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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Homogenous nucleation of sulfuric acid and water at atmospherically relevant conditions" *by* 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 the manuscript.

Report of reviewer #2

1. Experimental – this section should contain all relevant information on the measurements including more details of H2SO4 CIMS, the aerosol particle measurements by TSI CPC, and the loss of H2SO4 in the flow tube and sampling tube (these latter could be done in a separate section, but moved from the Results section as this paper aims at a presentation of nucleation results and the distribution of H2SO4 sets the experimental conditions).With respect to H2SO4-CIMS, a more thorough description is needed as

discrepancies show up and experimental issues related to this should be presented in the experimental. For example, no information about upper limits of measuring H2SO4 are given, depending on the CIMS system configuration, concentrations exceeding 109 molecules/cm3 might deplete the NO3- ion concentration in the ionisation zone of the CIMS and thus reduce the sensitivity. Furthermore, the principle of ionisation should be explained and it should be discussed which H2SO4 clusters can be ionised by NO3-. It should be clearly stated that dimers, trimers, etc. of H2SO4 are measured as one sulphuric acid molecule only. Furthermore, the rate constant for charging reactions with higher order acid clusters depend, according to Viggiano et al. (1982), on the reduced mass and the dipole momentum of the acid. As clusters are expected to arrange such that their dipole moments partly compensate each other, lower reaction rate constants and ionisation rates are expected. Accordingly, dimers and higher momentum acid clusters are not measured quantitatively, and estimates of dimer/monomer ratios etc. should be handled with great caution, e.g. ratios of monomer/dimers of 100 deduced from these observations are expected to be overestimated. Moreover, in usual operation, higher order acid clusters are decomposed in the collision dissociation chamber, and the experimental part needs to be accomplished by information on the method used to determine dimers. Finally, the use of the inlet line of 1 m should be described and characterized in the experimental part. Especially, care has to be taken to demonstrate that the flows in the CIMS and corresponding calibration factors are not affected by this inlet line.

RE: The experimental section was updated, we added information about the modifications made to TSI CPC 3025A and the H2SO4 loss part was moved from Results to Experimental section as suggested by reviewer. Furthermore the discussion on page 25970 was extended to reflect the latest progress in investigation of potential uncertainties in CIMS, the following paragraphs were added: "The discussion on the role of stabilizing compounds affecting the chemical ionization methods to determine sulfuric acid is currently ongoing (Kurtén et al. 2011). As these effects are potentially setup and instrument dependent and difficult to quantify, our concentration estimates have a larger uncertainty (factor of two) associated with them than presented earlier for the CIMS technique (30-35 %, Tanner and Eisele, 1995; Berresheim et al. 2000). Furthermore, the same calibration factor was used in converting the raw signal to monomer and dimer concentrations." and "In conclusion, we have no certain explanation for apparent loss. Also, it should be mentioned, that Sipilä et al. (2010) also observed an apparent additional loss of molecular sulfuric acid with high initial concentrations and longer residence times. That observation was explained by rapid conversion of concentrated sulfuric acid monomer to dimer and larger clusters, stabilized by proper, possibly basic compounds (Petäjä et al, 2011). The same process can take place also in our system even though it is difficult to perceive from the data." The maximum concentration of H2SO4 when nucleation rates were measured was 2e8 molec/ccm, so one order lower than mentioned depletion limit for NO3- ion. The WLF measurements were conducted at several, however relatively low concentrations, so the highest measured concentration (at 20 cm from beginning of flow tube) was about 3e8 molec/ccm. We agree with reviewer about the quality of dimer data. They are only qualitative; it is pointed out on p. 25964, l. 6 and also on p. 25969, l. 7. However the following sentence was added to part 2.1 CIMS: "Furthermore, our reported dimer signal comprises dimers formed both via neutral processes inside the flow tube and dimers formed by ion induced mechanism in the CIMS charger, for detailed discussion see Petäjä et al., (2011)." and also fit to dimer vs. monomer data was omitted.

2.a. The authors ascribe losses of H2SO4 in the flow tube (and the sample tube) mostly to wall losses, which appears questionable. A related point, the discrepancies between the different methods to determine H2SO4 remains largely unresolved, there is only a short and insufficient discussion of these issues on page 25970. Wall losses are presented which are according to Tables 1 and 2 in the range of factor 20 (combined loss in flow tube and sample tube CIMS). Such high loss rates principally bare the potential of high uncertainties in the H2SO4 concentrations, these uncertainties in the nucleation area need to be discussed. Furthermore, according to Brus et al. (2010), the observed losses relative to initial concentrations increase with increasing

concentration of H2SO4 (Figs. 12 and 13 in this reference). Such a dependency is not expected for a first order loss process to the wall surfaces.

RE: Unfortunately, we have to agree with reviewer that figures 12 and 13 in our previous publication Brus et al. (2010) are not the best ones; they might confuse the reader and lead to unexpected interpretation. We would like to provide the same data as in Brus et al (2010) but in different coordinates, see figure 1 A-C. There is a slight deviation at highest concentration of sulfuric acid, but this is probably only due to depletion of NaOH solution in the bubbler, so the bubbler could not trap any more sulfate.

2.b. On the other hand, it is clearly demonstrated that the H2SO4 mass in the observed particles is at most 3% of the initial gaseous H2SO4 (p. 25970). But the authors should consider and discuss the distribution of clusters containing H2SO4 and estimate the number of sulphuric acid molecules in all these clusters which are below the detection threshold of the particle counters. This sulphuric acid does not show up quantitatively in the CIMS measurements either (see above). Thus, the open part of the H2SO4 balance is expected to be in clusters and some small part also adsorbed to the walls. Furthermore, the discrepancies between CIMS, bubbler-IC quantification and mass balance of H2SO4 should be further addressed. To better separate effects, experimental set-ups with smaller H2SO4 concentrations could help to better understand the nature of the loss process, e.g. linear and non-linear processes. In comparing the CIMS and bubbler approach, it should also be thought of possible artefacts in the bubbler. As no information on the bubbler is provided, it is hard to estimate but the potential of a diffusion limitation of higher clusters to reach the interface in the bubbles should be considered which could underestimate the contribution of larger clusters. Finally, the mass balance approach can not address potential losses at the Teflon filter at the end of the furnace, and it does not differ between single acid molecules and clusters. Though some of these arguments remain speculative, they might be helpful in resolving or better discussing the discrepancies between the three methods for assessing the sulphuric acid concentration in these experiments. If the reason for the discrepancy is not resolved, the authors should think of new experiments in the flow tube to better understand what is going on. At least, the uncertainty of H2SO4 concentrations used in this paper should include the range of discrepancy between the different methods.

RE: First, we would like to make clear that in current manuscript the total sulfate was not estimated via bubbler method. The bubbler method was used only in Brus et al. (2010), and this is from simple reason, in the past time (around year 2005) we had no access to such sophisticated methods like CIMS. However Ion Chromatography was used in current manuscript to determine the total sulfate concentration from prepared liquid samples of H2SO4 and water, i.e. the concentration of weak sulfuric acid solution injected into system. These data, in principle, are not expected to suffer from any losses to walls, particles, clusters, and so on. Second, to answer reviewer's question concerning bubblers. The bubblers (usually pair) are connected to flow tube with short lines ($\sim$10 cm, 6 mm O.D.), the flow rate is $\sim$4 l/min through each. After the samples from bubblers are taken the bubblers are rinsed with pure water and this is added to total volume of the sample ($\sim$100 ml). If there are any diffusion losses to walls in the bubblers then they are minimal, and compared to CIMS, they are negligible. The statement of minimal losses is valid also to diffusion in the bubble itself. Third, "…clusters containing H2SO4 and estimate the number of sulphuric acid molecules in all these clusters which are below the detection threshold of the particle counters. This sulphuric acid does not show up quantitatively in the CIMS measurements either,…" Yes, this is our goal, but currently the theoretical backgrounds for such estimates are built (Kurtén et al. 2011), the actual experiments where we could quantify the estimates are not trivial but ongoing, data presented in current manuscript should be taken as first approximation to this problem.

3. The nucleation rates are calculated for a certain H2SO4 concentration. It is not made clear to the reader, how one can speak of a specific H2SO4 concentration in a flow tube when concentrations change by factors of 5 (table 1).

RE: Yes, the nucleation rates are provided for estimated initial concentrations in the flow

tube (Fig. 1. and 2.), because we tried to directly compare concentrations obtained by CIMS measurements + WLF and Ion Chromatography analysis. However with data (loss rate coefficient, residence time, WLF and WLF_inlet) provided in Tables 1. and 2. can anybody easily calculate measured sulfuric acid concentrations, concentration at the end or any arbitrary position in the flow tube.

4. It is not discussed why nucleation rates are identical at the lowest investigated H2SO4 concentration (Fig. 2) for all temperatures. The different slopes do not explain this phenomenon (p. 25968, l. 22, and conclusion) but only describe it. If real, this would imply that for atmospheric conditions with usually less than 5x10ˆ7 molecules /cm3 there is no temperature dependence of the nucleation mechanism discernable.

RE: Experiments at nucleation temperatures 15 and 5 C were really hard to conduct. Undoubtedly the reported slopes suffer from uncertainty and our only explanation for this behavior is provided in p. 25968, l. 22. All other explanations are possible but we are not able to provide any estimates of their uncertainty. We can hardly accept speculation of vanished temperature dependency at low sulfuric acid concentrations.

Technical/Minor Comments

1. Please check the given units for nucleation rates which should be given in /(cm3 s) and not cm3/s

RE: Corrected.

2. p. 25960, l. 19-20: the impact of anthropogenic emissions is rather vague, be more specific.

RE: Updated in new version of manuscript.

3. p. 25963, 1st §: this is a complete repetition from the Brus et al., 2010 paper, and should be shortened and referenced.

RE: We think this is very important information, because some of the readers (based on experience from personal communication) still do not fully understand the principle of H2SO4 production. We prefer to leave the paragraph as it is.

4. p. 25964, l. 3: the uncertainty should be further specified and it should be explained how it was derived (see also above).

RE: See references and comments above.

5. p. 25964, l. 21: spelling error in “diethyl-glygol”

RE: Corrected

6. section 3.1: It is recommended to move this to the experimental section (see above).

RE: Section 3.1 was moved to experimental as suggested by reviewer.

7. p. 25967, l. 26: a factor of “-2” would not make much sense, instead it should be uncertainty by factor 2.

RE: True, corrected.

8. p. 25968, l. 19: change to “. . . order of magnitude when decreasing. . .”

RE: Changed.

9. p. 25972, l. 2-4: Please, make clear that there were different CIMS systems involved

RE: Corrected to: ”The measurements in Hohenpeissenberg, Melpitz and San Pietro Capofiume were performed with the CIMS of German Weather Service (DWD), whereas in Hyytiälä the CIMS of the University of Helsinki (UHEL) was used. The two instruments are very similar, as the UHEL CIMS is built at the National Center for Atmospheric Research (NCAR, USA), and also the DWD CIMS is NCAR-type CIMS. They also rely on the same calibration procedure, for more details see Paasonen et al. (2010)”

10. p. 25972, l. 5: Please correct “Hohnepeissenberg” in “Hohenpeissenberg”

RE: Corrected.

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FIGURE CAPTION: Figure 1. Nucleation rate as a function of total sulfate (measured with bubblers + Ion Chromatography (IC) and calculated via mass balance (MB) from liquid samples analyzed by IC) at RH=10, 30 and 50%.

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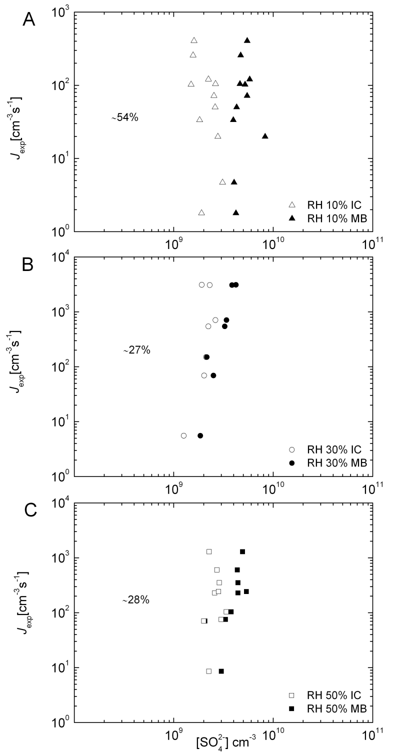
A
B
C
J_exp[cm^-3 s^-1]
~54%
~27%
~28%
RH 10% IC
RH 10% MB
RH 30% IC
RH 30% MB
RH 50% IC
RH 50% MB
10^0
10^1
10^2
10^3
10^4
10^9
10^10
10^11
[SO_4^2-] cm^-3

Fig. 1.