

Interactive comment on “Sulfuric acid nucleation: power dependencies, variation with relative humidity, and effect of bases” by J. H. Zollner et al.

Anonymous Referee #3

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The manuscript describes flow tube measurements to study the binary nucleation of sulfuric acid-water particles as a function of sulfuric acid concentration and as a function of relative humidity. Furthermore, some ternary nucleation experiments with two nitrogen containing bases are described. While the findings are interesting there are several major comments that need to be addressed in detail before the paper can be considered for publication in ACP.

Major comments:

The quantitative results of this study are all critically dependent on the validity of the fluid dynamics and chemistry model calculations that complement the measurements (e.g. the sulfuric acid concentration is estimated to be a factor of 5-10 higher in the nucleation zone than at the point of measurement, methyl amine is estimated to be a

C391

factor 100 higher!). All the features, results and assumptions of the model are left to an unpublished reference: Panta et al., manuscript in preparation. The calculations of the maximum concentration of nucleating vapors in the nucleation zone are very complex. All gas concentrations are strongly varying radially and longitudinally. The mixing process of the gases is difficult to describe, and how can the nucleation time be reliably estimated in the rapidly changing environment? It is necessary to publish the model calculations alongside to be able to judge the presented data (has the Panta et al. manuscript been submitted by now?). Otherwise the main findings of the paper cannot be reviewed at the required level of scrutiny.

While previous flow tube measurements (Ball et al., Young et al., Benson et al., Berndt et al., Sipilä et al., Brus et al., etc.) all faced similar problems (and they all disagree – varying over 4-5 orders of magnitude in $[H_2SO_4]$ for $J=1$, as demonstrated by Fig. 5), another data set should only be added if it is documented that substantial progress in the methods and in the quantitative results has been achieved! There is a large risk that concentrations and temperatures in the mixing and nucleation zone are not estimated correctly.

RH dependence of nucleation rate

Why do the measurements depicted in Fig. 3 not all line up? The measurements at 55-70% RH were made at a factor 2 lower flow rate but when multiplying the values by 2, the results still do not line up with the lower RH measurements. Why?

Furthermore, the purity of the water vapor addition could cause problems. Using de-ionized water without further purification might lead to substantial contamination with organics. These impurities can change the measured RH dependence. In addition, as both, water concentration and temperature, are not directly measured in the nucleation zone, I have doubts about the stated relative humidity.

NH₃ and MA measurements

C392

Here, just a few sample measurements have been made, far from a systematic analysis. All measurements are made at high sulfuric acid concentrations, much higher than any atmospheric conditions (in order to ensure the fast growth necessary to detect the particles with the CNC).

For all cases it is tried to measure the NH₃ and MA concentration with the mass spectrometer but only for one case an enhancement of signal corresponding to 0.4 pptv above the 3 pptv background is detected, which is converted to a mixing ratio of 35 pptv in the nucleation zone assuming a factor 100 of losses (p 1129, 5-9). Without a direct measurement and a more thorough investigation of the losses, the results of Table 4 are far from quantitative. I am sceptical that the stated mixing ratios in the nucleation zone are known, maybe within a factor of 10. I also do not understand how the mixing of the main flow and the flow from the top port is done. From the graph it seems that fairly separate (and asymmetric) flows can develop and there is no turbulent mixing zone as for the H₂SO₄ and H₂O injection. How can the concentrations in the nucleation zone be derived if the gases are not rapidly well mixed? Could the main nucleation take place in a zone where the amine/ammonia concentrations are still strongly enhanced over the stated mixing ratios, while sulfuric acid is not a limiting factor as it is supplied in fairly high concentration.

The authors note that for the NH₃ case substantial amounts of amines from a previous measurement were present. Can it be excluded that the contaminant amines aided the NH₃ nucleation? Therefore also the relative comparison between the role of NH₃ and MA for nucleation might be affected.

The authors state that "AmPMS detection of ammonia or amine when it was added at the top port was much less than that estimated by assuming what was added had mixed well with the main flow." (1124, 20-22). What is meant by this statement? Does this just refer to the large losses (factor 100 as stated above) or does it mean that the flows are not mixed? Did the H₂SO₄ signal change during these experiments?

C393

Apparently, the data only comprises the five individual measurements listed in Table 4. Were the authors able to repeated and confirm their measurements?

It is obvious that by addition of NH₃ or MA the nucleation rate will be increased over the neat sulfuric acid system, but, for the above arguments, I do not accept the stated mixing ratios and the quantitative statements.

Minor comments:

1120, 4-7: This sentence should also reference Kirkby et al., 2011. 1126, 2: "Above 1.5 sLpm, [H₂SO₄] does not increase in a linear fashion with QA." Why? Please discuss.

Technical corrections:

1118, 20: "Nels", change to "Nel"

1119, 3: "nucleation rates. . . have been presented."

1119, 10: "Zhang et al. report . . ."

1119,14: ". . . Young et al. (2008) report values of. . ."

1121, 10: STP is defined twice

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C394