

Interactive comment on “Atmospheric homogeneous nucleation of H₂SO₄ and H₂O” by D. R. Benson et al.

Anonymous Referee #2

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The group utilizes unique set of instrumentation (NH₃ and H₂SO₄ CIMS), that gives them huge potential to produce unique data and thus enrich the aerosol community. But I am afraid the current manuscript is not the case. The topic of the manuscript is misleading. There is nothing like atmospherically relevant conditions within the whole manuscript, one nucleation temperature (287K) and range of 35% from 6-41% in RH (average RH in atmosphere is ~50%, with no doubts it is depended on location), only H₂SO₄ concentration is about the same range that is observed in atmosphere. I was hoping for direct comparison of H₂SO₄-H₂O nucleation from laboratory to atmospheric new particle formation. The same group published recently “An atmospheric observation” paper in JGR (Erupe et al., 2010) where they used the same instrumentation as in laboratory experiment presented in this manuscript. They are supposed to have all the necessary data about particles characterization to be able to calculate nucleation

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rates of 3nm (J3) particles and compare them directly to their CPC TSI 3786 with 3nm cut-off. The concentration levels of H₂SO₄ and NH₃ can be mutually compared; also RH and nucleation temperate from meteorology should be available. It is really pity; I highly recommend to authors that they significantly revise their manuscript.

General comment on NH₃: the authors claim on the p.29053 l.14: “Depending on the material used in the nucleation reactor, the effects of such impurity NH₃ can be also defferent. Experimental tests have shown that whereas adsorption of NH₃ is most effective on stainless steel material, NH₃ adsorption is minimal on fluorinated ethylene propylene (FEP) or perfluoroalkoxy (PFA) Teflon surfaces.” Is not it then better to use stainless steel everywhere where it is possible to reduce NH₃ level, if you aim to measure “binary nucleation” with minimum NH₃? Of course considering subsequent desorption at elevated temperatures from the walls after each experiment to get rid of any adsorbed material including H₂SO₄, i.e. routine cleaning procedure of the flow reactor. Can authors quantify the losses of NH₃ in this manuscript when using FEP or PFA materials compared to stainless steel? What is the difference? Is it percents? Tens of percents? Orders of magnitude? It would be highly interesting and very important for other experimenters if the authors can provide rough estimates of wall loss factors, for example considering pipe made of above mentioned materials of the same diameter and the same length. This manuscript is anyway more technical than scientific.

I suggest authors to consider restatement of the whole paragraph dedicated to paper of Sipilä et al. (2010) or avoid it at all. The authors picked up just what they considered important for themselves; the whole paragraph suffers from hardly acceptable bias. In general and very shortly, in Sipilä et al. (2010) two different flow tubes from two different laboratories operated by two different groups (Ift and FMI) were used, however the same instrumentation (CIMS, PSM) was utilized in both cases. a) two particle counters for particles ~1.5 nm were used in Ift laboratory (PH-CPC and PSM) both based on different working principles and data evaluation methods and both are giving similar results. c) all together three different sources of H₂SO₄ were utilized [in Ift-LFT:

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1) continuous production in-situ with UV and 2) single point source from saturator at 15°C containing 98% H₂SO₄, 3) FMI experiment used diluted (very weak) solutions of H₂SO₄+H₂O injected into furnace and subsequently vaporized] resulting in figure 2 in there. All obtained data at different but close nucleation temperatures, slightly different RH, and different residence times, fall in to similar J vs. H₂SO₄ space with the similar slopes from 1-2. The counting efficiency of counters and their error estimates, error estimates in CIMS measurements and methods of H₂SO₄ production are discussed in supporting online material and references within in detail.

General comment on obtained slopes: The authors unfortunately do not provide any information about the particle sizes, the number of particles they are able to produce should be sufficient for any SMPS or DMPS measurements. In principle the authors should be able to produce figure of $D_p=f(\text{H}_2\text{SO}_4)$ for the initial concentrations of H₂SO₄ in the range $5 \cdot 10^6$ to $5 \cdot 10^7$ /ccm. This would give them rough estimate of the error and counting efficiency for their CPC TSI3786. The slopes they reported have no significant value without reference to particle size and discussion of estimated error of the slopes. The conclusions based on reported values are at leased controversial. From fig 4a, if you for example look at the blue points (down faced triangles, RH=12%, 60s) and take out three top points that suffer probably from vapour depletion in the flow reactor, the slope will be steeper then reported value of 4.2. Experimental data suffer from bow-shape, this is in principle alright, if you of course know why? I guess that at low concentrations of H₂SO₄ less than $5 \cdot 10^6$ their CPC TSI3786 is significantly undercounting. I would be very happy to be wrong and if the authors can provide solid evidence that their counting efficiency is not significantly changing along whole H₂SO₄ concentration range.

Comment on Fig. 1: I am not sure if I understand the schematic figure right. The distance between NH₃ inlet and H₂SO₄ sampling outlet is 9 cm, the nozzle is larger then 9 cm and is probably designed to block direct mixing of NH₃ with H₂SO₄ thus creating some kind of co-flow setup. My point is, the end of the nozzle is just at the

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beginning of the sampling outlet for the CIMS measurements. Does not the NH₃ flow create the sheath flow for the jet flow of H₂SO₄ from the nozzle? Thus leading to underestimated values of H₂SO₄ (initial) measured with CIMS, and to lower values of WLF? I understand the purpose of the nozzle, but not the position of the H₂SO₄ sampling outlet. If the authors insist on the results presented in their manuscript without correcting the schematic figure or clear justification of proper measurement setup (i.e. CFD or any model of dispersion from single source and/or measured radial profile from the wall towards center of the nozzle) I would be very skeptical about their results and conclusion.

Authors state on p.29059, l.22: “When only SO₂ (2.25 ppmv) was introduced, there were some low but still recognizable [H₂SO₄] and particle concentrations, . . .” Is it possible to quantify H₂SO₄ concentration at their SO₂ level, the background concentration for particles and H₂SO₄? and moreover I am very curious about the sensitivity of CIMS measurements to SO₂ alone, does anything like plot [H₂SO₄] vs. [SO₂] at different RH exist? Can authors comment it?

Authors state on p.29062, l.21: “Our results, together with [Berndt et al., 2005, 2006; Sipilä et al., 2010], show that [H₂SO₄] threshold for H₂SO₄-H₂O BHN is 10⁶ /ccm, as found in the atmosphere. . .”, I would like to know what is authors’ definition of “threshold”, is it H₂SO₄ concentration where they start to see particles? Usually in nucleation literature the authors refer to onset of nucleation defined as nucleation rate of 1 particle/ccm/s, definition is arbitrary, but you should state what it is in you case.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 29051, 2010.

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