**Atmospheric
Chemistry
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Discussions**

Interactive comment on "Ternary homogeneous nucleation of H_2SO_4, NH_3, and H_2O under conditions relevant to the lower troposphere" *by* D. Benson et al.

Anonymous Referee #1

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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:

-The THN parameterizations that include the formation of stable ammonium bisul-

fate monomers (NH_4HSO_4) are artefacts 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 underprediction 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 NH_3 unless drastically scaled or corrected by empirical terms. This might be mentioned in the discussion of THN models and experiments in the introduction.

-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 [NH_3] 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 (nH_2O) in critical clusters' are definitely overconfident, and should be

rephrased!)

-The real main charging ion in the CIMS setup is known to be $NO_3^-(HNO_3)$, not NO_3^-. This should be explicitly mentioned.

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

-The authors use the quantum chemical results (showing that pure sulfuric acid dimers evaporate quickly) to argue for a higher nH_2SO_4 slope than 2. But that just shows that the nucleating substance is not pure H_2SO_4 - 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.

-In the abstract, the authors claim that the enhancement factor EF (by ammonia) 'increases exponentially with decreasing H_2SO_4 and RH'. Yet later, on lines 163-164, it is claimed that high EFs require HIGH H_2SO_4, namely: 'Most EF values were largest at three orders of magnitude for H_2SO_4 from 10^8 –10^{10} cm^{-3}'. This seems very inconsistent. Must one set of data be wrong? Or is there some other explanation for the difference?

-The authors correctly note that there is always some background (sometimes below detection limit) NH_3 in any measurement system. As this background NH_3 may still

influence nucleation, the conclusions drawn from the effects of increasing NH_3 from this background may not necessarily reflect the full effect or role of NH_3 in nucleation. On the other hand, for parameterization purposes this probably doesn't matter that much since such background NH_3 is likely present almost everywhere in the atmosphere.

-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 H_2SO_4 concentrations? Explicit calculations showing that the clusters do have time to grow to detectable sizes even for $[H_2SO_4]$ in the 10^6...10^7 range would be necessary for the results to be believable. (The collision rate of H_2SO_4 with the clusters as a function of H_2SO_4 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.

-Can the authors suggest a reason for the difference in behavior (of e.g. nH_2SO_4) 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?

-On line 180, the estimated nNH_3 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 $nNH_3 = 1$ 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 nNH_3, except possibly a lower limit.)

-The discussion of NH_3 as a "catalysis agent" (lines 182-188) is very likely correct. NH_3 acts to "pull" further H_2SO_4 molecules into the cluster, and hence doesn't actually "nucleate" by itself (this is actually quite obvious from the vapor pressure of pure NH_3). However, note that the 'energy reduction due to exothermic heat releaed from the acid-base neutralization reaction' is just another way of expressing the same chemical mechanism, not really a separate phenomenon.

-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)...

-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 NH_3. This seems reasonable. However, in the abstract, the much stronger statement 'The composition of H_2SO_4 and H_2O in critical clusters and the threshold of H_2SO_4 concentrations required for the unit nucleation rate both do not vary in the presence and absence of NH_3.' 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.

Technical corrections:

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

-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?

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