Atmos. Chem. Phys. Discuss., 9, S999–S1001, 2009
www.atmos-chem-phys-discuss.net/9/S999/2009/

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.

Anonymous Referee #2

Received and published: 23 March 2009

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.

As pointed out by another reviewer (and this one in an initial quick review), a million 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 10ˆ-11 = 3x10ˆ-10 for A) and at low n there is a very low abundance of H3O+H2O clusters ($<<$ 10ˆ-16 atm) for atmospheric conditions.

I think the conclusion that should be drawn from the results are that ammoniated sulfuric acid water proton clusters are third:

ACPD

9, S999–S1001, 2009

Interactive Comment

(1) sulfuric acid (plus hydrates) are most abundant (roughly ˜10ˆ6 /cm3),

(2) ammoniated neutral clusters of sulfuric acid and water (on the order of 10ˆ3 cmˆ-3)

(3) ammoniated sulfuric acid water proton clusters (on the order of 10 cmˆ-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 deltaH values they and others have calculated. It would be good to have comparisons with experimental values as well.

Other questions: Very important calculations are missing:

H3O+ + H2SO4 -> H3O+.H2SO4

NH3 + H2SO4 -> NH3.H2SO4

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

ACPD

9, S999–S1001, 2009