



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, $\text{C}_2\text{H}_7\text{N}$) or oxidised products of pinanediol (PD, $\text{C}_{10}\text{H}_{18}\text{O}_2$). 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

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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 (Cur-
 5 tius, 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
 10 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
 15 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
 20 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 $[\text{H}_2\text{SO}_4]$ 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).
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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

3 Results

3.1 Sulphuric acid measurements during binary nucleation experiments

The focus of the performed binary experiments ($\text{H}_2\text{SO}_4\text{-H}_2\text{O}$) 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 $\sim 300 \text{ s}^{-1}$). 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 ($\sim 1800 \text{ s}$), the H_2SO_4 equilibrates back to the initial background concentration that was measured before starting the nucleation run.

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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 $\text{C}_{10}\text{H}_x\text{O}_y$ (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 $\text{HSO}_4^- \cdot \text{OxOrg}$ ion complex leads to a reduction in the ion mobility thereby enhancing the probability that the $\text{HSO}_4^- \cdot \text{OxOrg}$ 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 $\text{HSO}_4^- \cdot \text{OxOrg}$ clusters are visible in the mass spectrum (see Fig. 5). The APi-TOF, however, fragments the ions less strongly pronounced and therefore the mixed $\text{HSO}_4^- \cdot \text{OxOrg}$ 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

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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 (\pm 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	$51\,593 \pm 1$
a_1	$12\,953 \pm 1$
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

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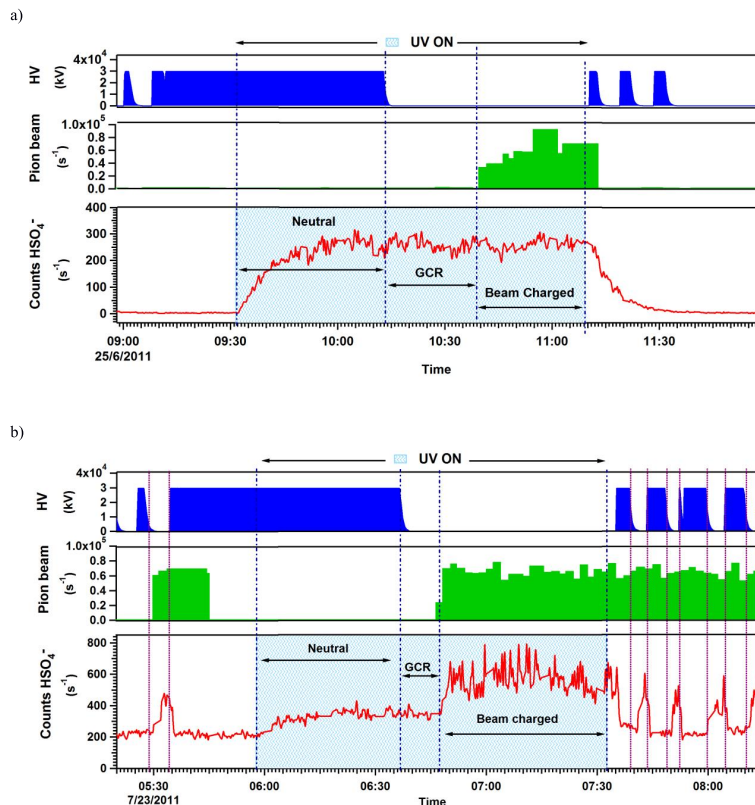


Figure 1. (a) Measurement of the CIMS bisulphate ion signal (HSO_4^- , red trace) during a typical binary nucleation experiment, displayed along with the variation of pion beam intensity (green) and clearing field high voltage (blue). (b) Measurement of the CIMS bisulphate ion signal for the ternary 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.

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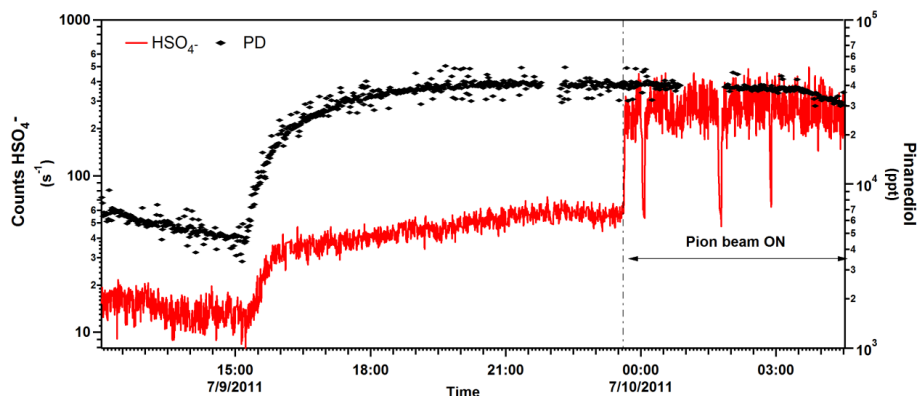


Figure 2. Enhancement of the HSO_4^- count rate in the presence of pinanediol (PD) during an experiment without the presence of UV light. The observed HSO_4^- enhancement in absence of UV light, indicates presence of a non-OH oxidant for SO_2 . The change of the PD concentration (factor of ~ 8), leads 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.

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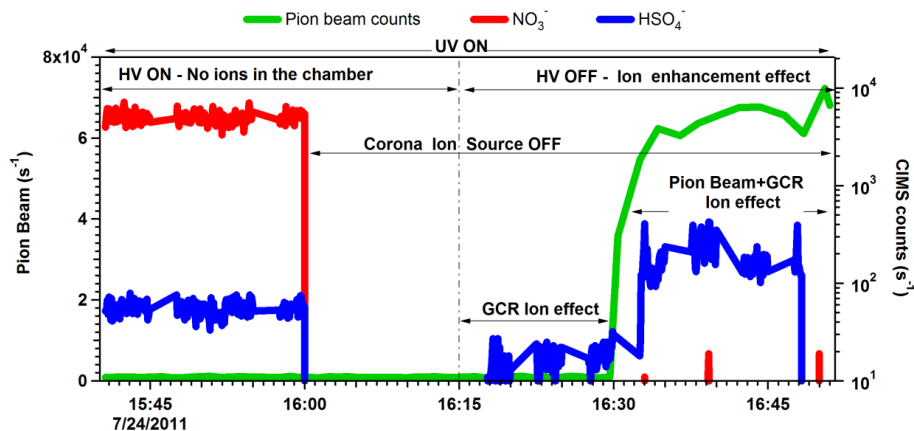


Figure 3. Example of the effect of the pion beam on the HSO_4^- count rate during a nucleation experiment. During the second part of this experiment (16:00 UTC and later) the CIMS corona ion source is switched off and only ions from the chamber can be detected.

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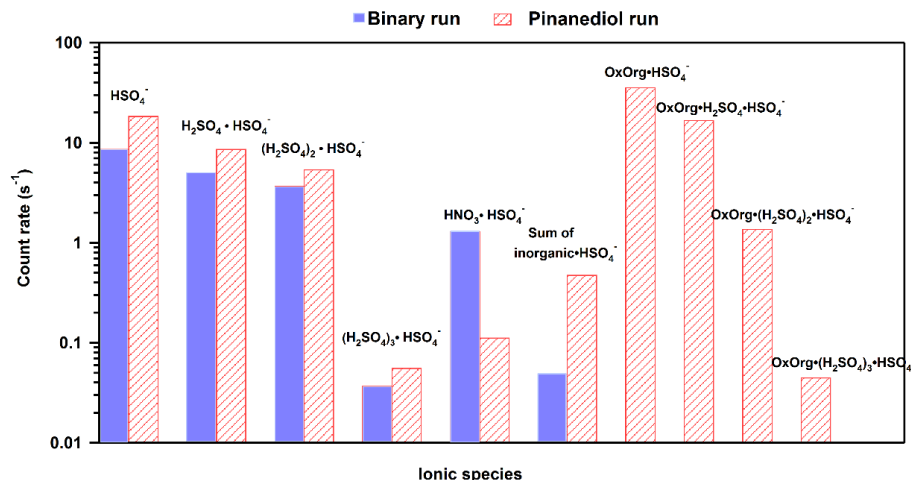


Figure 4. API-TOF negative ion mass spectrum for a H₂SO₄-H₂O, binary (blue) and a pinanediol nucleation experiment (red) under almost identical sulphuric acid concentration (6.6×10^6 molecule cm⁻³). The HSO₄⁻ signal is increased by a factor of ~ 2 , which confirms that these ions are detected with a higher sensitivity in case PD is present. Clustering with OxOrg molecules and subsequent fragmentation can explain the elevated HSO₄⁻ count rates.

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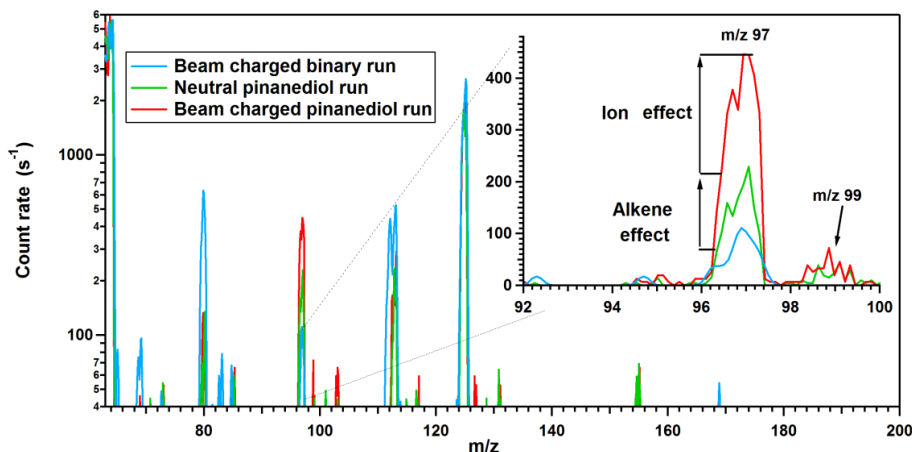


Figure 5. CIMS negative mass spectrum for a $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$, binary experimental run (blue) and a pinanediol experimental run in the presence of ions (red). For the pinanediol experimental run, the HSO_4^- signal is enhanced by a factor of 2.25 from the equivalent neutral run (green).

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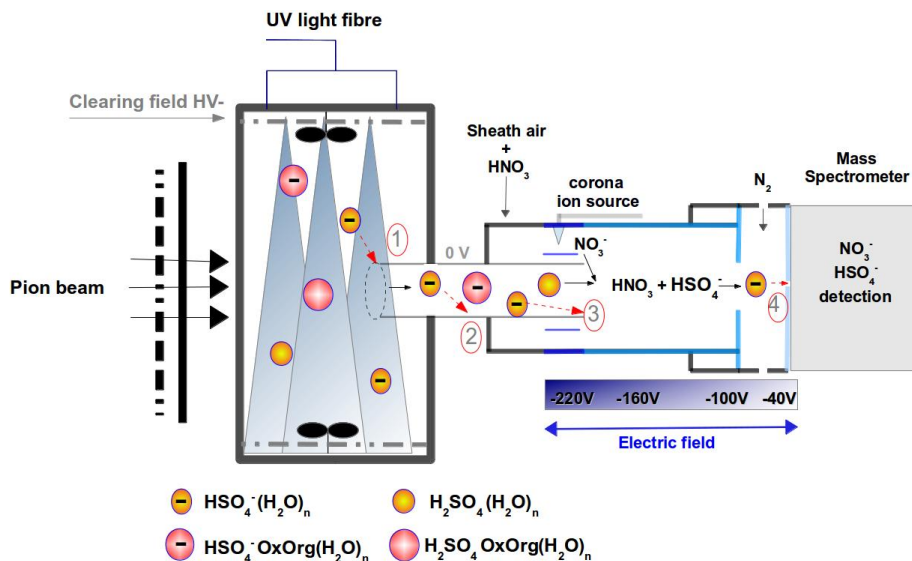


Figure 6. Schematic of the CLOUD chamber and the connected CIMS mass spectrometer. In a typical ion-induced binary (i.e. H₂SO₄ + H₂O) experiment (HV is switched off and the pion beam is on) not only H₂SO₄ neutral molecules are produced but also HSO₄⁻ ions, which are usually attached to water molecules (yellow) while for pinanediol runs the HSO₄⁻ 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.

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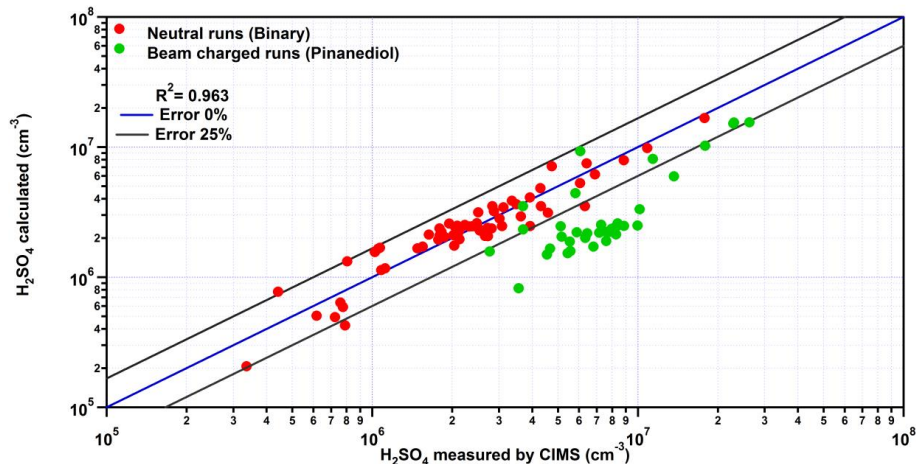


Figure 7. Calculated [H₂SO₄] vs. measured [H₂SO₄] for binary and ternary organic nucleation runs. The presence of ions during the pinanediol runs, leads to an excess of measured H₂SO₄. The deviation between the parameterized and the measured concentrations for the charged runs indicates the magnitude of the ion effect on the CIMS measurement.

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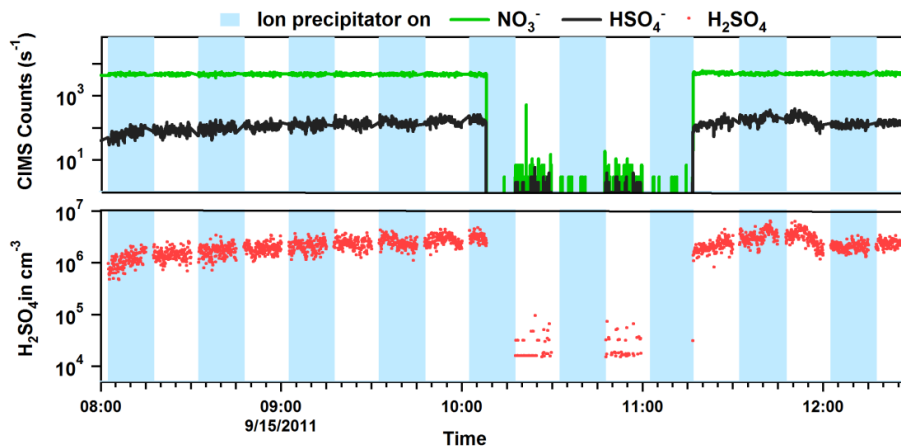


Figure 9. Daytime atmospheric $[\text{H}_2\text{SO}_4]$ measurements along with the setting of the ion precipitator. In the upper graph, the count rates of the primary ions NO_3^- and the HSO_4^- product ions are displayed while the ion precipitator is enabled every 15 min. While the corona ion source 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} .

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