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Effect of ions on the measurement of sulphuric acid in the CLOUD experiment at CERN

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Abstract

Ternary aerosol nucleation experiments were conducted in the CLOUD chamber at CERN in order to investigate the influence of ions on new particle formation. Neutral and ion-induced nucleation experiments, i.e., with and without the presence of ions, were carried out under precisely controlled conditions. The sulphuric acid concentration was measured with a Chemical Ionization Mass Spectrometer (CIMS) during the new particle formation experiments. The added ternary trace gases were ammonia (NH_3), dimethylamine (DMA, C_2H_7N) or oxidised products of pinanediol (PD, $C_{10}H_{18}O_2$). When pinanediol was introduced into the chamber, an increase in the mass spectrometric signal used to determine the sulphuric acid concentration (m/z 97, i.e., HSO_4^-) was observed due to ions from the CLOUD chamber. The enhancement was only observed during ion-induced nucleation measurements by using either galactic cosmic rays (GCR) or the proton synchrotron (PS) pion beam for the ion generation, respectively. The ion effect typically involved an increase in the apparent sulphuric acid concentration by a factor of ∼ 2 to 3 and was qualitatively verified by the ion measurements by an Atmospheric Pressure interface-Time Of Flight (APi-TOF) mass spectrometer. By applying a high voltage (HV) clearing field inside the CLOUD chamber the ion effect on the CIMS measurement was completely eliminated since, under these conditions, small ions are swept from the chamber in about one second. In order to exclude the ion effect and to provide corrected sulphuric acid concentrations during the GCR and PS beam nucleation experiments, a parameterisation was derived that utilizes the trace gas concentrations and the UV light intensity as input parameters. Atmospheric sulphuric acid measurements with a CIMS showed an insignificant ion effect.

1 Introduction

Atmospheric aerosols have an important effect on clouds and climate, with secondary aerosol particles contributing significantly to the global concentration of cloud

condensation nuclei (CCN) via new particle formation (Kulmala et al., 2004; Merikanto et al., 2010). From both field and laboratory measurements, it has been well established that sulphuric acid (H_2SO_4) plays a crucial role in atmospheric nucleation (Curtius, 2006; Riipinen et al., 2007; Kuang et al., 2008). However, binary nucleation of sulphuric acid and water vapour can be ruled out as a plausible mechanism to explain observed boundary layer nucleation rates (Kirkby et al., 2011). The presence of ternary substances like ammonia (Benson et al., 2009; Kirkby et al., 2011) or oxidised organic compounds (Zhang et al., 2004; Metzger et al., 2010; Riccobono et al., 2012, 2014; Schobesberger et al., 2013) can elevate the particle formation rates by orders of magnitude. Yet, so far the physico-chemical processes taking place in atmospheric boundary layer particle formation remain unknown and still questions remain on the exact contribution of ternary substances and on the role of ions in atmospheric nucleation (Kulmala, 2003; Lovejoy et al., 2004). One goal of the CLOUD (Cosmics Leaving OUtdoor Droplets) experiment at CERN is to investigate to what extent the presence of ions affects new particle formation at atmospherically relevant conditions (Kirkby et al., 2011; Schobesberger et al., 2013; Almeida et al., 2013). At CLOUD, neutral and ion-induced nucleation experiments are carried out in an aerosol chamber under precisely controlled conditions. Trace gases are added into the CLOUD chamber in order to investigate their influence on the nucleation. The source of ions in the chamber is either Galactic Cosmic Rays (GCR) or both GCR and the CERN's proton synchrotron (PS) pion beam (Duplissy et al., 2010; Kirkby et al., 2011). Highly accurate and precise measurements of gaseous [H_2SO_4] are required in order to interpret the data and for deriving parameterisations of the nucleation rate for certain conditions. Sulphuric acid concentration measurements are therefore performed with a Chemical Ionization Mass Spectrometer (Kürten et al., 2012).

In this paper, we describe the effect of ionising radiation on the sulphuric acid measurements performed by the CIMS instrument. During nucleation experiments with oxidation products of pinanediol, the mass spectrometric sulphuric acid signal (HSO_4^- ions) showed an increase due to the presence of ions in the chamber. The

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characteristics of the increased signal lead to the conclusion that HSO_4^- ions from the chamber were interfering with the product ions from the CIMS ion reaction zone. In order to verify this assumption, dedicated tests with the CIMS and the pion beam were performed. Surprisingly, the ion contribution was only detectably under the presence

5 of oxidised organic compounds. Additionally, the Atmospheric Pressure interface Time of Flight mass spectrometer (APi-TOF, Junninen et al., 2010) measurements of ionic clusters confirmed that the enhanced HSO_4^- signal is coming directly from the chamber in the presence of oxidised organic compounds. In order to exclude the ion effect and to derive the correct sulphuric acid concentration for the ternary pinanediol nucleation

10 runs, a parameterisation was developed.

2 Methods

2.1 CLOUD chamber measurements

Nucleation experiments were carried out using the CLOUD chamber at CERN (Kirkby et al., 2011). The electropolished stainless steel chamber of $26\,m^3$ volume provides an

15 ultra-clean environment where selected trace gases and ultrapure humidified synthetic air can be continuously supplied. Well-defined amounts of H_2SO_4 are produced in-situ from SO_2 and OH by means of internal ultra-violet (UV) illumination from a fibre-optic system producing OH from ozone and H_2O (Kupc et al., 2011). As a source of ionising radiation for ion-induced nucleation measurements, an adjustable pion beam from the

20 CERN Proton Synchrotron (PS) is used in order to simulate and enhance the natural cosmic radiation. For the so called GCR ion-induced nucleation experiments (GCR runs), the pion beam is turned off and the chamber is only irradiated by the natural GCRs that enter the chamber, while for ion-free nucleation experiments (neutral runs), an internal electric clearing field, with a total potential difference of 60 kV, was used to

25 sweep any ions out of the chamber within less than 1 s (Kirkby et al., 2011). The contents of the CLOUD chamber are continuously mixed by use of two fans (Voigtländer

et al., 2012) and are analysed by a wide variety of instruments, each connected to a separate 0.75 m long sampling probe protruding into the chamber. The instrumentation includes several condensation particle counters (CPCs), mass spectrometers, and electrical mobility analysers. Organic trace gases were monitored with a proton-transfer-reaction time of flight (PTR-TOF-MS; Schnitzhofer et al., 2013), and aerosol particle concentrations measured, starting at particle diameter sizes smaller than 2 nm (Wimmer et al., 2013).

During the CLOUD-04 campaign in June and July 2011, data of multi-component nucleation were obtained at the CLOUD chamber involving sulphuric acid and water vapour and adding either ammonia, dimethylamine or biogenic organic vapours (pinanediol, PD). PD is a surrogate first-generation product from the important biogenic vapour alpha-pinene, which is further oxidised by ozone and OH radicals to form more highly oxidised organic substances. Ammonia and dimethylamine concentrations were determined with an ion chromatograph (Praplan et al., 2012) while concentrations of organic compounds were measured with a proton-transfer-reaction time of flight (PTR-TOF-MS; Schnitzhofer et al., 2013). The nucleation events were started by switching on the UV light, which initialises the OH formation from ozone photolysis and leads to the production of H_2SO_4 (Kupc et al., 2011). While pinanediol is present in the chamber, the produced OH radicals would also contribute to reactions with pinanediol, competing in this way with the sulphuric acid production (Schobesberger et al., 2013; Riccobono et al., 2014).

2.2 H_2SO_4 measuring technique

A negative-ion detection CIMS instrument was used to measure the concentration of gaseous H_2SO_4 with a detection limit of $\sim 1 \times 10^5$ molecule cm^{-3}. This system utilises a specific ion-molecule reaction to convert electrically neutral H_2SO_4 molecules into bisulphate HSO_4^- (m/z 97) ions, using NO_3^- as the ionising agent. This technique has been used previously in many other studies for gaseous or aerosol measurements (Viggiano and Arnold, 1983; Eisele and Tanner, 1993; Berresheim et al., 2000; Petäjä et al.,

2009). The CIMS system (THS Instruments LLC, USA) contains a quadruple mass-filter and a channeltron detector for the quantification of analyte ions (Huey, 2007). In addition to the basic components, a collision dissociation chamber (CDC) consisting of an octopole, is used to remove weakly bonded water and nitric acid molecules from the core ions via energetic collisions (Tanner et al., 1997). The ion source that is used to generate the primary ions is a newly developed corona ion source (Kürten et al., 2011). For a known ion molecule residence time in the flow reactor and rate constant, the sulfuric acid concentration can be calculated by the ratio of the product ions (HSO_4^- ions) to educt ions (NO_3^- ions) count rates. In order to avoid a possible damage of the channeltron detector due to the high count rate of the NO_3^- ions, we measure the isotope at m/z 64, $N^{18}OO_2^-$ (Kürten et al., 2012). The ion-molecule reactions between the reagent ions and the neutral compound to be detected and quantified occur in the flow reactor. Electrostatic voltages applied to different parts of the ion source and the drift tube guide the primary ions into the sample flow where they can interact with the H_2SO_4 molecules. At the end of the drift tube primary and product ions are drawn into the vacuum chamber. Signals of the most prominent product and primary ions were recorded every few seconds while a complete mass spectrum (up to $m/z \sim 250$) was recorded every few minutes, allowing measurements in real time. Diffusion controlled wall loss in the CIMS sampling line has been taken into account (total length: 0.90 m, H_2SO_4 penetration: 44 %). The measured H_2SO_4 concentration is derived by multiplying the HSO_4^-/NO_3^- ratio with a calibration factor (Kürten et al., 2012). By performing a detailed calibration with a dedicated calibration source, uncertainties of reaction rate, reaction time and wall losses in the ion-molecule reactor do not influence the determination of the H_2SO_4 concentration. The calibration source is based on photolyzing water vapour with a mercury lamp to generate a known and stable amount of OH radicals in front of the inlet. The produced OH radicals react with the provided SO_2 in the presence of O_2, resulting in known sulphuric acid concentrations. The CIMS instrument was calibrated before and just after the end of the CLOUD-04 campaign in order to assure high accuracy of the measurement.

3 Results

3.1 Sulphuric acid measurements during binary nucleation experiments

The focus of the performed binary experiments (H_2SO_4-H_2O) was the measurement of the nucleation rate under neutral, GCR and charged pion beam conditions. Having the initial experimental conditions established in the chamber with constant SO_2 and O_3 concentration, temperature (T), relative humidity (RH), and stable UV lamp operation, a stable sulphuric acid concentration is typically reached within about 15 min after opening the shutter of the UV light source. Depending on the H_2SO_4 concentration, aerosol nucleation occurs at a constant rate (Kirkby et al., 2011; Riccobono et al., 2014). After switching off the UV light, the OH production stops and the H_2SO_4 concentration decreases to a background level due to condensation of H_2SO_4 on the chamber walls and dilution with freshly supplied air (Voigtländer et al., 2012). An overview of a typical binary run is given in Fig. 1a, which displays the clearing field voltage, the UV light intensity, the pion beam intensity, and the HSO_4^- count rate used for deriving the sulphuric acid concentration. While the UV lights are turned off, there is a background of 5 to 7 counts per second for HSO_4^- resulting in a background sulphuric acid concentration of 2.5×10^5 molecule cm^{-3}, which remains constant despite the changing clearing field voltage and pion beam intensity. Once the UV lights are switched on, the photo-oxidation of sulphur dioxide is taking place in the presence of O_3 and H_2O, producing an equilibrium sulphuric acid concentration around 2×10^7 molecule cm^{-3} (HSO_4^- count rate ~ 300 s^{-1}). Similar to the situation under background conditions, the H_2SO_4 concentration is identical for neutral, GCR and charged pion beam conditions. After the UV lights are turned off, the H_2SO_4 steady-state is disturbed and its concentration decreases due to loss onto the chamber walls and dilution. After some time (~ 1800 s), the H_2SO_4 equilibrates back to the initial background concentration that was measured before starting the nucleation run.

3.2 Sulphuric acid measurements during pinanediol nucleation experiments

In order to study the effect of oxidised organic compounds on the nucleation rates the pinanediol (PD, $C_{10}H_{18}O_2$) vapour (Sigma Aldrich, 99 %) was introduced into the chamber (Schobesberger et al., 2013; Riccobono et al., 2014). The concentration of the oxidation products (OxOrgs) is varied by changing the UV illumination and the concentration of pinanediol. The presence of PD (up to 500 ppbv) increased the HSO_4^- background intensity by as much as a factor of 40 in comparison to the chamber's neutral conditions without PD, i.e. during nucleation experiments using only H_2SO_4 and H_2O, or H_2SO_4, H_2O and NH_3 (Fig. 1a and b). In particular, the enhancement of the HSO_4^- background signal is confirmed by the data shown in Fig. 2. During this experiment no UV light was present. However, the increase of the PD level resulted in a clear enhancement of the bisulfate signal. An additional increase in the HSO_4^- count rate is observed in the presence of the pion beam. The first increase in Fig. 2 suggests that there exists another pathway for the production of H_2SO_4 besides the reaction between OH and SO_2. It has been shown recently that stabilized Criegee intermediates produced from reactions between alkenes and ozone have the capacity to oxidise SO_2 (Mauldin et al., 2012). However, since PD does not react with ozone due to its lack of a double-bond, organic impurities (alkenes) (Schnitzhofer et al., 2013) fed into the chamber along with the PD could account not only for the production of Criegee intermediates but also for the production of OH via ozonolysis of these alkenes (Kroll et al., 2001) and the subsequent generation of sulphuric acid (Riccobono et al., 2014). This dark production of sulphuric acid is not the focus of this study but will be studied in more detail in the future. Here we focus on the investigation of the ion effect on the CIMS sulphuric acid measurements in the presence of OxOrgs and ions (GCR and pion beam) for both background (UV off) and nucleation experimental runs (UV on).

An interesting feature in Fig. 1b, is that during background measurements in the presence of the pion beam (07:30 UTC and later), the HSO_4^- intensity measured by the mass spectrometer is increased by a factor of ~ 2 compared to neutral conditions

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(beam on or off but HV on). This observation indicates that there is an influence on the sulphuric acid measurement by additional HSO_4^- ions detected by the CIMS under these conditions (beam on and HV off). Thus, the CIMS is not only detecting the HSO_4^- ions being created in the CIMS flow reactor through reaction with NO_3^- ions, but is also detecting additional HSO_4^- ions coming directly from the chamber. In addition, the same effect is also taking place in the presence of the UV irradiation where the production of sulphuric acid is taking place through SO_2 oxidation by OH as well as stabilized Criegee intermediates (Riccobono et al., 2014). In both conditions (UV on and off), the observed enhancement of the detected HSO_4^- ions is about a factor of 2.

By activating the clearing field (CF), the influence of the HSO_4^- ions from the chamber is directly confirmed (Fig. 1b). When the clearing field is switched on, the measured HSO_4^- signal drops by a factor of 2 within about 1 s, which corresponds to the time to remove ions due to the presence of the strong electric field (Kirkby et al., 2011). The H_2SO_4 lifetime of ~ 400 to 500 s is substantially longer, therefore, the observed short lifetime of the increased HSO_4^- signal confirms that ions are responsible for it and not neutral sulfuric acid. In addition, a special experiment was performed by turning off the primary ion production in the CIMS corona ion source. The data in Fig. 3 unambiguously show that a substantial amount of HSO_4^- ions can be detected if the corona ion source is turned off while the pion beam is turned on.

Moreover, another vital confirmation of the ion effect is provided by the Atmospheric Pressure interface-Time Of Flight (APi-TOF) mass spectrometer measurements. The APi-TOF mass spectrometer measures the composition and concentrations of negative ions at mass-to-charge ratios ranging from about 50 to 3300 Th (Junninen et al., 2010; Schobesberger et al., 2013). A significant enhancement in the HSO_4^- signal measured by the APi-TOF is shown in Fig. 4 for the presence of oxidised organics. In this figure selected ion and cluster ion signals are displayed both for a binary (H_2SO_4-H_2O) and a ternary pinanediol nucleation experiment with very similar conditions. The concentration of H_2SO_4 is about 6.6×10^7 molecule cm^{-3} for both conditions, whereas the pion beam intensity is about 10 % higher for the PD experimental run. For the H_2SO_4-H_2O

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nucleation experiment (binary run, shown in blue), the negative ion spectrum is clearly dominated by sulfuric acid and other inorganic compounds. The strongest sulphate containing peak is from the HSO_4^- ion (m/z 97), which is seen to cluster with one, two or three H_2SO_4 molecules. The other main ions are HSO_4^- clustering with HNO_3 and other inorganic molecules. On the other hand, for the PD case (pinanediol run, shown in red), the most striking feature is that the HSO_4^- signal is raised by a factor of 2.2 although the measured neutral sulphuric acid concentration is almost identical. Here, the most abundant ions were complex cluster ions containing oxidised $C_{10}H_xO_y$ (where x = 12, 14, 16 and y = 2–12) organics and an HSO_4^- ion as well as 0–2 additional H_2SO_4 molecules.

4 Discussion

The APi-TOF mass spectrum clearly shows that HSO_4^- can cluster efficiently with oxidised organic products in case PD is present in the chamber. In the H_2SO_4-H_2O nucleation experiments these bisulfate-OxOrg clusters are absent and the mass spectrum is dominated by HSO_4^-. These observations suggest that the presence of OxOrg can enhance the transmission efficiency of the HSO_4^- core ions through the sampling line of the APi-TOF and the CIMS. The increase in the mass of the $HSO_4^- \cdot OxOrg$ ion complex leads to a reduction in the ion mobility thereby enhancing the probability that the $HSO_4^- \cdot OxOrg$ ions can eventually be detected. Fragmentation (i.e. evaporation of the OxOrg ligand) in the mass spectrometer leads to a rather strong increase in the HSO_4^- signal. Since the CIMS is using a collision dissociation chamber (CDC) to detect only the core product ions and the mass range is limited to $\sim m/z$ 250, no mixed $HSO_4^- \cdot OxOrg$ clusters are visible in the mass spectrum (see Fig. 5). The APi-TOF, however, fragments the ions less strongly pronounced and therefore the mixed $HSO_4^- \cdot OxOrg$ clusters are clearly detected. Taking a closer look at the sampling conditions of the CIMS reveals that for conditions without organics, a major part of the

bisulphate ions from the chamber, is probably being lost before reaching the ion drift tube due to diffusion or electrostatic forces. There are several possibilities for such effects to occur (see Fig. 6): (1) the entrance of the sampling probe, (2) the inner surface of the sampling line, (3) the section where the sampling line terminates and transitions into the CIMS drift tube and (4) the entrance to the vacuum chamber of the mass spectrometer (pinhole plate). Loss due to effects (3) and (4) are probably dominant for ions because electric fields separate the different regions of the CIMS inlet part (Kürten et al., 2011). Negatively charged ions in the sample gas experience a repulsing field when they enter the ion drift tube and ions with high mobility can very likely be precipitated efficiently at the end of the sampling line. This loss mechanism is likely less strongly pronounced when OxOrgs are bound to HSO_4^- and make the ion cluster less mobile. However, during binary and ternary (NH_3, DMA) experiments data from the APi-TOF show that HSO_4^- does not bind with DMA or NH_3 molecules (Schobesberger et al., 2013). Therefore, in presence of these gases there is no enhancement in the HSO_4^- detection efficiency with the CIMS.

5   Parameterisation of H_2SO_4 concentration during pinanediol experiments

From the discussion above it is clear that ions had an effect on the measured sulphuric acid concentrations during ternary ion-induced nucleation experiments involving pinanediol. Only during neutral runs, while the high voltage of the clearing field electrodes is enabled, the detected HSO_4^- ion signal can directly be used to determine the sulphuric acid concentration in the chamber. Any ion effect can be completely excluded as an additional source of HSO_4^- ions, since under these conditions small ions are swept from the chamber within less than 1 s. However, in order to derive the correct sulphuric acid concentration during the ion-induced nucleation experiments, one needs to be aware of ion effects and correct for them. Because not every ion-induced nucleation run was preceded by a neutral run with identical conditions, a parameterisation was derived, which can be applied to all ion-induced nucleation runs with pinanediol in

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order to derive a corrected sulphuric acid concentration. The parameterisation is only a simplification of the real sulphuric acid production process and it is not based on a physico-chemical modeled process. The chemistry behind the modeled processes is complicated and all affecting factors cannot be taken fully into account. For example, reactions in which SO_2 is oxidised into sulphuric acid in presence of UV radiation are known but the stabilized Criegee intermediates and the involved species like OH radicals interact also with several other compounds in the chamber, thus making it difficult to estimate how much sulphuric acid is actually formed when OH is not directly measured. The parameterization provides an estimate of the net effect of these sinks and sources acting in the CLOUD chamber. The results of the parameterisation indicate that the derived $[H_2SO_4]$ is able to represent the "true" sulphuric acid concentration adequately. For the parameterisation of the sulphuric acid a nonlinear regression analysis was used in this study in order to find a predictive model for the sulphuric acid concentration. Figure 7 shows that the predictive ability of the derived $[H_2SO_4]$ in an ion-free environment is good (red points). The developed parameterisation includes a combination of measured O_3, SO_2, relative humidity (RH), UV intensity, dimethylamine (DMA) and pinanediol (PD) mixing ratios. In more details, the parameterization relies on the following formula:

$$[H_2SO_4]_{calc,i} = Bg_i + \left(a_0 + a_1 \cdot UV_i + a_2 \cdot UV_i^2 + a_3 \cdot UV_i^3\right)$$
$$\cdot \left(k \cdot RH_i^b \cdot SO_{2,i}^c \cdot O_{3,i}^d + g \cdot PD_i^j + m \cdot DMA_i^l\right)$$

Here, the index i is representing an averaged value for one experimental run denoting each of the parameters, UV represents the aperture of the UV light system in % and RH the relative humidity in % (temperature was constant at 278 K). As for the gases used, SO_2 is the sulphur dioxide mixing ratio in ppbv, O_3 the ozone mixing ratio in ppbv, PD the pinanediol mixing ratio in pptv, DMA the dimethyalmine mixing ratio in pptv and Bg the background concentration of sulfuric acid just before an experimental run. Fitting the equation to the experimental data with the software IGOR yields the coefficients

shown in Table 1 (coefficient values ± 95 % confidence interval). From the comparison between parameterised and experimentally determined H_2SO_4 concentrations for the neutral runs it is shown that the data are in good agreement (R^2 = 0.963) (Fig. 6), which indicates that the parameterisation with a standard error of ±6.3 × 10⁵ cm⁻³ can be applied also to the GCR and charged beam experimental runs when no information on the [H_2SO_4] under neutral conditions is available. In order to confirm the good agreement between the parameterised and experimental data, in Fig. 8 the experimental neutral runs are displayed along with their equivalent GCR (galactic cosmic) and pion beam experimental runs that followed in sequence. The parameterised sulphuric acid concentration was of advantage not only for the current study but also for further analysis of nucleation studies from the CLOUD experiments (Riccobono et al., 2014).

6 Atmospheric implications

A question related to the discussed observations is to what degree atmospheric measurements could be affected by this phenomenon. As a consequence of our observations, we developed an ion precipitator which was installed inside of a new ambient sampling line (total length 1 m and flow rate 1800 L min⁻¹) and was located just before the entrance to the ion source. The ion precipitator uses a high voltage in the range of 2 kV and an applied grounding located opposite to the high voltage resulting in an electrostatic field which effectively removes ions from the ambient sample flow. This adjustment in the CIMS sampling line was developed in order to investigate the effect of ions on atmospheric measurements of gaseous sulphuric acid and for future CLOUD experiments to avoid the additional signal of HSO_4^- ions coming from the chamber.

During August and September 2011, the CIMS instrument participated in the PA-RADE campaign, which took place at the Kleiner Feldberg Taunus Observatory near Frankfurt, Germany. Figure 8 shows the measurement of sulphuric acid during daytime. In the lower part of the graph the sulphuric acid concentration is displayed along with the ion precipitator setting. The ion precipitator is set to be active every 15 min

in order to investigate if an effect from ambient ions can be detected. The performed measurements do not indicate a significant influence of ion effect, and we conclude the contribution of the atmospheric HSO_4^- ions is very small. Turning off the corona ion source allows estimating the maximum contribution due to ambient ions (lower panel of Fig. 9). If the ion precipitator is enabled all bisulphate ions are effectively eliminated ($0\,counts\,s^{-1}$). In contrast, for the case of having both the corona source and the ion precipitator switched off, the slight increase in the bisulphate ion signal (~ 4 to $5\,counts\,s^{-1}$) is noticeably observed relatively to the previous case. Using this measured HSO_4^- ion count rate together with the typical primary ion count rate one can translate the effect of the ambient ions to be equivalent to several $10^4\,molecule\,cm^{-3}$ during normal operation. This is typically smaller than the CIMS noise level.

During the entire PARADE campaign, the GCR ion effect was negligible for the CIMS H_2SO_4 concentration measurements. Nevertheless, since the exact nature of the bisulphate transmission enhancing ligand that is leading to the enhanced ion detection is not identified yet, for other environments, sampling conditions as well as ion source geometries and the applied electric fields, it cannot be ruled out that atmospheric measurements or chamber experiments are affected to some extent.

7 Conclusions

In this study the effect of ions on CIMS sulphuric acid concentration measurements in the presence of the organic vapour pinanediol (PD) and its oxidised products has been presented. We measured the sulphuric acid concentration during the CLOUD-04 campaign, in experiments studying nucleation from H_2SO_4-H_2O (binary) and H_2SO_4-H_2O-NH_3, H_2SO_4-H_2O-DMA, H_2SO_4-H_2O-DMA-PD or H_2SO_4-H_2O-PD (ternary) systems of vapours within the CLOUD chamber, where all parameters of the experiment were well controlled. In presence of pinanediol organic vapour and its oxidised products and while ions are introduced in the chamber, there is an amount of HSO_4^- produced within the chamber which is effectively detected leading to an overestimation of the H_2SO_4

monomer concentration by the CIMS measurement. We performed tests of the CIMS instrument in order to verify that we count more HSO_4^- ions in the presence of chamber ions. Moreover, data from the APi-TOF confirmed the enhanced detection efficiency of sulphuric acid ions, indicating a ligand that decreases the mobility of the bisulphate ion complex. As the HSO_4^- ions affect the CIMS H_2SO_4 measurement, we developed a parameterisation of the CIMS sulphuric acid measurements for the neutral case, when all ions are removed from the chamber within $< 1\,s$ and therefore no HSO_4^- is present in the chamber. Later on, the parameterisation was applied to the CIMS sulphuric acid measurements during GCR and pion beam-charged experimental runs. In this way, we corrected the CIMS sulfuric acid measurements for the ion effect. We also were interested in the atmospheric implications of this observation, so for this reason we performed atmospheric sulphuric acid measurements with the CIMS mass spectrometer which showed that for ground based ambient measurements the ion effect was negligible. Nevertheless, for future chamber experiments an ion precipitator should be applied in general in front of the CIMS for regular operation. Furthermore, more dedicated studies should be carried out to investigate the ion effect of complex bisulphate ions on the sulphuric acid CIMS measurements in presence of oxidised organics, focusing on the transmission efficiency of the bisulphate ions to the mass spectrometer.

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Table 1. Coefficients (±std. dev.) of parameters used in the H_2SO_4 parameterisation formula.

Parameter	Value
k	$2.3 \times 10^{-4} \pm 1.4 \times 10^{-6}$
a_0	51593 ± 1
a_1	12953 ± 1
a_2	-209.99 ± 0.001
a_3	$1.0934 \pm 1 \times 10^{-5}$
b	$2.0934 \pm 1 \times 10^{-5}$
c	0.82661 ± 0.127
d	0.56574 ± 0.0869
g	$-1.9897 \times 10^{-5} \pm 0.00025$
m	-0.747 ± 2.58
j	1.2766 ± 1.25
l	-0.087045 ± 1
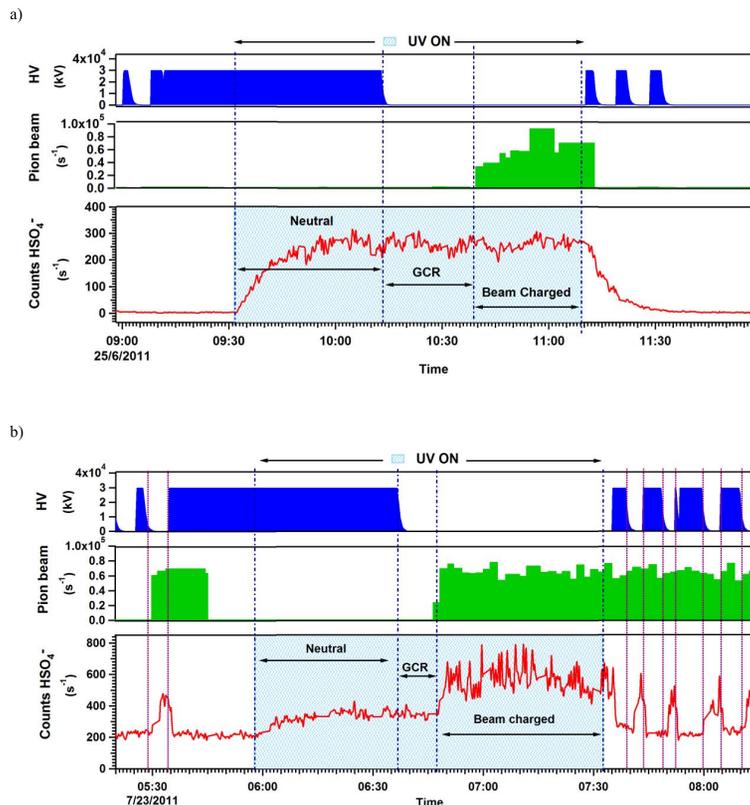
Figure 1. (a) Measurement of the CIMS bisulphate ion signal (HSO_4^-, red trace) during a typical binary nucleation experiment, displayed along with the variation of pion beam intensity (green) and clearing field high voltage (blue). **(b)** Measurement of the CIMS bisulphate ion signal for the ternary system (involving pinanediol) under the same beam condition as in **(a)** (red vertical lines show the ion effect under no-UV conditions). The CIMS signal is influenced by additional HSO_4^- ions from the chamber. This ion effect leads to an overestimation of the sulphuric acid concentration.
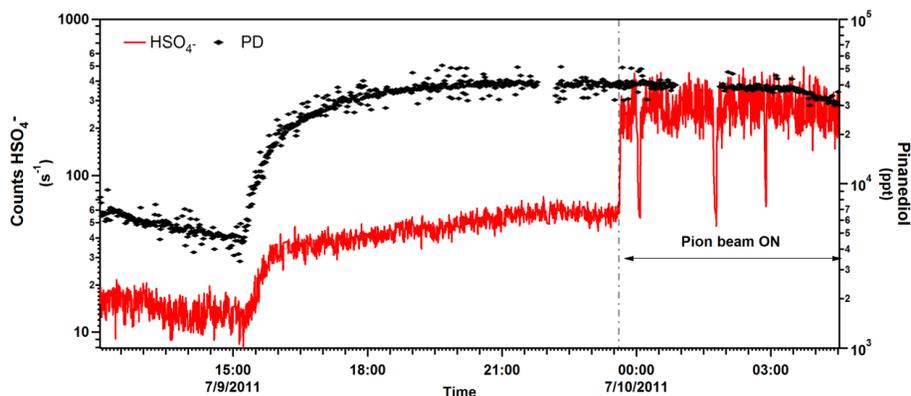
Figure 2. Enhancement of the HSO_4^- count rate in the presence of pinanediol (PD) during an experiment without the presence of UV light. The observed HSO_4^- enhancement in absence of UV light, indicates presence of a non-OH oxidant for SO_2. The change of the PD concentration (factor of ~ 8), leads to an enhancement (factor of ~ 5) of the sulphuric acid background concentration (HSO_4^- count rate). For the period shown the SO_2 (3 ppbv) and O_3 (50 ppbv) mixing ratios remained stable; the clearing field high voltage was turned off. The presence of ions, generated from the pion beam (23:40 UTC and later) increased the CIMS signal by another factor of 5, confirming the ion effect in the presence of PD.
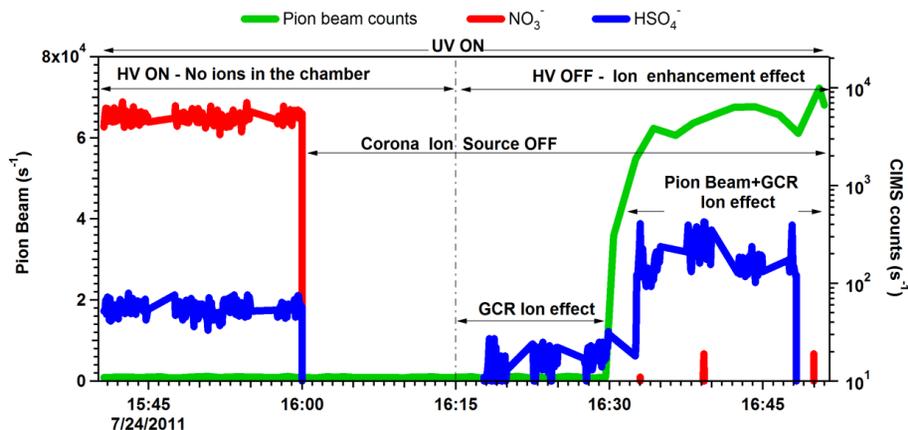
Figure 3. Example of the effect of the pion beam on the HSO_4^- count rate during a nucleation experiment. During the second part of this experiment (16:00 UTC and later) the CIMS corona ion source is switched off and only ions from the chamber can be detected.
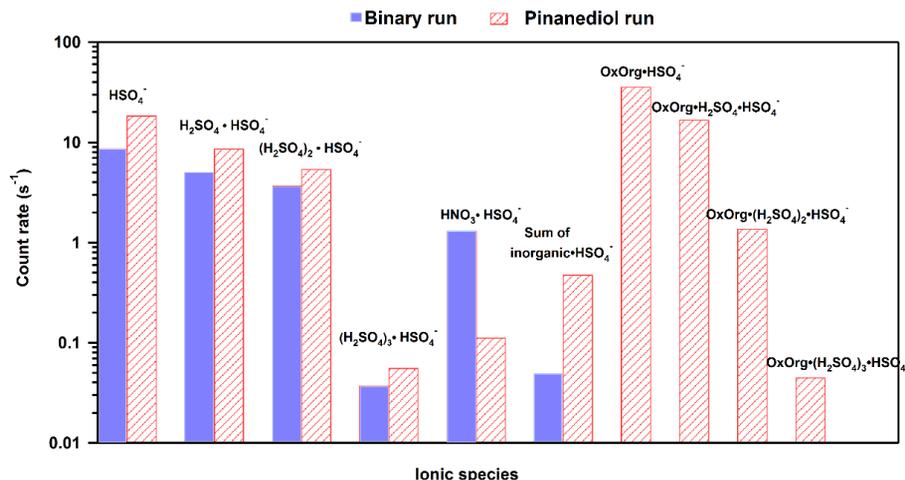
Figure 4. APi-TOF negative ion mass spectrum for a H_2SO_4-H_2O, binary (blue) and a pinanediol nucleation experiment (red) under almost identical sulphuric acid concentration (6.6×10^6 molecule cm^{-3}). The HSO_4^- signal is increased by a factor of ~ 2, which confirms that these ions are detected with a higher sensitivity in case PD is present. Clustering with OxOrg molecules and subsequent fragmentation can explain the elevated HSO_4^- count rates.

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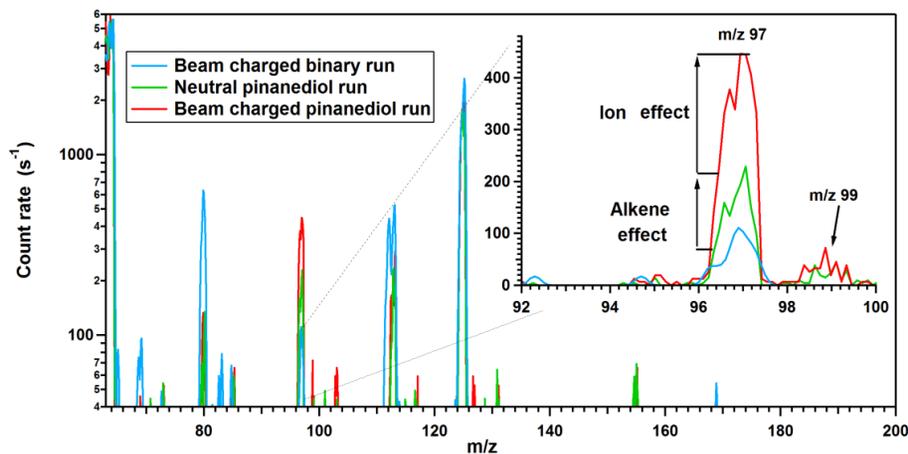
Figure 5. CIMS negative mass spectrum for a H_2SO_4-H_2O, binary experimental run (blue) and a pinanediol experimental run in the presence of ions (red). For the pinanediol experimental run, the HSO_4^- signal is enhanced by a factor of 2.25 from the equivalent neutral run (green).

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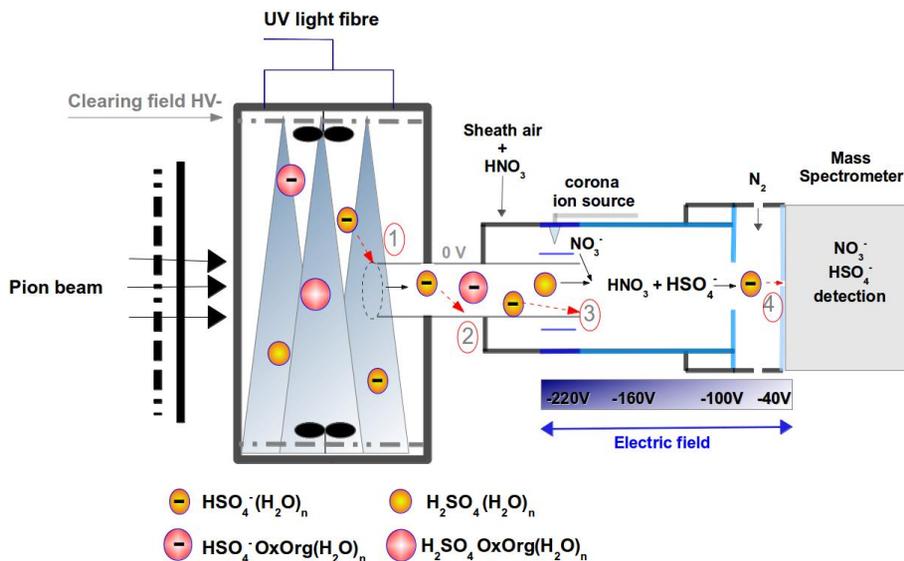
Figure 6. Schematic of the CLOUD chamber and the connected CIMS mass spectrometer. In a typical ion-induced binary (i.e. $H_2SO_4 + H_2O$) experiment (HV is switched off and the pion beam is on) not only H_2SO_4 neutral molecules are produced but also HSO_4^- ions, which are usually attached to water molecules (yellow) while for pinanediol runs the HSO_4^- ions are very likely bound to bigger OxOrg clusters (magenta). During binary experiments, the produced bisulphate ions are presumably efficiently lost before reaching the mass spectrometer. Losses can occur due to diffusion and/or electrostatic forces: (1) at the entrance of the sampling probe, (2) within the sampling line, (3) during the transfer into the CIMS ion drift region and (4) before entering into the mass spectrometer.
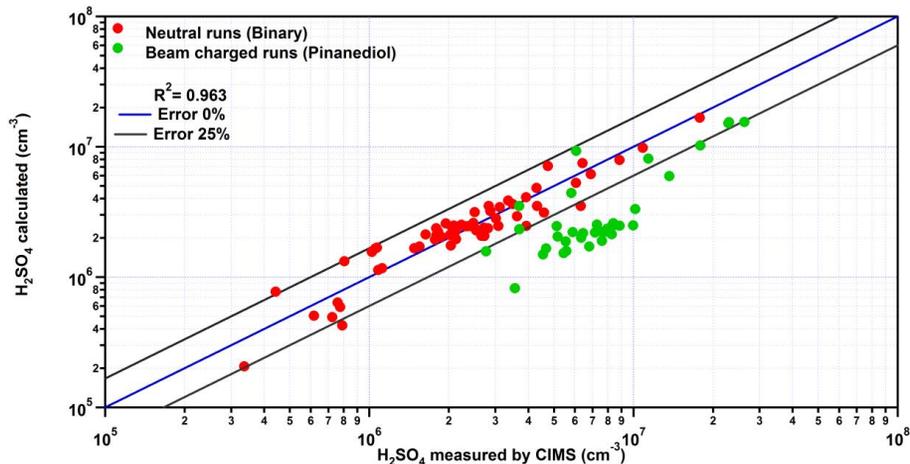
Figure 7. Calculated [H_2SO_4] vs. measured [H_2SO_4] for binary and ternary organic nucleation runs. The presence of ions during the pinanediol runs, leads to an excess of measured H_2SO_4. The deviation between the parameterized and the measured concentrations for the charged runs indicates the magnitude of the ion effect on the CIMS measurement.

Figure 8. For some GCR (galactic cosmic ray) and pion beam runs a neutral run was preceding where the conditions of the chamber were identical. This figure compares the parameterized $[H_2SO_4]$ for the GCR and beam runs to the value from the neutral stage. The good agreement indicates that the parameterization can be applied also to the GCR and beam runs when no information on the $[H_2SO_4]$ under neutral conditions is available.
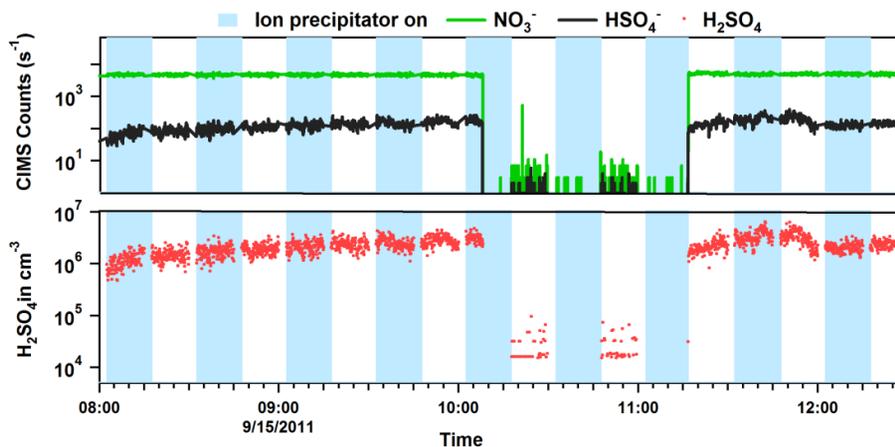
Figure 9. Daytime atmospheric [H_2SO_4] measurements along with the setting of the ion precipitator. In the upper graph, the count rates of the primary ions NO_3^- and the HSO_4^- product ions are displayed while the ion precipitator is enabled every 15 min. While the corona ion source is on, the signal of both NO_3^- and HSO_4^- is not noticeably influenced by the ion precipitator. When the CIMS corona ion source is off, the maximum contribution of the ambient HSO_4^- ions can be evaluated to be several 10^4 molecule cm^{-3}.