**Atmospheric
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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

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Reply to Referee #1

We appreciate the reviewer's constructive and helpful comments. Our point-to-point replies to the comments are given below.

1. "Introduction, line 7-9"

The importance of ion-mediated nucleation in the atmosphere remains controversial and further research is needed to resolve the controversy. The possible reasons behind the differences in the theories, interpretation and conclusion have been discussed in length in Yu et al. (ACP, 8, 2537, 2008), Yu and Turco (ACP, 8, 6085, 2008), and the

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Interactive Discussion

Discussion Paper

online discussion associated with this two papers. In the revised manuscript, we have pointed out the existence of controversy and the on-going debate with regard to the importance of ion-mediated nucleation.

2. “In Yu JPC 2007 the authors justify the use of a quasi-unary-nucleation (QUN) in base to the high concentration of water vapor in the system of interest…..So, how good valid are these assumptions in this case?”

The assumption that H2SO4 is responsible for cluster growing, and hence the nucleation is made based on numerous lower tropospheric nucleation measurements (e.g. Kulmala et al., 2004) in which measured nanoparticle concentration is clearly shown to closely correlate with H2SO4 concentration. Berndt et al. (2008) suggested that some unknown species other than H2SO4 is responsible for cluster growing. They came to this conclusion based on an experiment in which the measured particle size distributions were not changed when they switched on and off the background H2SO4 source. We examined the same experiment in this work and the results are presented in Fig. 5 in this work. We show that if background H2SO4 concentration is less than 5e08 cm-3, the difference in calculated particle size distributions between no and with background H2SO4 cases are within measurement uncertainties due to instrument limitations. So the particle size distributions would appear to be unchanged when the background H2SO4 source is switched on and off. We demonstrate in this work that there is a possibility that the measured particle size distributions would not change with background H2SO4 source switched on and off, if background H2SO4 concentration is smaller that 5e08 cm-3. It should be noted that the background H2SO4 concentration in the nucleation zone were not measured in Berndt et al. (2008)’s study. So a concentration range for background H2SO4 concentration is estimated and given in their paper, which is ˜ 1-2e09 cm-3. We show in Fig. 5 that only using 5e08 #/cm-3 H2SO4 background concentration, which differs from their estimated value only by a factor of 2-4, would change their conclusion on the role of H2SO4 in cluster growth. Therefore, we believe the statement that some unknown species other than H2SO4

is responsible for cluster growing needs to be much more carefully examined experimentally before we can really reach to this conclusion, given the known importance of H2SO4 in cluster growth observed in numerous ambient nucleation measurements and the fact that no actual background H2SO4 concentration measurements in nucleation zone was carried out by Berndt et al. (2008).

3. "I found the description of the method in this section quite confusing, authors should explain Eq (3) in more detail"

We have added more discussion about Eq (3) in the revised manuscript. In order to take into account the unknown species, a term dG(i) is added to DeltaG(i-1,i) of binary H2SO4-H2O homogeneous nucleation. dG(i) is a free parameter and supposed to be a function of cluster size (i). We choose different dG(i) in order to derive different DeltaG(i-1,i) for the ternary "unknown species-H2SO4-H2O" nucleation. dG(i) is chosen in such a way that the peak concentration of calculated particle size distribution matches that of measured particle size distribution.

4."Again the test here is quite confusing. How you calculate ER2 and ER3? In figure 1c you fix the evaporation rate to ER2, why?......Please clarify this point"

We calculated ER2 and ER3 based on Eq. (1-3). We first calculated DeltaG(i-1,i) of binary H2SO4 and H2O clusters. Then we varied parameters a, b and c in Eq. 3 to derive different dG(i) which is a function of cluster size. Then by adding dG(i) to DeltaG(i-1,i) of binary nucleation, we derived DeltaG(i-1,i) of ternary nucleation which takes into account the third unknown species. We then implemented it into Eq. 1 to derive the evaporation rate for a ternary "unknown species-H2SO4-H2O" nucleation. With different sets of parameters (a, b and c), one can have different ternary evaporation rates like ER2 and ER3. We used the same method to calculate ER in Fig. 3b.

The logic in Fig. 1(c-d) is as follows: based on simulations in Fig. 1(d), we found that with a fixed H2SO4 concentration profile, the mean size of calculated particle size

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Interactive Discussion

Discussion Paper

distribution stay unchanged and is insensitive to different evaporation rates used in simulations. This feature can be used to derive H2SO4 concentration profile. After we obtain the H2SO4 concentration profile, we then adjust dG(i) to derive a DeltaG(i-1,i) of ternary nucleation and thus gama of ternary nucleation in such a way that the peak concentration of calculated particle size distribution matches that of measured particle size distribution. This is how we derive DeltaG(i-1,i) of ternary nucleation and gama (i.e. ER2 in this case). We show that ER2 can represent the nucleation observed in Young et al. (2008). So Fig. 1(c) shows that with the same ER2, if assumed H2SO4 concentration profile is incorrect, the calculated particle size distribution will not match the measured one. We have re-organized the logic of discussion for Fig. 1 to clarify this point.

4. “Thermochemistry: implications for the underlying nucleation mechanism…are this values big enough to be representative?….Can be this differences induced by uncertainties in the estimation of evaporation rates or sulfuric acid concentrations instead of being caused by some unknown species?”

One should look at this energy difference in terms of evaporation rate which is critical for any nucleation process. It should be noted that the evaporation rate is exponential of Gibbs free energy change. Take dimer for example, the 0.7 kcal/mol in Gibbs free energy change leads to a difference in evaporation rate by as large as a factor of 3. This makes a big difference in the calculated nucleation rate. Therefore, those values are big enough to be representative.

We estimate the H2SO4 concentration and evaporation rate purely by matching calculated particle size distributions with measurements. For example, Fig. 1(c) shows that either a lower or higher estimation of H2SO4 concentration would lead to a clear mismatch with measurements. This suggests that the obtained values of H2SO4 concentration and evaporation rate in this work are constrained by particle size distribution measurements. Therefore, the difference in Gibbs free energy change is unlikely to be caused by uncertainties in our estimations of evaporation rate and sulfuric acid con-

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Interactive Discussion

Discussion Paper

centration, unless there are uncertainties in measurements, which is beyond the scope of this work.

5. "I don't see how the unrealistic values obtained for enthalpy can be a justification for proposing two different unknown species participating in nucleation"

If the unknown species involved in two different nucleation were the same, the derived dH and dS should be realistic. Both dH and dS should be negative, and absolute value of dH should not be as large as 176.53 kcal/mol.

6. "In line 29 the authors says that the chemical identities of the unknown speices has not yet been resolved………A comparison between the free energy stabilization calculated in that paper with the one proposed in this paper will be really interesting"

The authors agree with referee's idea. Actually we tried to do the comparison when this paper first came out. The obstacle we run into is that Salonen et al. studied non-hydrated sulfuric acid-free radical clusters; however, the clusters in our model are hydrated. Therefore, we cannot use their data to do the comparison.

7. Technical comments.

Corrected.

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