Atmos. Chem. Phys. Discuss., 10, C12789–C12800, 2011
www.atmos-chem-phys-discuss.net/10/C12789/2011/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Atmospheric homogeneous nucleation of H_2SO_4 and H_2O" *by* D. R. Benson et al.

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Received and published: 25 January 2011

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 rates of 3nm (J3) particles and compare them directly to their 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.

RE: Dr. Dave Benson is not immediately available because of personal circumstances and as co-corresponding author, I am responding to the reviews on his behalf. We thank the reviewer for helpful comments and we provided here point to point response.

We disagree with the reviewer's statement here: "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. These experimental conditions are within, and can be representative of, the typical conditions seen in the lower troposphere. Unlike in modeling studies, it is not possible to cover the entire atmospheric conditions in a single laboratory study and this is also not feasible from the practical viewpoint.

As we have discussed in this manuscript (Page 29062 lines 11-19), we do not think directly comparing laboratory BHN results with atmospheric observations can yield any new insights. This is because we don't know how other species than H2SO4 are involved in the real atmosphere and the RH and temperature also change in a large range for the ambient data which are used for this kind of comparisons. So just taking an ensemble data of Log J vs. Log H2SO4 from ambient measurements and comparing them with lab studies is not "apple and apple" comparison. Therefore, at present, we are not planning to make any direct comparison with atmospheric observations including even our own dataset. But as we mentioned in Discussion, when there is a more rigorous method that applies nucleation theories directly into atmospheric application, we will return this issue in the future.

For clarification on the reviewer's comment on our JGR [Erupe et al., 2010a]: there, we have provide J1 – instead of J3 stated by the reviewer. J1 was calculated with PARGAN inversion program by considering coagulation growth and loss and condensational growth.

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.

RE: These comments are related to how toflon material is less susceptible to ammonia adsorption and desorption, as compared to stainless steel. There are a large number of publications on this topic [Neuman et al., 2003; Nowak et al., 2002; Nowak et al., 2006; Nowak et al., 2007; Yokelson et al., 2003], which seems new to the nucleation community; these studies have made extremely detailed investigations to answer reviewer's technical questions. Some of these papers were cited in our manuscript (Experiments) – we added more in revision (Discussion section). These issues are beyond the focus of our nucleation study, and we direct the reviewer to our previous NH3-CIMS instrumentation paper [Benson et al., 2010a] where we have specifically addressed

NH3 contaminations with regard to various technical factors including material.

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 accepteble 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: 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.

RE: BHN is an extremely controversial subject (e.g., Zhang et al., Science 2010) and there are strong inconsistencies between different publications at present and there are many questions that still remain to answer and the community is segregated with different or often opposite opinions. This needs to be reconciled in the community by looking objectively at different data taken by different groups with different approach. Especially, currently we don't know what is the critical cluster both for BHN and multicomponent nucleation, in terms of their size and chemical composition. Here, we provided our experimental data with constrained precursor concentrations to draw a conclusion different from [Sipila et al., 2010] which concluded that BHN critical clusters contain only one or two H2SO4 molecules, contradicting thermodynamic principles.

We will include another PH-CPC (we only mentioned PSM, because as the reviewer has pointed out PH-CPC and PSM are giving similar results in terms of measuring small sizes and but this does affect in the context – please see below), but we believe our statement on [Sipila et al., 2010] did not contain any scientific errors or any bias:

(Page 4, lines 69-85) "(SipilÂÍa et al., 2010) have reported atmospherically observed nucleation threshold of 10ˆ6 cm−3 and the slope of Log J vs. Log [H2SO4] to be 1 – 2.1, from laboratory studies of H2SO4-H2O BHN. By comparing with previous laboratory observations (Ball et al., 1999; Benson et al., 2008; Berndt et al., 2005; Wyslouzil et al., 1991; Young et al., 2008), they concluded that this new finding is due to the following factors: (a) unique particle counters, particle size magnifier (PSM) and pulse height condensation particle counter (PH-CPC) which measure small particles down to 1.5 nm, as opposed to the common type of particle condensation counters (CPC; e.g., TSI 3025 and 3786) (measuring down to 3 nm) used in atmospheric observations (Kulmala et al., 2004) and previous laboratory studies, (b) a longer residence time (60 – 240 s), and (c) a continuous source of H2SO4 production in the entire nucleation reactor, as opposed to a local source used in (Benson et al., 2008; Young et al., 2008). Compared to (Berndt et al., 2005, 2006), (SipilaÂÍ et al., 2010) also used the same experimental approach, with the only difference in the type of particle counters used. While the BHN study by (Sipil ÂÍa et al., 2010) successfully reproduced the slope of Log J vs. Log [H2SO4] derived from field studies (1 – 2) (Kulmala et al., 2004), it is also difficult to understand how pure H2SO4 neutral monomers or dimers can act as critical clusters without a ternary species present, from a thermodynamics viewpoint (Zhang, 2010)."

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 Dp=f(H2SO4) for the initial concentrations of H2SO4 in the range 5.10ËĘ6 to 5.10ËĘ7 /ccm. This would give them rough es-

timate 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.

RE: We have included the following discussion in the revision:

(Page 11 lines 238-243) "The time difference between [H2SO4] and particles was nearly the same as the residence time (Figure 3). From this time difference, we derived a GR of ∼ 28 nm hour-1. But this GR should be regarded as the upper limit, since it was estimated by assuming that particles are larger than 3 nm. When we measured sizes with a nano-DMA (TSI 3085), however, the mode sizes were smaller than the cutting size (2.5-3 nm in CPC), indicated by the particle number concentrations decreasing from this cutting towards larger sizes."; (Page 16, lines 340-344) "Additionally, the current condensation theory does not incorporate the ternary species, the chemical interaction between acid and base and the possible catalytical effects of NH3 on H2SO4 cluster formation [Benson et al., 2010c]. With this current status of knowledge, we cannot quantitatively examine GR, especially without knowing the mode size (which is smaller than 2.5-3 nm cutting size in TSI 3085 nano-DMA)."

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 5.10ËĘ6 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.

RE: We have included this discussion in revision:

(Page 12 lines 258-266) "The slope of Log J vs. Log [H2SO4] was 4 – 6 for most of time. There is the possibility that J could be underestimated at the high [H2SO4] range due to saturation in particle counting; we have seen similar shapes also in our previous studies [Benson et al., 2008; Benson et al., 2009; Benson et al., 2010b], whereas at low [H2SO4], CPC has lower counting efficiencies which could also affect the slope. In comparison, in Figure 4a we also included data from [Sipilä et al., 2010]. Both these two studies show nucleation threshold of 106 cm-3 H2SO4, but the slopes are drastically different, because [Sipilä et al., 2010] utilized PSM which measures particles down to 1.5 nm."

Additionally (Page 16 line 365 – page 17 line 369): "Our laboratory observations also show that the slope of Log J vs. Log [H2SO4] ranges between 4 – 6. [Berndt et al., 2010; Sipila et al., 2010] have showed that using this new PSM or PH-CPC, as compared to CPCs, it can increase the particle concentrations at lower H2SO4 concentrations and will affect the slope of J vs. [H2SO4] in general. So there is the possibility that our measured Log J vs. Log [H2SO4] may also have been affected by low counting efficiencies at small sizes in CPC. However, whereas the slopes for J vs. [H2SO4] in our study with CPC was higher (3-5) than in [Berndt et al., 2010; Sipila et al., 2010] with PH-CPC/PSM (1-2), the slope of J vs. [NH3] was the same (1) with CPC [Benson et al., 2009; Benson et al., 2010c] and new particle counters [Berndt et al., 2010]. It is unclear why these different particle counters would only affect one slope and not the other(s). Cluster CIMS measurements also showed that the critical cluster for THN contains likely only one NH3 molecule [Hanson and Eisele, 2002]. Similarly to NH3, the slope of Log J vs. Log [trimethylamine] (measured by CPC) was also 1 [Erupe et al., 2010b]; considering the similar chemical properties and very similar effects on nucleation by trimethylamine and NH3, we believe this trimethylamine slope is also meaningful."

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 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. (Dave – can you answer these?)

RE: We want to clarify the purpose that we used this kind of "corn" is to reduce wall loss of H2SO4 – and not "to block direct mixing of NH3 with H2SO4 thus creating some kind of co-flow setup" as the reviewer stated here. This kind of design (corn in the center of the tube with high flows) has been in fact widely used in laboratory kinetics studies using radicals and short lived chemical compounds, and this concept is well proven by numerical and experimental studies ([Donahue et al., 1996] and references therein), as it was stated in the manuscript.

The reviewer's comment is whether H2SO4 measured with CIMS was underestimated by this corn-shape nozzle. We have included the following for clarification:

(Page 9 lines 187-191) "We have examined if this "corn-shaped" tube (i.d. 1 cm at the end of the corn) would affect the CIMS measurements near the entrance of the nucleation reactor. When we added NH3 before the nozzle, the measured concentration was the same as if we added it right before the CIMS inlet. From these results, we believe that the effects of the corn shaped tube on CIMS measurements can be minimal." Please also see additional information in revised Figure 1.

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 10ËĘ6 /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.

RE: The CIMS sensitivity does not dependent on whether we have only SO2 or H2SO4 in the flow tube (or on the RH in it) and is only determined within the CIMS by its own technical settings. CIMS only measures what we have in flow tube as a gas phase H2SO4. As we discussed in the manuscript in detail, there are several processes that are involved in production of H2SO4 in the flow tube: in addition to OH + SO2 process which we had in mind when we designed the setup, there is also OH recycling (amplifier) process with high OH and we also think there is some kind of heterogeneous dark oxidation processes without OH. The particle concentration was always less than 1 cm-3 (even less than 0.1 cm-3 most often) even when high SO2 (ppmv) was added – see Figure 3; they are much less than with OH and SO2 together. This was stated clearly in our manuscript (P29056 line 12 – P29057 line 6).

As explained in great detail in [Young et al., 2008], in addition to this kind of H2SO4 production channels (without OH in dark) in the flow tube, the CIMS can also artificially produce gas phase H2SO4 from the reaction of SO2 (introduced from flow tube, for example) and the artificially formed OH in the ionization region. This artificial OH radicals form by the radiation source and water molecules in the CIMS sheath air (which is not from our nucleation reactor and thus, has nothing to do with the RH in the flow reactor). But our CIMS has a very unique design in the ionization region to eliminate such artifact

H2SO4 very effectively [Young et al., 2008]. As for this artificial background H2SO4, it was highest only at about 1x10ˆ6 cm-3, not affecting our experiments. For example, it does not exceed 6-7*10ˆ5 for SO2 of 2.25 ppmv, again which is independent of RH in the flow tube.

With respect to the threshold we did define it as 1 cm-3 s-1 (on the graph, this is log J = 0); we have added this clarification in several places in the revision.

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