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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.

Anonymous Referee #3

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The manuscript details a theoretical study of the influence of base molecules (i.e. ammonia and dimethylamine) during detection of sulfuric acid with nitrate ion chemical ionisation mass spectrometry (CIMS). Using density functional methods, the authors have computed thermochemical energies for a number of different ions, molecules and clusters involved when analysing gas-phase sulfuric acid and also provide mass balance and equilibrium equations to estimate corresponding charging ratios. They conclude that despite different CIMS setups, base-containing sulfuric acid clusters are more difficult to charge. The authors have considered many issues for the charging efficiency, including the different proton affinity of clusters and the evaporation of amines from sulfuric acid clusters with the subsequent complex detection in CIMS. The work

reported is of interest to those researchers using nitrate ion CIMS for the detection of H2SO4 and to the scientific community studying atmospheric nucleation processes. It is therefore appropriate for publication in ACP. The paper is well written and the methodology is clear. However, I would recommend the following points/changes are addressed prior to publication.

Main comments:

Page 30543, line 14: The authors provide a general uncertainty for the quantum approximations of about 1-2 kcal/mol. This seems a significant value (if one compare the values given in tables) to be considered although they argue that the order-of-magnitude would provide a good qualitative estimate. It will be better if they provided more detailed uncertainties and included the uncertainties for the estimated concentration of nitrate ions.

Page 30546, line 3: I find the temperature for the example, 298K, very high for the clustering system whereas experimental studies have been focused on much lower temperatures (e.g. Hanson and Eisele, 2002). Is this temperature chosen in relation to the limitations of harmonic approximations?

Page 30552, line 7: the authors state that calculations of charging probabilities indicate that less than one fourth of the amine clusters will be charged, and 'hence measured by CIMS'. Given that the authors subsequently go on to note that many of the conditions within the CIMS environment do not correspond to the conditions assumed for these calculations, the statement 'hence measured by CIMS' is potentially misleading the reader at this point and I would recommend its removal. Similarly for page 30551 line 6, 'To assess the effect of this on the charging probabilities in CIMS'.

Minor comments:

Figure 1 is summarising the issues studied in the paper. I think the last statement is unnecessary: '. . .and are highly qualitative in nature'.

Page 30548, line 5 and 6: For consistency with the surrounding text, I suggest replacing the stated reaction formulas with the caption references, R1a and R1b.

Page 30552, line 27: Reference missing, Tanner and Eisele (1995).

References:

Hanson, D. R. and Eisele, F. L.: Measurement of prenucleation molecular clusters in the NH3, H2SO4, H2O system, J. Geophys. Res., 107, 4158, doi:10.1029/2001JD001100, 2002

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