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Atmospheric
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Interactive comment on “Atmospheric homogeneous nucleation of H_2SO_4 and H_2O” *by* D. R. Benson et al.

Anonymous Referee #3

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The paper reports laboratory results on homogeneous nucleation of H2SO4 and H2O under atmospherically relevant concentrations. The paper is revising previous findings by the group (Benson 2008, Young 2008), observing nucleation at lower H2SO4 threshold concentrations, due to modifications at the experimental setup (e.g. better RH control, longer residence times, nozzle to introduce the vapor in the center of the flow tube). H2SO4 and NH3-background concentrations are measured directly by CIMS, which is certainly the strength of the paper. However, a CPC (TSI3786) - cut off between 2.5 and 3nm -is used for particle detection. As outlined in Sipilä et al. (2010) and Berndt et al. (2010) the results might therefore be biased by the insufficient detection efficiency of the CPC and the limited residence time in flow tubes (nucleated particles do not have the time to grow to 3nm, thus are not detected). This would affect the slopes in the log(J) vs. log(H2SO4) plots and therefore the main result of the paper (critical cluster consists of 4-5 H2SO4 molecules). This is an important and crucial point and needs further verification before the paper is published in ACP.

Major comments: 1. To overcome these problems mentioned above (Sipilä et al. 2010) the authors argue that the real particle growth rate (GR) in their system is substantially higher (28nm/h) than expected from condensation of H2SO4 (1nm/h). Ammonia background concentrations might be responsible for the “observed” high growth rates (meaning: 1nm/h explained by H2SO4, 27 nm/h explained by NH3). It seems very unlikely that NH3 (20-100ppt) can explain such high GR. First of all, in a study by Zhang et al (2009) it was shown that NH3 (3×1014 molecule cm-3) contributed negligible to growth of freshly nucleated particles. And second, atmospheric observations typically report particle growth rates of 2-5nm/h in the presence of much higher NH3 concentrations (e.g. 1-10ppb of ammonia; Pryor et al., 2010). This leads to the following questions/conclusions: a. Is the system contaminated with other low volatile species that grow the particles to 3nm? What are those species? Do those species affect nucleation or only contribute to growth? Is it still homogeneous nucleation of sulfuric acid? b. Or are the results indeed biased by the issues reported in Sipilä et al. (2010) and therefore the slopes and critical cluster sizes are wrong? 2. Related to the same issue: In the response to the comments of reviewer 1 you state, “If values closer to the collision frequency are used, growth rates would be at least 40 nm hr-1”. Could you please provide the detailed calculations and references to support the statement? This would be a major step forward. 3. The technical improvements seem to be the key to the new results. More detailed information –similar to Young et al. (2008) - would be very valuable to assess the individual modifications e.g. The H2SO4 concentration profile in the flow tube? What is the effect of the “nozzle” on the H2SO4 profile or the nucleation region? Inhomogeneous air mixing as stated on page 29059? Minor comments: 29054: Sipilä et al. (2010): If I remember correctly, two type of new particle detectors have been used (PSM + pulse height CPC)! 29054 line 22/23: “While the BHN study by (Sipilä et al., 2010) successfully reproduced the slope of Log J vs. Log [H2SO4] derived from field studies (1 – 2) (Kulmala et al., 2004).” Kulmala et al (2004) is probably the wrong reference! P29055, Line 17-19: “this allows for an ozone-free system and so provides an advantage compared to other studies where OH was produced from ozone photolysis (Berndt et al., 2005, 2006; Sipilä et al., 2010).” Please explain what the advantage of Ozone free experiments should be? P29056: “20-100pptv” NH3: In Benson et al. (2010b) a 1min-detection limit of 60ppt is reported for the Ammonia-CIMS - mainly limited by chemical noise. How did you derive the 20 ppt background concentration? (longer integration times?) P29058: “Here, we make a correction that these initial [H2SO4] should be a factor of 4.6 lower (due to the 2.3 times lower k3 and the 2 times lower ion molecule reaction time) than the reported values, but this error does not affect the main conclusions of these papers, because of the high WLFs (up to 30).” Could you please explain why k3 (SO3+H2O=H2SO4) is a factor of 4.6 lower and please explain the “2 times lower ion molecule reaction time”. P29059: “It is also possible that inhomogeneous air mixing was present in the nucleation reactor which could affect our WLF measurements. In the future, we plan to investigate flow dynamics in the air mixing region and the nucleation reactor, in order to understand how different flow conditions affect nucleation experimental conditions.” As stated above the technical details should be assessed more rigorously. E.g. Is there inhomogeneous air mixing. If yes, how does this affect the derived H2SO4 concentrations, nucleation rates, etc. P29059, Line 20: “measured [H2SO4]”. Measured, at the entrance or the end section of the flow tube? P29060: The NH3 background concentration is a strong function of RH. Ammonia has an effect on nucleation. Moreover, if it is the dominating species for the particle growth please explain how you can measure any meaningful nucleation rates at different RH and any meaningful dependence of J on RH. Minor comments and technical comments: Please update the format of in-text-citations: e.g. 29053, line 25: (Berndt et al. 2005) should read Berndt et al. (2005), and so on throughout the whole manuscript! Also e.g. p29053, Line 25: “(Berndt et al., 2010;Kurten et al., 2008; Smith et al., 2009) and (Erupe et al., 2010b)” should read (Berndt et al., 2010;Kurten et al., 2008; Smith et al., 2009;Erupe et al., 2010b).

References: Benson, D. R., L. H. Young, et al. (2008). "Laboratory-measured nucleation rates of sulfuric acid and water binary homogeneous nucleation from the SO2+OHreaction." Geophysical Research Letters 35(11). Berndt, T., Stratmann, F., Sipilä, M., Vanhanen, J., Petäjä, T., Mikkilä, J., Grüner, A., Spindler, G., Lee Mauldin III, R., 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, Atmos. Chem. Phys., 10, 7101-7116, doi:10.5194/acp-10-7101-2010, Pryor, S. C., Barthelmie, R. J., Sørensen, L. L., McGrath, J. G., Hopke, P., and Petäjä, T.: Spatial and vertical extent of nucleation events in the Midwestern USA: insights from the Nucleation In ForesTs (NIFTy) experiment, Atmos. Chem. Phys. Discuss., 10, 23287-23344, doi:10.5194/acpd-10-23287-2010, 2010. Sipila, M., T. Berndt, et al. (2010). "The Role of Sulfuric Acid in Atmospheric Nucleation." Science 327(5970): 1243-1246. Young, L. H., D. R. Benson, et al. (2008). "Laboratory studies of H2SO4/H2O binary homogeneous nucleation from the SO2+OH reaction: evaluation of the experimental setup and preliminary results." Atmospheric Chemistry and Physics 8(16): 4997-5016. Zhang, R., L. Wang, et al. (2009). "Formation of nanoparticles of blue haze enhanced by anthropogenic pollution." Proceedings of the National Academy of Sciences 106(42): 17650-17654.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 29051, 2010.