

## ***Interactive comment on “Effect of ions on the measurement of sulphuric acid in the CLOUD experiment at CERN” by L. Rondo et al.***

### **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<sub>2</sub>SO<sub>4</sub> via nitrate CIMS. The manuscript outlines the various mechanisms for HSO<sub>4</sub><sup>-</sup> generation in the chamber. As one might expect the HSO<sub>4</sub><sup>-</sup> 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<sub>4</sub><sup>-</sup> production and when it is due to a real chemical process (e.g. H<sub>2</sub>SO<sub>4</sub> formation from dark reactions involving alkene impurities).

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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.

#### General Comments:

1) There was little discussion of the mechanism for primary HSO<sub>4</sub><sup>-</sup> ion generation in the chamber from the pion beam. Is it thought that it originates from H<sub>2</sub>SO<sub>4</sub>? 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<sub>4</sub><sup>-</sup>?

2) While the parameterization appears to capture the variability in H<sub>2</sub>SO<sub>4</sub>, 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<sub>4</sub><sup>-</sup> 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<sub>2</sub>SO<sub>4</sub> as opposed to attempting to parameterize H<sub>2</sub>SO<sub>4</sub> explicitly. I am curious how well this parameterization will translate to future experiments, especially since some fraction of the H<sub>2</sub>SO<sub>4</sub> 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?

#### 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<sub>3</sub><sup>-</sup> and H<sub>2</sub>SO<sub>4</sub> or through NO<sub>3</sub>-(HNO<sub>3</sub>) clusters). This will help with clarification of the future effects of ions.

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

Figure 9: The caption indicates that ambient HSO<sub>4</sub><sup>-</sup> ions are on the order of 1E4

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molecules/cm<sup>3</sup>. However, I thought the detection limit for such systems was closer to 1E5?

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Interactive comment on Atmos. Meas. Tech. Discuss., 7, 6595, 2014.

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