Atmos. Chem. Phys. Discuss., 8, S2720–S2722, 2008
www.atmos-chem-phys-discuss.net/8/S2720/2008/


Atmospheric Chemistry and Physics Discussions



# *Interactive comment on* "The role of ammonia in sulfuric acid ion induced nucleation" *by* I. K. Ortega et al.

**I. K. Ortega et al.**

Received and published: 15 May 2008

We would like to thank Dr. Hellmuth for his comments.

The use of quantum mechanical methods to study cluster structures relevant to the atmosphere presents several problems. The first of these is the computational effort needed to study large clusters with sufficient accuracy. The other main problem is the treatment of anharmonicity (both vibrational and configurational), which requires a really heavy computational effort . Our group is making big efforts to improve the existing strategies (Kurten et al. 2007b, Kurten et al. 2007c).

This work presents a new multi step strategy that can be applied to bigger cluster than before with good results., Naturally, there are still some points to improve, and we are working hard to fix them, but while some of them seems to be treatable in the near



Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

future, others, like the correct treatment of hydration, are likely to be more difficult. The main problem is the large number of water molecules that needs to be included in the cluster for a correct treatment of hydration. For example, for the largest clusters studied in this work, the number of water molecules can easily be around 16., Apart from the computational effort needed for calculations on such big clusters, the most difficult problem is scanning all the possible conformers of clusters containing 20 molecules. So far, the only way to look for the more stable conformers is using "chemical intuition" and then performing a low level calculation to choose the more adequate candidates among the initial guesses. We think that this is the step that needs more improvements, and we are working on it (e.g. by using classical potentials specifically developed for each system to perform the configurational search).

Specific comments (referee comments in italic):

-It would be helpful to insert some sentences (or footnotes) to relate the parameter input/output more clearly to the software modules. It has been done throughout the manuscript, but sometimes not unambiguously (cf. p. 5418, lines 8-9:Which of the listed parameters belong to TURBOMOLE?).

For thermodynamic calculations, we use vibrational frequencies from SIESTA, rotational constants from the geometries optimized with SIESTA, and electronic energies from TURBOMOLE. We will add more specific description of the input/output parameters in the revised manuscript.

- p. 5424, line 4-6: "This probably indicates that the presence of a second molecule of ammonia would lower this addition energy, allowing the cluster grow to larger sizes. In other words, clusters with four sulfuric acid molecules will probably contain 2 rather than 1 ammonia molecules in atmospheric conditions". I agree with the first sentence, but is the second one conclusive? I cannot see, that this conclusion is compelling here. In cases it is trivial, let me know without changing the sentence.

We agree with the referee, the sentence "In other words, clusters with four sulfuric



ACPD

8, S2720–S2722, 2008

acid molecules will probably contain more than 1 ammonia molecules in atmospheric conditions" makes more sense.

- p. 5434, Fig. 1 Most stable clusters: Compared the first version of the manuscript, Figs. 1b 1e have been replaced with new stable cluster configurations (n=3) (cf. location of the hydrogen bonds). I suspect, the new ones are a "bit" more stable than the previous ones. Please eventually comment principal problems of the identification of stable cluster configurations (in a footnote or so).

The errors in the figure were purely of a technical nature; the cluster structures shown in the first version were not the correct ones, and this was therefore corrected in the revised version. However, we agree with the referee that, in general, identifying the most stable cluster configuration can be problematic, as the energy difference between the two (or more) lowest-energy different conformers is often very small (less than 1 kcal/mol). A sentence on this topic will be added to the revised manuscript.

Technical

We will correct all the technical corrections pointed out by the referee in the revised manuscript.

References.

Kurtén, T., Torpo, L., Ding, C. G., Vehkamaki, H., Sundberg, M. R., Laasonen, K. and Kulmala, M.: A density functional study on water-sulfuric acid-ammonia clusters and implications for atmospheric cluster formation, J. Geophys. Res., 112, D04210, 2007b

Kurtén, T., Torpo, L., Sundberg, M. R., Kerminen, V. M., Vehkamaki, H. and Kulmala, M.: Estimating the NH3 : H2SO4 ratio of nucleating clusters in atmospheric conditions using quantum chemical methods, Atmos. Chem. Phys., 7, 2765-2773, 2007c

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 5413, 2008.