



On the composition of ammonia-sulfuric acid clusters

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

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substantiate previous evidence for acid-base reactions being the essential mechanism behind the formation of these clusters under atmospheric conditions and up to sizes of at least 2 nm. Our results also suggest that yet unobservable electrically neutral $\text{NH}_3\text{-H}_2\text{SO}_4$ clusters grow by generally the same mechanism as ionic clusters, particularly for $[\text{NH}_3]/[\text{H}_2\text{SO}_4] > 10$. We expect that $\text{NH}_3\text{-H}_2\text{SO}_4$ clusters form and grow also mostly by $\Delta m/\Delta n > 1$ in the atmosphere's boundary layer, as $[\text{NH}_3]/[\text{H}_2\text{SO}_4]$ is mostly larger than 10. We compared our results from CLOUD with APi-TOF measurements of $\text{NH}_3\text{-H}_2\text{SO}_4$ anion clusters during new particle formation in the Finnish boreal forest. However, the exact role of $\text{NH}_3\text{-H}_2\text{SO}_4$ clusters in boundary layer particle formation remains to be resolved.

1 Introduction

Atmospheric aerosol particles influence the Earth's radiation balance via aerosol-radiation and aerosol-cloud interactions, the latter effect being one of the largest sources of uncertainty in predicting the current and future climate change (IPCC, 2013). An important source of atmospheric aerosol particles is the formation of molecular clusters from gas-phase precursors (vapors) and their subsequent growth to larger sizes by vapor condensation and other processes. Such new particle formation gives a potentially large contribution to regional and even global cloud condensation nuclei (CCN) populations (Merikanto et al., 2009; Kerminen et al., 2012; Lee et al., 2013), thereby affecting aerosol-cloud interactions and ultimately climate (Kazil et al., 2010; Makkonen et al., 2012; Ghan et al., 2013). However, the very first steps of the atmospheric new particle formation process are still poorly understood and subject of ongoing research (Kulmala et al., 2014). An important task in this respect is to find out the factors and underlying mechanisms that determine the initial formation of molecular clusters and particles < 2 nm from vapors, and how this process varies throughout the atmosphere.

It is still largely unknown which vapors participate in atmospheric new-particle formation. The only compound that certainly plays a major role is sulfuric acid (H_2SO_4)

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(Weber et al., 1996; Kulmala et al., 2004b, 2006; Riipinen et al., 2007). Together with practically omnipresent water vapor (H_2O), H_2SO_4 is believed to be the main source of new particles in the middle and upper troposphere (Lovejoy et al., 2004). However, most measurements of new-particle formation have been made close to the ground, and these particle formation events have been observed to be confined into the lower tropospheric boundary layer (Kulmala et al., 2004b; Kulmala and Kerminen, 2008; O'Dowd et al., 2009; Schobesberger et al., 2013b). Within this relatively warm boundary layer, H_2SO_4 alone cannot explain either the particle formation or subsequent growth rate, because H_2SO_4 concentrations are too low, typically below one part per trillion by volume (<1 pptv, corresponding to 2.5×10^7 molecules cm^{-3}) (Kirkby et al., 2011). Other compounds are believed to participate in the process of new particle formation by stabilizing H_2SO_4 molecules during the formation of initial clusters (e.g., Petäjä et al., 2011; Sipilä et al., 2010). The candidate compounds for facilitating such stabilization are ions (Lovejoy et al., 2004; Kirkby et al., 2011), bases such as ammonia (NH_3) (Coffman and Hegg, 1995; Ortega et al., 2008; Kirkby et al., 2011) and amines (Kurtén et al., 2008; Paasonen et al., 2012; Almeida et al., 2013), and a possibly wide range of oxygenated organic molecules (Kulmala et al., 1998; Zhang et al., 2004; Metzger et al., 2010; Schobesberger et al., 2013a; Ehn et al., 2014; Riccobono et al., 2014).

Ammonia (NH_3) and its stabilizing effect on the H_2SO_4 - H_2O system is probably the most thoroughly researched among all those compounds. The saturation vapor pressure of H_2SO_4 is several orders of magnitude lower in bulk H_2SO_4 - H_2O - NH_3 solutions compared with H_2SO_4 - H_2O solutions (Marti et al., 1997). On the molecular scale, 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, both for electrically-neutral and for charged clusters (Kurtén et al., 2007; Ortega et al., 2008, 2012). Generally, these studies predict a maximum base:acid ratio of 1:1, even though the conducted studies have been computationally limited to clusters up to about 8 molecules. Experimentally, small ion clusters of the types $(\text{NH}_3)_m \cdot (\text{H}_2\text{SO}_4)_n \cdot \text{HSO}_4^-$ and $(\text{NH}_3)_m \cdot (\text{H}_2\text{SO}_4)_n \cdot \text{NH}_4^+$,

containing up to about 15 molecules, have been produced in various laboratory setups, allowing studies of their formation and stability (Hanson and Eisele, 2002; Bzdek et al., 2011; Froyd and Lovejoy, 2012). Ratios $m/n \leq 1$ were obtained, in agreement with the theoretical expectations.

Experiments at the Cosmics Leaving Outdoor Droplets (CLOUD) facility at CERN addressed new particle formation from NH_3 , H_2SO_4 and H_2O in an aerosol chamber setup. The results from these experiments connected the same $(\text{NH}_3)_m \cdot (\text{H}_2\text{SO}_4)_n \cdot \text{ion}^\pm$ clusters directly to new particle formation at atmospherically relevant rates (Kirkby et al., 2011). Formation rates comparable to those in the ambient atmosphere were only obtained when either H_2SO_4 concentrations were at least one order of magnitude higher than typical ambient concentrations, or when the temperature was very low (-25°C), ruling out NH_3 , H_2SO_4 and H_2O as the sole participants in new-particle formation in most regions of the atmospheric boundary layer.

Clusters of NH_3 , H_2SO_4 and H_2O may nevertheless play an important role in the very first steps of new-particle formation in the atmosphere. It was recently shown that the critical first step may be the stabilization of small H_2SO_4 -containing clusters by NH_3 , amines or organic compounds (Kulmala et al., 2013). In that study, these stabilized clusters grew relatively slowly up to an activation size (1.5–1.9 nm mobility diameter), and were only then able to grow faster by the enhanced uptake of additional compounds (likely organics). Indeed, the only clusters that have so far been unambiguously identified in the atmosphere and directly linked to new particle formation are clusters of H_2SO_4 plus NH_3 or amines or both (Ehn et al., 2010; Kulmala et al., 2013).

Gaseous NH_3 concentrations vary widely in the atmosphere, both with location and time, from <10 pptv to several ppbv (Ziereis and Arnold, 1986; Janson et al., 2001; Riipinen et al., 2007; Gong et al., 2011; Osada et al., 2011). In particular low concentrations of NH_3 remain challenging to measure accurately in the atmosphere (von Borutzki et al., 2010). Atmospheric measurements of other bases, such as amines, suffer from similar problems. However, recent laboratory experiments have shown a great enhancement of the formation of particles from H_2SO_4 by the addition of only either tens

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the chamber can be irradiated by UV light from the top of the chamber (Kupc et al., 2011). This UV light induces photolytic reactions, in particular the oxidation of SO₂ (at concentrations of 15 to 34 ppbv) to form H₂SO₄. The temperature inside the chamber is actively controlled and stable within 0.01 °C for the typical length of an experiment.

Some ionization always occurs inside the chamber via natural galactic cosmic rays (GCR). In addition, the chamber can be exposed to 3.5 GeV c⁻¹ pions (π⁺) that are provided by the CERN Proton Synchrotron in one to three spills per minute. The intensity of the spills can be regulated, and the mean total ion pair production rate in the chamber is therefore adjustable between 2 cm⁻³ s⁻¹ (π⁺ beam off) and 42 cm⁻³ s⁻¹ (at the usual maximum available π⁺ beam intensity). An electrical clearing field of 20 kV m⁻¹ can be applied by means of a pair of field cage electrodes, mounted at the top and the bottom of the chamber. This field will sweep out all ions in the chamber in about one second, providing an environment practically free of ions, when needed.

During the CLOUD 2 and CLOUD 3 campaigns, a wide array of instruments was arranged around the chamber, continuously analyzing its contents via 16 sampling probes. These sampling probes were mounted radially around the chamber and projected 0.5 m into the chamber. The instrumentation included an atmospheric pressure interface time-of-flight (APi-TOF) mass spectrometer to measure the chemical composition of ions (up to about 2 nm in size). Results from the APi-TOF are the main subject of this study, and the instrument is described below. The rest of the instrumentation included an Airborne Neutral cluster and Air Ion Spectrometer (NAIS) (Mirme et al., 2010), used to measure ions from 0.8 to 40 nm in mobility-equivalent diameter. A comprehensive suite of particle counting and sizing instruments facilitated aerosol number size distribution measurements, covering the range from 1.3 to 100 nm (Kirkby et al., 2011). A chemical ionization mass spectrometer (CIMS) (Kürten et al., 2011, 2012) measured H₂SO₄ concentrations down to about 10⁵ cm⁻³ at an accuracy of +100%/-50%. During CLOUD 3 only, a proton transfer reaction mass spectrometer (PTR-MS) (Norman et al., 2007) and a Long Path Absorption Photometer (LOPAP) (Bianchi et al., 2012) were used to measure NH₃ concentrations down to 35 pptv.

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ammonium bisulfate cluster ion at 3300 Th corresponds to about 2.1 nm in mobility-equivalent diameter, using the conversion procedure described by Ehn et al. (2011). The API-TOF's ion transmission efficiency was set to have its maximum at about 900 to 1400 Th for negative ions, and at about 100 to 300 Th for positive ions. In the CLOUD campaigns, we recorded spectra at a time resolution of 5 s. The signal-to-noise ratio usually resulted in a maximum practical time resolution of 30 s.

Sampled ions may be subject to fragmentation inside the API-TOF. Such fragmentation was mainly manifest by the usual near-absence of any H₂O clustered with, for instance, sulfuric acid. The evaporation rate of H₂O from these clusters is too rapid to survive detection in the non-equilibrium environment of the API-TOF. However, many more strongly bound clusters can be detected, as will be shown here and has been shown before (e.g., Ehn et al., 2010; Junninen et al., 2010). Also, comparisons with ion mobility spectrometers demonstrate a good agreement with the API-TOF's results (Ehn et al., 2011; Schobesberger et al., 2013a). Comparisons between the API-TOF and the NAIS for our measurements produce a similar agreement, so the ion mass spectra obtained by the API-TOF are, in general, representative of the actual population of small ions and ion clusters. However, a few molecules may anyway be lost from clusters during the sampling, as has also been suggested by comparisons between API-TOF results and cluster simulations (Olenius et al., 2013b; Ortega et al., 2014).

The data obtained from the API-TOF measurements were processed and analyzed using tofTools, a software package based on MATLAB and under continuous development, mainly at the University of Helsinki. Details on the analysis of API-TOF data are found elsewhere (Schobesberger et al., 2013a).

2.4 Gas-phase concentrations of NH₃

The primary means of obtaining the gas-phase concentration of NH₃ ([NH₃]) were the results from the LOPAP (Bianchi et al., 2012). It was only available during CLOUD 3 and above 0 °C. Below 0 °C, measurements of [NH₃] were available from the PTR-MS

for some experiments in CLOUD 3. Ammonia concentrations could also be estimated from the calibrated mass flow controller settings.

In practice, $[\text{NH}_3]$ was directly measured whenever NH_3 had been added during most of the CLOUD 3 campaign. Without the deliberate addition of NH_3 , values of $[\text{NH}_3]$ were below the detection limit of 35 pptv. More refined measurements during later campaigns showed that this contaminant level of $[\text{NH}_3]$ was in fact likely <2 pptv for experiments at 5°C (Almeida et al., 2013). The most plausible source of this contaminant NH_3 was evaporation from the inside walls of the chamber. Therefore, we assumed that contaminant levels of $[\text{NH}_3]$ were 2 pptv at 5°C and directly proportional to the desorption rate of NH_3 , assuming an activation energy of 33 kJ mol^{-1} . Thus calculated contaminant levels of $[\text{NH}_3]$ ranged from 0.3 pptv (at -24.7°C) to 4.3 pptv (at 19.7°C).

Ammonia concentrations also had to be calculated for a selection of experiments below 0°C when no direct measurement results of $[\text{NH}_3]$ were available. In the beginning of these experiments, $[\text{NH}_3]$ was above contaminant levels, but no NH_3 was being added to the chamber anymore. Therefore, a decay of $[\text{NH}_3]$ as measured previously by the LOPAP was used for our calculations, in addition to the proportionality to the desorption rate.

During the few experiments when NH_3 was added during CLOUD 2, estimates for $[\text{NH}_3]$ were made using the settings of the mass flow controllers that control the gas flows into and out of the CLOUD chamber.

2.5 Ambient measurements in the boreal forest

The same APi-TOF as in the CLOUD campaigns was deployed also at the Station for Measuring Ecosystem-Atmosphere Relations (SMEAR II) (Hari and Kulmala, 2005), where it measured negatively charged ions during spring 2011. The SMEAR II station is located in Hyytiälä, southern Finland, within a boreal forest, with Tampere being the closest larger town, 50–60 km southwest of the station. The station is the site of a host of continuing atmospheric observations, which includes extensive aerosol

mass. Therefore, it is advantageous to present mass spectra as mass defect diagrams (Fig. 2c). In such a diagram, the mass defect for each ion, i.e. the deviation from its nominal mass, is plotted against its mass-to-charge ratio. Any given ion will occupy a unique position in this diagram, and an addition of a specified atom or molecule will move an ion by a characteristic vector (e.g., see Fig. 2c insert).

During a typical new particle formation experiment in the CLOUD chamber, the dominant negatively charged ions were small sulfuric acid anion clusters, with the strongest signal, in most cases, from the trimer, $(\text{H}_2\text{SO}_4)_2 \cdot \text{HSO}_4^-$ (Fig. 2c). Heavier ion clusters (>350 Th; containing >3 sulfur atoms) were considerably less abundant for most experimental conditions. These heavier clusters consisted mostly of H_2SO_4 molecules. However, they were observed not only as “pure” sulfuric acid clusters but also as clusters with base molecules, specifically molecules of NH_3 or of various organic bases, mainly amines.

In general, larger clusters contained more base molecules. The predominant base in these clusters was NH_3 , yielding clusters of the form $(\text{NH}_3)_m \cdot (\text{H}_2\text{SO}_4)_n \cdot \text{HSO}_4^-$ (Fig. 2c). Only certain numbers of NH_3 molecules (m) were seen for each number of H_2SO_4 molecules (n), depending on experimental conditions. This dependency will be discussed below in more detail. Note that neither NH_3 nor amines had been deliberately fed into the chamber for these experiments. Instead, they were unintended impurities.

Some of the negatively charged clusters that grew by the addition of H_2SO_4 and base molecules had an additional oxygen atom (Fig. 2c). This can be explained by the growth starting from HSO_5^- instead of HSO_4^- . The role of HSO_5^- , as opposed to HSO_4^- , in the composition and growth of ion clusters, as well as its origin, will be described and discussed in Sects. 3.2 and 4.2.

Note that the APi-TOF did not detect any growing positively charged clusters under the typical experimental conditions discussed in this section, i.e. when no NH_3 was fed into the chamber, temperature was either 5 or 19 °C and RH was 40 %. This is

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$\text{NH}_3 \cdot (\text{H}_2\text{SO}_4)_3 \cdot \text{HSO}_5^-$, whereas the cluster $\text{NH}_3 \cdot (\text{H}_2\text{SO}_4)_2 \cdot \text{HSO}_4^-$ was totally absent. Subsequently, the average ratio between the number of NH_3 molecules (m) and the number of H_2SO_4 molecules (n) was initially higher in HSO_5^- -based clusters than in the corresponding HSO_4^- -based clusters. However, this difference decreased with an increasing cluster size, disappearing or staying approximately constant at about $n \geq 9$. The implications of these observations will be discussed in Sect. 4.2.

3.3 Contaminant amines in growing anion clusters

No amines were deliberately added into the chamber for the experiments discussed here, i.e. during the CLOUD 2 and CLOUD 3 campaigns. Amine contamination originated probably from the same source as NH_3 (see Sect. 2.4). We can give some estimate of the contaminant levels of the dominant amine, $\text{C}_2\text{H}_7\text{N}$, based on measurements from later CLOUD campaigns when dimethylamine was also added into the chamber in several experiments (Praplan et al., 2012; Almeida et al., 2013). These estimates are based on direct measurements of dimethylamine concentrations down to 0.2 pptv at the later experiments, and on measurements of the content of $\text{C}_2\text{H}_7\text{N}$ in clusters seen by the APi-TOF. Based on those results, we speculate that gas-phase contaminant concentrations of $\text{C}_2\text{H}_7\text{N}$ were between 0.1 and 1 pptv during the CLOUD 2 campaign, and about 0.1 pptv or even less during the CLOUD 3 campaign.

In the experiments discussed here, the highest abundance of the clusters containing contaminant organic bases (amines or amides) was usually seen on those clusters that contained a sulfuric acid tetramer anion. These clusters were observed either without any base, such as $(\text{H}_2\text{SO}_4)_3 \cdot \text{HSO}_4^-$, or clustered with NH_3 , or clustered with a basic organic compound. The most abundantly-observed organic base has the formula $\text{C}_2\text{H}_7\text{N}$ (dimethylamine or ethylamine). Other bases observed in these clusters were CH_5N (methylamine), $\text{CH}_4\text{N}_2\text{O}$ (urea) and larger amines or amides (Fig. 3). Note that in some cases, we are unable to resolve whether one oxygen atom was part of the organic constituent or whether the ion was HSO_5^- instead of HSO_4^- . $\text{C}_2\text{H}_7\text{N}$ was also

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At a given temperature and RH, $\Delta m/\Delta n$ generally increased with an increasing value of $[\text{NH}_3]/[\text{H}_2\text{SO}_4]$, then flattened off when approaching the value of 1, and eventually reached a saturation value slightly larger than 1. At 19 °C, the maximum value of $\Delta m/\Delta n$ of 1.1 to 1.2 was reached at the concentration ratio $[\text{NH}_3]/[\text{H}_2\text{SO}_4] \approx 100$ (Fig. 4). This concentration ratio was roughly coincident with the threshold for observing cation clusters (at 19 °C and 40 % RH) of the form $(\text{NH}_3)_m \cdot (\text{H}_2\text{SO}_4)_n \cdot \text{NH}_4^+$ with $m \approx n$ and $\Delta m/\Delta n \geq 1$. In an analogous way, the NAIS observed a formation of positively charged ions only when positively charged $\text{NH}_3\text{-H}_2\text{SO}_4$ clusters were observable by the APi-TOF. Note that for the cation clusters, $\Delta m/\Delta n$ was constant already from $n = 1$ onward and it was generally calculated over the range $1 \leq n \leq 17$.

The relationship between $\Delta m/\Delta n$ and $[\text{NH}_3]/[\text{H}_2\text{SO}_4]$ was similar under all experimental conditions, but the exact functional form of this relation was temperature dependent (Fig. 5a). For example, the value of $\Delta m/\Delta n = 0.2$ was reached at $[\text{NH}_3]/[\text{H}_2\text{SO}_4] \approx 0.1$ when the temperature was 19 °C, at $[\text{NH}_3]/[\text{H}_2\text{SO}_4] \approx 0.7$ when it was 5 °C, and at $[\text{NH}_3]/[\text{H}_2\text{SO}_4] > 1$ when it was –25 °C. Also, the maximum observed values of $\Delta m/\Delta n$ seemed to be reached at lower values of $[\text{NH}_3]/[\text{H}_2\text{SO}_4]$, and these maximum values were slightly higher at lower temperatures (e.g. a maximum $\Delta m/\Delta n$ of 1.1 to 1.2 at 19 °C, vs. a maximum $\Delta m/\Delta n$ of 1.3 at –25 °C).

Note that in practically all our experiments at $[\text{NH}_3]/[\text{H}_2\text{SO}_4] < 1$, only contaminant levels of $[\text{NH}_3]$ were present. These contaminant levels were not directly measured, but calculated under the assumptions described in Sect. 2.4. In particular the temperature dependence of these low values of $[\text{NH}_3]$ is subject to those assumptions. Note also that most experiments at CLOUD were run with the RH between 37 and 41 %, so the potential RH effects could not be thoroughly investigated. However, an increase of RH to >68 % increased the value of $\Delta m/\Delta n$ (Fig. 4). No significant effect on negatively charged clusters was observed due to RH changes in the range 30 % < RH < 60 %.

3.5 Negatively charged $(\text{NH}_3\text{-})\text{H}_2\text{SO}_4$ -clusters at very low $[\text{NH}_3]/[\text{H}_2\text{SO}_4]$

The role of NH_3 in the formation of clusters became negligible at very low values of $[\text{NH}_3]/[\text{H}_2\text{SO}_4]$, i.e. when $\Delta m/\Delta n$ dropped below 0.1 and the formation of pure binary clusters dominated (Fig. 5). Binary cluster formation is observed by the APi-TOF as pure sulfuric acid anion clusters, $(\text{H}_2\text{SO}_4)_n \cdot \text{HSO}_4^-$, because H_2O molecules are lost in the sampling process (Sect. 2.3). The fraction of pure, NH_3 -free sulfuric acid clusters was calculated over the same cluster range as was used for calculating $\Delta m/\Delta n$ ($4 \leq n \leq 18$), and like $\Delta m/\Delta n$, it was a function of $[\text{NH}_3]/[\text{H}_2\text{SO}_4]$. The fraction of NH_3 -free sulfuric acid clusters increased with a decreasing value of $[\text{NH}_3]/[\text{H}_2\text{SO}_4]$, and such clusters were observed only below some temperature-dependent threshold value of $[\text{NH}_3]/[\text{H}_2\text{SO}_4]$ (Fig. 5b). Taken together, the presence of pure, NH_3 -free sulfuric acid clusters was favored by lower $[\text{NH}_3]/[\text{H}_2\text{SO}_4]$ ratios and lower temperatures.

Note that the NH_3 contamination in the CLOUD chamber sets a lower limit to the minimum level of $[\text{NH}_3]$ that can be achieved. Therefore, pure binary sulfuric acid-water cluster formation can only be obtained at a sufficiently high $[\text{H}_2\text{SO}_4]$ level or at low temperatures. A low temperature both decreases the contaminant level of $[\text{NH}_3]$ (Sect. 2.4) and increases the threshold $[\text{NH}_3]/[\text{H}_2\text{SO}_4]$ below which binary cluster formation occurs (Fig. 5b).

4 Discussion

4.1 The composition of negative ions during new particle formation experiments (no NH_3 added)

Without adding any NH_3 into the CLOUD chamber, most anions during a new particle formation experiment in the CLOUD chamber were small sulfuric acid anion clusters. Heavier anion clusters, containing >3 sulfur atoms, were not only “pure” sulfuric acid clusters but also clusters associated with base molecules, namely NH_3 or

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various organic bases, mainly amines (Figs. 2c and 3). These findings agree qualitatively with observations made in the ambient atmosphere (Ehn et al., 2010), with independent measurements of such clusters in the laboratory (Bzdek et al., 2011), as well as with the results of simulations that consider classical collisions and evaporation rates based on quantum chemical methods (Olenius et al., 2013b). Both earlier experimental and theoretical studies, as well as our results here, show that NH_3 molecules can only cluster with anionic (= deprotonated) sulfuric acid clusters, i.e. form $(\text{NH}_3)_m \cdot (\text{H}_2\text{SO}_4)_n \cdot \text{HSO}_4^-$, if $n \geq 3$. This lower size limit for the inclusion of NH_3 molecules is explained by HSO_4^- itself acting as an electron donor (= Lewis base), in competition with regular bases such as NH_3 . Only when $n \geq 3$, the cluster is acidic enough to accept NH_3 molecules (Ortega et al., 2014).

The observation of both ammonia and amines in these clusters here is remarkable because neither NH_3 nor amines were deliberately fed into the CLOUD chamber for these experiments. All NH_3 and amines were unintended impurities ($[\text{NH}_3] < 5$ pptv, $[\text{C}_2\text{H}_7\text{N}] < 1$ pptv), yet they were found to play a crucial role in the chemistry of growing ion clusters.

4.2 The role of charge carriers different from HSO_4^-

In order of importance, the charge carriers in the observed base-sulfuric acid clusters were HSO_4^- , HSO_5^- , SO_5^- , and $\text{H}_2\text{O}_{11}\text{NS}_2^-$. The HSO_4^- ion strongly correlated with $[\text{H}_2\text{SO}_4]$ and was certainly formed by the de-protonation of H_2SO_4 . A formation mechanism for SO_5^- has been investigated by Möhler et al. (1992). The initial step of this mechanism is the formation of SO_3^- from SO_2 by the transfer of O^- from O_3^- . Subsequently, SO_5^- forms from SO_3^- and O_2 with a mediating N_2 or H_2O . We observed that O_3 in the CLOUD chamber was required for the formation of both SO_5^- and HSO_5^- , supporting these or similar ion-molecule reactions as a source. Possible origins of the HSO_5^- ions were the electronic charging of HSO_5 , while HSO_5 itself had possibly been formed as described in Kurtén et al. (2009), a proton-transfer reaction with peroxymonosulfuric

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acid H_2SO_5 , or ion-molecule reactions similar to those probably leading to the formation of SO_5^- . $\text{H}_2\text{O}_{11}\text{NS}_2^-$ was probably $\text{H}_2\text{S}_2\text{O}_8 \cdot \text{NO}_3^-$. $\text{H}_2\text{S}_2\text{O}_8$ might have been formed from hydrated SO_5 or from HSO_5^- (Kurtén et al., 2009). Nitric acid (HNO_3) and its conjugate base NO_3^- were present as contaminants in the chamber.

By far the most abundant ions during the new particle formation experiments at CLOUD that are discussed here were the clusters of type $(\text{NH}_3)_m \cdot (\text{H}_2\text{SO}_4)_n \cdot \text{HSO}_4^-$ and $(\text{NH}_3)_m \cdot (\text{H}_2\text{SO}_4)_n \cdot \text{HSO}_5^-$. The latter type gains relevance in conditions of high $[\text{NH}_3]$. Ammonia was present at $n \geq 2$ in the HSO_5^- -based clusters but at $n \geq 3$ in the HSO_4^- -based clusters. This suggests that sulfuric acid ion clusters will cluster more readily (i.e., build more stable clusters) with NH_3 when the charge-carrying component is HSO_5^- instead of HSO_4^- . Most likely, this was the primary reason for the observed increase of the fraction of HSO_5^- -based clusters at higher values of $[\text{NH}_3]$. A secondary reason was the usually coincidental lower $[\text{H}_2\text{SO}_4]$ during such experiments. The only other difference to the HSO_4^- -based clusters was an initially higher ratio m/n , as a direct consequence of the acceptance of NH_3 molecules already at $n=2$. Otherwise however, the composition of the clusters was the same, and the prevalent mechanism of cluster growth was not affected, namely the addition of a certain number of NH_3 molecules per H_2SO_4 molecule. Therefore, we conclude that the presence and actions of charge carriers other than HSO_4^- do not alter the conclusions of this study. Interestingly, when $n \geq 9$, differences in the ratio m/n disappeared or became approximately constant, suggesting that at about that size the ion cluster had become large enough to render any chemical effect of its charge-carrying component unimportant.

In conclusion, we suggest that HSO_5^- is a somewhat weaker Lewis base than HSO_4^- . Therefore, clusters containing HSO_5^- take up more readily bases and less readily acids, as compared with clusters containing HSO_4^- , which is in line with all our observations. Furthermore, the highest prevalence of HSO_5^- in all experiments at the CLOUD chamber to date has been in the dimethylamine- H_2SO_4 anion clusters that were produced during later experiments (in 2011 and 2012) following the addition of dimethylamine, a stronger base than NH_3 (Almeida et al., 2013).

4.3 The role of contaminant levels of amines in the formation and growth of anion clusters

Throughout our experiments, contaminant levels of amines were below the limit of direct detection. We estimate the gas-phase contaminant concentrations of C_2H_7N between 0.1 and 1 pptv during the CLOUD 2 campaign, and about 0.1 pptv during the CLOUD 3 campaign, but they may have been even smaller. The most abundant contaminant amine observed in anionic clusters was C_2H_7N , and the most abundant cluster containing C_2H_7N was $C_2H_7N \cdot (H_2SO_4)_3 \cdot HSO_4^-$ (Fig. 3). Note that $C_2H_7N \cdot (H_2SO_4)_2 \cdot HSO_4^-$ was observed, whereas $NH_3 \cdot (H_2SO_4)_2 \cdot HSO_4^-$ was not. Nevertheless, the growth of the clusters at contaminant levels of amines proceeded almost exclusively by the addition of NH_3 and H_2SO_4 molecules. 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).

The effect of higher gas-phase concentrations of amines, in particular of dimethylamine, on the composition of growing clusters and on particle formation rates has since been 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. The same reason can account for the observation (here, as in Almeida et al., 2013) that dimethylamine binds first to the sulfuric acid trimer anion, whereas NH_3 requires one more H_2SO_4 in the cluster and binds first to the sulfuric acid tetramer anion. Specifically, dimethylamine competes more successfully than NH_3 against HSO_4^- , which acts as a strong Lewis base in these clusters.

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However, in the experiments presented here, no effect on the rate of new particle formation was observed due to the contaminant levels of amines (<1 pptv). Also, the composition of the growing ion clusters was dominated by NH_3 and appeared to be unaffected by the optional inclusion of an amine.

5 Interestingly, a similar dominance of NH_3 over amines is also apparent in the composition of base-sulfuric-acid ion clusters that were observed during new particle formation in the ambient atmosphere, specifically in a boreal forest environment (Kulmala et al., 2013; Schobesberger et al., 2013a). However, it was also shown that other, oxidized organic compounds participate in those atmospheric new particle formation events as well from an early stage on (Schobesberger et al., 2013a; Ehn et al., 2014), suggesting more complex mechanisms of formation and growth of clusters, which have not yet been determined in detail.

4.4 The composition of NH_3 - H_2SO_4 clusters in the CLOUD laboratory experiments

15 The API-TOF measurements of NH_3 - H_2SO_4 clusters during particle formation experiments at the CLOUD chamber revealed how these clusters grow by the accretion of certain numbers of NH_3 and H_2SO_4 molecules. The measurements covered the range up to clusters containing about 27 sulfur atoms. This maximum size corresponds to 2.1 nm in mobility equivalent diameter, when converted according to Ehn et al. (2011) using the bulk density of ammonium bisulfate (1780 kg m^{-3} ; and neglecting a likely involvement of H_2O).

25 The anion clusters were mainly of the form $(\text{NH}_3)_m \cdot (\text{H}_2\text{SO}_4)_n \cdot \text{HSO}_4^-$. The HSO_4^- ion acts as a strong Lewis base, so stable bonds with NH_3 molecules are only possible for $n \geq 3$. For larger clusters ($n \geq 4$), the cluster growth was well characterized by the ratio of added NH_3 molecules per added H_2SO_4 molecule, $\Delta m / \Delta n$, which we found to be dependent on the ratio $[\text{NH}_3] / [\text{H}_2\text{SO}_4]$ and temperature (Fig. 5a). At high enough values of $[\text{NH}_3] / [\text{H}_2\text{SO}_4]$, $\Delta m / \Delta n$ saturated at just above unity. Note that a ratio of $\Delta m / \Delta n = 1$ corresponds to the stabilization of each H_2SO_4 molecule by an NH_3

consistent with the increased value of $[\text{NH}_3]/[\text{H}_2\text{SO}_4]$ required at lower temperatures to add NH_3 molecules to under-saturated $\text{NH}_3\text{-H}_2\text{SO}_4$ or H_2SO_4 clusters (Figs. 5 and 6).

At high values of $[\text{NH}_3]/[\text{H}_2\text{SO}_4]$, the ratio $\Delta m/\Delta n$ usually exceeded 1, approaching saturation in terms of the cluster NH_3 content (Figs. 5a and 6). This relationship appeared independent of the temperature within uncertainties and the investigated temperature range (-25 to 20°C). However, our data set may not be sufficiently complete to resolve possible dependencies on temperature. In this regime of high values of $[\text{NH}_3]/[\text{H}_2\text{SO}_4]$, also cation clusters of the form $(\text{NH}_3)_m \cdot (\text{H}_2\text{SO}_4)_n \cdot \text{NH}_4^+$ were observable, again with $\Delta m/\Delta n \geq 1$ (Fig. 5a). 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. 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 that we cannot exclude (Olenius et al., 2013a, b).

Since both the anion and cation clusters had $\Delta m/\Delta n$ slightly above unity when $[\text{NH}_3]/[\text{H}_2\text{SO}_4] \geq 10$, the clusters become slightly less acidic as they grew. The mass defect diagrams of the corresponding ion mass spectra illustrate the details on the increase of the clusters' base content as they grow (Fig. 7a and b). The anion clusters were seen to grow first by the addition of acids due to the high basicity of HSO_4^- . From the tetramer onwards ($\#S \geq 4$; see Sect. 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 (Fig. 7b). For the cation clusters, NH_3 was already present for the monomer, i.e. $\text{NH}_3 \cdot \text{H}_2\text{SO}_4 \cdot \text{NH}_4^+$, and the clusters grew slightly more basic already from the first step onwards (Fig. 7a). Interestingly, we observed a wider range of the number of NH_3 molecules m for any n in anion clusters than in cation clusters. We hypothesize that this observation follows from the requirement that $\text{NH}_3\text{-H}_2\text{SO}_4$ clusters be basic enough to accept an additional proton (therefore becoming or staying positively charged), whereas they need to be acidic enough to donate a proton

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(therefore becoming or staying negatively charged). Sulfuric acid can form clusters with only itself (plus H₂O) much more readily than can NH₃. Therefore, highly acidic (NH₃-) H₂SO₄ clusters can be formed, and they were indeed observed as anion clusters when [NH₃]/[H₂SO₄] was sufficiently low (e.g., Fig. 2c). For these clusters $\Delta m/\Delta n$ was < 1 , i.e. they continuously became more acidic as they grew. The possibility of such relatively acidic anion clusters leads to the wider range of observed m even at relatively high [NH₃]. On the other hand, the maximum basicity of NH₃-H₂SO₄ clusters is apparently limited, even at the highest investigated [NH₃] (Fig. 5a). Only such relatively basic clusters can be observed as cation clusters.

Note that almost all our experiments were performed at the RH between 37 and 41 %. Indeed, the data presented in Fig. 4 show that the observed NH₃-H₂SO₄ clusters contained more NH₃ at RH > 68 %. It remains a task for future studies to thoroughly investigate how the composition of these clusters changes with changing RH. It is also worth noting that the API-TOF was set to measure positively charged clusters in only few experiments; only for experiments at 19 °C did these experiments include conditions with [NH₃]/[H₂SO₄] < 100 .

4.5 Comparison to the composition of electrically neutral clusters from the ACDC model

In this work we hypothesize that the growth mechanism of NH₃-H₂SO₄ clusters is governed chiefly by hydrogen bonds and ionic bonds formed by acids and bases and the availability of the gas-phase precursors NH₃ and H₂SO₄. The electrical charge somewhat increases the stability (Olenius et al., 2013a), but most importantly it provides an additional base in the form of HSO₄⁻, whereas the NH₄⁺ ion seems to behave neither basic nor acidic. At relatively high [NH₃], both positively and negatively charged NH₃-H₂SO₄ clusters grow by adding NH₃ and H₂SO₄ molecules at a ratio of about unity, once the cluster is large enough that the effect of the HSO₄⁻ or NH₄⁺ ion is neutralized in terms of its basicity or acidity (Figs. 5a, 7a and b). Therefore we would expect electrically neutral clusters to grow by the same mechanism already from the

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5 first bond-formation onwards. At relatively low $[\text{NH}_3]$, only negatively charged clusters were observed in our experiments, growing mainly by the uptake of H_2SO_4 molecules (Fig. 5a), whereas positively charged clusters were not seen to be formed. Electrically-neutral $\text{NH}_3\text{-H}_2\text{SO}_4$ clusters must form under these conditions as well, since new particle formation occurred also without any ions in the CLOUD chamber (Kirkby et al., 2011).

10 We could not measure electrically neutral $\text{NH}_3\text{-H}_2\text{SO}_4$ clusters in this study. However, the difficulties in measuring such neutral clusters do not concern computer simulations. ACDC is a kinetic collision and evaporation model to study the formation dynamics and concentrations of molecular (charged and neutral) clusters (McGrath et al., 2012). In this study, we used ACDC to simulate the steady-state distribution of neutral clusters $(\text{NH}_3)_m \cdot (\text{H}_2\text{SO}_4)_n$ up to $m = 5$ and $n = 5$, as described in Almeida et al. (2013). Cluster evaporation rates were calculated from quantum chemical Gibbs free energies of formation of the clusters. We calculated the $\Delta m/\Delta n$ ratio for the simulated neutral clusters in the same way as for the measured data, covering the different combinations of temperature, $[\text{NH}_3]$ and $[\text{H}_2\text{SO}_4]$ of the measurement conditions. A single neutral H_2SO_4 molecule was taken as the starting point. The results are shown as dashed lines in Fig. 5a. The results from the simulations of neutral clusters agreed with the measurements of charged clusters in several respects: a maximum $\Delta m/\Delta n$ of 1.2 to 1.3 was reached at high values of $[\text{NH}_3]/[\text{H}_2\text{SO}_4]$ and $\Delta m/\Delta n$ decreased when $[\text{NH}_3]/[\text{H}_2\text{SO}_4] < 10$. Over the whole range, the simulations also reproduced the chief dependence of $\Delta m/\Delta n$ on the ratio $[\text{NH}_3]/[\text{H}_2\text{SO}_4]$ only. At low values $[\text{NH}_3]/[\text{H}_2\text{SO}_4]$, however, the simulated neutral clusters took up much more NH_3 as they grew than the measured negatively charged clusters. This discrepancy may arise from the following reasons: (1) H_2O molecules were not included in the model simulations, though they are abundant at $\text{RH} = 40\%$ and may play a more important role at relatively low $[\text{NH}_3]$; (2) small neutral clusters indeed contain more NH_3 than their negatively charged counterparts. The former reason would imply that H_2O molecules are able to compete with NH_3 at relatively low $[\text{NH}_3]$ for acting as the critical bases that stabilize sulfuric acid

clusters. The latter reason 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).

4.6 Comparison of $\text{NH}_3\text{-H}_2\text{SO}_4$ clusters from CLOUD to ambient observations

Negatively charged $\text{NH}_3\text{-H}_2\text{SO}_4$ clusters are commonly observed during new particle formation events in the boreal forest when using APi-TOF mass spectrometers (Kulmala et al., 2013; Schobesberger et al., 2013a). A typical anion mass spectrum obtained from those ambient APi-TOF measurements is presented in Fig. 7c, with the $(\text{NH}_3)_m \cdot (\text{H}_2\text{SO}_4)_n \cdot \text{HSO}_4^-$ clusters shown colored. The majority of the larger ions (shown in grey) likely contain mainly a variety of oxidized organics, and some probably also H_2SO_4 molecules (Schobesberger et al., 2013a; Ehn et al., 2012). However, most H_2SO_4 molecules in these anion clusters are found in the $(\text{NH}_3)\text{-H}_2\text{SO}_4$ clusters. Amines are present in some of these clusters as well, but most of the larger of these clusters ($n > 3$) contain only NH_3 and H_2SO_4 .

Figures 5a and 6 include a comparison of the CLOUD results with the observations of negatively charged $\text{NH}_3\text{-H}_2\text{SO}_4$ clusters during new particle formation events in the boreal forest during spring-time. The ambient measurements were made at conditions comparable to those covered by the CLOUD experiments, with mean values of 4°C for the temperature and 47 % for the RH. The $\text{NH}_3\text{-H}_2\text{SO}_4$ clusters from the boreal forest measurements always showed a high NH_3 content, with $\Delta m/\Delta n > 1$. The $[\text{NH}_3]/[\text{H}_2\text{SO}_4]$ ratios measured in the boreal forest at the same times were relatively high as well, with $[\text{NH}_3]$ ranging from 28 to 134 pptv (0.8 to $3.6 \times 10^9 \text{ cm}^{-3}$) and $[\text{H}_2\text{SO}_4]$ from 0.5 to $2.1 \times 10^7 \text{ cm}^{-3}$. In these terms, therefore, the ambient observations fully agree with the expectations from the laboratory experiments at CLOUD (Figs. 5a and 6). That specific $[\text{H}_2\text{SO}_4]$ range is well within the values of $[\text{H}_2\text{SO}_4]$ during new particle formation events recorded around the world, those values ranging from about 10^5 to 10^8 cm^{-3} (e.g., Kuang et al., 2008). The $[\text{NH}_3]$ range observed during the boreal

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ratio of unity). On the other hand, pure binary $\text{H}_2\text{O}-\text{H}_2\text{SO}_4$ clusters (without contribution of NH_3) only form at values of $[\text{NH}_3]/[\text{H}_2\text{SO}_4]$ smaller than about 0.1 (depending also on temperature). In our experiments, these binary clusters were only observed as negatively charged H_2SO_4 clusters. In the ambient atmosphere, their formation must be largely restricted to higher regions of the troposphere, where NH_3 concentrations are low.

A detailed comparison of model results on the growth of negative, positive and neutral $\text{NH}_3-\text{H}_2\text{SO}_4$ clusters is presented in Olenius et al. (2013a). So far, the quantum chemical data used to calculate the cluster evaporation rates restricted the model simulations to clusters containing up to ten molecules, whereas the API-TOF measurements could measure negatively and positively charged clusters up to clusters containing >50 NH_3 and H_2SO_4 molecules. The model simulations and API-TOF measurements are consistent and in good agreement with each other, particularly for cases of $[\text{NH}_3]/[\text{H}_2\text{SO}_4] > 10$. Under these conditions, also electrically-neutral $\text{NH}_3-\text{H}_2\text{SO}_4$ clusters grow principally by adding, on average, 1 to 1.4 NH_3 molecules for each added H_2SO_4 molecule. Note that the recombination of anion and cation clusters can also contribute to the population of neutral clusters (Olenius et al., 2013a; Kontkanen et al., 2013).

In combination, measurement and model results strongly suggest that acid-base interactions are the dominant clustering mechanism for all $\text{NH}_3-\text{H}_2\text{SO}_4$ clusters. These interactions allow for the initial formation of clusters and facilitate additional intermolecular bonds as the clusters grow to 2 nm in size and larger, i.e. sizes that are nowadays accessible by condensation particle counters (Lehtipalo et al., 2014). The presence of an electric charge implies a missing or extra proton, i.e. the creation of a conjugate base or acid. In particular, the basic properties of HSO_4^- have an important impact on the composition of the small negatively charged clusters. We identified the HSO_5^- ion as an important alternative ion in these clusters for the conditions in the CLOUD chamber. It appears to be slightly less basic than HSO_4^- and similarly affects cluster composition. Besides the stabilizing effect of the electric charge on the cluster,

the property of HSO_4^- (or HSO_5^-) as a Lewis base is probably crucial to the enhancements of particle formation rates attributed to ions (Kirkby et al., 2011).

In the atmospheric boundary layer, the composition of formed $\text{NH}_3\text{-H}_2\text{SO}_4$ clusters will mostly be in the regime of saturation that we observed with respect to the clusters' NH_3 content, i.e. they will be seen growing by the addition of in average >1 NH_3 molecule per added H_2SO_4 molecule. This prediction is due to H_2SO_4 concentrations in the boundary layer being comparatively low, mostly at sub-pptv levels, leading to typical vapor concentration ratios $[\text{NH}_3]/[\text{H}_2\text{SO}_4]$ of larger than 10. Ambient API-TOF measurements during new particle formation events in the Finnish boreal forest indeed confirm this prediction.

Another general requirement for the formation of $\text{NH}_3\text{-H}_2\text{SO}_4$ clusters is the sufficiently low abundance of compounds competing with NH_3 in forming clusters with H_2SO_4 . One such class of compounds has been shown to be amines, in particular dimethylamine (Bzdek et al., 2011; Almeida et al., 2013). The measurements in the boreal forest have shown that large $\text{NH}_3\text{-H}_2\text{SO}_4$ clusters do not usually contain any amines. This observation suggests relatively low amine concentrations at the boreal forest measurement site in Hyytiälä (Schobesberger et al., 2013a). In fact, the prevalence of NH_3 over amines is similar to the observations in the CLOUD chamber at the presence of contaminant levels of amines, indicating ambient amine concentrations in the boreal forest of <1 pptv.

It remains unsolved what is the exact role of $\text{NH}_3\text{-H}_2\text{SO}_4$ clusters, and NH_3 in general, in the initial steps of the boundary layer events of new particle formation and growth that are frequently observed in the Finnish boreal forest and elsewhere (Kulmala et al., 2004b). Such clusters have been observed, but laboratory experiments suggest that they are not stable enough to fully account for the bulk of boundary layer particle formation (Kirkby et al., 2011). Other experiments conclude that clusters of two to three H_2SO_4 molecules plus a mix of basic molecules (NH_3 and amines) can in fact account for particle formation in polluted conditions (Chen et al., 2012).

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At least in clean environments rich in α -pinene, such as boreal forests, recent experimental evidence hints at an important role of highly-oxidized organic compounds with extremely low volatility already in the first steps of boundary layer particle formation (Kulmala et al., 1998; Schobesberger et al., 2013a; Ehn et al., 2014; Riccobono et al., 2014). These organic compounds probably feature several functional groups that facilitate hydrogen bonds with each other and with H_2SO_4 molecules, in the same way as the bonds between H_2SO_4 and NH_3 (Donahue et al., 2013). However, the inclusion of dimethylamine in these sub-2 nm clusters has been observed as well (Riccobono et al., 2014). Our ambient observations in the boreal forest suggest that a large fraction of H_2SO_4 molecules in sub-2 nm clusters are found in clusters with NH_3 . Therefore, it is very likely that mixed sub-2 nm NH_3 - H_2SO_4 -organics clusters are also stable and indeed commonly contributing to particle formation in the boreal forest.

The measurement results presented here substantially extend our knowledge on how NH_3 and H_2SO_4 interact in detail when forming and growing clusters under atmospheric conditions. The results are in general agreement with results from model simulations (e.g., Olenius et al., 2013a), as well as with previous experimental work (e.g., Bzdek et al., 2011, 2013; Froyd and Lovejoy, 2012). Altogether, we are moving closer to gaining a more complete and detailed understanding of this subject. The most important contribution of the present study is a detailed examination of cluster compositions under a wide range of atmospherically relevant conditions, and experimentally covering the whole sub-2 nm size range. Supported by simulations of cluster population dynamics, the results also allow for inferences to be made on electrically neutral NH_3 - H_2SO_4 clusters.

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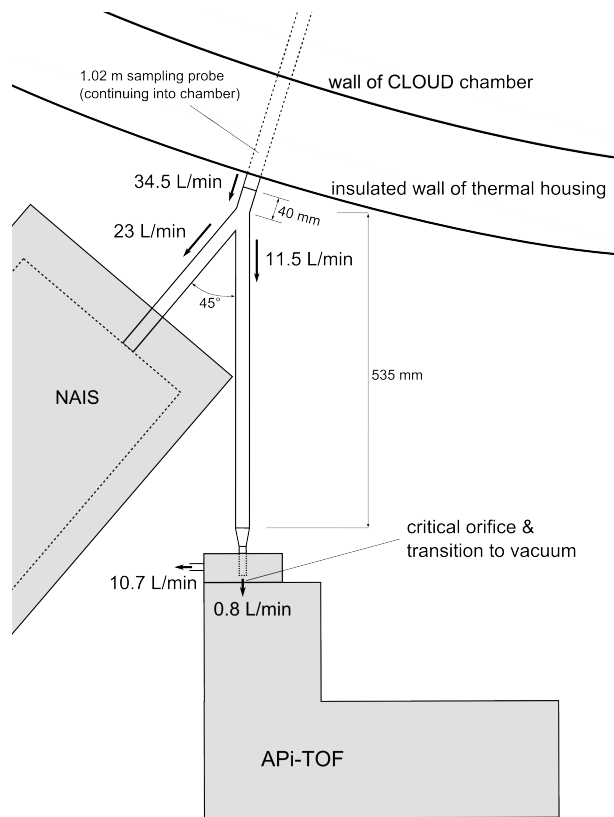


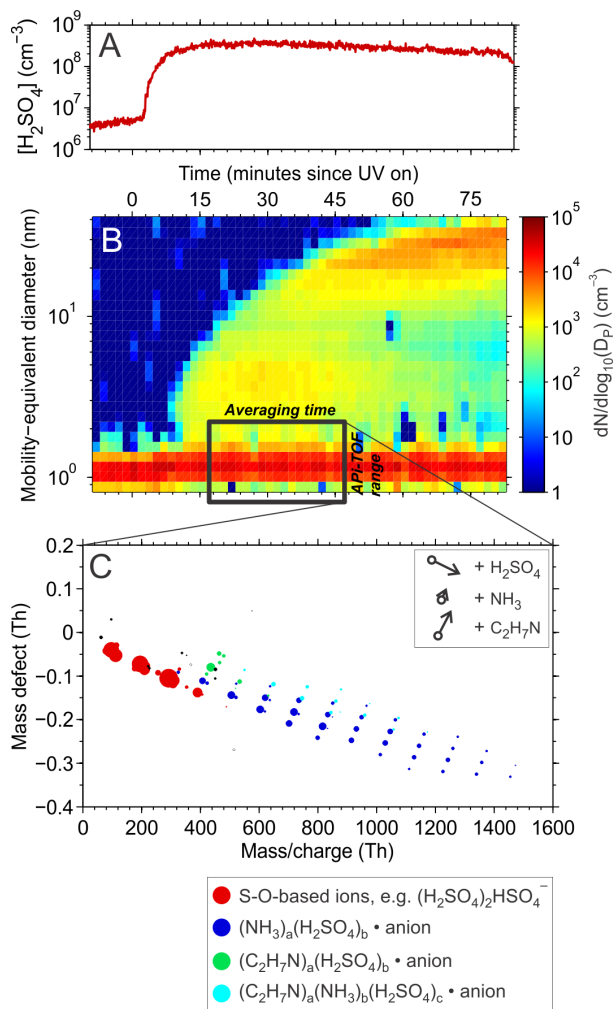
Figure 1. Setup of the API-TOF at the CLOUD chamber during the CLOUD 2 and CLOUD 3 campaigns. The API-TOF shared one sampling probe (22.1 mm ID) with the NAIS. The flow was split via a Y-splitter. Before reaching the critical orifice inlet of the API-TOF, the inner tube diameter reduced from the Y-splitter's 21.2 to 7 mm.

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Figure 2. Summary of a typical new particle formation experiment in the CLOUD chamber during the CLOUD 2 campaign, with no added NH_3 , at 20°C , 60 % relative humidity, $3.7 \times 10^8 \text{ cm}^{-3}$ $[\text{H}_2\text{SO}_4]$, 4 pptv $[\text{NH}_3]$, <1 pptv $[\text{C}_2\text{H}_7\text{N}]$, pion beam on. **(A)** Measurements of sulfuric acid concentration ($[\text{H}_2\text{SO}_4]$) by CIMS, showing the marked increase in $[\text{H}_2\text{SO}_4]$ after the start of UV illumination. **(B)** Consequent new particle formation event as observed by the NAIS negative ion channel, showing negatively charged ions that grow from originally well below 2 nm to larger sizes. The black box marks the time period of steady new particle formation that was used for averaging APi-TOF data, and the size range covered by the APi-TOF mass spectra. **(C)** Mass defect diagram for the APi-TOF mass spectrum, averaged over the shown particle formation event. The diagram reveals the composition of the growing negatively charged ions between about 1–2 nm. These are ion clusters, growing by the addition of H_2SO_4 and contaminant NH_3 molecules (red and blue). Some clusters also contain contaminant amines (green and light blue).

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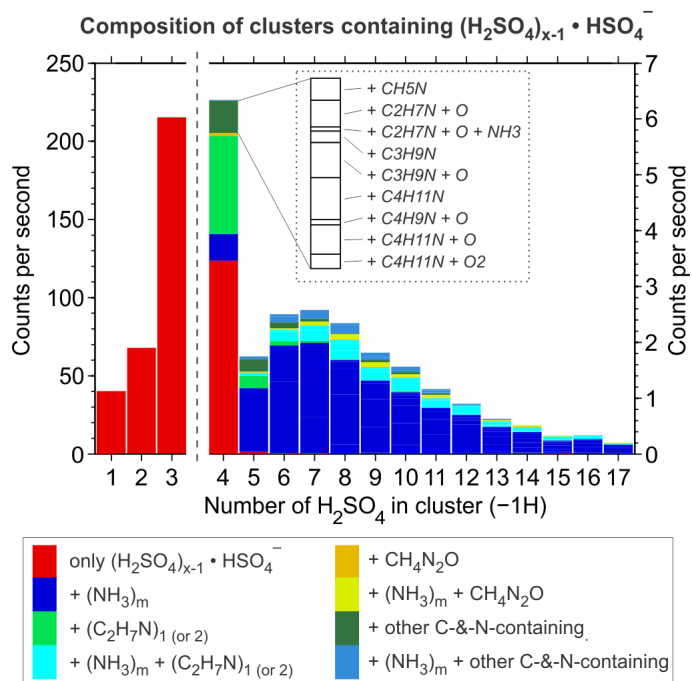


Figure 3. Details on the composition of the growing negatively charged clusters during the new particle formation experiment presented in Fig. 2, binned by the number x of H_2SO_4 molecules in the cluster. Note that only ion clusters based on the HSO_4^- ion are shown, for simplicity. However, these ions constitute the majority of all ions, and practically all ions at $x > 3$ (i.e. beyond 350 Th, as can be seen in Fig. 2c). Besides contaminant NH_3 , a wide range of contaminant nitrogen-containing organic compounds are seen in these clusters if $x > 3$, especially for $x = 4$. By far the most observed of these compounds is $\text{C}_2\text{H}_7\text{N}$ (dimethylamine or ethylamine). Most likely all these organics are amines or amides (such as $\text{CH}_4\text{N}_2\text{O}$, probably urea), their high proton affinities facilitating the formation of clusters with H_2SO_4 .

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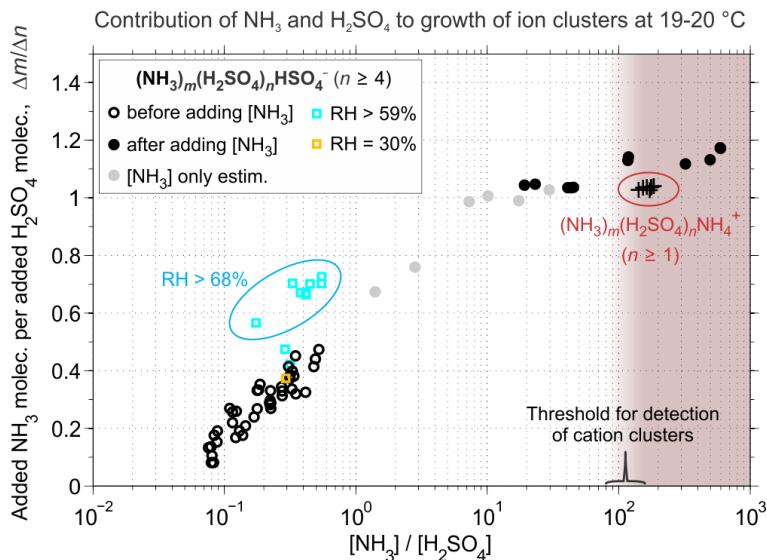


Figure 4. Number of gained NH₃ molecules per gained H₂SO₄ molecule, $\Delta m/\Delta n$, plotted against the ratio of NH₃ and H₂SO₄ gas-phase concentrations, $[\text{NH}_3]/[\text{H}_2\text{SO}_4]$, for particle formation experiments at 19 to 20 °C, showing a positive correlation. Circles are for anion clusters $(\text{NH}_3)_m \cdot (\text{H}_2\text{SO}_4)_n \cdot \text{HSO}_4^-$ and experiments at a relative humidity (RH) of 37 to 40%. Colored squares denote experiments at lower RH (30%) or higher RH (>59%). Red pluses show $\Delta m/\Delta n$ for cation clusters $(\text{NH}_3)_m \cdot (\text{H}_2\text{SO}_4)_n \cdot \text{NH}_4^+$, which are only observed at sufficiently high $[\text{NH}_3]/[\text{H}_2\text{SO}_4]$, as marked by the shaded area, at an RH of 39 to 40%. Values for $\Delta m/\Delta n$ were determined for anion clusters in the range $4 \leq n \leq 18^*$, and for cation clusters in the range $1 \leq n \leq 17^*$. The lower limits of these ranges correspond to the sizes, from which onward $\Delta m/\Delta n$ were constant. The upper limits were chosen, because up to these sizes a good signal was obtained for most experiments.

* Actual upper limits varied depending on obtained signals. The median maximum n was 16 for anion and 17 for cation clusters.

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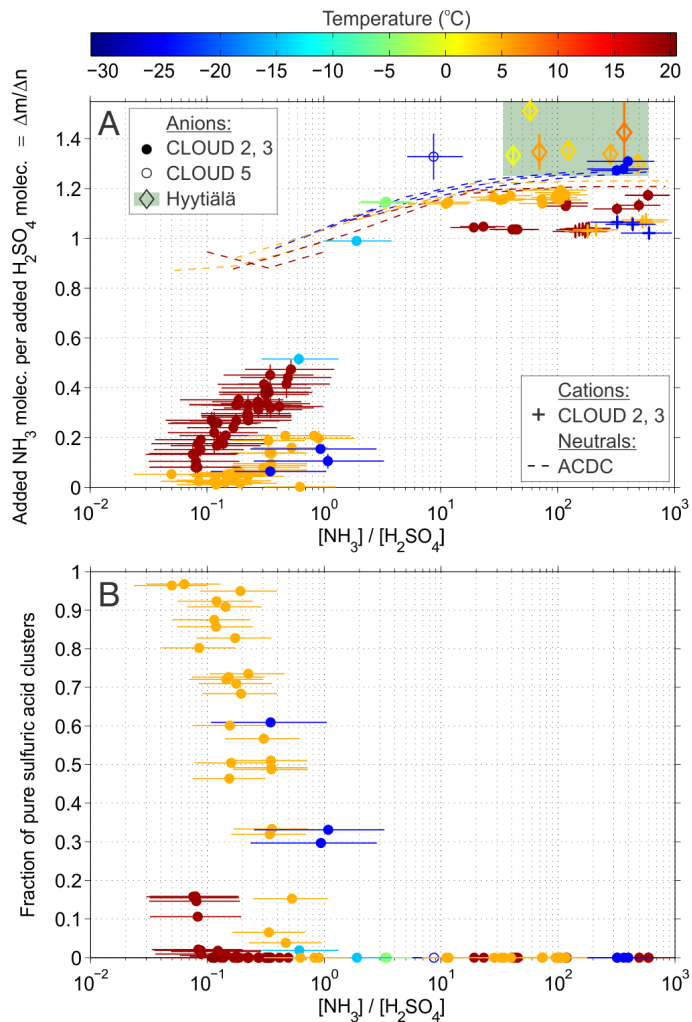
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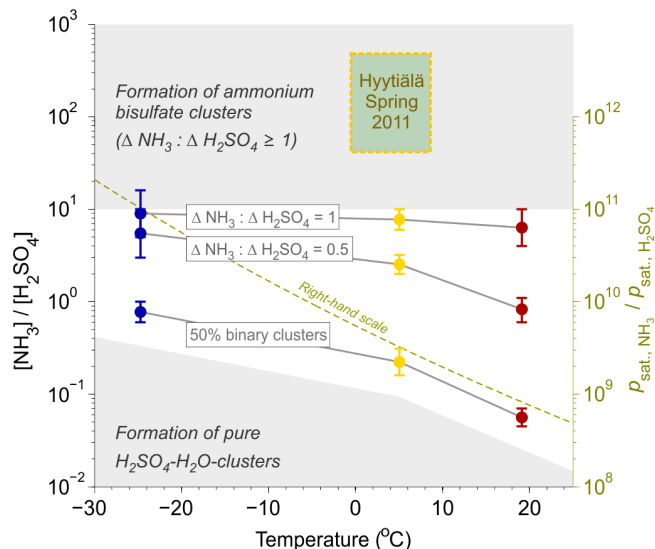
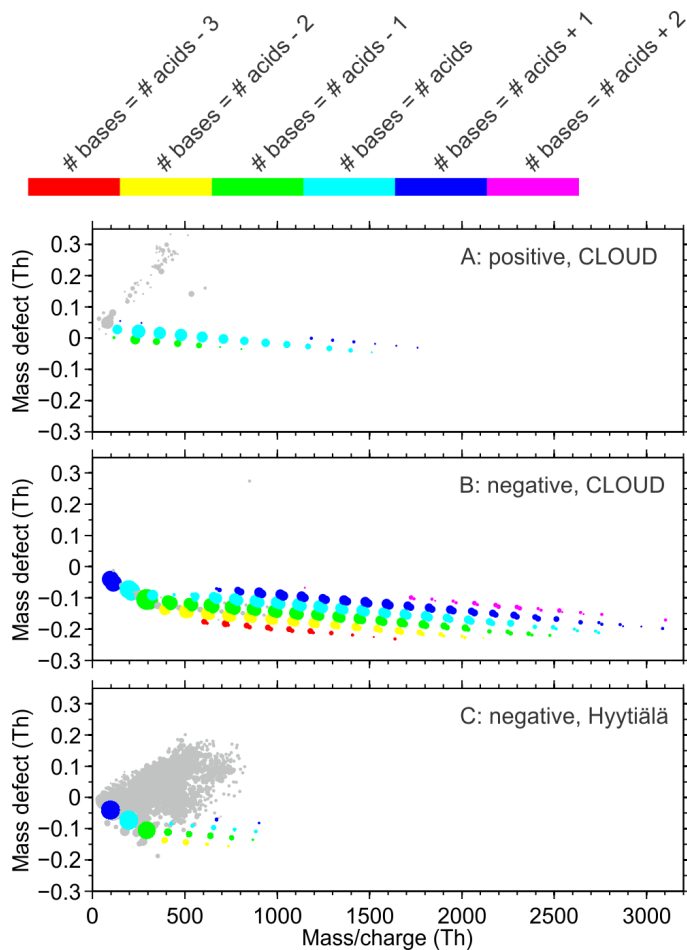


Figure 6. Summary of the observed composition of $(\text{NH}_3)_m \cdot (\text{H}_2\text{SO}_4)_n \cdot \text{HSO}_4^-$ anion clusters for the covered experimental conditions: varying vapor concentration ratios $[\text{NH}_3]/[\text{H}_2\text{SO}_4]$ (left vertical axis) and temperatures (horizontal axis and same color scale as for Fig. 5). Three specific features of cluster composition are presented at three investigated temperatures each, by a total of nine circles. These three features are (1) a fraction of 50% of pure, NH_3 -free sulfuric acid clusters, (2) a ratio of added NH_3 molecules per added H_2SO_4 molecule, $\Delta m/\Delta n = 0.5$, and (3) $\Delta m/\Delta n = 1$. Values and uncertainties are based on the data shown in Fig. 5. Consequently, the grey shaded area at the bottom covers conditions allowing the formation of pure binary (NH_3 -free) H_2O - H_2SO_4 clusters. The grey shaded area at the top covers conditions that allow for the formation of clusters with about equal numbers of NH_3 and H_2SO_4 molecules (as in ammonium bisulfate). The position of the green box and the color of its dashed edge line mark the conditions during the measurements in the boreal forest (Hyytiälä). Shown in brown (right vertical axis and line) is the ratio of saturation vapor pressures of NH_3 and H_2SO_4 ($p_{\text{sat.},\text{NH}_3}/p_{\text{sat.},\text{H}_2\text{SO}_4}$).

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Figure 7. Mass defect diagrams of ion mass spectra during new particle formation. The NH_3 - H_2SO_4 ion clusters are colored, other ions are shown in grey. The colors reflect the relative numbers of acids and bases in the cluster, counting NH_3 , HSO_4^- , HSO_5^- and SO_5^- as bases, and H_2SO_4 as acid, and not counting NH_4^+ . **(A)** Positively charged clusters $(\text{NH}_3)_m \cdot (\text{H}_2\text{SO}_4)_n \cdot \text{NH}_4^+$ during new particle formation at CLOUD at $[\text{NH}_3]/[\text{H}_2\text{SO}_4] = 185$, temperature (T) = 19 °C. Other ions (in grey) are mostly organic, N-containing contaminants, such as pyridine, charged by protonation. **(B)** Negatively charged clusters $(\text{NH}_3)_m \cdot (\text{H}_2\text{SO}_4)_n \cdot \text{HSO}_4^-$ and $(\text{NH}_3)_m \cdot (\text{H}_2\text{SO}_4)_n \cdot \text{HSO}_5^-$ during new particle formation at CLOUD at $[\text{NH}_3]/[\text{H}_2\text{SO}_4] = 118$, $T = 19$ °C. **(C)** Negatively charged clusters $(\text{NH}_3)_m \cdot (\text{H}_2\text{SO}_4)_n \cdot \text{HSO}_4^-$ during a new particle formation event in the boreal forest, Hyytiälä, at $[\text{NH}_3]/[\text{H}_2\text{SO}_4] = 485$, $T = 1$ to 5 °C. Most of the signal of other ions (in grey) has a more positive mass defect and likely arises from ions containing mainly a variety of oxidized organics.

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