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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Ammonia in positively charged pre-nucleation clusters: a quantum-chemical study and atmospheric implications" *by* A. B. Nadykto et al.

A. B. Nadykto et al.

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The authors appreciate the Reviewer's thoughtful and constructive comments, which helped to improve the paper. We have revised the paper with the reviewer's comments taken into account. The responses to the comments accompanied by the original comments (in Italic) are given below.

The manuscript presents quantum chemical data on positively charged sulfuric acid containing clusters (with either NH+4 or H3O+ as the core ion) on which little previous data is available. The methods used are more or less appropriate to the topic of study, and the calculations seem to have been planned and carried out diligently and carefully. The manuscript is fluently written, and the data is presented clearly and concisely. The

manuscript is well suited to publication in ACP after a few minor issues are addressed. -As a general comment, some of the "main conclusions" seem rather trivial, e.g. the qualitative fact that (NH+4)(H2O) clusters are more stable than (NH3)(H3O+) clusters (whatever the rest of the cluster composition) can be deduced from known pKa valu though the precise numerical values for the free energy changes are naturally valuable data. The results on the binding of ammonia to positively charged sulfuric acid - water - clusters (and the binding of sulfuric acid to protonated water-ammonia clusters) are, nevertheless, new, interesting and definitely worthy of publication.

The authors appreciate the referee's positive comments on the manuscript and the values of the data obtained in the present study.

-Some references could be added, e.g. the claim by Froyd and Lovejoy (JPC A 107, 9800, 2003) that water will tend to displace sulfuric acid from small protonated sulfuric acid - water clusters should be at least briefly addressed. Also, the reference to Napari et al. (2002) as a "prediction" should be accompanied by a note that the paper in question contained both theoretical and numerical errors (described e.g. in the Merikanto et al. 2007 reference given in the manuscript).

In order to address the Reviewer's concerns, references to Froyd and Lovejoy (JPC A107,9800, 2003) and Lovejoy, E. R., J. Curtius, and K. D. Froyd (J. Geophys. Res., 109, D08204, 2004) have been added to the revised manuscript. The remarks on numerical and theoretical errors in Napari et al. (2002) have also been included in the revised manuscript.

-Also, some further critical discussion on the overall importance of positively charged sulfuric acid clusters in the atmosphere would be warranted. The authors claim that a large fraction of positively charged sulfuric acid clusters contain ammonia. While this is very probably true, the atmospheric relevance of the claim crucially depends on the total concentration of positively charged sulfuric acid clusters, which is likely to be quite low, for example compared to the concentration of negatively charged clusters. A large

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fraction of a very small number is still a very small number! The affinity of sulfuric acid to positively charged clusters seems to be quite low overall, as shown by the modest free energy changes for sulfuric acid addition reactions in Table 2 and by recent computational studies (both by the authors and by others) on the sign preference of sulfuric acid nucleation. The authors focus on ion-ion recombination, in which clusters with relatively small absolute concentrations may still play an important role, so their interest in the positively charged sulfuric acid clusters is quite understandable and justifiable.

Nevertheless, some rough estimates of the ambient concentrations of positive sulfuric acid clusters (or at least the ratio of positive to negative sulfuric acid - containing cluster concentrations) would be warranted. This could easily be computed based on data published earlier by the same authors.

In order to address the Reviewer's concerns, we estimated the concentrations of various positive ion clusters under typical conditions and discussed the implications in the revised paper.

-The authors might want to consider providing more of their computational data (cluster geometries in z-matrix or Cartesian format, absolute values for electronic energies, enthalpies and entropies, and/or vibrational frequencies) as a supplement file. This is customary (and often even obligatory) in many journals specializing in computational chemistry, even though e.g. ACP does not seem to have any specific policies on the subject. The authors have, during the past few years, built up an impressively large cluster energetics dataset by consistently applying the same level of theory to different cluster types. Unfortunately, the usefulness of this dataset to other researchers remains somewhat limited, as the authors have often chosen to provide only selected parts of their thermodynamic data, e.g. reaction energies for some small subset of the possible cluster formation routes. A somewhat more extensive data publication strategy would be of significant assistance to nucleation modelers around the world, and probably also benefit the authors themselves.

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The authors are thankful to the Reviewer for a very good idea concerning the database. It is true that we have built up a large database of cluster geometries and energetics in the past couple of years. We will organize and compile these data and find a practical and convenient way to make these extensive data available to others in the future. At this point, to address the Reviewer's concerns, the Supplementary Information including Cartesian coordinates for the isomers shown in Figure 1 has been added to the revised manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 4231, 2009.

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