**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Ternary homogeneous nucleation of H$_2$SO$_4$, NH$_3$, and H$_2$O under conditions relevant to the lower troposphere" *by* D. Benson et al.

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-Nucleation of sulfuric acid particles and the effects of different additional compounds to nucleation have been investigated by numerous laboratory studies within past two decades. However, the results have shown significant divergence and the detailed understanding of nucleation mechanisms even in controlled laboratory systems has been pending. Effect of ammonia on sulfuric acid water nucleation has been studied previously but the results from the different experiments have been, to some extent, conflicting and more work is required before the potential role of ammonia in atmospheric new particle formation can be decoded. Thus, the topic of the present study

suits well within the scope of ACP, but there are several crucial issues mainly related to the quality of data that authors should answer before this manuscript can be published.

RESPONSE: We would like to thank the reviewer for their helpful comments in revising our manuscript. Below is our point by point response to the comments including the major revisions; (1) addressing the growth processes in the tube, (2) discussion of the mixing and the wall losses in the new flow tube, (3) highlighting the differences between this study and the Benson 2009 study, and (4) discussion of changing SO_2 vs. changing OH.

Additionally, in our second manuscript (ACPD) on BHN involving H_2O-H_2SO_4 (Atmospheric homogeneous nucleation of H_2SO_4 and H_2O, Atmos. Chem. Phys. Discuss., 10, 29051-29073, 2010, http://www.atmos-chem-phys-discuss.net/10/29051/2010/acpd-10-29051-2010-discussion.html), many of the issues brought are also addressed.

-Nucleation rates J are measured in the [H_2SO_4] range 2×10^6 - 2×10^7 cm-3 (which is equivalent to a mean [H_2SO_4] in the growth region of below 1×10^6 - 1×10^7 cm-3, after accounting for wall losses). This corresponds to a growth rate due to sulfuric acid condensation of about 0.1 - 1.0 nm/hr (see e.g. Nieminen et al., 2010, Sub-10 nm particle growth by vapor condensation – effects of vapor molecule size and particle thermal speed, Atmos. Chem. Phys., 10, 9773-9779.). Even at the maximum residence time (240 s), the mean particle growth (by sulfuric acid) is therefore only 0.007 - 0.07 nm. Please explain how you can measure any meaningful nucleation rate in your experiment using a CPC with a _3 nm threshold, when the mean time to grow from nucleation size (1-2nm) to detection size is at least 1-10 hours. How significantly particle undercounting affect the measured slopes? This is a highly fundamental question, to which the authors should be able to provide a satisfactory answer.

RESPONSE: We added two paragraphs in Discussions Section:

"It is important to know the kind of growth processes that can occur in the flow tube (Benson et al., 2010a; Berndt et al., 2010; Brus et al., 2010; Sipilä et al., 2010). As discussed also in (Benson et al., 2010a), the growth rates in our flow tube (28 nm hr-1) are much larger than can be explained by H2SO4 condensation alone (1 nm hr-1 at 107 cm-3 H2SO4 (Erupe et al., 2010). Therefore it is possible that the background NH3 present (e.g., $\sim$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 $7 \times 10^{\hat{}}6$ cm-3, Berndt et al. (2005, 2006) have also seen a $\sim$13 nm hr-1 growth rate in their nucleation reactor. This could have been also due in part to NH3 impurities in the system. As eliminating background NH3 is unavoidable, on the other hand, any EF values found or given will actually be an underestimation due to pptv level NH3 being present. This effect will be stronger at lower NH3 used in THN studies. Another possibility is that not every collision results in the formation of a critical cluster (Kuang et al., 2008). 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 to 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 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." (Lines 160 – 178)

-Related to above comment, authors refer to their earlier studies (Benson et al., 2008; Young et al., 2008; Benson et al., 2009) for description of the experimental setup. However, authors have modified the way that sulfuric acid is introduced into the flow tube. My concern is that if sulfuric acid is introduced from the center of the flow reactor, diffusion is not fast enough that concentration near the tube wall (where CIMS inlet is located according to cited studies) would be representative for the concentration in the nucleation region. This might yield in serious underestimation of sulfuric acid concentration. Authors should discuss their experimental setup in more detail, potentially with help of a drawing. Same comment applies for ammonia measurements.

RESPONSE: The experimental setup is discussed more in depth in a paper just recently published in ACPD (Benson et al., 2010a). In that paper, Figure 1 shows where all the gases are added. If we add NH3 to the port labeled N2/H2O (before the flow is centered) we see that the [NH3] is the same as if we added it directly before the NH3 CIMS inlet. This design allows for less wall losses but also for correct measurements and complete mixing. Also, in a previous NH3-CIMS instrumental paper (Benson et al., 2010b), it was shown that losses in the flow tube are minimal and that complete mixing does take place, which is now clarified in our revised manuscript (Lines 98 – 99).

-How is sulfuric acid CIMS calibrated? And what is the calibration coefficient used to convert measured m97/m62 ratio to sulfuric acid concentration?

RESPONSE: The measurement of [H2SO4] is based on (Young et al., 2008). $[H2SO4] \approx [HSO4^-]/([NO3^-]*kt)$ (7) k is the rate constant (2.3×10^{-9} cm3 s-1) and t is the reaction time (0.1s). So $[H2SO4] = C [HSO4^-] / [NO3^-]$ with C being the calibration factor (C = 1/kt, C = 4.35×10^9 cm-3). This is described more in depth in (Benson et al., 2010a).

-After addressing the above mentioned points, I presume that numbers and/or accuracy of the numbers given in the text might need to be revised. At present, no conclusions on the composition of critical cluster in the experiment can be drawn from the data.

RESPONSE: We disagree. Our measurements are complimentary to (Hanson and Eisele, 2002) that show nNH3 is only one, which was shown from cluster measurements; also complement with (Berndt et al., 2010) THN study performed at higher NH3 ($\sim$10-100 ppbv). Our study is the first THN laboratory experiment that reproduces atmospheric observations, using the conditions relevant to the lower troposphere.

-Abstract: l.3: "..laboratory experiments have failed to reproduce atmospheric observations". This is not completely true as Berndt et al. (2010) and Sipilä et al. (2010) reproduced atmospheric J vs. [H2SO4] even in absence of added ammonia and Metzger et al. (2010) by adding organics in the system. Berndt et al. (2010) observed a

promoting though not strong effect of ammonia on nucleation rate.

RESPONSE: We are discussing NH3-THN laboratory experiments made under atmospherically relevant conditions. As we have discussed in the manuscript (Discussion), (Sipilä et al., 2010) was a BHN study. (Berndt et al., 2010) performed a THN study, but [H2SO4] was 8×10^8 cm-3 and NH3 was also much higher (NH3 ($\sim$10-100 ppbv) than most of the atmospheric conditions. (Metzger et al., 2010) was on multicomponent nucleation involving an organic compound (trimethylbenzene) of petroleum industry origin. We revised to:

"Ternary homogeneous nucleation (THN) of H2SO4, NH3 and H2O has been used to explain new particle formation in various atmospheric regions, yet laboratory measurements of THN have failed to reproduce atmospheric observations." L10 – 12

-Determining the critical cluster composition from the measured slopes has been discussed by referee 1 and I will not repeat it here.

RESPONSE: Please see the response to referee 1.

-l.12: "..threshold for of H2SO4 concentrations . . . do not vary in the presence or absence of NH3." This is too strong statement and not even correct. Certainly, it does not vary orders of magnitude but it still varies.

RESPONSE: Agree -we have reworded to:

"„ vary only fractionally in the presence and absence of NH3."

-Experiments, l.23.: It is unclear why changing [H2SO4] by adjusting [OH] is an "improvement" in comparison to adjustment of [SO2]. By adjusting [OH] also reaction products from any trace species present in the gas capable of reacting with [OH] will change. These species can potentially participate in nucleation or growth.

RESPONSE: Unlike other experimental setups used for homogeneous nucleation studies, such as (Berndt et al., 2005, 2006, 2010) where OH is produced from ozone and

the OH is measured with titration reactions with various organic compounds, we produce OH from water photolysis and measure OH directly from photon flux, and therefore, our system is ozone- and organics-free so there is no such concern that OH might react with any trace species to produce ternary species (Benson et al., 2010; Young et al., 2008). This has been explained in detail in (Benson et al., 2010) (Page 29055, last paragraph). From our previous studies (Benson et al., 2008, 2009; Young et al., 2008), we also found that H2SO4 concentrations were also dependent [SO2], even when [SO2] » [OH]. The reason behind this is explained in (Benson et al., 2010a)(Page 29056-29057), as the following:

"The following reactions occur in the flow tube: SO2 + OH →HSO3 (R1) HSO3 + O2 → SO3 + HO2 (R2) SO3 + H2O →H2SO4 (R3) HO2 + SO2 → SO3 + OH (R4)

R4 is less important in the atmosphere at the moderate [SO2] (ppbv or less), but in the flow tube when we used high [SO2] (ppmv or higher), this reaction should be taken into account. Therefore, it is possible that in the flow tube, more than one H2SO4 molecule is formed from each OH radical due to the recycle (or amplification) between OH and HO2. Because the OH recycling process depends on k4, this explains why [H2SO4] were dependent not only on [OH], but also [SO2]. By adjusting [OH] only, only reactions R1-R3 are important and production of H2SO4 becomes SO2 independent. Additionally, there is also the possibility that some H2SO4 vapor can be produced in the absence of OH and UV, via heterogeneous oxidation or dark oxidation processes on surfaces (including on nanopaticles)."

However, [H2SO4] produced without OH are much lower than the concentration (10ˆ6 - 10ˆ7 cm-3) we are using in the experiments and in most cases particles are not seen in the absence of OH and SO2, as shown in Figure 3 in (Benson et al., 2010a). In order to minimize such unknown, complex effects of SO2 on H2SO4 production, we kept SO2 constant.

-Discussions l.17. and Conclusions l.22.: "using the same instrument used in field

studies to measure particles (TSI CPC 3876)" It sounds that use of same instrument in laboratory experiment is somehow an advantage and makes the results more representative for the ambient atmosphere. Fact is, though, that in ambient air the particles grow and the particles are detected after their growth above some ∼3 nm. In lab system, if particles do not have time to grow above 3 nm they just are not detected. Formation rate at 3 nm in flow tube is not comparable to formation rate at 3 nm in atmosphere.

RESPONSE: We agree that the formation rate cannot be directly compared between flow tube studies and atmospheric measurements due to different times for growth. However the statement regarding "using the same instrument used in field studies to measure particles (TSI CPC 3876)" is meant to convey that it is important to compare studies using the same instrument so there is no bias due to having different measurement techniques. Sipilä et al. (2010) have shown particle counters with different detection efficiencies can produce different results. Recently (Kuang et al., 2010) have also shown quantitatively that there is one order of magnitude discrepancy in atmospheric nucleation rates between those calculated from the measurements using commercial TSI SMPS combined with "conventional" time difference method and those measured directly with diethylneglycol nano-DMA (based on a similar principle in Sipila's PSM) developed by McMurry and co-workers (Zhao et al., 2010). Therefore it is crucial to compare results using the same instrument to be able to make direct correlations between different studies. Especially considering the fact that at present there has been so far no intercomparison between these new type of cluster instruments, such as Sipilä's PSM, ion mobility spectrometer used in (Kulmala et al. 2007), and McMurry's diethylneglycol nano-DMA (Kuang et al., 2010; Zhao et al., 2010), the conclusions drawn with these instruments need further verifications.

-Data presented in this paper are conflicting with earlier data reported by the authors (Benson et al., 2008; Benson et al., 2009; Young et al., 2008): 1) Onset sulfuric acid concentrations are clearly lower, and 2) EF's reported in the present work are clearly

smaller as could be expected based on Benson et al., (2009) with exponentially increasing EF with lowering SA, and 3) the slopes are different. These differences and reasons for differences are not yet discussed appropriately.

RESPONSE: The main difference between the two studies is the flow reactor used for nucleation experiments. A detailed discussion of this is also given in (Benson et al., 2010a). We added this new paragraph in Discussion Section:

"There are also differences, especially in the threshold of H_2SO_4 and the slope, between the current and the early THN study (Benson et al., 2009). The main difference between the two studies is the flow reactor used for nucleation experiments, as discussed in a great detail in (Benson et al., 2010a). Because the flow reactor is much larger in the present study (I.D. 12.8 cm vs 5.08 cm previously), we had much higher residence times in the current study (up to 240 s). The difference in residence times will cause the slopes to be different so the behavior with respect to relative humidity may also be altered. The effect residence time has on the slopes is discussed more in detail in (Benson et al., 2010a). As for the differences in EF, in the previous study (Benson et al., 2009) it was shown that EFs increase exponentially with decreasing H_2SO_4 and the same trend was also found in the present study. From these results, one would expect that EFs in the current study should actually be higher due to lower H_2SO_4 used. However, because of the differences between these two studies (including larger I.D. for the nucleation region and higher residence times), direct extrapolation between the studies is inconclusive. It seems only when all conditions are the same that EFs are higher for lower H_2SO_4." Lines 179 – 193."

-Technical comments: monomer cannot evaporate, in references/citations: Antilla->Anttila, Boge -> Böge, Vehkamaki/Vekhamaki -> Vehkamäki, Plass-Dulmer-> Plass-Dülmer,.

ADDITIONAL REFERENCES: Benson, D. R., Erupe, M. E., Yu, J. H., Markovich, A., and Lee, S.-H.: Atmospheric Homogeneous Nucleation of H_2SO_4 and H_2O Atmo-

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