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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The formation of new particles in the atmosphere is still a hot topic in atmospheric science. Although in the last time there is a lot of progress open questions remain. The authors show experimental findings from a flow-tube experiment investigating the role of NH$_3$ additions for H$_2$SO$_4$/H$_2$O nucleation. H$_2$SO$_4$/H$_2$O is formed via the reaction of OH with SO$_2$. Experimental conditions are close to atmosphere, the residence time in the tube is in the range 60 – 240 sec. H$_2$SO$_4$ and NH$_3$ concentrations are obtained by means of a mass spectrometer. This manuscript is one of a series of papers by this group. A paper with similar topic was already published last year, Benson et al., GRL,
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) highlighting the differences between this study and the Benson 2009 study (2) addressing the growth processes in the tube, (3) discussion of how particle counting efficiency can affect the results, and (4) discussion of background of amines and organics.

Additionally, in our second manuscript (ACPD) on BHN involving H2O-H2SO4 (Atmospheric homogeneous nucleation of H2SO4 and H2O, 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 here are also addressed.

-1. I am very confused by comparing the data given in this manuscript with earlier results from the same group using more or less the same experimental approach. The only change in the setup seems to be the enlargement of the tube diameter from 2.54 or 5.08 cm to 13 cm at present. With the smaller tubes a H2SO4 concentration of 108-109 molecule cm$^{-3}$ was reported for a nucleation rate of unity (Young et al., ACP, 2008). But in this manuscript data are shown for $J = 1$ cm$^{-3}$ s$^{-1}$ for a few of $10^6$ molecule cm$^{-3}$ of H2SO4 (also in the absence of NH3 addition). Nothing is given in the manuscript explaining this discrepancy! Lowering of the importance of wall losses with the new tube cannot be the reason for this large difference, in the former studies the H2SO4 wall loss was intensively discussed by the authors.

RESPONSE: The reviewer's comment that “But in this manuscript data are shown for $J = 1$ cm$^{-3}$ s$^{-1}$ for a few of $10^6$ molecule cm$^{-3}$ of H2SO4 (also in the absence of NH3 addition)” is not correct, as we have mentioned clearly in our manuscript, it is unavoidable to have NH3 impurities from water vapor (Experimental Section, Lines 107 – 112). We have explained explicitly:
“One issue that must be taken into account in the nucleation experiments is the amount of NH3 that comes from the flow tube system, which was most likely originated from water vapor (Nowak et al., 2006). This background NH3, measured with CIMS, increased linearly with RH in the flow tube, but for RH from 6 – 40 %, the NH3 from water vapor in the flow tube was \(\sim 20 – 100\) pptv. These concentrations are actually similar to NH3 found in some remote areas (Dentener and Crutzen, 1994).

From this reason, it is possible that this NH3 can affect BHN results including the threshold of H2SO4 concentration and also the enhancement factor reported here is likely underestimated. We added this new paragraph in Discussion Section:

“There are also differences, especially in the threshold of H2SO4 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 H2SO4 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 H2SO4 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 H2SO4.” Lines 179 – 193

-2. The authors used for particle monitoring a TSI 3786 counter and they are stating that particles with a diameter > 3nm were detected. Assuming a critical cluster size of 1-1.5 nm a growth of about 1.5-2nm in diameter is needed. This cannot be explained by
106-107 molecule cm$^{-3}$ of H$_2$SO$_4$. A clear statement regarding the growth processes in the tube incl. the H$_2$SO$_4$ limited growth is needed.

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 H$_2$SO$_4$ condensation alone (1 nm hr$^{-1}$ at 107 cm$^{-3}$ H$_2$SO$_4$ (Erupe et al., 2010). Therefore it is possible that the background NH$_3$ present (e.g., $\sim$20 – 100 pptv at RH from 6 - 40% in our case) contributes to this growth even for the BHN case. At similarly low H$_2$SO$_4$ of $7 \times 10^6$ 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 NH$_3$ impurities in the system. As eliminating background NH$_3$ is unavoidable, on the other hand, any EF values found or given will actually be an underestimation due to pptv level NH$_3$ being present. This effect will be stronger at lower NH$_3$ 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 H$_2$SO$_4$ 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

In recently published papers (Sipilä et al., Science, 2010; Berndt et al., ACP, 2010; Brus et al., ACPD, 2010) the importance of high efficiency counters with a cut-size of about 1.5 nm for nucleation experiments with low growth times was clearly shown. Application of less efficient counting devices should result in an underestimation of total particle numbers and in an overestimation of the slope log(J) vs. log (H$_2$SO$_4$).
The authors are stating slopes of 3.6-4.6 being definitely higher than those given in the three papers above. On the other hand, the given values for J are close to (or somewhat higher than) the observation from the other experiments in literature. Also this topic should be discussed in this paper.

RESPONSE: We have cited (Brus et al., 2010; Sipilä et al., 2010) in the revised manuscript; please also see the above response. We agree that the efficiency of counting devices is important and can affect the measurement of total particle numbers. Underestimation due to a lower efficiency would cause the higher slopes of Log J vs. Log H2SO4. As shown in Figure 4a in (Benson et al., 2010a), when comparing our data to (Sipilä et al., 2010) we saw that for lower [H2SO4], our particle numbers were lower than their data, confirming that our particle counter had less efficiency for smaller sizes. However, because the different new cluster instruments, such as PSM used in the cited papers here by the review, 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, the conclusions made from these instruments need further verifications. Particle measurements are not the only factor that affects the slope. Besides the uncertainties in particle measurements, there are uncertainties in H2SO4 (reported from different studies, especially those not measured directly) which affect J values non-linearly, and therefore, the slope is also sensitively affected by H2SO4 measurements.

4. Was NH3 measured only at the entrance or also at the tube outlet? What was the NH3 loss in the tube?

RESPONSE: The [NH3] was measured only before the nucleation region (see Figure 1 in (Benson et al., 2010a)). But, there were no significant losses from where ammonia was introduced to where it was measured. For example, this 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 also clarified in the revised manuscript (Lines 93 – 101).

-5. It is stated that NH3 was flushed into the tube together with the water vapour resulting in NH3 mixing ratios of 20-100 pptv. What are the background concentrations of amines and organics in the flow tube? Especially in the case of amines, very low concentrations of these substances can clearly influence nucleation.

RESPONSE: We currently have only measured background concentrations of NH3. Initially, we tried to measure the concentration of amines (Erupe et al., 2010). (Benson et al., 2010b) explains more about CIMS instrument background). We also have found that even when the flow tube is purged with nitrogen, there was still 17 pptv amines (which could originate from deionized water since the RH was 6 %), as included in revised manuscript (in Experiments Section). There is no other sources of organics from are experiments the setup should be free of organics. This is because 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 organics-free (Benson et al., 2010a; Young et al., 2008). In the future we do plan to take more extensive measurements of both NH3 and amines using the CIMS as these compounds are of more importance in terms of background concentrations of any possible trace species.

-From my point of view a main revision is needed.


Interactive comment on Atmos. Chem. Phys. Discuss., 10, 22395, 2010.