	2.28×10^4
$(H_2SO_4)_4 \cdot (NH_3)_4 \cdot NH_4^+$	6.86×10^{-1}	NH_3	6.906×10^{-1}
$(H_2SO_4)_5 \times (NH_3)_4 \cdot NH_4^+$	1.20	H_2SO_4	1.23
$(H_2SO_4) \cdot (CH_3)_2NH_2^+$	7.65×10^2	H_2SO_4	7.65×10^2
$(H_2SO_4)_2 \cdot (CH_3)_2NH_2^+$	7.08×10^1	H_2SO_4	7.11×10^1
$(CH_3)_2NH \cdot (CH_3)_2NH_2^+$	1.66×10^{-2}	$(CH_3)_2NH$	1.66×10^{-2}
$H_2SO_4 \cdot (CH_3)_2NH \cdot (CH_3)_2NH_2^+$	1.630×10^{-10}	H_2SO_4	1.630×10^{-10}
$(H_2SO_4)_2 \cdot (CH_3)_2NH \cdot (CH_3)_2NH_2^+$	1.63	H_2SO_4	1.63
$((CH_3)_2NH)_2 \cdot (CH_3)_2NH_2^+$	1.04×10^4	$(CH_3)_2NH$	1.04×10^4
$H_2SO_4 \cdot ((CH_3)_2NH)_2 \cdot (CH_3)_2NH_2^+$	2.71×10^{-2}	$(CH_3)_2NH$	2.71×10^{-2}
$(H_2SO_4)_2 \cdot ((CH_3)_2NH)_2 \cdot (CH_3)_2NH_2^+$	5.79×10^{-10}	H_2SO_4	8.14×10^{-10}
$(H_2SO_4)_3 \cdot ((CH_3)_2NH)_2 \cdot (CH_3)_2NH_2^+$	1.26×10^2	H_2SO_4	1.26×10^2
$(H_2SO_4)_4 \cdot ((CH_3)_2NH)_2 \cdot (CH_3)_2NH_2^+$	1.74×10^{-1}	H_2SO_4	1.74×10^{-1}
$(H_2SO_4)_2 \cdot ((CH_3)_2NH)_3 \cdot (CH_3)_2NH_2^+$	1.54×10^{-2}	$(CH_3)_2NH$	1.54×10^{-2}
$(H_2SO_4)_3 \cdot ((CH_3)_2NH)_3 \cdot (CH_3)_2NH_2^+$	1.46×10^{-8}	H_2SO_4	1.79×10^{-8}
$(H_2SO_4)_4 \cdot ((CH_3)_2NH)_3 \cdot (CH_3)_2NH_2^+$	4.25×10^3	H_2SO_4	4.25×10^3
$(H_2SO_4)_4 \cdot ((CH_3)_2NH)_4 \cdot (CH_3)_2NH_2^+$	1.53×10^{-5}	$H_2SO_4 \cdot (CH_3)_2NH$	1.54×10^{-5}

molecules (including the bisulfate ion) is not directly comparable to the most stable clusters predicted by B3RICC2 method, which contain two molecules of ammonia. Therefore we have not included those values in the comparison.

The stability of the $HSO_4^- \cdot (CH_3)_2NH$ cluster is similar to the corresponding ammonia cluster. However, in DMA-containing clusters, the stability increases much faster as the number of sulfuric acid molecules increases than in ammonia-containing clusters. The $(H_2SO_4)_2 \cdot HSO_4^- \cdot (CH_3)_2NH$ cluster is already close in stability to the pure charged three sulfuric acid cluster, and $(H_2SO_4)_3 \cdot HSO_4^- \cdot ((CH_3)_2NH)_2$ is more stable than the $(H_2SO_4)_3 \cdot HSO_4^-$ cluster.

Similar trends have been observed in several experimental studies. Hanson and Eisele (2002) saw that all dimers and most three sulfuric acid clusters con-

tained no ammonia, while larger clusters contained at least one ammonia molecule. Bzdek et al. (2011) observed mostly ammonia-free clusters up to the tetramer $(H_2SO_4)_3 \cdot HSO_4^-$, and for larger clusters mostly a composition, $(H_2SO_4)_{i+3} \cdot HSO_4^- \cdot (NH_3)_i$. A similar composition was found also for mixed sulfuric acid–ammonia–DMA clusters, but clusters consisting only of sulfuric acid and DMA had a higher ratio of DMA. Kirkby et al. (2011) measured pure negatively charged sulfuric acid clusters up to 20 molecules at 248 K when almost no base contaminants were present, but at higher temperatures and higher base concentrations they also saw ammonia and DMA molecules in the clusters beginning from the four sulfuric acid cluster. Using the same setup but with a higher DMA concentration, Almeida et al. (2013) saw DMA molecules already in clusters with three sulfuric acid molecules.
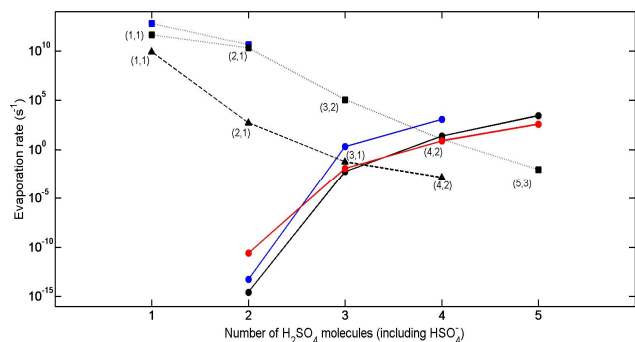
Figure 2. Total evaporation rates at 298.15 K (s^{-1}) for most stable negatively charged clusters versus the number of sulfuric acid molecules in the cluster including the bisulfate ion; that is, 1 corresponds to HSO_4^-, 2 corresponds to $H_2SO_4\ HSO_4^-$ etc. Solid lines represent pure sulfuric acid clusters, dashed lines represent sulfuric acid–DMA clusters and dotted lines represent sulfuric acid–ammonia clusters. Black lines represent evaporation rates from this work, blue lines represent evaporation rates obtained using the theoretical formation free energies by Herb et al. (2013) and red lines represent evaporation rates obtained using the semi-experimental formation free energies reported by Froyd and Lovejoy (2003). Numbers in parentheses indicate the composition of the cluster (acids, bases).
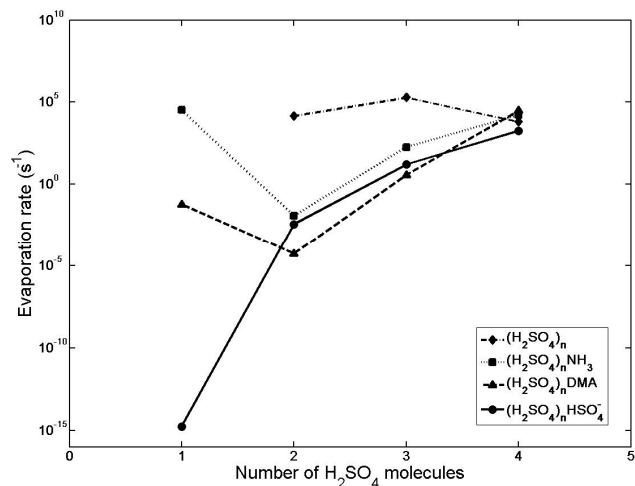
Figure 3. Total evaporation rates at 298.15 K (s^{-1}) of sulfuric acid clusters containing one Lewis base versus the number of sulfuric acid molecules in the cluster (not including the bisulfate ion). The dash-dotted line represents pure neutral sulfuric acid clusters, the dotted line represents neutral sulfuric acid clusters with one ammonia molecule, the dashed line represents neutral sulfuric acid clusters with one DMA molecule and the solid line represents pure sulfuric acid clusters with one HSO_4^- ion. Note that, unlike in Fig. 2, 1 now corresponds to $H_2SO_4 \cdot X$, 2 corresponds to $(H_2SO_4)_2 \cdot X$ etc., where $X = NH_3$, DMA or HSO_4^-.

These results confirm that while sulfuric acid is able to form up to anionic trimers on its own, in a similar way to neutral clusters, some additional stabilizing compound is
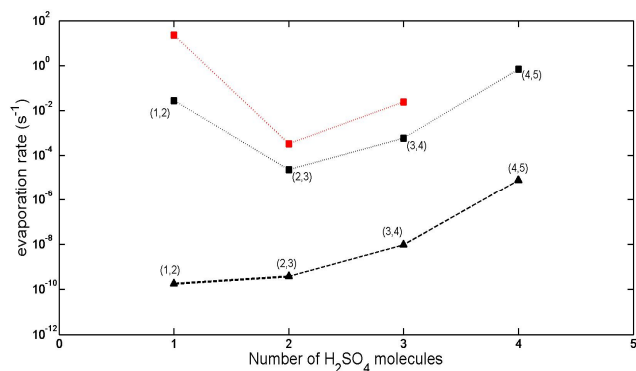

Figure 4. Total evaporation rates at 298.15 K (s^{-1}) for most stable positively charged clusters versus the number of sulfuric acid molecules in the cluster. Dashed lines represent sulfuric acid–DMA clusters and dotted lines represent sulfuric acid–ammonia clusters. Black lines represent evaporation rates from this work and the red line represents evaporation rates obtained using the formation free energies reported by Froyd and Lovejoy (2012). Numbers in parentheses indicate the composition of the cluster (acids, bases).

needed to enable further growth by addition of sulfuric acid molecules. This is not surprising, since the bisulfate ion itself is a Lewis base, and thus able to stabilize the cluster. Figure 3 compares the evaporation rates of pure neutral sulfuric acid clusters and clusters containing one stabilizing base (including the bisulfate ion as a base). In all cases, one base molecule is able to stabilize only clusters with up to three sulfuric acid molecules, and additional base molecules are needed to stabilize larger clusters. HSO_4^- is able to form very stable clusters with one sulfuric acid molecule compared to DMA and NH_3, but clusters with two sulfuric acid molecules are already better stabilized by DMA. As sulfuric acid molecules are added to the cluster, the evaporation rate approaches that of pure neutral sulfuric acid clusters. Clusters containing four sulfuric acid molecules are not stabilized sufficiently by just one base, and thus the evaporation rate of clusters containing four sulfuric acids and a base is similar to the evaporation rate of the pure sulfuric acid tetramer. As already shown by Ortega et al. (2012), further base molecules are needed to stabilize larger clusters. It is not possible to add a second bisulfate ion to a small cluster due to electrostatic repulsion, but a neutral nitrogen-containing base (ammonia or DMA) can be added.

4.1.1 Positive clusters

For each number of sulfuric acid molecules, the most stable positively charged clusters (Fig. 4) have evaporation rates below $1\,s^{-1}$. In the case of positive sulfuric acid–ammonia clusters, the most stable cluster is $(H_2SO_4)_2 \cdot (NH_3)_2 \cdot NH_4^+$. As cluster size increases, the evaporation rate increases. As in negatively charged clusters, DMA clusters are more stable than ammonia clusters. For DMA the most stable cluster

is $H_2SO_4 \cdot (CH_3)_2NH \cdot (CH_3)_2NH_2^+$, and, as in the case of ammonia, as cluster size increases, so too does the evaporation rate. The acid : base stoichiometry of positively charged clusters is the same for ammonia and DMA. The most stable clusters are formed by the cation and an equal number of sulfuric acid and base molecules.

This same optimal stoichiometry has also been observed experimentally by Bzdek et al. (2010) for clusters where the acid was either sulfuric acid or nitric acid and the base was either ammonia, methylamine, dimethylamine or trimethylamine. Almeida et al. (2013) found this stoichiometry to be dominant for small sulfuric acid–DMA clusters, but, starting from four sulfuric acids, clusters with a higher DMA content were seen to dominate. Froyd and Lovejoy (2012) detected positively charged sulfuric acid–ammonia clusters with a wider variety of acid : base ratios, but all clusters contained more ammonia than sulfuric acid molecules and most stable ones had the same optimal stoichiometry found in this work and by Bzdek et al. (2010). The evaporation rates obtained using the formation free energies reported by Froyd and Lovejoy (2012) present the same trend that the ones calculated from B3RICC2 formation free energies, though B3RICC2 evaporation rates seem to be systematically underestimated.

In this case NH_4^+ and $(CH_3)_2NH_2^+$ cations (or technically the protons bound to the nitrogen atoms) are Lewis acids, so there will be competition for bases between the cation and the sulfuric acid, instead of competition between bases for the available acids.

4.1.2 Charging neutral clusters

To evaluate the effect of charging in the detection of neutral clusters by mass spectrometry techniques, we have compared the evaporation rates of the most stable base-containing neutral clusters to the evaporation rates of the charged clusters obtained by adding or removing a proton from the neutral clusters (Figs. 5–7).

Figure 5 shows the most stable ammonia-containing neutral clusters and the corresponding negatively charged ones. We can see that if the most stable neutral ammonia-containing clusters become charged, their charged counterpart is unstable. For example, the $(H_2SO_4)_2 \cdot NH_3$ cluster is stable, but its negatively charged counterpart, $H_2SO_4 \cdot HSO_4^- \cdot NH_3$, is extremely unstable and the ammonia molecule will evaporate, resulting in the charged pure sulfuric acid dimer. The situation for charged clusters containing three sulfuric acid molecules is similar. Neutral ammonia-containing clusters will lose the ammonia molecules when charged, and will be detected as pure charged trimers. Once the cluster has four sulfuric acid molecules, only one ammonia molecule is likely to evaporate from the cluster. Thus, although some ammonia molecules will stay in the cluster, the composition of the resulting charged cluster will be different from the original neutral
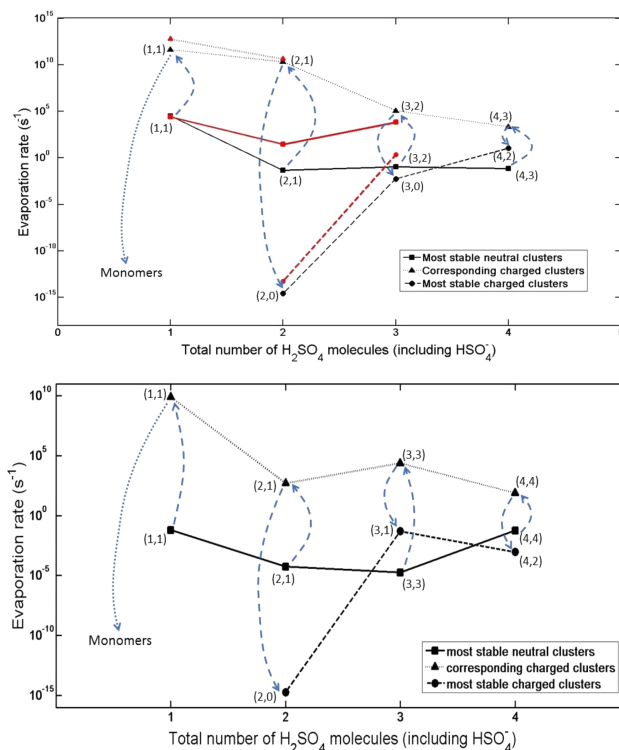

Figure 5. Comparison of the total evaporation rates at 298.15 K (s^{-1}) of neutral clusters (solid lines), negatively charged clusters obtained by removing a proton (dotted lines) and the most stable negatively charged clusters with the same number of sulfuric acid molecules (including the bisulfate ion, dashed lines). Black lines represent evaporation rates from this work and red lines represent evaporation rates obtained using the formation free energies by Herb et al. (2013). Numbers in parentheses indicate the composition of the cluster (acids, bases). Blue arrows illustrate the charging process and the resulting most stable charged cluster. Top panel: ammonia-sulfuric acid clusters. Bottom panel: DMA-sulfuric acid clusters.

cluster. Evaporation rates based on the computational cluster energies by Herb et al. (2011, 2013) have been included for comparison. While they predict the clusters to be overall less stable, the trends of cluster composition and stability as a function of sulfuric acid content are very similar to our results. As in Fig. 2, only clusters with comparable composition have been included in the comparison. Similarly, in the case of DMA-containing clusters, the most stable neutral cluster $(H_2SO_4)_2 \cdot (CH_3)_2NH$ will lose the DMA molecule when it is charged, ending up as a charged pure sulfuric acid cluster. The main difference between ammonia and DMA clusters is that three sulfuric acid molecules are enough to keep some DMA molecules in the cluster after negative charging. As in the case of ammonia, the number of DMA molecules in a stable neutral cluster will decrease when the cluster is charged. This has important implications, since according to recent modeling studies (Olenius et al.,
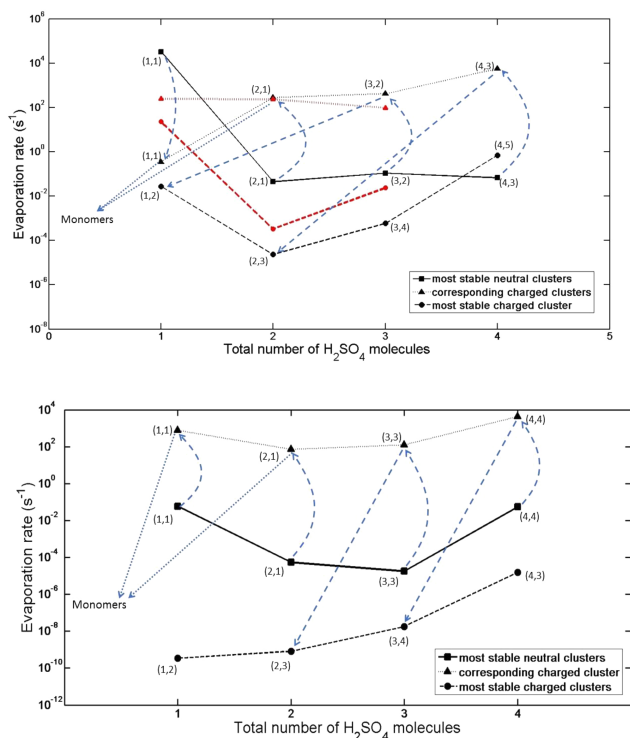
Figure 6. Comparison of the total evaporation rates at 298.15 K (s^{-1}) of neutral clusters (solid lines), positively charged clusters with one proton added (dotted lines) and the most stable positively charged clusters with the same number of sulfuric acid molecules (dashed lines). Numbers in parentheses indicate the composition of the cluster (acids, bases). Black lines represent evaporation rates from this work and red lines represent evaporation rates obtained using the formation free energies by Froyd and Lovejoy (2012). Numbers in parentheses indicate the composition of the cluster (acids, bases). Blue arrows illustrate the charging process and the resulting most stable charged cluster. Top panel: ammonia-sulfuric acid clusters. Bottom panel: DMA-sulfuric acid clusters.

2013b; Kupiainen-Määttä et al., 2013), $H_2SO_4 \cdot DMA$ and $(H_2SO_4)_2 \cdot DMA$ clusters might be relatively abundant under atmospheric conditions, but they will not be detected by mass spectrometry techniques as DMA-containing clusters.

Charging base-containing clusters positively will also affect their composition (Fig. 6). The $H_2SO_4 \cdot NH_3$ cluster (which is very unstable although it is the most stable neutral ammonia-containing cluster with one sulfuric acid molecule) is stabilized by being ionized positively, but for all larger sizes the most stable neutral clusters will not remain stable when charged positively. The $(H_2SO_4)_2 \cdot NH_4^+$ cluster will evaporate one sulfuric acid molecule, leading to the stable $H_2SO_4 \cdot NH_4^+$ cluster. In the case of neutral clusters, the number of sulfuric acid molecules in stable clusters is one higher than the number of ammonia molecules, while in the most stable positively charged clusters the number of ammonia molecules (including the NH_4^+ ion) is one higher than number of sulfuric acid molecules. Therefore clusters con-

taining three and four sulfuric acids need to evaporate two sulfuric acid molecules after being charged in order to reach a favorable composition. Here the results are compared to evaporation rates based on the semi-experimental cluster energies by Froyd and Lovejoy (2012), and again the main trends are in agreement with our conclusions.

In the case of DMA-containing clusters, all the charged counterparts of the most stable neutral clusters are unstable. $H_2SO_4 \cdot (CH_3)_2NH_2^+$ and $(H_2SO_4)_2 \cdot (CH_3)_2NH_2^+$ clusters will most probably evaporate into monomers. In the case of larger clusters, which in the neutral case favor the same number of DMA and sulfuric acid molecules, positively charged clusters will evaporate one sulfuric acid molecule, leading to the formation of the stable clusters $(H_2SO_4)_2 \cdot (CH_3)_2NH \cdot (CH_3)_2NH_2^+$ and $(H_2SO_4)_2 \cdot ((CH_3)_2NH)_2 \cdot (CH_3)_2NH_2^+$.

Figure 7 schematically represents the effect of charging on the composition of the most stable neutral ammonia/DMA-containing clusters. In Fig. 7, the decay of a neutral cluster is presented as a step-wise evaporation process determined by the highest evaporation rate of each cluster on the evaporation pathway. In the figure we have included evaporation pathways until the resulting cluster has an evaporation rate lower than $10 \, s^{-1}$, and therefore the last cluster on the pathway may not be the most stable one in terms of total evaporation rate (Figs. 5 and 6). This limit is arbitrary and has been chosen for figure clarity. The relative concentration of different clusters is not only determined by their evaporation rates but also by the collision frequency of different species with the cluster. In other words, the most stable cluster (in terms of evaporation rate) will not always be the most abundant. However, in the case of clusters with extremely high evaporation rates, for example in the case of $HSO_4^- \cdot NH_3$, the concentration of those clusters will be close to zero in any atmospherically relevant conditions. In a similar way, if the evaporation rate is close to zero, like for $H_2SO_4 \cdot HSO_4^-$ cluster, the cluster will not evaporate under any atmospherically relevant conditions.

5 Conclusions

In this work we present the evaporation rates of both positively and negatively charged sulfuric acid–ammonia and sulfuric acid–DMA clusters. We found that the most stable positively charged base-containing clusters have evaporation rates below $1 \, s^{-1}$, while in the case of the smallest negatively charged clusters the pure sulfuric acid clusters with evaporation rates on the order of 10^{-15}–$10^{-3} \, s^{-1}$ are more stable than the most stable base-containing clusters (for which the evaporation rates are 10^5–$10^{11} \, s^{-1}$), and bases become important only when the cluster contains more than 3–4 sulfuric acid molecules. DMA-containing positively charged clusters are more stable than the ammonia-containing clusters, and in both cases the stability decreases when the cluster size
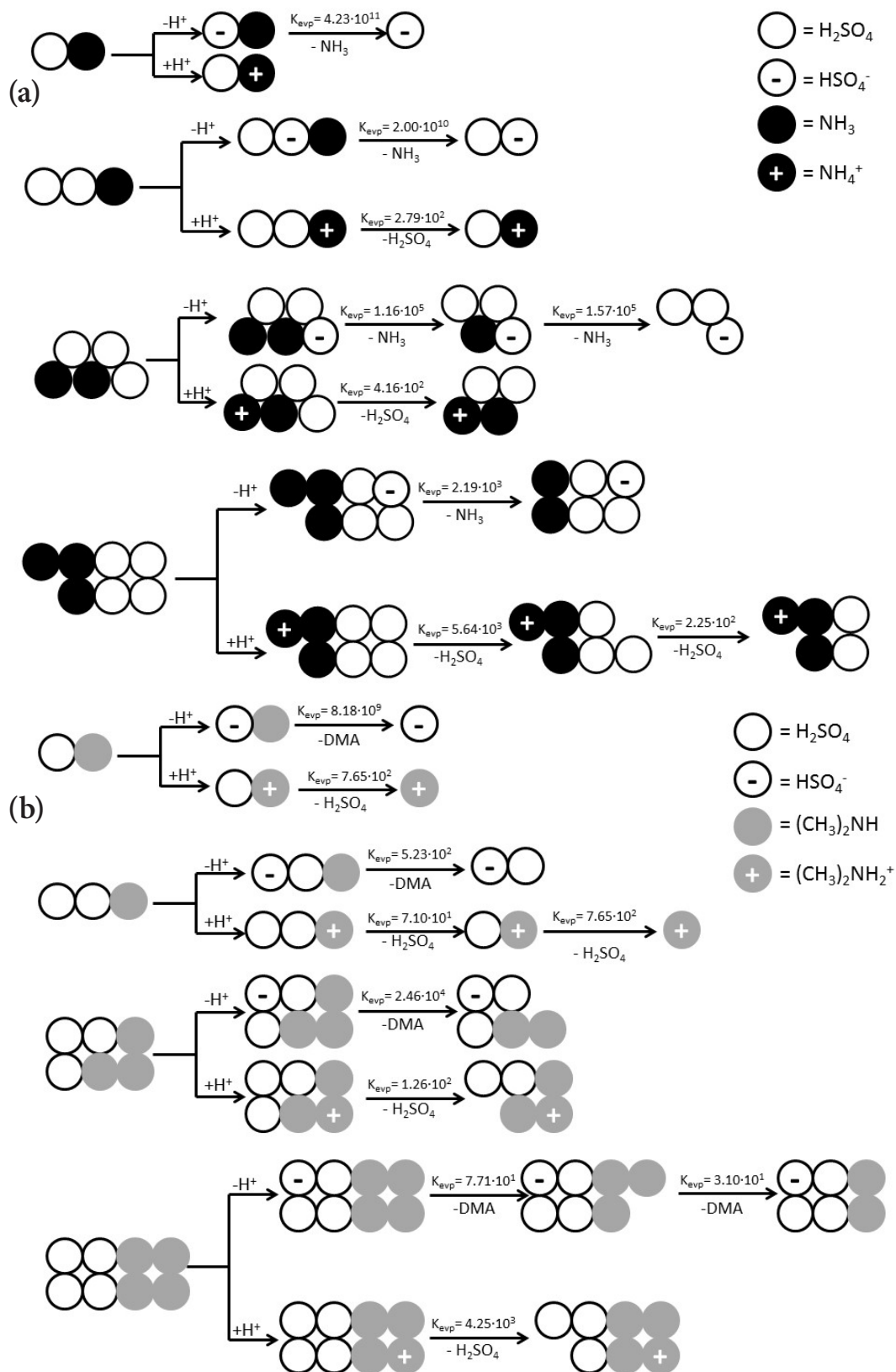
Figure 7. Schematic representation of the evaporation pathways after charging of the most stable neutral base-containing clusters. White circles represent sulfuric acid, white circles with a minus sign represent the bisulfate ion, black circles represent ammonia, black circles with a plus sing represent the ammonium ion, grey circles represent dimethylamine and grey circles with a plus sign represent the dimethylammonium ion.

increases. In the case of negatively charged clusters, HSO_4^- acts as a Lewis base, and is able to stabilize the smallest cluster effectively. Similar to neutral clusters, one base is able to bind to only a few (around two) sulfuric acid molecules. To prevent the fast evaporation of subsequently added sulfuric acid molecules, the addition of further base molecules is needed. In the case of HSO_4^-, the addition of a second ion is not possible due to electrostatic repulsion, and thus an electrically neutral base molecule is needed. This base competition makes base-containing negatively charged clusters unstable until they reach a certain number of sulfuric acid molecules. Ammonia-containing clusters need four sulfuric acid molecules (including the bisulfate ion) to prevent the evaporation of the ammonia molecule from the cluster, while only three acids are needed in the case of DMA-containing clusters.

We have studied how charging processes (in this case, addition or removal of one proton, for example, by chemical ionization) affect cluster composition by comparing the evaporation rates of the most stable neutral sulfuric acid–ammonia and sulfuric acid–DMA clusters to the evaporation rates of the corresponding charged clusters. Our calculations show that the composition of the stable base-containing clusters will change after they are charged. All positively charged clusters will retain their base molecules but will lose a number of sulfuric acid molecules. After becoming negatively charged, neutral ammonia-containing clusters with one to three sulfuric acid molecules will lose all ammonia molecules. In the case of DMA-containing clusters, one and two sulfuric acid clusters will lose all DMA molecules after charging. These results are in good agreement with experiments by Zhao et al. (2011), Hanson and Eisele (2002), Kirkby et al. (2011) and Almeida et al. (2013) in which the smallest detected base-containing negatively charged clusters contained three to four sulfuric acid molecules.

The results presented in this work help in the interpretation of experimental data on neutral cluster distributions obtained via chemical ionization APi-TOF mass spectroscopy, a state-of-the-art instrument in which naturally neutral clusters are charged in order to determine their composition by mass spectrometry. The theoretical predictions on the different effects of positive and negative charging can be validated by distribution measurements performed by both positive and negative ionization of the same sample of neutral clusters. As the chemical ionization techniques are likely to become more common in the chemical characterization of atmospheric molecular clusters (Jokinen et al., 2012; Kulmala et al., 2013), we propose this type of measurement to experimentally verify the effect of charging on the composition of small acid–base clusters.

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References

Ahlrichs, R., Bar, M., Häser, J., Horn, H., and Kölmel C.: Electronic structure calculations on workstation computers: the program system TURBOMOLE, Chem. Phys. Lett., 162, 165–169, 1989.

Almeida, J., Schobesberger, S., Kürten, A., Ortega, I. K., Kupiainen-Määttä, O., Praplan, A. P., Adamov, A., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Donahue, N. M., Downard, A., Dunne, E., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, Ale., Guida, R., Hakala, J., Hansel, A., Heinritzi, M., Henschel, H., Jokinen, T., Junninen, H., Kajos, M., Kangasluoma, J., Keskinen, H., Kupc, A., Kurtén, T., Kvashin, A. N., Laaksonen, A., Lehtipalo, K., Leiminger, M., Leppä, J., Loukonen, V., Makhmutov, V., Mathot, S., McGrath, M. J., Nieminen, T., Olenius, T., Onnela, A., Petäjä, T., Riccobono, F., Riipinen, I., Rissanen, M., Rondo, L., Ruuskanen, T., Santos, F. D., Sarnela, N., Schallhart, S., Schnitzhofer, R., Seinfeld, J. H., Simon, M., Sipilä, M., Stozhkov, Y., Stratmann, F.,Tomé, A., Tröstl, J., Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Virtanen, A., Vrtala, A., Wagner, P. E., Weingartner, E., Wex, H., Williamson, C., Wimmer, D., Ye, P., Yli-Juuti, T., Carslaw, K. S., Kulmala, M., Curtius, J., Baltensperger, U., Worsnop, D. R., Vehkamäki, H., and Kirkby, J.: Molecular understanding of sulphuric acid-amine particle nucleation in the atmosphere, Nature, 502, 359–363, 2013.

Becke, A. D.: Density-functional thermochemistry. III. The role of exact exchange, J. Chem. Phys., 98, 5648–5652, 1993.

Benson, D. R., Yu, J. H., Markovich, A., and Lee, S.-H.: Ternary homogeneous nucleation of H_2SO_4, NH_3, and H_2O under conditions relevant to the lower troposphere, Atmos. Chem. Phys., 11, 4755–4766, doi:10.5194/acp-11-4755-2011, 2011.

Bzdek, B. R., Ridge, D. P., and Johnston, M. V.: Amine exchange into ammonium bisulfate and ammonium nitrate nuclei, Atmos. Chem. Phys., 10, 3495–3503, doi:10.5194/acp-10-3495-2010, 2010.

Bzdek, B. R., Ridge, D. P., and Johnston, M. V.: Amine reactivity with charged sulfuric acid clusters, Atmos. Chem. Phys., 11, 8735–8743, doi:10.5194/acp-11-8735-2011, 2011.

Chapman, S. and Cowling, T. G.: The Mathematical Theory of Non Uniform Gases, University Press, Cambridge, 1970.

Dunning Jr., T. H., Peterson, K. A., and Wilson, A. K.: Gaussian basis sets for use in correlated molecular calculations. X. The atoms aluminum through argon revisited, J. Chem. Phys., 114, 9244–9253, 2001.

Ehn, M., Junninen, H., Petäjä, T., Kurtén, T., Kerminen, V.-M., Schobesberger, S., Manninen, H. E., Ortega, I. K., Vehkamäki, H., Kulmala, M., and Worsnop, D. R.: Composition and temporal behavior of ambient ions in the boreal forest, Atmos. Chem. Phys., 10, 8513–8530, doi:10.5194/acp-10-8513-2010, 2010.

Friedlander, S. K.: Smoke, Dust and Haze, John Wiley & Sons, New York, 1977.

Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery Jr., J. A., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, N., Millam, J. M., Klene, M., Knox, J. E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J.,Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, O., Foresman, J. B., Ortiz, J. V., Cioslowski, J., and Fox, D. J.: Gaussian 09, Revision B01, Gaussian, Inc., Wallingford CT, 2009.

Froyd, K. D. and Lovejoy, E. R.: Experimental thermodynamics of cluster ions composed of H_2SO_4 and H_2O. 2. Measurements and ab initio structures of negative ions, J. Phys. Chem. A, 107, 9812–9824, 2003.

Froyd, K. D. and Lovejoy E. R.: Bond Energies and Structure of Ammonia – Sulfuric Acid Positive Cluster Ioms, J. Phys. Chem. A, 116, 5886–5899, 2012.

Hanson, D. R., and Eisele, F. L.: Measurement of prenucleation molecular clusters in the NH_3, H_2SO_4, H_2O system, J. Geophys. Res., 107, D124158, doi:10.1029/2001JD001100, 2002.

Hattig, C. and Weigend, F.: CC2 excitation energy calculations on large molecules using the resolution of the identity approximation, J. Chem. Phys., 113, 5154–5161, 2000.

Herb, J., Nadykto, A .B., and Yu, F.: Large Ternary Hydrogen-Bonded Pre-nucleation Clusters in the Earth's Atmosphere, Chem. Phys. Lett., 518, 7–14, 2011.

Herb, J., Xu, Y., Yu, F., and Nadykto, A. B.: Large Hydrogen-Bonded Pre-nulceation $(HSO_4^-)(H_2SO_4)_m(H_2O)_k$ and $(HSO_4^-)(NH_3)(H_2SO_4)_m(H_2O)_k$ Clusters in the Earth's Atmosphere, J. Phys. Chem. A, 117, 133–152, 2013.

IPCC, The Intergovernmental Panel on Climate Change: Climate Change 2007: The Physical Science Basis, Cambridge University Press, New York, 2007.

Jokinen, T., Sipilä, M., Junninen, H., Ehn, M., Lönn, G., Hakala, J., Petäjä, T., Mauldin III, R. L., Kulmala, M., and Worsnop, D. R.: Atmospheric sulphuric acid and neutral cluster measurements using CI-APi-TOF, Atmos. Chem. Phys., 12, 4117–4125, doi:10.5194/acp-12-4117-2012, 2012.

Junninen, H., Ehn, M., Petäjä, T., Luosujärvi, L., Kotiaho, T., Kostiainen, R., Rohner, U., Gonin, M., Fuhrer, K., Kulmala, M., and Worsnop, D. R.: A high-resolution mass spectrometer to measure atmospheric ion composition, Atmos. Meas. Tech., 3, 1039–1053, doi:10.5194/amt-3-1039-2010, 2010.

Kirkby, J., Curtius, J., Almeida, J., Dunne, E., Duplissy, J., Ehrhart, S., Franchin, A., Gagne, S., Ickes, L., Kurten, A., Kupc, A., Metzger, A., Riccobono, F., Rondo, L., Schobesberger, S., Tsagkogeorgas, G., Wimmer, D., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Downard, A., Ehn, M., Flagan, R. C., Haider, S., Hansel, A., Hauser, D., Jud, W., Junninen, H., Kreissl, F., Kvashin, A., Laaksonen, A., Lehtipalo, K., Lima, J., Lovejoy, E. R., Makhmutov, V., Mathot, S., Mikkila, J., Minginette, P., Mogo, S., Nieminen, T., Onnela, A., Pereira, P., Petaja, T., Schnitzhofer, R., Seinfeld, J. H., Sipila, M., Stozhkov, Y., Stratmann, F., Tome, A., Vanhanen, J., Viisanen, Y., Vrtala, A., Wagner, P. E., Walther, H., Weingartner, E., Wex, H., Winkler, P. M., Carslaw, K. S., Worsnop, D. R., Baltensperger, U., and Kulmala, M.: Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation, Nature, 476, 429, doi:10.1038/nature10343, 2011.

Kulmala, M., Kontkanen, J., Junninen, H., Lehtipalo, K., Manninen, H. E., Nieminen, T., Petäjä, T., Sipilä, M., Schobesberger, S., Rantala, P., Franchin, A., Jokinen, T., Jarvinen, E., Aijälä, M., Kangasluoma, J., Hakala, J., Aalto, P. P., Paasonen, P., Mikkila, J., Vanhanen, J., Aalto, J., Hakola, H., Makkonen, U., Ruuskanen, T., Mauldin, R. L., Duplissy, J., Vehkamaki, H., Bäck, J., Kortelainen, A., Riipinen, I., Kurten, T., Johnston, M. V., Smith, J. N., Ehn, M., Mentel, T. F., Lehtinen, K. E. J., Laaksonen, A., Kerminen, V. M., and Worsnop, D. R.: Direct observations of atmospheric aerosol nucleation, Science, 339, 943–946, doi:10.1126/science.1227385, 2013.

Kupiainen, O., Ortega, I. K., Kurtén, T., and Vehkamäki, H.: Amine substitution into sulfuric acid – ammonia clusters, Atmos. Chem. Phys., 12, 3591–3599, doi:10.5194/acp-12-3591-2012, 2012.

Kupiainen-Määttä, O., Olenius, T., Kurtén, T., and Vehkamäki, H.: CIMS sulfuric acid detection efficiency enhanced by amines due to higher dipole moments: a computational study. J. Phys. Chem. A, 117, 14109–14119, 2013.

Kurtén, T.: A comment on Nadytko et al.: Amines in the Earth's atmosphere: a density functional theory study of the thermochemistry of pre-nucleation cluster, Entropy, 2011, 13, 554–569, Entropy, 13, 912–923, 2011.

Kurtén, T., Noppel, M., Vehkamäki, H., Salonen, M., and Kulmala, M.: Quantum chemical studies of hydrate formation of H_2SO_4 and HSO_4^-, Boreal Environ. Res., 12, 431–453, 2007.

Kurtén, T., Loukonen, V., Vehkamäki, H., and Kulmala, M.: Amines are likely to enhance neutral and ion-induced sulfuric acid-water nucleation in the atmosphere more effectively than ammonia, Atmos. Chem. Phys., 8, 4095–4103, doi:10.5194/acp-8-4095-2008, 2008.

Kurtén, T., Petäjä, T., Smith, J., Ortega, I. K., Sipilä, M., Junninen, H., Ehn, M., Vehkamäki, H., Mauldin, L., Worsnop, D. R., and Kulmala, M.: The effect of H_2SO_4 – amine clustering on chemical ionization mass spectrometry (CIMS) measurements of gas-phase sulfuric acid, Atmos. Chem. Phys., 11, 3007–3019, doi:10.5194/acp-11-3007-2011, 2011.

Loukonen, V., Kurtén, T., Ortega, I. K., Vehkamäki, H., Pádua, A. A. H., Sellegri, K., and Kulmala, M.: Enhancing effect of dimethylamine in sulfuric acid nucleation in the presence of water – a computational study, Atmos. Chem. Phys., 10, 4961–4974, doi:10.5194/acp-10-4961-2010, 2010.

McGrath, M. J., Olenius, T., Ortega, I. K., Loukonen, V., Paasonen, P., Kurtén, T., Kulmala, M., and Vehkamäki, H.: Atmospheric Cluster Dynamics Code: a flexible method for solution of the birth-death equations, Atmos. Chem. Phys., 12, 2345–2355, doi:10.5194/acp-12-2345-2012, 2012.

Merikanto, J., Napari, I., Vehkamäki, H., Anttila, T., and Kulmala, M.: New parameterization of sulfuric acid-ammonia-water ternary nucleation rates at tropospheric conditions, J. Geophys. Res., 112, D15207, doi:10.1029/2006JD007977, 2007.

Merikanto, J., Spracklen, D. V., Mann, G. W., Pickering, S. J., and Carslaw, K. S.: Impact of nucleation on global CCN, Atmos. Chem. Phys., 9, 8601–8616, doi:10.5194/acp-9-8601-2009, 2009.

Montgomery, J. A., Frisch, M. J., Ochterski, J. W., and Petersson, G. A.: A complete basis set model chemistry. VI. Use of density functional geometries and frequencies, J. Chem. Phys., 110, 2822–2827, 1999.

Mäkelä, J. M., Yli-Koivisto, S., Hiltunen, V., Seidl, W., Swietlicki, E., Teinila, K., Sillanpää, M., Koponen, I. K., Paatero, J., Rosman, K., and Hameri, K.: Chemical composition of aerosol during particle formation events in boreal forest, Tellus B, 53, 380–393, doi:10.1034/j.1600-0889.2001.530405.x, 2001

Nadykto, A. B., Yu, F. Q., Jakovleva, M. V., Herb, J., and Xu, Y. S.: Amines in the Earth's atmosphere: a density functional theory study of the thermochemistry of pre-nucleation clusters, Entropy, 13, 554–569, 2011.

Olenius, T., Schobesberger, S., Kupiainen-Määtä, O., Franchin, A., Junninen, H., Ortega, I. K., Kurtén T., Loukonen, V., Worsnop, D. R., Kulmala, M., and Vehkamäki, H.: Comparing simulated and experimental molecular cluster distributions, Faraday Discuss., 165, 75–89, doi:10.1039/C3FD00031A, 2013a.

Olenius, T., Kupiainen, O., Ortega, I. K., Kurtén, T., and Vehkamäki, H.: Free energy barrier in the growth of sulfuric acid-ammonia and sulfuric acid-dimethylamine clusters, J. Chem. Phys., 139, 084312, doi:10.1063/1.4819024, 2013b.

Ortega, I. K., Kurtén, T., Vehkamäki, H., and Kulmala, M.: The role of ammonia in sulfuric acid ion induced nucleation, Atmos. Chem. Phys., 8, 2859–2867, doi:10.5194/acp-8-2859-2008, 2008.

Ortega, I. K., Kupiainen, O., Kurtén, T., Olenius, T., Wilkman, O., McGrath, M. J., Loukonen, V., and Vehkamäki, H.: From quantum chemical formation free energies to evaporation rates, Atmos. Chem. Phys., 12, 225–235, doi:10.5194/acp-12-225-2012, 2012.

Sipilä, M., Berndt, T., Petäjä, T., Brus, D., Vanhanen, J., Stratmann, F., Patokoski, J., Mauldin, R. L. I., Hyvarinen, A.-P., Lihavainen, H., and Kulmala, M.: The Role of Sulfuric Acid in Atmospheric Nucleation, Science, 327, 1243–1246, 2010

Smith, J. N., Barsanti, K. C., Friedli, H. R., Ehn, M., Kulmala, M., Collins, D. R., Scheckman, J. H., Williams, B. J., and McMurry, P. H.: Observations of ammonium salts in atmospheric nanoparticles and possible climatic implications, P. Natl. Acad. Sci. USA, 107, 6634–6639, 2010.

Su, T. and Chesnavich, W. J.: Parametrization of the ion-polar molecule collision rate constant by trajectory calculations, J. Chem. Phys. 76, 5183, doi:10.1063/1.442828, 1982.

Viggiano, A. A., Seeley, J. V., Mundis, P. L., Williamson, and J. S., and Morris, R. A.: Rate Constants for the Reactions of XO_3^- $(H_2O)n$ (X = C, HC, and N) and NO_3^- $(HNO_3)n$ with H_2SO_4: Implications for Atmospheric Detection of H_2SO_4, J. Phys. Chem. A, 101, 8275–8278, 1997.

Weber, R. J., Marti, J. J., McMurry, P. H., Eisele, F. L., Tanner, D. J., and Jefferson, A.: Measured atmospheric new particle formation rates: Implications for nucleation mechanisms, Chem. Eng. Commun., 151, 53–64, doi:10.1080/00986449608936541, 1996.

Zhao, J., Smith, J. N., Eisele, F. L., Chen, M., Kuang, C., and McMurry, P. H.: Observation of neutral sulfuric acid-amine containing clusters in laboratory and ambient measurements, Atmos. Chem. Phys., 11, 10823–10836, doi:10.5194/acp-11-10823-2011, 2011.