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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 thank the referee for the constructive comments, which helped to improve the paper. Our responses to the comments accompanied by the original comments (in Italic) are given below. We have revised the paper accordingly.

This paper presents the results of quantum mechanical calculations. Unfortunately, it does not attempt to evaluate their accuracy by comparison to experimental data and its main conclusion does not seem to be supported by the present results. Besides being too self-referential, the paper left out previous calculations (Ianni and Bandy, for example), it has made no reference to the sulfuric acid ion experimental thermodynamic data from Lovejoy and coworkers, it neglects also the experimental data on ammonia

and water proton clusters , and it left out some key reactions.

The accuracy of the method used in the present study has been evaluated via the comparison with the experimental data in a number of recent studies, and its performance in the case of atmospheric clusters has been found to well beyond satisfactory (see also comments by Reviewer 1). The statement concerning the predictivity of the method accompanied by the key corresponding references has been included in the original manuscript in the section of Computational Details. Moreover, the comparison of the data obtained using by PW91PW91/6-311++G(3df,3pd) with data by Lovejoy and coworkers have been made in e.g. Nadykto et al. (2008a, b, 2009) and it has been found that our results are in good agreement with the experiments of Lovejoy and others. The experimental data of Piccard et al. (2005) on ammonia proton clusters is shown in Table 1. The comparison with experimental data for water proton clusters has been given in Nadykto et al. (2006) and thus is not repeated here.

The statement that our work is to self-referential is not well justified because we have cited most of the relevant studies. The articles of Bandy and Ianni, which are among the pioneering works considering small neutral sulfuric acid hydrates and bisulfate clusters, were not cited in the paper because their predictions were found to be inconsistent with experimental data. The reason of the failure (problem with dispersion in functional selected by Ianni and Bandy in their studies) has been discussed in e.g. Nadykto and Yu (2007) and Kurten et al. (2007), and is out of the scope of the present work.

In order to address the Reviewer's concerns, the references to studies by Froyd and Lovejoy (2003) and Lovejoy et al. (2004) have been included in the revised manuscript. In Table 2, we added a column comparing our calculated Gibbs free changes at T=270K for the reaction of H2SO4 molecules with water proton clusters with those estimated by Froyd and Lovejoy (2003) from fitting simulated ion mass spectrum to the measured one. We have also included the reaction suggested by the Reviewer.

As pointed out by another reviewer (and this one in an initial quick review), a million

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times a very small number can still be a very small number. The authors' conclusion that ammoniated sulfuric acid positive ions are more abundant than neutral ammoniated sulfuric acid clusters is not supported by the facts. Another of their conclusions is, by inference, that charged clusters are more important than uncharged clusters in atmospheric nucleation. Fig. 4 is misleading and the preceding claim is essentially unverifiable. We are only left to use true abundances to evaluate this inferential claim. Figure 4 should present ratios for the species but the ratios should all have the same denominator. Therefore the authors must present in detail an abundance calculation such as the following in (A) and (B) where neat sulfuric acid is chosen as the denominator:

*(A) The ratio of ammoniated to non-ammoniated sulfuric acid water proton cluster ions is about 2.5 million (from Table 3 yet Figure 4 indicates 30 million?) for n = 3 at 295 K and 1 ppbv ammonia. The ratio of sulfated water proton clusters to neat sulfuric acid is about 6e-13 (Table 2 data for n = 3 and using 5e-17 atm for the abundance of the n=3 water proton clusters.) Thus the abundance of ammoniated sulfuric acid water proton clusters relative to neat sulfuric acid will be 2.5million*6e-13 = 1.5e-6.*

(B) From Table 3 (and figure 3) the ratio of neat sulfuric acid neutrals for ammoniated vs. non-ammoniated is 5e-4.

(B/A) This leads to a ratio for neutral ammonia H2SO4 clusters to positively charged ammonia H2SO4 clusters (via a proton) of 5e-4/1.5e-6 = a few hundred.

The ammoniation of neat sulfuric acid appears to be a suitable reference compound here as the ammonia sulfuric acid cluster appears to have a high abundance even at high RH (using values in Table 1.) It seems that the water content of the clusters will not change the overall impact of my concerns: i.e., the situation changes for the worse at high n (n= 5: 30 times 1e-11 = 3x1e-10 for A) and at low n there is a very low abundance of H3O+H2O clusters (« 1e-16 atm) for atmospheric conditions.

I think the conclusion that should be drawn from the results are that ammoniated sul-

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furic acid water proton clusters are third:

(1) sulfuric acid (plus hydrates) are most abundant (roughly 1e6 cm-3), (2) ammoniated neutral clusters of sulfuric acid and water (on the order of 1e3 cm-3) (3) ammoniated sulfuric acid water proton clusters (on the order of 10 cm-3.) (4) lastly, sulfuric acid water proton clusters.

The order is for T = 298 K. Are there temperatures where this order might change? The authors should evaluate this with the delta H values they and others have calculated. It would be good to have comparisons with experimental values as well.

The focus of this paper is on the conversion of (H3O+)(H2O)n-1 into (NH4+)(H2O)n and (H3O+)(H2SO4)(H2O)n-1 into (NH4+)(H2SO4)(H2O)n. We didn't state anywhere in the manuscript that "ammoniated sulfuric acid positive ions are more abundant than neutral ammoniated sulfuric acid clusters". Our conclusions that "a large fraction of positive sulfuric acid monomer ions may contain ammonia" and "most of neutral and negative hydrated sulfuric acid monomers do not contain ammonia" are based on the ratios of equilibrium concentrations of ternary (ammonized) clusters to those of corresponding binary clusters (Fig. 4). Nevertheless, the referee raised a good and valid point that the absolute concentrations are important.

Following the referee's suggestion, we added a figure in the revised manuscript showing the absolute concentrations of sulfuric acid (and hydrates), ammoniated neutral clusters of sulfuric acid and water, ammoniated sulfuric acid water proton clusters, sulfuric acid water proton clusters, ammoniated water proton clusters, and water proton clusters. The referee is correct that the concentrations of ammoniated and unammoniated sulfuric acid water proton clusters are quite low, at least for those clusters containing 6 or less water molecules that we have thermodynamic data. Our calculations showed that the concentrations of ammoniated water proton clusters are high and comparable to those of ammoniated neutral sulfuric acid and water clusters. The implications of these additional results have been discussed in the revised manuscript.

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Other questions: Very important calculations are missing:

H3O+ + H2SO4 -> H3O+.H2SO4 NH3 + H2SO4 -> NH3.H2SO4

The first one has been added into Table 2 in the revised manuscript. The second one has already been included in the Table 3 of original manuscript.

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