

Interactive comment on “Ternary homogeneous nucleation of H₂SO₄, NH₃, and H₂O 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 NH₃ additions for H₂SO₄/H₂O nucleation. H₂SO₄/H₂O is formed via the reaction of OH with SO₂. Experimental conditions are close to atmosphere, the residence time in the tube is in the range 60 – 240 sec. H₂SO₄ and NH₃ 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,

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2009.

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 $J = 1 \text{ cm}^{-3} \text{ s}^{-1}$ for a few of 10⁶ 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 $J = 1 \text{ cm}^{-3} \text{ s}^{-1}$ for a few of 10⁶ 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:

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“One issue that must be taken into account in the nucleation experiments is the amount of NH_3 that comes from the flow tube system, which was most likely originated from water vapor (Nowak et al., 2006). This background NH_3 , measured with CIMS, increased linearly with RH in the flow tube, but for RH from 6 – 40 %, the NH_3 from water vapor in the flow tube was $\sim 20 - 100$ pptv. These concentrations are actually similar to NH_3 found in some remote areas (Dentener and Crutzen, 1994).”

From this reason, it is possible that this NH_3 can affect BHN results including the threshold of H_2SO_4 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 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

-2. The authors used for particle monitoring a TSI 3786 counter and they are stating that particles with a diameter $> 3\text{nm}$ 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

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106-107 molecule cm⁻³ of H₂SO₄! A clear statement regarding the growth processes in the tube incl. the H₂SO₄ 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 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., ~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 7×10^6 cm⁻³, (Berndt et al., 2005, 2006) have also seen a ~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

-3. 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 (H₂SO₄).

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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 $\text{Log } J$ vs. $\text{Log H}_2\text{SO}_4$. As shown in Figure 4a in (Benson et al., 2010a), when comparing our data to (Sipilä et al., 2010) we saw that for lower $[\text{H}_2\text{SO}_4]$, 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 H_2SO_4 (reported from different studies, especially those not measured directly) which affect J values non-linearly, and therefore, the slope is also sensitively affected by H_2SO_4 measurements.

-4. Was NH_3 measured only at the entrance or also at the tube outlet? What was the NH_3 loss in the tube?

RESPONSE: The $[\text{NH}_3]$ 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 NH_3 to the port labeled $\text{N}_2/\text{H}_2\text{O}$ (before the flow is centered) we see that the NH_3 is the same as if we added it directly before the NH_3 -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.

ADDITIONAL REFERENCES: Benson, D. R., Erupe, M. E., Yu, J. H., Markovich, A., and Lee, S.-H.: Atmospheric Homogeneous Nucleation of H₂SO₄ and H₂O Atmospheric Chemistry & Physics Discussion, 10, 29051-29073, 2010a.

Benson, D. R., Markovich, A., Al-Refai, M., and Lee, S.-H.: A Chemical Ionization

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Mass Spectrometer for ambient measurements of Ammonia, Atmospheric Measurement Techniques, 3, 1075-1087, 2010b.

Berndt, T., Boge, O., Stratmann, F., Heintzenberg, J., and Kulmala, M.: Rapid formation of sulfuric acid particles at near atmospheric conditions, Science, 307, 671-698, 2005.

Berndt, T., Boge, O., and Stratmann, F.: Formation of atmospheric H₂SO₄/H₂O in the absence of organics: A laboratory study, Geophys. Res. Lett., 33, L15817, doi:15810.11029/12006GL026660, 2006.

Berndt, T., Stratmann, F., Sipilä, M., Vanhanen, J., Petaja, T., Mikkilä, J., Gruner, A., Spindler, G., Mauldin III, R. L., Curtius, J., Kulmala, M., and Heintzenberg, J.: Laboratory study on new particle formation from the reaction OH + SO₂: influence of experimental conditions, H₂O vapour, NH₃ and the amine tert-butylamine on the overall process, Atmospheric Chemistry and Physics, 10, 7101-7116, 2010.

Brus, D., Hyvarinen, A.-P., Viisanen, Y., Kulmala, M., and Lihavainen, H.: Homogeneous nucleation of sulfuric acid and water mixture: experimental setup and first results, Atmospheric Chemistry and Physics, 10, 2631-2641, 2010.

Dentener, F. J., and Crutzen, F.: A three-dimensional model of the global ammonia cycle J. Atmos. Chem., 19, 331-369, 1994.

Erupe, M. E., Viggiano, A. A., and Lee, S.-H.: The effect of trimethylamine on atmospheric nucleation involving H₂SO₄, Atmospheric Chemistry and Physics Discussions, 10, 27673-27693, 2010.

Kuang, C., Wang, J., and McMurry, P. H.: Measurements of Newly Formed 1 – 3 Nanometer Particles Using a High-Time Resolution Nanoparticle Size Spectrometer. AAAR 29th Annual Conference, Portland, Oregon, 2010.

Kulmala, M., Riipinen, I., Sipilä, M., Manninen, H. E., Petäjä, T., Junninen, H., Dal Maso, M., Mordas, G., Mirme, A., Vana, M., Hirsikko, A., Laakso, L., Harrison, R. M., Hanson, I., Leung, C., Lehtinen, K. E. J., and Kerminen, V.-M.: Toward Direct

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10, C12392–C12399,
2011

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Interactive Discussion

Discussion Paper



Measurement of Atmospheric Nucleation, *Science*, 318, 89-92, 2007.

Sipilä, M., Berndt, T., Petäjä, T., Brus, D., Vanhanen, J., Stratmann, F., Patokoski, J., Mauldin, R. L. I., Hyvärinen, A.-P., Lihavainen, H., and Kulmala, M.: The Role of Sulfuric Acid in Atmospheric Nucleation, *Science*, 327, 1243 - 1246, 2010.

Vehkamäki, H.: Molecular Modeling of Atmospheric Clusters. 2010 International Aerosol Conference, Helsinki, Finland, 2010.

Young, L. H., Benson, D. R., Rifkha, F., Pierce, J. R., Junninen, H., Kulmala, M., and Lee, S.-H.: Laboratory studies of sulfuric acid and water binary homogeneous nucleation: Evaluation of laboratory setup and preliminary results, *Atmos. Chem. Phys.*, 8, 1-20, 2008.

Zhao, J., Eisele, F. L., Titcombe, M., Kuang, C., and McMurry, P. H.: Chemical Ionization Mass Spectrometric Measurements of Atmospheric Neutral Clusters using the Cluster-CIMS, *Journal of Geophysical Research*, 115, D08205, 2010.

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

ACPD

10, C12392–C12399,
2011

Interactive
Comment

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