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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 #1

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Title: Chemical ionization mass spectrometry (CIMS) may not measure all gas-phase sulfuric acid if base molecules are present Authors: Kurten et al.

This manuscript reports on a theoretical study into the mechanistic aspects of a chemical ionization mass spectrometry (CIMS) method based on the nitrate reagent ion. This method is widely utilized in the aerosol nucleation community for detection of atmospheric sulfuric acid and its various neutral clusters. Using thermodynamic data obtained from density functional theory (DFT) electronic structure calculations, it is concluded that in the presence of strong bases, such as amines, a significant fraction of gaseous sulfuric acid may remain undetected. Another conclusion from this work is

that amines are not likely to affect the detection of clusters that contain more than one sulfuric acid molecule.

The manuscript, as revealed in its title, raises a relevant question regarding the actual fraction of atmospheric sulfuric acid detected by CIMS, but the paper does not provide sufficient data to address such an issue. Initially, a bold statement is made that only one quarter of gaseous sulfuric acid would be detected by CIMS in the presence of 1 ppt of amine. Later, it appears that the authors step back from this statement, showing that for a number of reasons (assumptions of thermodynamic equilibrium and constant amine concentration) the actual detected fraction could be significantly higher. However, in the end, no quantitative estimate, accounting for the above factors, is provided, leaving the detection problem unresolved.

I find it rather puzzling that the bulk of the manuscript focuses heavily on the ionization efficiencies of different clusters, while only a brief consideration is given to the ABSOLUTE concentrations of those clusters. I suggest that a thorough account of the calculation of the absolute cluster concentrations should be presented in the manuscript instead of merely referring to the data obtained in a previous study (Loukonen et al., 2010). Also, the uncertainties associated with the binding energies and resulting concentrations of clusters should be explicitly included and discussed. For instance, according to Loukonen et al. (2010), bare and hydrated sulfuric acid dimers are significantly more stable than it was found in a recent experimental study (Hanson and Lovejoy, 2006), giving a reason to suspect that the stability of the sulfuric acid – amine clusters may also have been overestimated by DFT. If the concentration of the sulfuric acid - amine clusters is actually low (i.e., only a small fraction of sulfuric acid is bound to amines), the low charging efficiency of those clusters would not matter and the conclusion would be that all sulfuric acid will be detected by CIMS.

The conclusions made in this paper rely on DFT electronic structure calculations to obtain thermodynamic properties of charged and neutral clusters. However, only superficial information is provided about the computational details. DFT calculations of

complexes and clusters often require the use of an ultrafine integration grid and tight convergence criteria in order to obtain accurate energies and structures. Have default energy and geometry convergence criteria mentioned in the manuscript been sufficient to locate true minima and obtain accurate thermodynamic data for the complexes considered in this study?

Overall, the manuscript is well written, the subject of this study is relevant to the area of ACP, and the results may have important implications to the measurements of atmospheric sulfuric acid and its clusters. I suggest revision of the manuscript by including an additional section (after section 3.2), which would present a detailed calculation and analysis of cluster concentrations. Also, depending on the results of this analysis, the title may have to be modified.

References:

Loukonen, V., T. Kurten, I. K. Ortega, H. Vehkamaki, A. A. H. Padua, K. Sellegri, and M. Kulmala, Enhancing effect of dimethylamine in sulfuric acid nucleation in the presence of water - a computational study, Atmos. Chem. Phys., 10(10), 4961-4974, 2010, 10.5194/acp-10-4961-2010.

Hanson, D. R., and E. R. Lovejoy, Measurement of the thermodynamics of the hydrated dimer and trimer of sulfuric acid, J. Phys. Chem. A, 110(31), 9525-9528, 2006, 10.1021/jp062844w.

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