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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.

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Response to Dr. F. Khosrawi's interactive discussion comment

Benson et al. present laboratory measurements of the binary homogeneous nucleation of H2SO4 and H2O which are quite important for understanding the binary homogeneous nucleation of H2SO4 and H2O in the atmosphere. However, I am somewhat dissapointed about the present study. In their previous studies Benson et al. discussed measurements and showed very interesting results on the binary homogeneous nucleation, but here solely laboratory measurements are shown and the entire study is rather a technical than a scientific one.

General RESPONSE: It is correct that in the current paper, we discuss mainly technical issues raised in BHN lab studies, as stated in Abstract and throughout the manuscript. This is because there are several technical issues and challenges and limitations in homogeneous nucleation lab experiments, and it is important to properly address these issues and understand their implications and resolve them, and this will help us to make correct comparisons between different lab studies and between lab studies and atmospheric field observations. This has become increasingly important when considering the fact that there are some misunderstandings and misinterpretation of experimental data, which causes or even intensifies "mystery", "dilemma" or "puzzles" and generates some prompt attempts to solve them hurryingly.

First of all I am wondering why Benson et al. do not use any atmospheric measurements together with their laboratory measurements?

RESPONSE: As we have stated in our paper, we believe that directly comparing lab BHN results with ambient nucleation observations, with the current knowledge of the field, would not bring significant insights into the field. For example, as we have stated: "There is a difference in the method used to make these slopes in the laboratory studies and field observations. The atmospherically derived slopes are usually from ensemble data obtained at various RH and temperatures and different saturation ratios of possible ternary precursors (which are unknown currently). On the other hand, laboratory values are derived from the data taken under a constant temperature and RH, and presumably in the absence of, or at least in the possibly lowest amount of, ternary species in the binary case. Such a difference has been neglected when comparing the slopes derived from field and laboratory studies. Perhaps, a more rigorous approach directly applying the first nucleation theorem in atmospheric observations is needed."

Further, it is not clear what the goal of this study is and what is new compared to previous studies, e.g. there has just a few months earlier a study on laboratory measurements of the nucleation of sulfuric acid and water in ACPD being published by Brus et al. (2010). It would be worth if Benson et al. would discuss what the differences between their study and the study by Brus et al. (2010) are.

RESPONSE: Again, our goal is to discuss technical issues raised in BHN lab studies and provide new results taken at H2SO4 at the range from 10ˆ5 to 10ˆ7 cm-3. The Brus et al. (2010) paper came out at ACPD within the same week as our manuscript and we plan to include this new paper in our revision.

Benson et al. state that their measurements of nucleation are made for atmospheric relevant conditions. However, the sulfuric acid concentrations used in this study are only representative for clean air. Air masses in the boundary layer are quite often polluted and thus polluted conditions should be also considered under atmospheric relevant conditions. Measurements have shown that in polluted air H2SO4 concentrations can reach up to 108 cm−3 (Weber et al., 2001, Berresheim et al., 2002, Bardouki et al., 2003; Weber et al., 2003, Mauldin et al., 2002).

RESPONSE: Atmospheric H2SO4 is usually at 10ˆ5-10ˆ7 cm-3 (noontime peak). Lower range of 10ˆ8 cm-3 (highest 2 x 10ˆ8 cm-3 at noontime peak) is possible but very rare and only for very for short time span. This includes the cases both in clean and pollution conditions. This is because as H2SO4 chemistry shows, H2SO4 molecules have very short atmospheric lifetimes (10-20 minutes), and especially in the polluted region H2SO4 would instantly be scavenged to large surface area pre-existing aerosols, as shown by observations and models (e.g., Chen et al., JGR 2005; McMurry et al., JGR 2005). Therefore, even in the polluted condition, H2SO4 noontime peak would be at the middle 107 cm-3 level at highest. This is also actually systematically shown in the papers mentioned by Dr. Khoswari above. All these cited studies consistently show (either in figures and tables) that their noontime H2SO4 noonpeaks are in 10ˆ6-10ˆ7cm-3 range, with the maximum values of (1-2) x 108 cm-3 (also very occasionally shown by spikes). Also in our previous BHN studies, these papers were actually on the 10ˆ8 cm-3 H2SO4 range (Benson et al., GRL 2008; Young et al., ACP 2008).

Chen et al., An investigation of the chemistry of ship emission plumes during ITCT 2002, JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 110, D10S90, doi:10.1029/2004JD005236, 2005

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McMurry, et al. A criterion for new particle formation in the sulfurâĂŘrich Atlanta atmosphere, J. Geophys. Res., 110, D22S02, doi:10.1029/2005JD005901, 2005

Further, covering atmospheric relevant conditions would also mean to perform the laboratory measurements under different temperatures and humidities relevant for the atmosphere as it was done by e.g. Brus et al. (2010) and not just at one temperatures as it was done by Benson et al. This is rather a snapshot and only represents certain conditions in the atmosphere and not a set of atmospheric relevant conditions.

RESPONSE: Our RH ranged from 6-40% (Figure 1) representing one of the largest RH ranges amongst published BHN lab studies, with H2SO4 ranges from 10ˆ5-10ˆ7 cm-3. Temperature dependence is an important aspect, but this is not the focus of our current study.

Some detailed comments on the manuscript text:

P29052, L2: As stated above clean air sulfuric acid concentrations and only one temperature do not represent all atmospheric relevant conditions. Different temperatures, relative humidities and higher sulfuric acid mixing ratios should be taken into account. As stated above measurements of H2SO4 show that concentrations can reach up to 108 cm−3. Further, the binary homogeneous nucleation is strongly dependent on temperature and humidity and different values applied for the measurement surely will change the results.

RESPONSE: Please see the above response.

Abstract in general: It should be more clearly pointed out what the goal of this study is what the differences concerning previous studies are and what is new in this study compared to previous studies.

RESPONSE: Please see above responses. The difference between the current and previous studies is mainly at different H2SO4 concentrations and different setup.

P29052, L8: I am not convinced of this statement. I do not believe that only getting a

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higher slope in the nucleation rate vs. H2SO4 is an indicator for the need of ternary aerosol precursor to reduce the slope in the atmosphere. This should be discussed more clearly and probably compared with atmospheric measurements. How does you know that this slope difference is not caused by errors in the measurements?

RESPONSE: It is not clear why “only getting a higher slope in the nucleation rate vs. H2SO4 is an indicator for the need of ternary aerosol precursor to reduce the slope in the atmosphere”. To show differences in slope, we have specifically included standard deviations of x and y axes in Figures 4a and 4b.

Another general question: Dynamical effects in the boundary layer can also strongly affect the nucleation of sulfuric acid and water. Can such processes be treated in laboratory measurements? If yes, how is it done?

RESPONSE: How atmospheric dynamics affect boundary layer nucleation is not the focus of our current laboratory study.

P29053, l5: That nucleation is a non-linear process has been known since at least a decade, thus the reference of Lee et al. (2003) is here not adequate or should, if cited, be cited with adding e.g. The non-linear behaviour goes back to publications by Easter and Peters (1994), Bigg et al. (1997) and Nilsson and Kulmala (1998). I not know sure which is the correct references, but this fact is known since that time the mentioned publications were published or even earlier than that.

RESPONSE: We will include an appropriate reference on nonlinearity.

P29063, l6: Binary homogeneous nucleation is not that often occurring in the boundary layer. As was stated by Weber et al. (1999) observations of particle formation can be well explained by the binary homogeneous nucleation of H2SO4 and H2O above 4 km.

RESPONSE: Assuming that ”Binary homogeneous nucleation is not that often occurring in the boundary layer” is a correct statement, then we don’t need to consider those polluted conditions with higher H2SO4 concentrations.. In fact, recent lab studies (e.g.,

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Sipila et al., 2010) have shown that BHN is possible in boundary layer conditions. Weber et al., (1999) conclusion was based on classical homogeneous nucleation theory, which is now known to be incorrect. (There are also a large group of publications similar to Weber et al., 1999 study). But, this does not mean Weber et al.'s conclusion is incorrect – rather this implies that we need more experiments to understand the BHN process. This is the reason we present the current study.

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Weber, R. J. et al. (1999), New particle formation in the remote troposphere: A comparison of observations at at various sites, Geophys. Res. Lett., 26, 307-310.

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Weber, R. J. et al. (2001), Nucleation in the equatorial Pacific during PEM-Tropics B: Enhanced boundary layer H2SO4 with no particle production, J. Geophys. Res., 106, D23, 32,767-32,776.

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