

Interactive comment on “Laboratory studies of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ binary homogeneous nucleation from the SO_2+OH reaction: evaluation of the experimental setup and preliminary results” by L.-H. Young et al.

L.-H. Young et al.

Received and published: 15 July 2008

Response to Reviewer II

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We thank the reviewer for helpful comments and revised our manuscript accordingly. The summary of our major revisions are described in our summary response file, separately. Please also see the revised manuscript for detail. Below, we provide detailed point-to-point response to the review.

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Anonymous Referee #2

General comments:

This paper presents valuable laboratory work of binary homogeneous nucleation relevant to atmospheric new particle formation. The instrumentation used in the study is novel, and the construction of the new instrument is well documented. Experimentally measured, accurate nucleation rates of sulfuric acid + water are very much needed, as questions still arise of this nucleation pathway. Therefore, the paper is well suited for publication in the ACP.

There are, however, some concerns over the methodology used in this study, and the following items should be addressed in the revised paper. My main concern over the experiments conducted is the stability of the instrument. In flow based nucleation experiments, nucleation is assumed to take place in a steady state. In principle, the steady state could be maintained as long as needed, several hours at least. However, the authors show no proof of the operating stability. In stead, looking at figures 4,5,6,10 and 12 it appears that the measured particle concentration is typically exhibiting a rising trend. The authors should perform a stability test on their instrument, or at least explain why they assume their instrument to be in a steady state only minutes after changing the experimental parameters such as the SO₂ concentrations.

RE: This stability issue is an important comment and we have performed stability tests of H₂SO₄ and particles (Figure 3 and Section 2.3). H₂SO₄ measurements show very high stability with relative standard deviation of < 10 % (Figure 3a). On the contrary, we found some stability issue with particle measurements (Figure 3a). The particle concentrations often rise in the beginning taking a few minutes then decline slowly with time to become stabilized. These stabilization times are often quite long (e.g., 3 hours). But the initial concentrations are usually about a factor of 5 higher than those under steady state conditions after 3 hours (Figure 3b). We have taken into account this difference for particle measurements and nucleation rate calculations. In the Intro-

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duction, we also included how other studies have dealt with stability (also summarized in Table 1).

Another general comment is about the figures. Nearly all figures are presented as timelines. I would suggest presenting more figures as quantitative relations and only the most necessary figures as timelines. Which figures might be changed is in the discretion of the authors.

RE: We agree. Figures are revised as a function of $[H_2SO_4]$ (as opposed to as a function of time previously). Also for $[H_2SO_4]$, we have also included WLFs, so that we can estimate the initial $[H_2SO_4]$ from the method mentioned above (Section 3.2).

Specific comments:

The orders of the paragraphs in the introduction should be considered. Now there is first discussion about sulfuric acid vapor generation (starting at line 12, page 6905), then discussion about flow based methods (from the line 22) and then focus is again on sulfuric acid vapor generation (line 10, page 6906). Furthermore, the authors should make a note that sulfuric acid vapor from liquid samples can be made by two ways: saturating a carrier gas with the vapor from a liquid pool or vaporizing the sulfuric acid liquid at high temperature. This has direct effect on the corrosion problem mentioned line at 10, page 6906.

RE: Agree. Introduction is reconstructed according to this comment.

Page 6909, line 14. The authors assume that nucleation occurs on the whole length of the nucleation chamber. Is it possible that nucleation occurs already in the mixer? Could this have an impact on the results or would this effect be negligible?

RE: We agree. In order to estimate the nucleation zone, we have conducted numerical simulations of aerosol nucleation as a function of the axial axis of the nucleation reactor based on the nucleation and condensation growth processes and from the measured aerosol size distributions and $[H_2SO_4]$ (Section 3.3). These calculations show that

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nucleation zone is within about 40 cm (a half of the nucleation tube length) (Figure 7). This factor of 2 (residence time vs nucleation time) has been taken into account for nucleation rates in our revised manuscript.

2.3 Particle measurements. The five to ten times lower particle concentrations obtained with the DMA + CPC compared to a stand-alone CPC are worrying. Some questions come to mind to validate the data. Did the authors make an intercomparison for example from the lab air? Was inversion made on the SMPS data? Was the RH of the sheath air controlled? If the differences of the concentrations cannot be consolidated, I would recommend using only the stand-alone CPC data for concentration. SMPS size distribution data are still likely valid, and very valuable information.

RE: We agree. We did intercomparison experiments with laboratory room air and with new particles generated in the nucleation reactor and these results show that for room air these two modes show nearly the same concentrations (combination vs. stand-alone = 0.66:1) but for particles generated from the nucleation reactor, stand-alone vs. combination = 0.1:1 or 0.2:1 (Section 2.3, the 3rd paragraph). We included only CPC data for nucleation rate measurements in this manuscript and SMPS data are shown for aerosol sizes only (Section 2.3, the 1st paragraph). As for SMPS inversion: the commercial software (Aerosol Instrument Manager) that comes with the SMPS does all the data inversion, including charge probability, transfer function width, flow rates, CPC and DMA efficiencies, etc. and we did not do any addition inversion on the SMPS output results. Also, the RH of the sheath air is not controlled; however, the SMPS has a built-in heat exchange unit and temperature sensor to maintain the temperature of the sheath air.

Page 6911, line 8. "when condensation and coagulation growth are negligible". Only coagulation should be negligible.

RE: Corrected.

3.1 SO₂, OH, H₂O and O₂ effects on H₂SO₄ and particle production. The authors say

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that step (3) illustrated in figure 4a is not expected from the reactions R1-R3, as both sulfuric acid concentration and particle number should show zero. From figure 4b, a clear decrease of both can be seen in step (3). What would happen if step three was kept on a longer time? Complementary to that; did the authors make test runs starting with SO₂ on, but UV light off? Did particles/ sulfuric acid appear? If so, this could be an indication of an unknown production process of sulfuric acid/particles (just as the authors correctly suggest and further elaborate in chapter 4.6) and should be a subject of further studies later on. It would be interesting to see if the problem remains if SO₂ concentrations were on the same order of magnitude as the OH-concentrations. According to the authors, the minimum RH attained was 4%. Where does the humidity come to the system? What is the accuracy of the RH sensor/has it been calibrated? The authors state that the standard SO₂ gases were diluted for the experiments. How was this made? The resulting nucleation behavior should really be independent of the original gas concentration, as long as the concentration entering the mixing chamber is the same. If I understood correctly this is not the case. Any ideas behind this? Which measurements should be considered more valid; the ones from 1ppm SO₂ or 100ppm SO₂?

RE: H₂SO₄ and particle formation from SO₂ without OH is one of the results we want to explore in our future work, but here we only briefly mention these results. Section 5.4: "There are several experimental results related to this feature. Firstly, as shown in Figure 8, there were some measurable amounts of H₂SO₄ and particles when UV was off; we also saw the same feature when starting with SO₂ but UV off. Such a feature consistently appears over different time periods and even after we washed the flow tube with distilled water overnight to remove all sulfuric acid and particles deposited on it from previous experiments. In addition, the measured [H₂SO₄] and particles were also directly related to the initial [SO₂] (Figures 9 - 15), even though [SO₂] >> [OH] and therefore, the produced [H₂SO₄] from R1 should be the same as [OH] and independent from [SO₂]. These results may suggest that there are some other pathways for H₂SO₄ and particle formation, independent from R1-R3. But we do not understand

the reaction and nucleation mechanisms from these qualitative results at present and it is also difficult to know if these results have something to do with Berndt and Stratmann (2007)'s speculation of an alternative path for new particle formation involving HSO_5 . Note that the residual $[\text{H}_2\text{SO}_4]$ measured without OH and UV were usually at least one or two orders of magnitude lower than those produced in the presence of UV and OH." Section 3.1, the 3rd paragraph: "The minimum RH of 4% (as opposed to 0%) was reached by simply *not* bubbling the water but water was still there; note, RH sensors also have $\pm 4\%$ accuracy. Note, as will be discussed in Section 4.4, there were RH effects on both the measured particle number concentrations and particle sizes." Section 2.2, the last paragraph: "The RH sensors were calibrated and are NIST and (National Physical Laboratory) NPL traceable and have an accuracy of $\pm 4\%$ over RH from 0 – 100%; comparison results with several RH sensors with the laboratory room air and the air in the nucleation reactor showed a good agreement within this accuracy." Dilution of SO_2 was made with standard SO_2 gases, after taken from MKS flow controllers for a certain amount then mixed with high purity nitrogen gases (vaporized from liquid nitrogen tank) of a certain amount. When the same concentrations of SO_2 are achieved from these two different bottles of SO_2 gases (1 and 100 ppm), nucleation rates are quite different. Section 4.1, the last paragraph: "This difference occurs probably because of the incomplete mixing of SO_2 gases with other gas species in the fast flow reactor. Because SO_2 molecules were released near the centerline of the flow reactor, it would take a longer time for SO_2 molecules to be vigorously mixed with OH radicals at lower mixing ratios than at higher mixing ratios. The flow ratios of Q_{SO_2} to Q_{total} were from 0.03 - 0.15 and from 0.025 - 0.04 for the 1 ppmv- and 100 ppmv- SO_2 cylinder experiments, respectively. Because its Q_{SO_2} to Q_{total} ratios were larger than that for the 100-ppmv cylinder experiment, we can expect a better mixing with the 1-ppmv cylinder."

3.2 Nucleation time (t_n) dependence of particle numbers (N) and $[\text{H}_2\text{SO}_4]$. These

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measurements are interesting. I was wondering, in principle, the residual sulfuric acid concentrations could be linked to the initial OH-concentrations with the wall loss factors, thus consolidating the different sulfuric acid concentrations observed with different nucleation times (at these particle concentrations, the condensational loss of vapor should be close to negligible). Did the authors try to do this?

RE: This is an important comment. We did test experiments to see how the [OH] are related to the residual [H₂SO₄] measured at the end of the nucleation reactor and WLFs (Table 2 and Figure 6). In conclusion, the [OH] produced from water vapor photolysis are on the same order as the initial [H₂SO₄] calculated from the CIMS-measured residual [H₂SO₄] and wall loss of H₂SO₄, within experimental uncertainties (Table 2 and Figure 6). First, The CIMS-[H₂SO₄] determination is based on Huey (2007) (Section 2.4) from the measured NO₃⁻ and HSO₄⁻ ion signals and the reaction time in the ion-molecule reaction region of the CIMS. Field studies have proven that this method is valid (Huey 2007; Eisele and Tanner, 1993) (Section 2.4). Our experimental results also show the CIMS measurements also have a high stability over an 8 hour measurement period (relative standard deviation of < 10 % (Figure 3a). We have calculated the initial [H₂SO₄] from the residual [H₂SO₄] measured by CIMS and wall loss factors (WLFs) (Section 3.2). Table 2 shows these initial [H₂SO₄], along with the CIMS-measured residual [H₂SO₄] and WLFs. Table 2 also includes the initial [OH] produced from water vapor photolysis experiments. Since for all experimental conditions [SO₂] >> [OH], one can expect that the produced [OH] are the same as the initial [H₂SO₄], when CO impurities are negligible (our CO scrubber tests show that [CO] is only at the 200 ppbv level). As shown in Table 2, the produced [OH] are indeed on the same order as the initial [H₂SO₄] within experimental conditions, estimated from WLFs and the CIMS-measured residual [H₂SO₄]. Figure 6 also shows how gas phase species evolve as a function of time in the nucleation reactor for the typical experimental conditions and gives an example of [OH] = initial [H₂SO₄]. OH dilution with SO₂, O₂, and N₂ in the mixer is not important under our experimental conditions, as the main flow is N₂ used to bubble water (Section 2.2). In addition, the OH and + SO₂ reaction time is very

short under our experimental conditions (e.g., 1 ms) (Figure 6). So it is reasonable to assume that the majority of [OH] is converted to [H₂SO₄] and our results show this is the case (Table 2 and Figure 6). We have also verified our WLFs calculations with the simultaneous measurements of [H₂SO₄] at the beginning and at the end of the nucleation reactor with two CIMSs and found that WLFs, calculated by assuming H₂SO₄ wall loss is diffusion limited, are consistent with observations (Section 3.1; Figure 5). For the detail, please see the mentioned sections in the revised manuscript.

Page 6917, line 25. "...larger N and D_p at higher t_n , consistent with the predictions from nucleation theories." I do not see a point making this relation, larger N is quite trivial ($N \propto J$) and larger D_p occurs due to there being more time for condensational growth. Please elaborate? The same sentence occurs in the abstract, by the way.

RE: We agree. Section 4.3: "These results also show that both N and D_p become higher at longer t_r ; N becomes higher because of nucleation and D_p higher because of condensation growth. But since both D_p and N are affected by t_r , this makes estimation of "apparent" J from different nucleation studies less comparable, especially when particles have different D_p under different t_r (or t_n) conditions.."

3.5 The ³⁴SO₂ experiments. The authors should consider whether this chapter brings any added value to the manuscript.

RE: We agree and removed this section.

4.1 Uncertainties in the particle measurement. According to the authors the reproducibility of the instrument can be examined when the same experimental condition is repeated several times. While this is certainly true, I would still draw attention in making sure that the instrument is really at steady state when repeating the experiment. In the referee's opinion, this might not be the case in figure 10.

RE: We agree and we discuss CPC measurement stability in detail in Section 2.3 (the second paragraph; Figure 3). Briefly, usually it took 3 hours to completely stabilize

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the system when using water-UCPC and the initial concentrations were approximately a factor of 5 higher than that after a steady state has been achieved. For nucleation rates reported here, this factor of 5 has been taken into account.

Page 6921, line 17. "On the other hand, enhanced condensation growth will allow more particles to grow larger than 3 nm, leading to an increase of N and subsequently an overestimated (Kulmala et al., 2006)". This is very confusing. The paper by Kulmala 2006 deals with activation of clusters (NOT necessarily pure sulfuric acid clusters.), and the situation is quite different from the experiment. Surely the nucleation rate cannot be overestimated, this is the only way particles form in the experiment. The authors should carefully revise the remaining paragraph as well especially when talking about condensation.

RE: We removed this rather confusing discussion.

Page 6921, line 26. "...condensation is needed for nucleation." This term is not correct. Nucleation is the very first step of the phase transition, only after nucleation can condensation take place. The authors are correct that condensation in the experiment is unavoidable; otherwise no particles would grow big enough to be detected!

RE: We meant to state that "H₂SO₄ vapor is needed for nucleation." But now we removed this misleading discussion.

Page 6923, line 26. "A recent refined kinetic quasi-unary nucleation model...[H₂SO₄] has to be at least 10¹¹ cm⁻³ to observe significant binary J ...". Would be nice to see the same for classical nucleation theory. I think this should be also in the paper by Yu (2006).

RE: Agree. Section 5.2, the 1st paragraph: "In comparison, predictions from classical nucleation theory show that the initial [H₂SO₄] has to be at least 10¹⁰ cm⁻³ to observe significant binary J at RH < 20% and 298 K (Vehkamäki et al., 2002). A recent kinetic quasi-unary nucleation model for H₂SO₄/H₂O also shows that the initial [H₂SO₄] has

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to be at least 10^{11} cm^{-3} to observe significant binary J at $\text{RH} < 20\%$ and 300 K (Yu, 2006).”

Fig 3. Should the y-axis really be log WLF, or just WLF in logarithmic scale?

RE: Corrected.

Fig 5. Is there a reason why the axis values for H_2SO_4 are different in figures a and b? Also time axis's are different.

RE: Corrected.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 6903, 2008.

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