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Atmospheric
Chemistry
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Discussions

Interactive comment on "Kinetic modeling of nucleation experiments involving SO_2 and OH: new insights into the underlying nucleation mechanisms" *by* H. Du and F. Yu

H. Du and F. Yu

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Reply to Referee #2 We appreciate the constructive comments of the reviewer which help to improve this manuscript. Our point-to-point replies to the comments are given below.

1. “Generally, it is hard to reproduce the calculations done by the authors. In practice, the corresponding rate coefficients for beta and gamma are needed explicitly. It should be described more in detail how these coefficients were obtained. Equations as a function of I would be helpful.”

We don’t think that it is hard to reproduce the calculations as all the information needed to build the model to solve the cluster formation and evolution have been well documented (Yu, J. Chem. Phys., 127, 054301, 2007; Du and Yu, ACP, 8, 4729, 2008). The method and equations to calculate rate coefficients for beta and gamma (as a function of i) have been described in detail in the reference we cited (Equations 14 and 15 in Yu, J. Chem. Phys., 127, 054301, 2007). In this work, we only modified DeltaG(i-1,i) of binary nucleation to take into account the unknown species and the procedure is presented in the manuscript.

To address the referee’s concern, we have explicitly pointed out in the revised paper that beta and gamma (as a function of i) were calculated based on Equations 14 and 15 in Yu (2007).

2. “The unit of the rate of these steps is [cm(-3) s(-1)] or [molecules cm(-3) s(-1)]. In Fig. 1b and 3b the unit [s(-1)] is given. Please give an explanation.”

Both Fig. 1b and 3b show the Beta (Beta = K(1,i)N(1)) and Gama. The K(1,i) (coagulation kernel) has the unit of [molecules cm(-3) s(-1)]. But when it multiplies N(1) which is monomer number concentration, Beta has the unit of [s(-1)]. Gama, which considers how fast H2SO4 molecules evaporate away from the hydrated cluster, should have the unit of [s(-1)].

3. “The equation at P.1278, line 5 shows the reaction of a monomer with an existing cluster, like A+A3=A4. Do the authors only consider forward reactions of the monomer? Are reactions like A2+A2=A4 neglected?

The equation referee mentioned is an illustration of nucleation process. In our model, we calculate collisions among clusters. In other words, we consider collisions like A2+A2=A4 in our model. Generally, A + A(i-1) = Ai dominates the nucleation process because [A1]$>>$[A2]$>>$[A3] … (see Figures 2 and 4). We have pointed this out in the revised version.

4. “Comparison with Young et al. (2008): Young et al. measured H2SO4 concentrations at the outlet of the flow tube as well as simultaneously at the inlet in

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order to evaluate the theoretical WLF. And the measured WLF was in line with the gas kinetic limit. These measurements should be accepted! The authors should show graphically what the result of modeling is using the WLF and the H2SO4 levels detected by Young et al. By adjusting the gama value a description of the experimental H2SO4 profile should be possible.”

Young et al. (2008) measured inlet and outlet H2SO4 concentration at only one experimental condition (t=19 s, and RH=16%). Based on our simulation, we found that at t=24 and 37 s, our derived WLFs differs from those calculated in Young et al. (2008) within a factor of 2. Considering the difficulty in detecting [H2SO4] and the associated uncertainties, we think that our derived WLF is reasonable at least at t=24 and 37 s. At t=54 s, the difference becomes larger, which is 7.6. So we think the difference in WLFs between our work and Young et al. (2008) grows larger as the residence time becomes longer. Unless the measurement of WLF for t=54 s is also carried out, it is hard to identify the source of the difference. In this paper, we seek to derive the WRF independently from a model point of view based on measured particle size distributions and residual [H2SO4]. As we have shown in Figure 1, adjusting the gama values will not change the simulated mean size of nucleated particles.

5. “ Comparions with Berndt et al. (2008): The authors used experimental findings from runs given in Berndt et al. (2008) but for modeling an OH profile from another experiment given in Berndt et al. (2005). Why?.....H2SO4 concentrations stated in Berndt et al. (2008) are average concentrations in the reactor and not peak concentrations.”

The method to calculate H2SO4 concentration profile used Berndt et al. (2008) and in Berndt et al. (2005) are the same. That’s why we can reproduce their H2SO4 simulation which is shown in Fig. 3(a). OH profile is explicitly given in Berndt et al. (2005) but not available in Berndt et al. (2008). In order to give more useful information to readers who are interested in H2SO4 concentration derivation, we cited their 05 paper instead of 08 paper. We have clarified this in the revised paper.

6. “The authors came to the conclusion that critical cluster composition……..It should be noted that these slopes can represent clear overestimations caused by the counting efficiency curve of the counters used, see also the notice in Berndt et al. (2005).”

On Page 1283 line 16, we wrote “the agreement is reasonable” not “well in line with experimentally observed slopes”. The reason we describe the agreement to be reasonable is that we do notice the uncertainties in the experiments, as mentioned by the referee. In addition to the uncertainty in the particle concentration measurement which is Y-axis in the plot, the H2SO4 concentration in the X-axis also has uncertainty. H2SO4 concentration in the plot should be the one when nucleation takes place. However, no measurements are available at present. Given all these factors, we think “reasonable agreement” is a more appropriate phrase to describe the agreement between our study and those based on measurements. This “reasonable agreement” also indicates that the derived beta and gama which are used to determine the critical cluster size can be considered to be good.

7. “Atmospheric measurements indicate that obviously only 1-2 H2SO4 molecules are need in the critical clusters……The authors should discuss this topic and the consequences for the model given, the gama values and the corresponding Gibbs free energy.”

As far as we know, the conclusion that the critical cluster in the atmosphere contains only 1-2 molecules is based on the empirical fitting of the dependence of nucleation rates (J) derived from measured particle concentrations on measured [H2SO4]. While the reasons behind the linear or square dependence of J on [H2SO4] remain to be investigated, it doesn’t necessarily imply that the critical clusters contain only 1-2 molecules. Actually, the measurements reported in Kulmala et al. (Science, 2007) showed that the critical clusters have diameters of ˜1.5 nm (containing ˜ 7-10 sulfuric acid molecules).

We believe that it is too early to discuss the results in terms of their atmospheric significance. Through our simulations in this work, we feel that we don’t know yet how close are Berndt et al. and Young et al.’s study to the nucleation occurring in the atmosphere. Both studies start nucleation via OH induced SO2 oxidation; however, we find that the stabilizing effect of this unknown species in two studies varies significantly. This leads to a logic question: which experiment can be representative of nucleation occurring in the atmosphere?

8. “Personally, I guess it sounds better to say “best agreement between model and measurement is found assuming a 2-4 fold H2SO4 concentration” than “H2SO4 concentration was underestimated in those studies by a factor of 2 to 4.”

We have modified the sentence as suggested.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 1273, 2009.

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