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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.

1)We agree that the uncertainties are significant. The problem is that there is not really any way of reliably assessing the uncertainty of quantum chemical values - some method may perform very well for a test set of molecules, but fail dismally for some other system. A case in point is the PW91 method used here, which works very well for sulfuric acid - water binding, but seems to perform much worse for sulfuric acid - amine binding. The G3 method which we have used for the smallest clusters in the

revised manuscript has a mean error of about 1 kcal/mol for a test set of formation enthalpies of single molecules, but again, this is not proof that its error is this small for the systems we have studied here. Therefore, we are hesitant to add explicit error margins (e.g. "+- 1 kcal/mol") into the tables, as these are not really true statistical error margins in the same sense as for some experimental results. Similarly, we do not really know the uncertainty of the nitrate ion concentration - we have simply performed calculations with what we believe to be reasonable maximum and minimum limits (the latter in the "sensitivity analysis" section).

2)The temperature of 298K has been chosen as the CIMS experiments are typically performed at room temperature. Errors due to the harmonic approximation do tend to grow as the temperature increases, but to predict chemistry at room temperature, the calculations have to be done at room temperature. The charged clusters as well as the amine-acid clusters are fairly strongly bound, so the effect of anharmonicity is overall much smaller than for e.g. water clusters, and also small compared to many other error sources.

3)These statements have been removed as part of the overall rewriting of the manuscript.

Minor comments: addressed as suggested. The 1995 reference was a typographical error, it should have read 1993.

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