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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

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The topic of the (title of the) manuscript, binary homogenous nucleation of H2SO4 and H2O in the atmosphere, is an important topic, where inconsistencies between observations, laboratory work and theories still exist - and is a topic well within the scope of ACP. However, the results presented, in my view, do not remove any of these inconsistencies (but only add to the 'confusion').

The title itself has two inaccuracies: 1. The work presented is a laboratory study and necessarily does not have much to do with 'atmospheric homogeneoous nucleation'. 2. The nucleation experiments presented are very probably not binary H2SO4/H2O nucleation. The carrier gas has inpurities, most probably a significant amount of ammonia and thus the particle formation is very likely (at least) ternary.

The major (and very serious) problem of this work is point 2 mentioned above. The

authors themselves acknowledge at the top of page 29060 that of the observed growth rate of 28 nm/h, sulfuric acid can explain only about 1 nm/h - and 'it is possible that these studies also had some low concentrations of NH3'. The authors state that the detection limit of NH3 in their measurements is 93 pptv, which corresponds to a molecule concentration of roughly 2*10ˆ9 #/cm3 !!! This is a couple of orders of magnitude higher than the sulfuric acid concentration. How can you then claim that you are measuring binary nucleation???

As the authors have at the same time another manuscript (p. 22395-22414) under evaluation in ACPD, showing results of ternary H2SO4/NH3/H20-nucleation (including several of their 'binary' results also), I strongly suggest combining these two manuscripts - but with a careful investigation/discussion on which vapors are/can be present and account for the observed nucleation and growth rates.

Another important thing (which concerns both this manuscript and the ternary one)... The first nucleation theorem is used quite loosely to compare with previous studies and interpret nucleation mechanisms. Actually, as I understand, the main conclusion of the paper, written in the abstract as well as in the conclusions, is that impurities cause the results that show a slope 1...2 (e.g. Sipila et al.), but 'pure binary' experiments, as in this manuscript, result in a higher slope. This is wrong! In addition to the possible contamination by NH3 of these experiments (also), the measurements here were done with a TSI 3786 CPS (cutoff = 3 nm), and Sipila et al. clearly showed that a higher cutoff will lead to a higher slope in logJ-log[H2SO4]-space. In other words, the slopes that the authors are observing are resulting from nucleation+condensation and not nucleation alone.

Minor comments:

Please discuss what are the uncertainties in a) the H2SO4 measurement, b) the NH3 measurement ?

In the discussion section it is stated that the slopes (which result from both nucleation

and condensation) are thermodynamically consistent with the quantum chemical calculations by Kurdi and Kochanski. This is a very loose statement and by browsing through the reference I cannot understand why this is stated.

In the discussion section it is stated that the observed BHN threshold of 10ˆ6 cm-3 agrees with the observed atmospheric one. How is this threshold obtained from a) these laboratory results and b) atmospheric observations?

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