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

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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 #1 Received and published: 8 July 2014

Overall, this is a very well written paper. It presents new insights into the CERN CLOUD chamber nucleation measurements revealing a positive ion adduct interference when measuring H₂SO₄ with CIMS in the presence of organics (pinanediol, PD).

C2896

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



As a consequence of these observations the authors developed an ion precipitator device and present relevant measurements confirming its efficiency at removing ions from the chamber and thereby suppressing the CIMS interference.

1. Although some measurements have been conducted in ambient air it seems quite preliminary to exclude ion effects in general. For example, early work by Eisele and coworkers has shown significant ion generation in the vicinity of power lines. Therefore, the authors should formulate their conclusions more cautiously in this respect.

We thank the referee for mentioning earlier work related to the study of ion generation in the vicinity of power lines by Eisele F.L. (1989). In order to improve our statement on the atmospheric ion effect we introduced a few sentences including the findings from previous studies. Page 6608, line 1: ...performed measurements do not indicate a significant influence of ion effect, and we conclude that during the PARADE measurements the contribution of the atmospheric HSO₄⁻ ions is very small.

Page 6608, line 13: Nevertheless, earlier studies showed e.g. that significant ion production can occur in the vicinity of high-voltage power lines (Eisele F.L., 1989a, b; Matthews et al., 2010). Therefore, in other environments with a strong local source of ions it is not clear whether CIMS measurements could potentially be affected more strongly. Still, during the entire PARADE campaign, the GCR ion effect was negligible for the CIMS H₂SO₄ concentration measurements. Hence, 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 sulphuric acid atmospheric measurements or chamber experiments are affected to some extent.

Added reference: Eisele, F.L.: Natural and atmospheric negative ions in the troposphere, *J. Geophys. Res.*, 94, 2183-2196, 1989a.

Eisele, F.L.: Natural and transmission line produced positive ions, *J. Geophys. Res.*,

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94, 6309-6318, 1989b.

Matthews, J. C., Ward, J. P., Keitch, P. A. and Henshaw, D. L.: Corona ion induced atmospheric potential gradient perturbations near high voltage power lines, *Atmos. Environ.*, 44, 5093–5100, doi:10.1016/j., 2010.

2. Did the authors vary the CDC voltage to break up the ligand (HSO_4^-) clusters?

No, in fact we did not change the settings of the CDC voltages. The performed CDC voltage settings that was applied during the CLOUD experiment, was set to break up the sampled ligands. Thus, the bisulphate ion HSO_4^- that was originally attached to the OxOrg cluster enhanced the signal of the sampled H_2SO_4 . One other possibility would be to turn off the CDC voltage so the CIMS could potentially detect the OxOrg- HSO_4^- ion as well but in this case we would be limited by the mass range which has a maximum of ~ 250 amu in our instrument.

3. Why is [DMA] part of the parameter equation, as it does not cluster with HSO_4^- ?

The reason that DMA is used in the sulphuric acid parameterization equation, is that we have to consider any further chemistry reactions of DMA that take place in the chamber which can influence the sulphuric acid concentration. Note that, DMA is thought to be an additional source of H_2SO_4 , through the additional OH production via DMA and O₃ reaction, with a reaction rate of $k_{\text{O}_3} = 1.67 \times 10^{-18} \text{ cm}^3/\text{sec}$ at 298 K (Tuazon et al., 1994). In addition, there is also DMA reaction with OH that takes place with a reaction rate of $k_{\text{OH}} = 6.54 \times 10^{-11} \text{ cm}^3/\text{sec}$ at 298 K (Atkinson et al., 1978). Nevertheless, due to the fact that DMA concentrations were really low (~ 10 pptv) its effect to the sulphuric acid parameterization was considered low (DMA parameter taken from Table 1, I = -0, 08). We included the following sentence in order to clarify why DMA was used in the parameterization, page 6606, line 9:

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

Full Screen / Esc

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Interactive Discussion

Discussion Paper



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. In addition, DMA chemistry should also be considered since it reacts not only with O₃, producing OH (Tuazon et al., 1994) but also consumes OH radicals (Atkinson et al., 1978). The parameterization provides an estimate of the net effect of these sinks and sources acting in the CLOUD chamber.

Added reference: Tuazon, E. C., Atkinson, R., Aschmann, S. M., Arey, J.: Kinetics and products of the gas-phase reactions of O₃ with amines and related compounds, Res. Chem. Intermed., 20, 303-20, 1994.

Atkinson, R., Perry, R. A., Pitts, J. N., Jr.: Rate constants for the reactions of the hydroxyl radical with dimethylamine, trimethylamine, and ethylamine over the temperature range 298-426 K, J. Chem. Phys., 68, 1850-3, 1978.

4. Explain k in Table 1 and include a reference.

We would like to clarify that the parameter k as well as the rest of the used parameters in Table 1 are used in the parameterization formula as a best estimate, which can fit the observed sulphuric acid concentrations and not as published constant rate coefficient. For this reason, there is no reference attributed to parameter k .

The following are minor comments:

p. 6598, line 25: Could the sweep (cleaning) 60 kV field in the chamber affect the (non-ionic) nucleation process, e.g., in case of oxidized polar molecules?

There is experimental evidence from the latest nucleation studies of sulphuric acid and oxidized products of pinanediol (CLOUD-04 campaign) (Schobesberger et al. 2013; Riccobono et al., 2014), where nucleation rates for both ion induced and neutral conditions does not show significant difference. In particular, there is proof from the combined information of a PSM (particle size magnifier), an APi-TOF (Atmospheric Pressure interface-Time Of Flight) and a NAIS (neutral cluster and air ion spectrometer)

which indicate a similarity of the nucleation process in presence and absence of the electric field (60 kV).

With OH + SO₂ and OH + PD reactions occurring concurrently, how might this affect H₂SO₄/HSO₄⁻ production?

Although the main reaction of OH, for the binary case, is considered to be with SO₂ for the production of sulphuric acid, this was not the case when pinanediol was introduced into the CLOUD chamber. Since pinanediol does not react with O₃, its main reaction would be with the available OH. For a constant OH production, given the differences in the reaction rate coefficients, $k_{\text{SO}_2\text{-OH}} < k_{\text{PD-OH}}$ ($k_{\text{SO}_2\text{-OH}} = 9 \times 10^{-13}$ cm³/sec and $k_{\text{PD-OH}} = 3.9 \times 10^{-11}$ cm³/sec, Riccobono et al., 2014), the produced sulphuric acid from OH+SO₂ reaction would be lower compared to that of the binary case. Nevertheless, the bisulphate ion production is not affected significantly since the negative charge will be always associated with the strongest acid (in our case sulphuric acid). Since the sulphuric acid concentration ($\sim 10^6$ molecules/cm³) is much higher than the ion concentration (pion beam produces $\sim 10^3$ cm⁻³ ions/cm³) the produced HSO₄⁻ will also result to the range of the $\sim 10^3$ cm⁻³. However, the ratio between H₂SO₄ and HSO₄⁻ is probably lower for the pinanediol case because PD consumes part of the available OH and therefore leads to a lower sulphuric acid production.

p. 6599, line 24: Quote the detection limit together with the relevant signal integration time (30 sec?).

We included the integration time within the main text, page 6599, line 24: A negative-ion detection CIMS instrument was used to measure the concentration of gaseous H₂SO₄ with a detection limit of $\sim 1 \times 10^5$ molecule cm⁻³ and 30 seconds integration time.

p. 6600, line 20: Describe how diffusion-controlled losses were estimated and include uncertainty. We modified the sentence as below (page 6600, line 20):

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



For diffusion controlled wall losses within the CIMS sampling line the H₂SO₄ diffusion coefficient ($D = 0.078 \pm 0.0546 \text{ cm}^2/\text{s}$ for $T = 278 \text{ K}$ and $\text{RH} = 38\%$, see Hanson and Eisele, 2000), the sample flow rate ($Q = 7.5 \pm 0.1 \text{ slpm}$) and the length of the sampling line ($L = 0.9 \text{ m}$) were taken into account. The transmission efficiency was calculated as $44\% \pm 0.12\%$ for laminar flow in a straight tube using the empirical equations given in Baron and Willeke (2001).

Added reference:

Hanson, D. R., Eisele, F. L.: Diffusion of H₂SO₄ in Humidified Nitrogen: Hydrated H₂SO₄, J. Phys. Chem. A, 104, 1715–1719, 2000.

Baron & Willeke, Aerosol Measurement: Principles, Techniques, and Applications, John Wiley and Sons, 2nd edition, page 580, 2001

p. 6600, line 25: “provided SO₂” = provided from the Cloud chamber?

The calibration is a stand-alone system which uses its own SO₂ gas bottle. In order to clarify this we modified the sentence slightly (page 6600, line 25): . . .The produced OH radicals react with SO₂ from a gas bottle in the presence of O₂ and water vapor resulting in known sulphuric acid concentrations.

p. 6602, line 22: Can you really assume that the “dark” production of H₂SO₄ and the additional ion-induced production are completely separate processes, i.e., not mutually influenced? Criegee radicals are breakdown products. Could their concentration be enhanced by ions?

In our study, we state that for the CLOUD-04 experiments in the presence of pinanediol and its oxidized products we observed the enhancement of the sulphuric acid concentration due to the “dark” production via sCI oxidation as well as the ion effect on the CIMS measurements separately. The expectation of the possibility that these two effects would mutually influence the sulphuric acid production in total would not be consistent with the findings of the study by Schobesberger et al. (2013), as we already

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mentioned in the previous question (1st minor comment). So in this way, the possibility of ion enhancement on the Criegees breakdowns can be ruled out since there was not observed a significant difference between neutral and ion-induced nucleation measurements.

p. 6604, line 2: What “other inorganic” compounds? Impurities?

Actually here the “other inorganic” compounds are not referred to impurities but to water molecules coupled to sulphuric acid/bisulphate clusters ((H₂O)_n·HSO₄⁻ and (H₂O)_n·H₂SO₄·HSO₄⁻) while for the PD case most of “other inorganic” clusters were H₂S₂O₇·HSO₄⁻. We added this information to the main text as below (page 6604, line 2): ..the negative ion spectrum is clearly dominated by sulfuric acid and other inorganic compounds, which include water molecules associated with sulphuric acid or bisulphate.

p. 6604, line 16: Quantify this statement. Transmission efficiency > 44% ? Has this been parameterized?

We calculated the transmission efficiency due to diffusion losses of OxOrg·HSO₄⁻ (59%) and OxOrg·(H₂SO₄)₃·HSO₄⁻ (69%) for laminar flow along the sampling line of the APi-TOF (Baron & Willeke, 2001). Similarly, for the CIMS sampling line the transmission efficiency for OxOrg·HSO₄⁻ is 64% and 72% for OxOrg·(H₂SO₄)₃·HSO₄⁻, respectively. We will include the following information in the manuscript (page 6604, line 16):

These observations suggest that the presence of OxOrg can enhance the transmission efficiency of the HSO₄⁻ core ions through the sampling line of the APi-TOF and the CIMS. In particular, the sampling line transmission efficiency due to diffusional losses (Baron & Willeke, 2001) varies from 59 to 69% for OxOrg·HSO₄⁻ and OxOrg·(H₂SO₄)₃·HSO₄⁻, respectively, while the transmission efficiencies for the CIMS sampling line are 64% and 72% for the same ions.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Please also note the supplement to this comment:
<http://www.atmos-meas-tech-discuss.net/7/C2896/2014/amtd-7-C2896-2014-supplement.pdf>

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

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