

We would like to thank the reviewers for their constructive comments in order to make the paper more complete. We have revised and improved the manuscript by considering their points. Our replies to each comment are given below in blue font, following the reviewer's comment in black font. The text from the revised manuscript is set in black and red font (red for the applied changes in the text).

Anonymous Referee #2

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Rondo et al present a detailed analysis of the impact of ions generated in the CLOUD chamber on the measurement of H_2SO_4 via nitrate CIMS. The manuscript outlines the various mechanisms for HSO_4^- generation in the chamber. As one might expect the HSO_4^- production rate and transmission of these ions from the chamber to the various instruments is complicated by clustering reactions within the chamber and the subsequent transport and dissociation of these clusters. As such, it is a difficult to communicate this to the reader and at times the manuscript was challenging to follow. My primary suggestion is to add in reaction mechanisms for each of the processes such that the reader can follow the mechanisms for HSO_4^- production and when it is due to a real chemical process (e.g. H_2SO_4 formation from dark reactions involving alkene impurities).

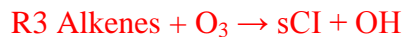
It appears that the effect of ions on ambient measurements is negligible, which narrows the scope of the manuscript as its implications are primarily for a small subset of the community. Nonetheless, I think it is within the scope of AMT, and could certainly have future implications for measurements made beyond CLOUD.

We thank the referee for his kind comments and useful suggestions for our manuscript. We also agree with the above suggestion to add the overall reaction mechanisms that lead to the production of sulphuric acid (''dark'' production via sCI) and bisulphate ions. Thus, we included the requested reactions in section 3.2 (page 6602, line 2), trying this way to give a clearer picture of the sulphuric acid and bisulphate ion production (as explained below).

In case of the ''dark production of sulphuric acid, we introduced the reaction schemes as given below (page 6602, line 2):

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). The following simplified scheme summarizes the possible reactions:

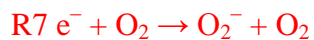


General Comments:

1) There was little discussion of the mechanism for primary HSO_4^- ion generation in the chamber from the pion beam. Is it thought that it originates from H_2SO_4 ? If so, what impact does this have on the experiment and what fraction of the sulfur in the chamber is in the form of HSO_4^- ?

We agree with referee#2 that there was little discussion on the exact mechanism of the bisulphate ion (HSO_4^-) generation in the chamber. Therefore, in order to clarify this point we introduced a new paragraph on page 6603, line 10 where we explain in more detail the production of bisulphate ions, which originate from the interaction of ions and neutral sulphuric acid molecules:

The formation of HSO_4^- ions within the chamber in the presence of GCRs or the pion beam is a result of ion–molecule reactions. The ions and free electrons created by the pion beam rapidly interact with the gas molecules within the chamber and convert to complex positive and negative cluster ions and therefore induce radical chemical reactions (Kirkby, 2007). A chain of reactions is initiated by the rapid attachment of a free electron to an oxygen molecule O_2 which possesses an appreciable electron affinity, leading to O_2^- as the most important primary negative ion as shown in reaction R7 below. When an O_2^- ion collides with a sulphuric acid molecule, it charges the molecule or cluster negatively by removing one proton (Almeida et al., 2013).



Reference to be added:

Kirkby, J.: Cosmic rays and climate, *Surveys in Geophysics*, 28, 333-375, 2007.

Nevertheless, as we previously replied also to the 5th comment of referee #1, the measured nucleation and growth process of particles was not influenced by the presence of the bisulphate ions in the chamber (Schobesberger et al. 2013; Riccobono et al., 2014). The applied pion beam produces about 80 ion pairs $\text{cm}^{-3} \text{sec}^{-1}$, which corresponds to a steady-state negative ion concentration of about $7 \times 10^3 \text{cm}^{-3}$ for the CLOUD chamber. So, in this way, we can assume that the bisulphate ion concentration, produced from the ions, would be in the range of $7 \times 10^3 \text{cm}^{-3}$.

2) While the parameterization appears to capture the variability in H_2SO_4 , I was surprised that an attempt at modeling the mechanism was not made. Specifically, it would be more valuable to track the production of HSO_4^- in the chamber and the subsequent cluster formation en route to the API-ToF and CIMS to build a model for the effect of ions on H_2SO_4 as opposed to attempting to parameterize H_2SO_4 explicitly. I am curious how well this parameterization will translate to future experiments, especially since some fraction of the H_2SO_4 production is acknowledged to be from impurities in the PD source. Also, will it then be required to develop and test parameterizations for all of the organics that are used beyond PD?

We acknowledge that, the ideal evaluation of the HSO_4^- effect on the sulphuric acid measurements in presence of oxidized products would be based on a detailed model where all the possible reactions are taken into account. However, developing a model that would take into account all reactions related to pinanediol, its oxidized products and the possible alkene impurities, would be very challenging since it requires developing detailed chemical reaction schemes that are still not fully understood. The explicit description of large C10 hydrocarbons is expected to be a complex mechanism with a very large number of chemical schemes. Therefore, we developed a practical tool (the parameterization) in order to estimate the sulphuric acid concentration for the ongoing ion-induced nucleation experiments. This straightforward quantification of sulphuric acid was a result of the awareness of the bisulphate ion effect which has an impact on the CIMS sulphuric acid measurements but not on the particle nucleation. So in this way, we decided to develop and include the ion precipitator in the sampling line in order to exclude any future bisulphate ion artifacts on the sulphuric acid measurements for oxidized organics experiments.

Specific Comments:

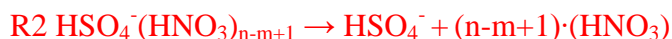
Section 2.2: I think it would be helpful to include the ion molecule reaction and subsequent dissociation reactions specifically here (e.g., does the reaction proceed directly through NO_3^- and H_2SO_4 or through $\text{NO}_3^-(\text{HNO}_3)$ clusters). This will help with clarification of the future effects of ions.

We agree with the above suggestion. The following ion molecule and subsequent dissociation reactions are introduced in page 6600, line 13 (section 2.2):

....The ion-molecule reactions between the reagent ions and the neutral compound to be detected and quantified occur in the flow reactor according to:



Subsequent to the formation of the bisulphate ion and nitric acid clusters within the CIMS flow reactor, the dissociation (R2) of the bisulphate cluster takes place in the collision dissociation chamber, resulting in the detection of HSO_4^- .



Page 6606, line 20: Why is DMA included in the parameterization? Was the parameterization applied more generally to other experiments?

The reason that DMA was used in the parameterization was discussed previously in the context of the 3rd comment by referee #1. As for the application of the parameterization on other experiments: no it was not used, since in later CLOUD experiments we used the additional ion precipitator in order to exclude any ion effect on sulphuric acid measurements.

Figure 9: The caption indicates that ambient HSO_4^- ions are on the order of $1\text{E}4$ molecules/ cm^3 . However, I thought the detection limit for such systems was closer to $1\text{E}5$?

Indeed, as stated in the manuscript, the detection limit of our system for neutral sulphuric acid measurements is 1×10^5 molecules/ cm^3 . What is illustrated at Figure 9 (for the time period 10:20-11:05), involves results of ion measurements (HSO_4^-) and not neutral sulphuric acid (H_2SO_4). In case of ion measurements, the ion sensitivity is much higher compared to the neutral measurements because no charging is needed, therefore the detection limit can be lower than 1×10^5 molecules/ cm^3 .