

***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)The title has been changed, and the original work by Eisele and Tanner has now been more explicitly credited in the introduction.

2)As the equilibrium constants correspond to the ratio of the forward and reverse reaction rates, even the equilibrium distributions give some indication of the relative charging probability of different cluster types. However, the reviewer is entirely correct that the kinetics of the process should be addressed in more detail. Several paragraphs

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discussing the kinetics have now been added to the manuscript. The sentence recommending other users to repeat the calculations has also been removed, as suggested.

3) We agree with the reviewer that more discussion on kinetics/dynamics is needed. A new section on the acid - base clustering has been added to the manuscript, including both more accurate (G3-level) thermodynamics, and discussion on the dynamics of the process. The clustering of amines and acids presumably occurs at fairly close to the collision rate (there are no major kinetic barriers to cross as the clustering reaction involves H-bond formation, which is usually close to barrierless). With this assumption, both thermodynamics and kinetics now suggest that the threshold amine concentration for significant clustering to occur is in the 1-10 ppt range.

4) The reviewer is correct that the CIMS charging process is kinetically limited, and that the predominant reaction ion is likely the $\text{NO}_3\text{-(HNO}_3\text{)}$ cluster in almost all steps. However, the charging efficiency still depends on the concentration of neutral HNO_3 both from a thermodynamic and kinetic viewpoint (the latter via the net rate of the reverse reaction of R2b in the manuscript). Thus, some differences between CIMS setups with strongly different HNO_3 concentrations may still be observed. However, this difference can not be larger than the maximum overall effect of the amine contamination on the HSO_4^- signal, which according to the more accurate (G3MP2) thermodynamics is only on the order of some tens of percent even for high amine and HNO_3 concentrations. The section concerning instrument comparison has been revised accordingly, and the issues raised by the reviewer have been discussed.

The structure of the manuscript has also been changed to match the reviewer's suggestion: first, the cluster distribution as a function of the amine concentration is discussed, and subsequently the charging of the clusters, followed by a discussion on amine evaporation after charging.

Minor comments: -Mention of malonic and methane sulfonic acids has been added. -Repetitions of the nitrate ion and nitric acid concentrations have been removed as

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suggested. -The 1995 reference was a typographical error, it should have read 1993.

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

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