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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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Response to Anonymous Referee #1

-The topic of the (title of the) manuscript, binary homogenous nucleation of H2SO4 and H2O in the atmosphere, is an important topic, where inconsistencies between observations, laboratory work and theories still exist - and is a topic well within the scope of ACP. However, the results presented, in my view, do not remove any of these inconsistencies (but only add to the ’confusion’).

RE: We thank the reviewer for helpful comments and below we provide the point to point response to the comments.

-The title itself has two inaccuracies: 1. The work presented is a laboratory study and necessarily does not have much to do with 'atmospheric homogeneoous nucleation'. 2. The nucleation experiments presented are very probably not binary H2SO4/H2O nucleation. The carrier gas has impurities, most probably a significant amount of ammonia and thus the particle formation is very likely (at least) ternary.

RE: 1. Homogeneous nucleation is a very broad term and we intend to refer to the one that is taking place in the atmosphere. 2. Ammonia and amines always exist as impurities from 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. More specifically, in (Berndt et al., 2010) background NH3 impurities in the system were reported to be < 100 pptv (below the instrument detection limit); similarly, for (Brus et al., 2010), NH3 impurities < 500 pptv. (Sipila et al., 2010) have used these two instruments. 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 $\sim$15 - 85 pptv in the nucleation reactor at RH of 6%. Both ammonia and TMA were measured by CIMS. These experiments with controlled experimental conditions will complement with other studies. These data together will become a valuable basis to test and improve theories. To reflect this comment, we have included in the revision: "While we have used loosely the term of BHN in this study, due to the impurities of NH3 and amines, the nucleation rates were also definitely affected by these base molecules present as background impurities in the nucleation reactor; which is the case also for other nucleation studies. However, we also believe the background NH3 concentrations present in our nucleation reactor were generally lower than in other studies where stainless steel material was used in the experimental setup (Berndt et al., 2005; Brus et al., 2010; Sipilä et al., 2010) and we have also provided a systematic detection of background impurity NH3 with CIMS as a function of RH, in addition to a preliminary result of trimethylamine concentrations measured by CIMS. However, to accurately measure trace concentrations of these base molecules, there are several technical challenges in CIMS instrumentation we need to overcome; especially, we will need to significantly lower the "CIMS-background signals" which are different from background impurity concentrations present in the nucleation reactor (Benson et al., 2010b)."

-The major (and very serious) problem of this work is point 2 mentioned above. The authors themselves acknowledge at the top of page 29060 that of the observed growth rate of 28 nm/h, sulfuric acid can explain only about 1 nm/h - and 'it is possible that these studies also had some low concentrations of NH3'. The authors state that the detection limit of NH3 in their measurements is 93 pptv, which corresponds to a molecule concentration of roughly 2*10ËĘ9 #/cm3 !!! This is a couple of orders of magnitude higher than the sulfuric acid concentration. How can you then claim that you are measuring binary nucleation???

RE: Please also see the above comment. As we have discussed in the manuscript in detail, the growth rates in our flow tube (28 nm hr-1) are much larger than can be explained by H2SO4 condensation alone (e.g., 1 nm hr-1 at 10ˆ7 cm-3 H2SO4). Therefore it is possible that the background NH3 present (e.g., 20 – 100 pptv at RH from 6 - 40% in our case) contributes to this growth even for the BHN case. At similarly low H2SO4 of 7x10ËĘ6 cm-3, (Berndt et al., 2005, 2006) have also seen roughly 13 nm hr-1 growth rate in their nucleation reactor. This could have been also due "in part" to NH3 or amine impurities in the system. As eliminating background NH3/amine is unavoidable, on the other hand, any EF values found or given will actually be an underestimation due to pptv level NH3 being present. Another possibility is that not every collision results in the formation of a critical cluster (Kuang et al., 2010). In a study showing the dependence of the nucleation rate on H2SO4 in various atmospheric locations (Kuang et al., 2008), it was found that the kinetic prefactor values were 1 – 4 orders of magnitude below the hard-sphere collision frequency. If values closer to the collision frequency are used, growth rates would be at least 40 nm hr-1, which could

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explain growth in our flow tube. At present, however, only a limited number of growth theories exist, none of which incorporate a third species or take into account chemical interactions that occur between precursors.

-As the authors have at the same time another manuscript (p. 22395-22414) under evaluation in ACPD, showing results of ternary H2SO4/NH3/H20-nucleation (including several of their 'binary' results also), I strongly suggest combining these two manuscripts - but with a careful investigation/discussion on which vapors are/can be present and account for the observed nucleation and growth rates.

RE: Benson et al. (2010a) focuses on the relative importance of NH3 on nucleation – and the experiments were conducted in the new nucleation reactor with longer lifetimes and lower wall losses. On the other hand, the current manuscript focuses on how various experimental conditions affect nucleation results using the case of BHN; and the experiments were made with a large range of nucleation times (60-400 s) and with two different nucleation reactors. This is extremely important in order to correctly interpret experimental results correctly from different studies.

-Another important thing (which concerns both this manuscript and the ternary one)... The first nucleation theorem is used quite loosely to compare with previous studies and interpret nucleation mechanisms. Actually, as I understand, the main conclusion of the paper, written in the abstract as well as in the conclusions, is that impurities cause the results that show a slope 1...2 (e.g. Sipila et al.), but 'pure binary' experiments, as in this manuscript, result in a higher slope. This is wrong! In addition to the possible contamination by NH3 of these experiments (also), the measurements here were done with a TSI 3786 CPS (cutoff = 3 nm), and Sipila et al. clearly showed that a higher cutoff will lead to a higher slope in logJ-log[H2SO4]-space. In other words, the slopes that the authors are observing are resulting from nucleation+condensation and not nucleation alone.

RE: We agree with the comment with regard to first nucleation theorem and have in-

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cluded: “While we have used the slope of Log J vs. Log [H2SO4] to determine the number of H2SO4 molecules (nH2SO4) in the critical cluster based on the classical nucleation theory by assuming that there is only one maximum of Gibbs free energy for nucleation (Kashchiev, 1982; McGraw and Zhang, 2008), a recent theoretical study has also suggested that such assumption may not be valid for a multicomponent nucleation system and there may be several local minima and maxima (Vehkamäki, 2010).”

The following statement of the reviewer is inconsistent with the statement made in our manuscript: “Actually, as I understand, the main conclusion of the paper, written in the abstract as well as in the conclusions, is that impurities cause the results that show a slope 1...2 (e.g. Sipilä et al., 2010), but ’pure binary’ experiments, as in this manuscript, result in a higher slope. This is wrong!”. Instead, we have mentioned that all nucleation studies were affected by ammonia impurities including our and (Sipilä et al., 2010) We stated: “For example, in binary homogeneous nucleation (BHN) studies that usually use water vapor to produce different RH values in the nucleation reactor, it is usually assumed that ternary species do not exist in the nucleation system (Ball et al., 1999; Benson et al., 2008; Berndt et al., 2005, 2006; Sipilä et al., 2010; Young et al., 2008), but in fact NH3 impurities are unavoidable, because even highly purified water contains some amounts of NH3 as impurities (Benson et al., 2010a; Nowak et al., 2006). Depending on the material used in the nucleation reactor, the effects of such impurity NH3 can be also different. (Page 29053; Lines 9-16)” Also, “Our results, together with (Berndt et al., 2005, 2006; Sipilä et al., 2010), show that [H2SO4] threshold for H2SO4-H2O BHN is 10ˆ6 cm$-$3, as found in the atmosphere (Erupe et al., 2010; Kulmala et al., 2004). As discussed in the present study, it is likely that all these studies were under the influence of certain levels of impurities of NH3 at least, which is also easily available in the atmosphere. (Page 29062, Lines 21-25).”

For a clarification, we believe that (1) all homogeneous nucleation experiments reported so far in the literature were all affected by base impurities, but at substantially different levels; (2) it is difficult to understand why (Berndt et al., 2005, 2006) and (Sip-

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ilä et al., 2010) showed the same threshold of H2SO4 (10ˆ6 cm-3) for J =1 cm-3 s-1, but the slopes were so different (5-7 vs. 1-2)? (3) to our knowledge, the different new cluster instruments, such as PSM used in (Sipilä et al., 2010) here, ion mobility spectrometers (Kulmala et al., 2007) and McMurry's new type of ethyleneglycol nano-DMA (Zhao et al., 2010) have not been inter-compared yet, and therefore, the conclusions made from these instruments need further verifications; (4) a monomer or dimer of H2SO4 alone is thermodynamically unstable and cannot be the critical cluster.

-Minor comments: -Please discuss what are the uncertainties in a) the H2SO4 measurement, b) the NH3 measurement ?

RE: a) The detection limit of H2SO4-CIMS was 2 × 10ˆ5 cm−3 and the uncertainty associated with our ambient measurements were estimated to be about 60% at maximum. (Erupe et al., 2010). b) Typically, the detection limit of NH3-CIMS was about 60 pptv and the overall uncertainty associated with the instrument background and the sensitivity was 30 pptv ± 30% (Benson et al., 2010b). These values were both derived from ambient measurements, but we can assume similar performances for flow tube studies or somewhat better, because of less complication and interference due to the sampling inlet.

-In the discussion section it is stated that the slopes (which result from both nucleation and condensation) are thermodynamically consistent with the quantum chemical calculations by Kurdi and Kochanski. This is a very loose statement and by browsing through the reference I cannot understand why this is stated.

RE: This is a correct reference.

-In the discussion section it is stated that the observed BHN threshold of 10ËĘ6 cm-3 agrees with the observed atmospheric one. How is this threshold obtained from a) these laboratory results and b) atmospheric observations?

RE: As it was stated in Discussion: "Our results, together with (Berndt et al., 2005,

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2006; Sipilä et al., 2010), show that [H2SO4] threshold for H2SO4-H2O BHN is 10ˆ6 cm−3, as found in the atmosphere (Erupe et al., 2010; Kulmala et al., 2004)."

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