**Atmospheric
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Discussions**

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

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This manuscript describes a new model of aerosol nucleation and growth that considers charged and neutral H2SO4-H2O clusters. This is an extension of earlier work by the author. The major improvement in the present work is an empirical treatment of the thermodynamics of cluster evaporation. Proper treatment of cluster evaporation is absolutely necessary to make accurate predictions of particle formation rates. The author derives cluster thermodynamics based on a modified liquid drop/Thomson equation and parameterized cluster composition. The accuracy of this approach is unclear, and a careful analysis and discussion of the uncertainties is needed. This work is an improvement over the first generation model published by the same author, and is worthy of publication once the following specific issues have been addressed.

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1. The recent sulfuric acid-water cluster ion experimental and modeling work by Sorokin et al (2006) should be referenced and discussed in some detail.

2. There are several qualitative statements suggesting that model predictions are in "reasonable agreement" with observations or measurements. What is "reasonable agreement"? This should be quantified explicitly. See lines 9-10 abstract, page 3053 line 29, p. 3057 line 4, page 3062 line 1, p. 3063 line 14, p. 3068 line 17 etc.

3. What are "secondary" particles? (p. 3051, lines 7,18)

4. The measurements of nanoparticle growth rates from the McMurry group (e.g. Stolzenburg et al. 2005) should be referenced in the introduction p. 3051, line 16.

5. The derivation of thermodynamic data by using thermodynamic cycles is not an "approximation", and the wording on page 3053 line 10 and page 3069 line 13 should be improved.

6. Page 3053, line 12 "various extrapolations, etc." is vague and should be clarified. See next comment.

7. It would be more accurate to describe the method of deriving the thermodynamics of intermediate size ion clusters by Lovejoy et al. as "interpolation" not "extrapolation" (p3069, line 13).

8. The statement that Lovejoy et al. (2004) suggest that nucleation on ions in the lower troposphere is negligible is misleading. Lovejoy et al. (2004) state that "the HSO4-/H2SO4/H2O mechanism does not generally explain the nucleation events observed in the boundary layer". They showed that one out of six boundary layer events that they analyzed was consistent with their ion H2SO4/H2O nucleation model. The statements on page 3053 line 13, page 3067 line 22, and page 3074 line 6 should be rewritten to be more specific and accurate.

9. The author has apparently used NO3- as the negative core ion (Y-) throughout his reaction scheme. This is not accurate, since when H2SO4 (stronger acid than HNO3)

reacts with NO3- the core ion becomes HSO4-. It is not clear how this affects the thermodynamics derived in the present work. Certainly the statement on p. 3054 line 20 and possibly figure 1 should be corrected.

10. Page 3056 line 3: It is stated that H2SO4 and H2O are known to play an important role in particle formation in the atmosphere. Some references to support this statement would be useful. To my knowledge no one has explicitly shown this to be true. This would require measuring the composition of molecular clusters during an atmospheric nucleation event, which has not been achieved.

11. Throughout the paper, the author references Froyd (2002) for thermodynamic data of ionic H2SO4 H2O clusters. This reference is a PhD thesis, and there are also several peer-reviewed manuscripts that present these data. The peer-reviewed manuscripts should also be referenced as appropriate (Froyd and Lovejoy (2003a,b), Curtius et al. (2001), Lovejoy and Curtius (2001)).

12. Page 3057. The author parameterizes the cluster composition to use in the estimation of cluster thermodynamics. The parameterized compositions are compared with experimental predictions for some atmospheric conditions in figure 2. In general the parameterized compositions agree pretty well with the experimental predictions. However there are some important differences e.g. for the small negative clusters at low RH. The parameterization overestimates the hydration of these clusters and will overestimate the stability of these clusters. Also the parameterization does a poor job for most conditions for the composition of the a=1 cluster, always predicting AMF=1, where the experimental data gives values less than 1. The consequence of these discrepancies should be addressed.

13. Page 3060 line 3: Is the hydration of the "H2SO4 monomers" considered when calculating the condensation coefficients?

14. Page 3063. In figure 3 the author compares predicted Gibbs free energy changes for evaporation of H2SO4 from HSO4-(H2SO4)n, and for HNO3 evaporation from NO3-

(HNO3)n with experimental values near room temperature. These are interesting plots, but have little relevance to the accuracy of the thermodynamics used in this work for the growth/evaporation of ionic H2SO4 H2O clusters. I suggest eliminating the NO3-(HNO3)n thermodynamics, because the model predictions are not sensitive to the thermodynamics of these clusters. The HSO4-(H2SO4)n thermodynamics are generally relevant only at low RH. I strongly suggest that the author use figure 3 to show stepwise Gibbs free energy changes as a function of both temperature and RH for the evaporation of H2SO4 from HSO4-(H2SO4)a(H2O)w, and compare these with the experimental values averaged over the appropriate "equilibrium" water distributions. A wide range of atmospheric RH and temperature should be explored. This will give the reader an idea of the accuracy of the parameterization for predicting ion cluster evaporation for atmospheric conditions, and ultimately a feeling for the accuracy of the model.

15. In the present study, the author parameterizes the composition of the small clusters and then uses a modified version of the liquid drop/Thomson equation to derive the cluster thermodynamics. I assume that the parameterized composition represents an average composition with respect to water, since there will be a distribution of hydrates e.g. HSO4-(H2SO4)n(H2O)m for each number of H2SO4 n. It should be recognized that each hydrate has a characteristic lifetime with respect to evaporation of H2SO4, and that these lifetimes can be a very strong function of the number of H2O ligands. Minor hydrates can carry the majority of the evaporation flux. In this case using an average composition can be problematic. In the present work, uncertainty in the derived thermodynamics may overwhelm this detail, but this point should be considered.

16. The author states that the fundamental physics of the sign preference in ion nucleation remains to be investigated. It should be noted that Froyd (2002,2003), Wilhelm et al. (2004), and Sorokin et al. (2006) describe the origin of the negative ion preference in ion nucleation of H2SO4 H2O, based on their cluster ion observations and thermodynamic measurements. They point out that H2SO4 is a strong acid and therefore is a

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good proton donor that solvates negative charge extremely effectively. Therefore, the binding of H_2SO_4 to small negative H_2SO_4 clusters is strong. Conversely, H_2SO_4 is a weak base, similar to water (proton affinities are essentially the same), and H_2SO_4 binds to protonated water clusters with energies very similar to that of water. Hence for atmospheric conditions, water tends to drive H_2SO_4 out of the positive clusters, due to overwhelming H_2O concentrations. This inhibits the growth of the positive ions, particularly at the high atmospheric temperatures.

17. Page 3067 point 1. The author discusses possible reasons why the second generation model predictions are different from the predictions of Lovejoy et al. The author points out that the neutral thermodynamics used by Lovejoy et al. are calculated with an empirical correction to the liquid drop model based on experimental room temperature nucleation rates. He argues that this may lead to significant uncertainties for atmospheric conditions (i.e. lower temperatures). However, it should be noted that the ion nucleation rate is most sensitive to the size of the neutral critical cluster and that this empirical approach does successfully reproduce the size of the neutral H_2SO_4 H_2O critical cluster measured by Eisele and Hanson (2000) at 240 K. The author then states that he uses a series of parameterizations and the liquid drop model to derive the neutral thermodynamics, and the calculated neutral nucleation rates are "in reasonable agreement with experimental data" (also at room temperature). Both approaches probably give neutral critical clusters of about the same size, at least at room temperature, since the size of the critical cluster is not a particularly strong function of the neutral thermodynamics. The model predictions will be most sensitive to the thermodynamics of the ion clusters (point 3, see below) and point 3 should be emphasized over points 1 and 2.

18. Page 3068 point 2. The author points out that atmospheric measurements of positive ions show a distribution peaked at 1nm in a Boreal forest, and suggests that this observation supports his model predictions that the positive ions contain 4 H_2SO_4 for these conditions. It should be recognized that mass resolved measurements of

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ambient positive ions (see e.g. Tanner and Eisele (1991)) show that the positive ion spectrum is extremely complex, suggesting that treatment of the positive ions as the simple binary H2SO4 H2O system is probably not correct. It should also be noted that Froyd's experimental work shows that for T>270K and [H2SO4]< 1e08 molec. cm-3 there is negligible H2SO4 incorporated into protonated water clusters. So treating the positive ions as containing H2SO4 and H2O is problematic. Granted, the positive ions may contain nonvolatile compounds that help stabilize the neutral clusters formed upon recombination. However, in this case the neutrals are no longer a simple binary H2SO4 H2O system, and the size of the critical cluster is even less well defined. On the other hand, it may be the case that the positive ion material is volatile, as Lovejoy et al. (2004) assumed.

19. Page 3070. The author includes the contribution of organics to the growth of ultrafine particles in his model. What is the origin of the condensable organic diurnal profile used in the model (eqn 20 and fig. 9). A reference and some justification for the profile would be interesting.

20. Page 3071 line 28. "Charge fraction" should probably be defined.

21. This work carefully points out potential errors in other related work. Equal attention should be given to the uncertainties in the present modeling approach. I would suggest adding a thorough discussion of the estimated errors of the present model predictions. In particular, addressing the uncertainties related to the parameterization of the cluster ion thermodynamics (point 14 above) is paramount.

Suggested technical and grammatical corrections:

1. p. 3051 line 14: "numbers"

2. p. 3051 line 21: "has been considered"

3. p. 3052 line 7: "all the above"

4. p. 3057 line12: "and negatively charged (AMF-)"

5. p. 3061 line 17: "concentration of H2SO4"

6. p. 3072 line 21: "particles lose their memory"

7. p. 3074 line 26: "quantum mechanical"

8. Fig. 2: caption and text uses "AMF" and the axis label is "AMOF".

9. Fig. 3: Fehsenfeld reference is misspelled.

10. Fig. 5. Need units for y axis. Font is too small.

11. Fig. 6. Font is too small. Insets are too small. Caption: 1.5 x106 should be 1.5x107?

12. Fig. 9. "concentration" is misspelled on the y axis.

References:

Eisele FL, Hanson DR, First measurement of prenucleation molecular clusters, J. Phys. Chem. A., 104, 830-836 (2000).

Sorokin A, Arnold F, Wiedner D, Formation and Growth of sulfuric acid-water cluster ions: Experiments, modeling, and implications for ion-induced aerosol formation, Atm. Env. 40, 2030-2045 (2006).

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Tanner DJ, Eisele FL, Ions in oceanic and continental air masses, J. Geophys. Res. Atm. 96 (D1): 1023-1031 JAN 20 1991.

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