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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Chemical ionization mass spectrometry (CIMS) may not measure all gas-phase sulfuric acid if base molecules are present" *by* T. Kurtén et al.

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We thank the reviewer for his or her thorough work and constructive comments and suggestions. We have revised the manuscript accordingly.

The "bold statements" the reviewer refers to have been revised in light of the recalculated thermodynamics (see below), and the manuscript has been extensively rewritten. While some issues (such as the degree of amine-acid clustering) are now better resolved, we are unfortunately still not any closer to a truly quantitative estimate of the central issues related to the charging process itself - hopefully this is made more clear in the revised manuscript.

The reason for focusing on relative rather than absolute concentrations is that predictions for relative values of thermodynamic parameters are in general easier to do than for absolute values. Also, the relative results tend to be somewhat more reliable. However, we agree with the reviewer that the absolute extent of acid-amine clustering should be addressed in more detail. In addition, we have found that both the PW91 data and the data by Loukonen et al (2010) contain large errors in the acid-amine binding energies (though in different directions), requiring us to recompute the cluster distribution at a higher level of theory (G3). The kinetics of the clustering process has also been given more attention. A entire new section on this issue has been added to the manuscript, as suggested by the reviewer.

(As a side note, the reviewer is correct that the data by Loukonen et al overestimates the binding of some clusters. This is likely due to the vibrational scaling approach used, as described briefly in the revised manuscript. In contrast, the PW91 approach seems to significantly underestimate the amine-acid binding, despite good performance for acid-water and acid-acid binding.)

We have tested the effect of using tight convergence criteria and an ultrafine integration grid, and found them to be small - on the order of 0.1 kcal/mol with respect to the binding energies. Given the massive increase in computational effort associated with the tighter grid, as well as the large differences between e.g. PW91 and G3 or G3MP2 for the acid-amine binding, recalculating all clusters with the tighter criteria is clearly not cost-effective. However, carrying out the test , as suggested by the reviewer, was definitely warranted, and the test results have been discussed briefly in the manuscript.

The title has been changed as suggested by both reviewers 1 and 2.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 30539, 2010.