

Interactive comment on “From molecular clusters to nanoparticles: second-generation ion-mediated nucleation model” by F. Yu

F. Yu

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The author thanks Ned Lovejoy for the detailed, insightful, and constructive comments which are very useful to improve the paper. My point-to-point replies to the comments are given below.

1. The named work will be referenced and discussed in the revised manuscript.
2. Due to the difficulty in determining accurately the sulfuric acid gas concentration in the nucleation zone, the laboratory study on H₂SO₄-H₂O binary homogeneous nucleation has large uncertainty. For example, the uncertainty in the nucleation rate at given [H₂SO₄] in Ball et al. (1999)'s measurements could be as large as 10 orders of magnitude. “Reasonable agreement” means that the predicted nucleation rates are within the experimental uncertainty range. This was pointed out in lines 9-10 abstract.

I will modify the text to make it clearer. Several sentences containing the redundant “reasonable agreement” statement will be deleted.

3. “Secondary” particles refer to those particles grown from the nucleated particles in the ambient atmosphere. To avoid confusion, I will change “secondary” in page 3051 to “atmospheric”.

4. The reference will be added.

5-7. I will change the wording in two sentences to “. . . via a combination of derivations from measurements of small ion clusters, ab initio calculations, thermodynamic cycle, and approximations (adjustment of Gibbs free energy for neutral clusters calculated based on liquid droplet model, interpolation, etc.)”.

8. I will change the wording in the mentioned sentences to something like “Lovejoy et al. (2004) state that the nucleation of H₂SO₄ (and H₂O) on negative ions does not generally explain the observed nucleation events in the boundary layer”.

9. This is a good point. In the atmosphere, charged clusters may be composed of multiple species including sulfuric acid (A), water (W), and others (X, Y) as illustrated in Figure 1. Measurements of nature negative ion mass spectrum (Eisele and Tanner, 1990) indicate the presence of NO₃⁻, HSO₄⁻, SO₄NO₂⁻, SO₄NO₃⁻, malonate ion, etc. The negative ions are dominated by NO₃⁻ core ions at low sulfuric acid gas concentration but are generally dominated by HSO₄⁻ core ions when sulfuric acid gas concentration is high. The modified Kelvin Thomson equation used to calculate the charge effect considers the effect of the size of core ions but is not able to take into account the effect of core ion composition (see equations 15-17 in section 2.3). In this study, I assume that the core of negative ions to be NO₃⁻. However, during the nucleation events when [H₂SO₄(g)] is relatively high, the negative ions may be dominated by HSO₄⁻ core ions. The uncertainty in charge effect associated with core ion sizes (NO₃⁻ versus HSO₄⁻) for small ions is smaller than the uncertainty in experimental data (see Figure 3) and is likely to be small for larger cluster ions. I will expand line 20

on page 3054 to include the above discussion.

10. Two references provided by referee #2 will be cited in the revised paper.

11. In addition to Froyd's thesis, the peer-reviewed papers mentioned by the referee will be referenced in proper places in the revised manuscript.

12. I agree. The parameterization appears to overestimate the hydration of small negative ions at low RH when compared to those calculated based on data from Froyd (2002). However, as I pointed out in the paper, there exists large difference between Froyd' data and Wilhelm et al. (2004)'s measurements at low RH. It should be noted that Wilhelm et al. (2004)'s measurements are available only at low RH (~5%). At this point, it is hard to determine the reason for the difference and the uncertainty in the measurements. Our parameterization should be considered as an approximation which may contribute to the uncertainty in the predicted nucleation rates. I will emphasize in the revised paper the uncertainty in our model associated with composition parameterization and the necessity to obtain more data to constrain the model. The underestimation of hydration of $a=1$ clusters shall have little effect on nucleation as the charge effect dominates the thermodynamics when clusters are very small (see Figure 5). I will point this out in the revised paper.

13. Yes. The average composition (and hence size) of monomers is used in calculating the coefficients.

14. One of the major features of the model presented in this paper is that I use the modified Kelvin-Thomson (MKT) equation to calculate the evaporation of H_2SO_4 from charged clusters. MKT takes into account of the physics of dipole-charge interaction (Yu, 2005). The purpose of showing $NO_3-(HNO_3)_n$ thermodynamics was to demonstrate that MKT equation is in reasonable agreement with experimental data not only for $HSO_4-(H_2SO_4)_n$ ions but also for $NO_3-(HNO_3)_n$ ions. Following the referee's suggestion, I will eliminate $NO_3-(HNO_3)_n$ thermodynamics. The referee also suggests to "use figure 3 to show stepwise Gibbs free energy changes (ΔG) as a function of

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both temperature and RH for the evaporation of H_2SO_4 from $\text{HSO}_4\text{-(H}_2\text{SO}_4)_a(\text{H}_2\text{O})_w$, and compare these with the experimental values averaged over the appropriate equilibrium water distributions.” While ΔG based on MKT equation as a function of T and RH can be readily calculated, there is not enough experimental data available for making the named comparisons. In order to obtain experimental values averaged over the appropriate equilibrium water distributions for $\text{HSO}_4\text{-(H}_2\text{SO}_4)_a(\text{H}_2\text{O})_w$ with $a=1, 5$, experimental enthalpy and entropy changes for $\text{HSO}_4\text{-(H}_2\text{SO}_4)_a(\text{H}_2\text{O})_w \rightarrow \text{HSO}_4\text{-(H}_2\text{SO}_4)_{a-1}(\text{H}_2\text{O})_w + \text{H}_2\text{SO}_4$ with w from 1 to ~ 10 are needed. As far as I know, the truly experimental enthalpy changes for the evaporation of H_2SO_4 from negative ions are available ONLY for $\text{HSO}_4\text{-(H}_2\text{SO}_4)_a$ with $a=1-5$ (Froyd and Lovejoy, 2003). Based on entropy changes for $\text{HSO}_4\text{-(H}_2\text{SO}_4)_a$ ($a=1,5$) obtained from an initio calculation and using thermochemical reaction cycle, Froyd and Lovejoy (2003) derived enthalpy and entropy changes for $\text{HSO}_4\text{-(H}_2\text{SO}_4)_a(\text{H}_2\text{O})_w \rightarrow \text{HSO}_4\text{-(H}_2\text{SO}_4)_{a-1}(\text{H}_2\text{O})_w + \text{H}_2\text{SO}_4$ with $a=1, 5$ and $w=1, 4$. These data are not enough to carry out the comparisons suggested by the referee. Instead, I will use Fig. 3(b) to show the stepwise Gibbs free energy change for $\text{HSO}_4\text{-(H}_2\text{SO}_4)_a(\text{H}_2\text{O})_w \rightarrow \text{HSO}_4\text{-(H}_2\text{SO}_4)_{a-1}(\text{H}_2\text{O})_w + \text{H}_2\text{SO}_4$ ($a=1,5$; $w=0,3$). Both MKT predictions and calculations based on data from Froyd and Lovejoy (2003) will be given. Except for $a=1$, the differences between MKT predictions and data are within 2 kcal/mol which is likely the uncertainty range of experimental data.

15. This is a good point. In our current model, I use the parameterized composition as average cluster composition with respect to water and don't consider the effect of hydration distribution on the evaporation flux. Same approximation has been applied in our kinetic model of binary $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ homogeneous nucleation (Yu, 2006). I agree with the referee that the major uncertainty of the model is likely to be dominated by the uncertainty in H_2SO_4 clustering thermodynamics (as well as hydration thermodynamics). The effect of hydration distribution on evaporation should be evaluated in the future when more data on hydration and H_2SO_4 clustering thermodynamics become available. I will point the issue out in the revised paper.

16. The sentence will be modified to take into account the information provided by the referee.

17. Surface tension and density of binary H₂SO₄-H₂O solution and H₂SO₄ vapor pressure over the solution are all strong functions of temperature. While our calculated neutral nucleation rates are compared to experimental data also at room temperature, I expect the model behaves properly at other temperatures as the dependences of key parameters (vapor pressure, surface tension, etc) on temperatures are parameterized based on experimental results. The point I want to make in this paragraph is that the empirical terms $4\exp(-a/5)$ and $5\exp(-w/5)$ used in Lovejoy et al.' model don't depend on temperature and there is no physics behind the terms that will ensure their validity at other temperature. In the revised paper, I will replace the sentence "it may be invalid . . . ones" with "there is no physics behind the terms that will ensure their validity at other temperature". Also to address the referee's concern, I will exchange the position of point 1 with point 3.

18. I agree with the referee that the spectrum (and hence compositions) of positive ions in the atmosphere is extremely complex. Species other than water and sulfuric acid such as ammonia and certain organic compounds may contribute to the mass of positive ions. The treatment of positive ions as simple binary H₂SO₄-H₂O is an approximation. While nucleation of H₂SO₄-H₂O on negative ions is generally favored, laboratory study by Wilhelm et al. (2004) indicates that H₂SO₄-H₂O can also nucleate on positive ions though at lower rates. In our model, the evolution of positive H₂SO₄-H₂O clusters is calculated with the thermodynamics parameterization as discussed in the text. Our parameterization appears to be in good agreement with the limit experimental data available for H⁺(H₂SO₄)_a(H₂O)_w (a=1, w=1, 3) (see Fig. 4). I agree that if the major component (besides H₂O) of the observed positive ions around 1 nm is not H₂SO₄, the neutral clusters resulting from recombination are no longer a simple binary H₂SO₄-H₂O system. If the positive ions contain NH₃ (which is very likely due to high ammonia proton affinity and the abundance of NH₃ in the boundary atmosphere),

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the ternary neutral clusters resulting from recombination are more stable than binary cluster and thus will enhance the nucleation. If organic compounds dominate the mass of positive ions, I feel that these organics will remain in the neutral clusters (e.g., non-volatile). Our quantum mechanism calculations indicate that some common organic species in the atmosphere (such as formic and acetic acids) form thermodynamically stable complexes with sulfuric acid (Nadykto and Yu, 2006). As we pointed out at the end of the paper, the possible involvement of species other than H₂SO₄ and H₂O in the nucleation process remains to be investigated.

19. While organics are known to be involved in the growth of nucleated particles, little is known about the properties of these organics and their concentration variation. As we pointed out in the paper, Fig. 9 (equ. 20) represents only one of possible scenarios.

20. Charged fraction = number of particle charged (positively or negatively) divided by total particles in the size range. Will be defined in the revised paper.

21. As pointed out in the paper, the current model is subject to uncertainties associated with the uncertainties in the thermodynamic data for small neutral and charged clusters. More discussion on the possible uncertainties will be added in the revised paper (see points 12 and 15 above). Due to the limit of data available (and uncertainties in the data), it will be hard to estimate the errors of the present model at this point. The revised Fig. 3(b) shall address some of the referee's concern (point 14 above). The uncertainties related to the parameterization of cluster ion thermodynamics have already been demonstrated in Figure 7 (Figures 3 and 5 as well) and discussed in the text (page 3067). Around 2 kcal/mol difference in clustering stepwise Gibbs free energy changes (Figure 3) leads to about one and four order of magnitude difference in the predicted nucleation rates for case (b) and case (a) shown in Figure 7, respectively. The sensitivity of nucleation rates to the uncertainties in thermodynamics data decrease as the nucleation rates increase.

Suggested technical and grammatical corrections: I thank the referee for identify the

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typos and errors. These will be corrected in the revised paper.

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