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Atmospheric
Chemistry
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Discussions

# *Interactive comment on* “Homogenous nucleation of sulfuric acid and water at atmospherically relevant conditions” *by* D. Brus et al.

**D. Brus et al.**

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We thank to reviewers for constructive review of our manuscript, we do also highly appreciate reviewers’ suggestions to improve our manuscript.

Report of reviewer #1

1) I guess, this is the first experimental work describing temperature-dependent measurements of J using a high efficient particle counter with a cut-off-size of 1.5 nm. This fact should be highlighted also in the Abstract. Moreover, a discussion is missing regarding the T-dependence of sulphuric acid/water nucleation generally and a comparison with other literature data published so far.

RE: We emphasized the uniqueness of first temperature dependent measurements with high efficient particle counter in the abstract. The following paragraph was added: “To the best of our knowledge, this is the first experimental work providing temperature dependent nucleation rate measurements using a high efficiency particle counter with a cut-off-size of 1.5 nm together with direct measurements of gas phase sulfuric acid concentration.” The following paragraph was added to section 3.2.Temperature dependency: “The temperature dependency was already studied earlier by Wyslouzil et al. (1991) in temperature range of 20 – 30 °C. These measurements are provided in the plot of nucleation rate vs. relative acidity, which complicates the direct comparison to our dataset, however their data indicate that a 5 °C decrease in nucleation temperature would lead to a decrease in nucleation rate of two to four orders in magnitude.“ We did not find necessary to provide comparison to other previous literature data since the detailed comparison is already given in our previous publication Brus et al. 2010 (fig. 16 in there), and the initial concentrations of sulfuric acid (prepared solutions) used in our current manuscript are the same, i.e. the overall picture will not change. Following sentence was added to section 3.4. Comparison to our previous data: ”The detailed comparison to other literature data concerning sulfuric acid – water system is given in our previous publication Brus et al. (2010), however the discrepancy was found in the results of this study compared to data published earlier (Brus et al., 2010).”

2) It should be stated what kind of changes were done to improve the 50% cut-off-size of TSI3025 from normally 3 nm to 2.28 nm. In tables and figure captions there should be a note pointing to the improved counting efficiency

RE: The following paragraph was added to experimental part: “The following modification to UCPC TSI 3025A has been done to obtain a d50 cut-off of 2.28 nm. The saturator temperature was increased from a nominal 37 °C up to 38 °C, the condenser temperature was decreased from a nominal 10 °C down to 8 °C. At these new temperatures no homogeneous nucleation was observed inside the counter.”

3) Nucleation rates observed by means of PSM are higher than those from TSI3025 measurements. This fact is more pronounced for relatively low sulphuric acid con-

centrations and is qualitatively in line with measurements given by Sipilä et al., Science, 2010. Can the observed differences of both counters be explained by particle growth from 1.5 nm to 2.28 nm governed by sulphuric acid or are additional substances needed?

RE: At the moment we do not have any systematic growth rate measurements available. There is probably no straightforward answer to this problem, for example just to pick the right concentration of sulfuric acid itself. If we consider initial sulfuric acid concentration determined with CIMS + WLF in the flow tube then additional vapor(s) is probably needed to explain higher growth rate. On the other hand if we use for growth rate estimation initial sulfuric acid concentration obtained from total sulfate (Ion Chromatography) analysis then no presence of additional vapor is needed at all, e.g. Fluent + Fine Particle Model simulations made for FMI flow tube by Hermann et al. (2010).

4) For ammonia an upper limit of 0.5 ppb is stated. Can the author give a rough estimated regarding the background concentrations of amines in the carrier gas?

RE: The limit of 0.5 ppb of ammonia in our system would be reached if the lower detection limit of the Ion Chromatography (0.02 mg/l) is passed. Such situation never happened; we have always got only blanks (zeros). The paragraph will be restated to make the statement unambiguous. Unfortunately at the moment we do not have any direct analytical method to measure concentrations around levels of tens ppt for ammonia, neither for amines.

5) The given slope from PSM measurements at 25C and RH=57% in table 3 is 1.7. In table 4 a slope of 1.2 is given for 25C and RH ca.50%. More information is needed with respect to the precision/repeatability of the experiments. The error limits of deduced parameters (slopes, k-values) are helpful. What are the consequences for the trends measured by varying RH or temperature?

RE: In our opinion the R-squared are sufficient for the purpose of linear slope fit. Undoubtedly the reported values of slopes suffer from uncertainty. In this case the simple statistics might not shed the light on this topic. For example the lower sulfuric acid concentration the lower particle size and particle counting efficiency, in case when we measure particle number as a function of sulfuric acid concentration with CPC TSI 3025A the statistics might be perfect but the slope will be too steep due to undercounting of small particles.

6) Sulphuric acid measured by CI-MS accounts for only 20% (RH=50%) or 1% (RH=16%) of the theoretical value expected from sulphate balance. Insufficient CIMS detection efficiency of bound sulphuric acid is discussed. In the former paper of the FMI experiment, Brus et al., ACP, 2010, there were also shown a strong disagreements between measured sulphuric acid (bubbler with subsequent IC analysis instead of CI-MS!) and the sulphate balance. Here, a more detailed discussion of the experimental findings with both approaches is necessarily needed. Nevertheless, the proposed “shielding effects” are very interesting also with respect to atmospheric sulphuric acid measurements!

RE: We updated the discussion in section 3.4 Comparison to our previous data. We cannot agree on “strong disagreements” between measured sulphuric acid (bubbler with subsequent IC analysis instead of CI-MS) and the sulphate balance in our previous publication (Brus et al., ACP, 2010), according to our experience the opposite is true. Please see Brus et al., ACP, 2010 and Figure 13 in there, which shows the ratios of H2SO4 concentration determined by Ion Chromatography and initial H2SO4 concentration calculated by Mass Balance as a function of the initial H2SO4 concentration calculated by Mass Balance. The Mass Balance calculation provides a concentration of sulfuric acid at the beginning of the nucleation chamber and does not include any losses connected to diffusion to walls at any part (i.e. at the furnace and the mixing unit). Included figure 1 is plotted in the same coordinates as figure 5 in current manuscript to have direct comparison. The lines in included figure 1 are the estimated wall losses for 10 % RH are about 54 %, for 30% RH about 27 %, and for 50 % RH about 28% under assumption of first order and H2SO4 concentration independent losses. The overall error of the method of sulfuric acid concentration determination was estimated to be ±17 %, including the inherent error of Ion Chromatography analysis. The wall loss factor (WLF) of sulfuric acid is there directly derived from WLF=[H2SO4]0/[H2SO4]t, where [H2SO4]0 is the initial concentration of sulfuric acid obtained from Mass Balance calculations, and [H2SO4]t is the concentration of sulfuric acid at residence time, t, in this case it is at 140 cm in the nucleation chamber. The scatter of data points in included figure 1 is relatively big but it is hard to talk about "strong disagreement" considering that y-avis data represent losses on 140 cm in the flow tube and x-axis no losses, the beginning of the flow tube.

7) There are some typos, e.g. notation of nitrate ions, etc RE: corrected.

REFERENCES:

Brus, D., Hyvarinen, A.-P., Viisanen, Y., Kulmala, M., and Lihavainen, H.: Homogeneous nucleation of sulfuric acid and water mixture: experimental setup and first results, Atmos. Chem. Phys., 10, 2631-2641, doi:10.5194/acp-10-2631-2010, 2010.

Herrmann, E., Brus, D., Hyvarinen, A.-P., Stratmann, F., Wilck, M., Lihavainen, H. and Kulmala, M.: A computational fluid dynamics approach to nucleation in the water-sulfuric acid –system, J. Phys. Chem. A, 114 (31), 8033–8042, 2010.

Wyslouzil B. E., Sienfeld J. H., Flagan R. C., and Okuyama K.: Binary nucleation in acid-water systems. II. Sulphuric acid-water and a comparison with methanesulphonic acid-water, J. Chem. Phys., 94, 6842-6850, 1991.

FIGURE CAPTION: Fig. 1. Total sulfate concentration obtained with bubblers and subsequent IC analysis (at 140 cm in flow tube) as a function initial total sulfate concentration obtained from Mass Balance calculations. Dotted (1:1) black line means no losses.

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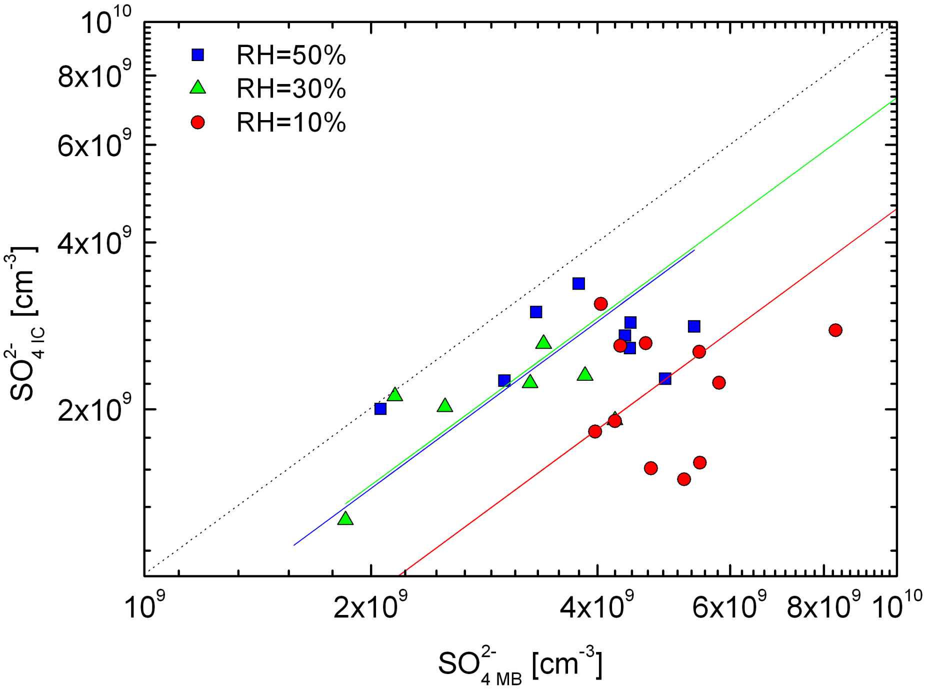
Interactive comment on Atmos. Chem. Phys. Discuss., 10, 25959, 2010.



$10^{10}$
$8x10^9$
$6x10^9$
$4x10^9$
$2x10^9$
$10^9$
$2x10^9$
$4x10^9$
$6x10^9$
$8x10^9$
$10^{10}$
■ RH=50%
▲ RH=30%
● RH=10%
$SO_{4\ IC}^{2-}$ [$cm^{-3}$]
$SO_{4\ MB}^{2-}$ [$cm^{-3}$]

**Fig. 1.**