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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.

D. Benson et al.

dbenson2@kent.edu

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Sulfuric acid - water nucleation, and the effect of ammonia (or other third components) on it, is one of the most popular atmospheric physics/chemistry research topic of the past decade. Despite the large amount of pre-existing literature, there are still surprisingly large gaps in both the experimental and theoretical evidence. For example, most (though not all) experimental studies are typically performed with sulfuric acid concentrations considerably larger than those found in the atmosphere. This study helps fill those gaps, and is therefore worthy of publication in ACP. However, a number of issues in the manuscript need to be resolved first. Some comments:

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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 nucleation tube, (2) highlighting the differences between this study and the Benson et al. 2009 study, and (3) the effect of residence time on the results. 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.

-The THN parameterizations that include the formation of stable ammonium bisulfate monomers (NH4HSO4) are artifacts of the liquid drop model thermodynamics, which fails catastrophically for this particular system due to the implicit assumption of bulk proton transfer (and the corresponding under-prediction of the evaporation rate by over 10 orders of magnitude compared to high-level computational data). See e.g. the IAC 2010 plenary talk abstract by Vehkamäki (available online at http://www.atm.helsinki.fi/IAC2010/abstracts/abstbook.html) for discussion on this. So it is not very surprising that classical models have difficulties to match experimental observations on sulfuric acid - ammonia - water nucleation, typically tending to over-predict the effect of NH3 unless drastically scaled or corrected by empirical terms. This might be mentioned in the discussion of THN models and experiments in the introduction.

RESPONSE: We agree and have included this in our introduction:

"Later THN parameterizations included the effects of stable ammonium bisulfate (NH4HSO4) formation (Antilla et al., 2005; Merikanto et al., 2007) to match the available laboratory THN observations in the NH3 range from $0 - 170$ pptv (Ball et al., 1999); but these parameterizations also fail quite drastically due to overestimation of the degree of proton transfer from bulk liquid properties (Vehkamäki, 2010) $L49 - 54$."

-As in many other nucleation studies, the first nucleation theorem is applied a bit too enthusiastically and uncritically. The simplest formulation of the theorem (slope of log J versus log [X] gives the number of X in the critical cluster) only applies in an idealized case where the N-dimensional (where N is the number of compounds, e.g. 3 in this case) free energy surface has precisely one saddle point, corresponding to the critical cluster, and no minima, at least not on the nucleation path. For a chemically complicated real system like sulfuric acid - ammonia - water, it is likely that there exist local minima (and possibly local maxima) smaller than the actual critical cluster. (They are explicitly known to exist for the case of sulfuric acid hydrates, which can fortunately be fairly simply corrected for in the theory.) In this case, the log J versus log [X] slopes will not directly correspond to the number of molecules of X in the critical cluster. For example, if there exists a local minimum cluster, smaller than the critical cluster, and containing one or more ammonia molecules, then the critical cluster may well contain more than one ammonia despite a log J versus log [NH3] slope of one. This is not to say that the slope information is useless - it is still definitely valuable information - but a note of caution on the interpretation of the slope data would be warranted. (And statements like 'The slope of Log J vs. Log RH, which is the same as the number of water molecules (nH2O) in critical clusters' are definitely overconfident, and should be rephrased!)

RESPONSE: We agree that directly applying the first nucleation theorem can be an issue due to lots of limits associated with it as the referee points out. The goal of our experiments is to provide observation data that can be used to develop new, more appropriate theories, but there is lacking such new theories found in the literature. We have rephrased the appropriate areas in the manuscript to reflect that it is not an exact interpretation:

"„, based on the first nucleation theorem by assuming the free energy surface has only one saddle point and no minima (Kashchiev, 1982; McGraw and Zhang, 2008)." (L130 – 132 in revised manuscript)

-The real main charging ion in the CIMS setup is known to be NO3−(HNO3), not NO3−. This should be explicitly mentioned.

RESPONSE: While NO3−(HNO3) may be the main charging ion, because of the CDC this ion (as well as any other cluster ions) is broken down to NO3- and this is the only reagent signal we see. This has been discussed in detail in (Erupe et al., 2010a) and (Benson et al., 2010). For example, in (Benson et al., 2010) in Experimental Section (Pages 29057-29058):

"[H2SO4] were detected with CIMS, using the following ion-molecule reaction: NO3- + H2SO4 → HNO3 + HSO4- (R5) at atmospheric pressure, using 210Po as the ion source (Benson et al., 2009; Benson et al., 2008; Eisele and Tanner, 1993; Erupe et al., 2010b; Young et al., 2008). The CIMS can detect [H2SO4] as low as 105 cm-3. The rate constant of R5 (k5) is 2.32 × 10-9 cm3 s-1 with a factor of 2 uncertainties (Viggiano et al., 1997); the ion-molecule reaction time was 0.1 s. As discussed in (Erupe et al., 2010b), it is also possible that in the ion molecule reaction region, NO3- ions can make clusters, such as NO3-âŰł(HNO3)m, where m = 1, 2, 3. . . etc., and NO3-âŰł(H2O)n, and n = 1, 2, 3. . . etc. Laboratory measurements have showed that these clusters also react with H2SO4 to produce corresponding clusters (Viggiano et al., 1997): NO3-âĂć(HNO3)m + H2SO4 → HNO3 + HSO4-âĂć(HNO3)m (R6) NO3-âĂć(H2O)n + H2SO4 → HNO3âĂć(H2O)m + HSO4-âĂć(H2O)n-m (R7) But their reaction rates, k6 and k7, are approximately 1.8 × 10-9 cm3s-1, very similar to k5 (Viggiano et al., 1997). A collision dissociation chamber (CDC) was also used to effectively dissociate these clusters in our CIMS. Therefore, the presence of possible clusters of ion reagents would not affect the CIMS sensitivity. This is the case for the gas phase H2SO4 detection, but for the measurements of atmospheric neutral or charged clusters containing H2SO4, these ion reagent clusters can affect the mass peak identification and the instrument sensitivity of individual H2SO4 clusters sampled from ambient air."

-The authors are certainly correct when they claim that 'quantum chemical calculations'...' show that a monomer [sic] or dimer of H2SO4 would spontaneously evaporate

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and is difficult to form critical clusters by themselves'. However, none of the three papers that they then cite actually contain original quantum chemical data. It would be appropriate to cite the original sources; certainly there is no shortage of computational data on H2SO4 dimers and trimers, as close to 20 papers with data on this have been published so far (starting from Kurdi and Kochanski in 1989, and continuing to the ongoing work of the Yu and Kulmala groups today).

RESPONSE: We have cited the original source (Kurdi and Kochanski, 1989).

-The authors use the quantum chemical results (showing that pure sulfuric acid dimers evaporate quickly) to argue for a higher nH2SO4 slope than 2. But that just shows that the nucleating substance is not pure H2SO4 - e.g. the evaporation of sulfuric acid from a cluster containing a base molecule (such as ammonia or amines) is already much lower. Even the presence of just one ammonia molecule (which even this study supports) will change the situation significantly. So while the statement ('quantum chemical calculations...show') is correct, it does not necessarily support the authors' claim that the slope should be much higher than 2.

RESPONSE: There are two points convoluted each other. First point is whether we discuss ternary nucleation vs. binary nucleation, and the referee's comments are correct that a ternary species would make the slope of Log J vs. Log H2SO4 smaller. The second point is looking at binary nucleation in terms of laboratory vs. ambient measurements. Laboratory measurements are restricted in terms of holding all parameters constant except [H2SO4], whereas for ambient measurements, these restrictions are not followed, as there are wide fluctuations in RH, temperature and other parameters, as discussed in (Benson et al., 2010) – also see blow. Also, ambient measurements may have ternary species present which we cannot detect or are not even aware of their identities this moment. So, for BHN, this shows that slopes have to be greater than 3. We have rephrased the appropriate area in the manuscript:

"The slopes $(3 - 5$, as compared to $1 - 2)$ found in BHN are, however, thermody-

namically consistent with quantum chemical calculations which show that a dimer of H2SO4 would spontaneously evaporate and is difficult to form critical clusters by themselves (Kurdi and Kochanski, 1989). These results also indicate that other condensable species (ammonia, amines or organics) leading to THN would have to explain a slope of $1-2$ found in the atmosphere." (L212 − 217)

Additionally, we have stated in (Benson et al., 2010) in Discussion Section (Pages 29061-29062):

"Our slope taken from laboratory studies is higher than those found from the atmospheric observations $(1-2)$ (Erupe et al., 2010a; Kulmala et al., 2004). 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 to better understand the chemical composition of critical clusters in the atmosphere."

-In the abstract, the authors claim that the enhancement factor EF (by ammonia) 'increases exponentially with decreasing H2SO4 and RH'. Yet later, on lines 163-164, it is claimed that high EFs require HIGH H2SO4, namely: 'Most EF values were largest at three orders of magnitude for H2SO4 from 108 −1010 cm−3'. This seems very inconsistent. Must one set of data be wrong? Or is there some other explanation for the difference?

RESPONSE: Valuable comment. We added a new paragraph:

"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." (L187 – 195)

-The authors correctly note that there is always some background (sometimes below detection limit) NH3 in any measurement system. As this background NH3 may still influence nucleation, the conclusions drawn from the effects of increasing NH3 from this background may not necessarily reflect the full effect or role of NH3 in nucleation. On the other hand, for parameterization purposes this probably doesn't matter that much since such background NH3 is likely present almost everywhere in the atmosphere.

RESPONSE: We added:

"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" (Lines 168 – 170).

-I'm not convinced that this study is free of the issues and problems described by Sipilä et al (2010). The residence time in the tube used in this experiment is longer (240 s) than in many other experiments, but do the nucleating (or nucleated) clusters still have time to grow to the detection limit (3nm in this setup) during this residence time, especially for the lower H2SO4 concentrations? Explicit calculations showing that the clusters do have time to grow to detectable sizes even for [H2SO4] in the 106...107 range would be necessary for the results to be believable. (The collision rate of H2SO4 with the clusters as a function of H2SO4 concentration is well known, and upper-limit estimates for growth are easily obtained by ignoring evaporation.) Otherwise the high slopes may simply be an artifact, as described by Sipilä et al. Note that this problem

is in addition to the general problem with slope interpretation described above. On the other hand, the main conclusions concerning the role of ammonia - which are probably the main new result of this study - may still be valid even if the slopes with respect to sulfuric acid are artificially large.

RESPONSE: We added the following two paragraphs in Discussion Section:

"It is important to know the kind of growth processes that can occur in the flow tube (Benson et al., 2010; Berndt et al., 2010; Brus et al., 2010; Sipilä et al., 2010). As also discussed in (Benson et al., 2010), 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 $\times$ 106 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)

-Can the authors suggest a reason for the difference in behavior (of e.g. nH2SO4) with respect to relative humidity (lines 107-110) compared to the Benson 2009 study? Is there some difference in setup that is likely to have caused this difference?

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RESPONSE: We added a new paragraph:

"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., 2010). 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., 2010)." L179 – 186

-On line 180, the estimated nNH3 of one is said to be 'consistent with cluster measurements by (Hanson and Eisele, 2002)'. However, these measurements were made on negatively charged clusters, from which ammonia molecules tend to evaporate quite rapidly, at least if the clusters are small. This is actually explicitly noted in the same Hanson and Eisele paper. Thus, conclusions about the likely ammonia content of the neutral clusters nucleating in this study can NOT be drawn from the measurements on small charged clusters. (This is not to say that the result of nNH3 = 1 is wrong. It may, or may not be, correct - the only claim I'm making here is that charged cluster measurements do not really predict anything about neutral cluster nNH3, except possibly a lower limit.)

RESPONSE: The (Hanson and Eisele, 2002) measurements were made on neutral clusters. The charged clusters they refer to are the reactions occurring in the CIMS which produce ions to be measured by the mass spectrometer.

-The discussion of NH3 as a "catalysis agent" (lines 182-188) is very likely correct. NH3 acts to "pull" further H2SO4 molecules into the cluster, and hence doesn't actually "nucleate" by itself (this is actually quite obvious from the vapor pressure of pure NH3). However, note that the 'energy reduction due to exothermic heat released from the

acid-base neutralization reaction' is just another way of expressing the same chemical mechanism, not really a separate phenomenon.

RESPONSE: Actually the two mechanisms are different because the catalyst mechanism would affect the system kinetically while the energy reduction implicates thermodynamic effect.

-Apparently different experiments were done with varying residence times. This is not made very clear in the text - various residence times are quoted seemingly randomly. Some coherent discussion on the effect of residence time would help a non-expert reader. Especially as the residence time may crucially affect the slopes as noted by Sipilä et al (2010)...

RESPONSE: Please see the above comments, with regard to residence time.

-In the main text, the authors show that the sulfuric acid and water content of the critical cluster (obtained by a rather uncritical application of the nucleation theorem, see above) does not "change drastically" by the addition of NH3. This seems reasonable. However, in the abstract, the much stronger statement 'The composition of H2SO4 and H2O in critical clusters and the threshold of H2SO4 concentrations required for the unit nucleation rate both do not vary in the presence and absence of NH3.' This statement is too strong, and is not supported by the presented data. As many people tend to read only the abstract, this statement must be rephrased.

RESPONSE: We agree that this statement is too strong and have rephrased this in the abstract: "„ vary only fractionally in the presence and absence of NH3."

Technical corrections:

"Antilla" in the references should read "Anttila". Corrected

-On line 154, the authors talk about a "monomer or dimer" of H2SO4 spontaneously evaporating. Surely they mean "dimer or trimer" - how does a monomer evaporate from itself? Corrected

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, 2010.

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., Sipila, M., Vanhanen, J., Petaja, T., Mikkila, 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.: Homogenous 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

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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 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.

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

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