Atmos. Chem. Phys. Discuss., 10, C12779–C12784, 2011
www.atmos-chem-phys-discuss.net/10/C12779/2011/

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 authors replies to my comments are unsatisfactory on a couple of crucial points:

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 re-review and we provide here point to point response for each comment. BHN is an extremely controversial subject (e.g., [Zhang, 2010]) and there are strong inconsistencies between different publications at present and there many questions that still remain to answer and the community is somehow segregated with different or often opposite opinions. The nucleation community has to reconcile them, by looking at different data taken by different groups with different approach objectively. Especially, we don’t know what is the critical cluster, in terms of their size and chemical composition. Here, we have provided our experimental data with constrained precursor concentrations and these observation data, we made a conclusion different from [Sipilä et al., 2010] which concluded that BHN critical clusters contain only one or two H2SO4 molecules; from thermodynamics viewpoint, a monomer (gas phase free molecule) or a dimer cannot act the critical cluster.

1. The authors ’justify’ having un-quantified impurities in their system by the fact that other previous research have had the same ’problem’ also. I feel that every scientific paper should have some important new information that adds to the existing knowledge. When looking into new things (as the first one, or among the first) it is ok/natural to be ’not perfect’ (have uncertainties, impurities etc.). However, as progress is made, these uncertainties are typically decreasing (or hopefully removed altogether) – and progress is made. This is not the case here.

RE: The reviewer’s following statement “The authors ’justify’ having un-quantified impurities in their system by the fact that other previous research have had the same ’problem’ also” is inconsistent with what we have stated in our response to the reviewer and in our manuscript; we did provide systematic, quantitative investigation of impurity NH3 measured directly with CIMS as a function of RH – thus, this is NOT “unquantified”. For example, in our manuscript (from page 29055 lines 24-25 to page 29056 lines 1-3):

“The impurity NH3 gases in the system, mostly likely originated from deionized water, were systematically determined as a function of RH in the system with the CIMS (Benson et al., 2010b; Nowak et al., 2006). Under the typical experimental conditions, the mixing ratio of NH3 existing in the nucleation reactor was estimated to be between 20 – 100 pptv for RH from 6 – 40%.” In the revision, we also included the background trimethylamine concentration measured with CIMS: approximately 15-85 pptv at RH 6% (Page 10, line 213).

Also, in our response to reviewer (C12523, lines 12-19), we stated: “In our study we have managed to minimize (yet not eliminate) the lowest ammonia contamination in the system (using TFA material as opposed to stainless steel) and provided systematic measurements of these impurity concentrations (as opposed to roughly estimate): e.g., 20 – 100 pptv at RH from 6 - 40% in typical experimental conditions used in the current study. Unique to this study, we will also provide amine concentrations (trimethylamine) to about 15 - 85 pptv in the nucleation reactor at RH of 6%."

For a further clarification, as we stated in our initial response to the review, we stated this contamination exists in all (C12523, lines 6-10): "Ammonia and amines always exist as impurities form water vapor in the nucleation system – and it is unavoidable. This is an inherent problem and common to all different groups and not unique to this study, as we have stated in our manuscript." However, we believe our group is the only group which has so far provided both the measured NH3 and amine concentrations, quantitatively, directly with CIMS.

2. Still, the authors present a set of (possibly) valuable experimental data. It should be, however, much more thoroughly quantified/analyzed. My suggestion is to spend much more time on the growth rate. Now, the authors' response to my criticism of having a factor of 28 unknown cause in the growth rate is, again, 'other researchers have had uncertainties also' and 'only a limited number of growth theories exist' (which is an odd statement). Condensation-theory is much more 'well established' than theories on nucleation - of course there are uncertainties related to thermodynamical quantities, however. In any case, for the ternary system of water-sulfuric acid-ammonia, it should be possible to estimate growth rates for specified conditions and concentrations. The same, apparently (by the references mentioned in the nice comment by Jianxin Ma), is true also for amines. So why not play with condensational growth models and see what kind of ammonia/amines concentrations (or are other significant concentrations of 'impurities' needed?) are needed to explain the observed growth rates - and compare them with e.g. the detection limits of the instruments.

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 $\sim$ 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., 2010b]. 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)."

3. The main value of the Berndt et al. and Sipila et al. papers is the fact that both works carefully try to find out possible causes for the different slopes in the logJ-logH2SO4-plots. The explanations on effects of detection limit and residence time are easy to grasp and clear now. One other thing (removing much of the effect of growth) is using new devices with low detection limits, so that measurements gradually approach 'nucleation size'. Since here a 3nm-cutoff CPC is used, any conclusions on the slopes are affected both by a) a longer range to cover by growth and b) other vapors participating on both nucleation and growth.

RE: We agree that PSM measures 1.5 nm which is close to 'nucleation size'– yet, this instrument still cannot provide direct information on critical clusters. Moreover, as we have mentioned early in our response, one needs to see how this instrument is intercompared with Kulmala et al. Science (2007)'s neural ion mobility instrument which also covers similar size range, as this will provide more validity of these instruments. With these instrument validations, we will be able to verify these new findings. Also, [Berndt et al., 2005] and [Sipila et al., 2010] showed the same threshold (at 10ˆ6 cm-3 H2SO4), but with the entirely different slopes (5 vs. 1-2); so they seem to contradict each other.

4. I still also protest the fact that the authors refer to binary nucleation at all, when writing about these experiments. For many previous works (in which there has been other participating vapors also) this is ok because at the time the researchers did not know any better. Now the situation is different.

RE: We would need to know what situation has changed – we would like literature backup on this comment – so that we cannot refer to BHN in the present study while there are papers continuously being published from other groups with the same situations.

On whether these impurities (e. g., 20-100 pptv NH3 and 85 pptv trimethylamine in our system) is affecting BHN we have added the following paragraph in Discussion:

(Page 16, lines 345-355) "Whether these impurities can affect BHN or not is unclear. But as discussed above, from our THN studies with MH3 and tirmethylamine, sub-ppbv level of base species had very moderate effects on nucleation [Benson et al., 2010b; Erupe et al., 2010b]. We have seen only significant effects with high [NH3] at the tens ppbv level [Benson et al., 2009]. There is also another important theoretical aspect we should take into account in homogeneous nucleation studies. Even if the system has multiple chemical species, we cannot simply assume that nucleation would take place through THN or multicomponent processes; rather this depends on several conditions including how much we have these ternary species in the system, for example, and sometimes, nucleation can take place solely via BHN even in the presence of ternary species [McGraw and Zhang, 2008], which certainly does not exclude the case of these NH3 or amine impurities."

5. (minor point) When I asked for more reasoning about the 'threshold' of 1.e+6 for particle formation, I meant how (in detail) it is seen from the results presented in this manuscript - so please write a couple of lines of advice to the readers what to look for in the figures...

RE: We refer the review to Results Section where this issue has been explained in great detail. For other cited studies, we cannot speak for other papers and would like to direct the reviewer to those references.

References: Benson, D. R., et al. (2009), Laboratory-measured H2SO4-H2O-NH3 ternary homogenous nucleation rates: Initial observations, Geophysical Research Letters, 36.

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