

## ***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 #2**

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Kurten et al. present a theoretical study on the ability of CIMS systems designed for the measurement of gaseous sulfuric acid in the atmosphere to also measure sulfuric acid in neutral clusters with other molecules. They use quantum chemical approximations to derive cluster binding energies between various molecules and between molecule (-clusters) and ions. By further using mass balances and chemical equilibrium considerations they try to characterize the charging probability of various neutral clusters by nitrate-nitric acid clusters in CIMS. As a result of this study, certain amine containing clusters and some of the ammonia containing clusters may not be charged quantitatively by nitrate based ionization, and the efficiency of charging further depends on the experimental conditions of the CIMS system.

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The paper is of interest for particle nucleation studies though it mainly addresses issues related to a highly specialised measurement technique, and it might be thought of better presenting this paper in a journal focussing on measurement techniques. On the other hand side, a lot of theoretical estimations of binding energies and reactions of clusters are presented which are of importance also for nucleation processes in the atmosphere. Subject, language, style and presentations are generally appropriate for ACP. However, there are some general comments concerning title and focus of this study, the relation of this theoretical study to experimental data, and the implications of this study.

1. The title is in my opinion misleading as it states that not all gaseous sulfuric acid is measured by CIMS in the presence of base molecules. It should better say that CIMS may not measure all sulfuric acid that exists in specific clusters with base molecules in the atmosphere. This, however, is not new. In the original paper by Eisele and Tanner (1993), it is clearly stated that this technique is only appropriate for sulfuric acid in the “. . . gas phase. This includes monomers and may be some dimers and trimers, all of which may be hydrated but with diminishingly small contributions from the larger clusters. . .”. They also address the ability to measure gas phase ammonium bisulfate, but point out that “. . . preliminary studies in our laboratory suggest that such a contribution if present would probably be quite small”. The original papers by the Eisele group should be spent more credit, and the authors should think of changing the title and focus of the paper into “Theoretical study on clusters containing H<sub>2</sub>SO<sub>4</sub> and base molecule in the atmosphere and their potential to be detected by nitrate based CIMS”.

2. The section 3.1 “charging mechanism in CIMS” does not appropriately consider the short time constant for charging reactions of typically 0.1 sec. Thus, charge transfer is kinetically limited and only a very small fraction of sulfuric acid is ionized (see Eisele and Tanner, 1993). The authors, however, discuss an equilibrium distribution which is not justified. Their conclusion that unionized to ionized sulfuric acid is below 0.1% is not correct. Furthermore, it is hard to understand why the authors “. . . recommend

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other CIMS users repeat these calculations using appropriate NO<sub>3</sub>- and HNO<sub>3</sub> concentration estimates.” They themselves admit to have an uncertainty of the nitrate concentration by some 4 orders of magnitude and that HNO<sub>3</sub> is determined by its ambient air abundance.

3. The same principle objection also holds for the following section 3.2. An equilibrium assumption is not appropriate for the short encountered reaction times. Thus, the ionization estimates on page 30552, 1st paragraph, are very crude and do not really tell about the fraction of ionized sulfuric acid – base molecule clusters detected by CIMS. Furthermore, the authors estimate that for 1 ppt amine concentration more than 98% of H<sub>2</sub>SO<sub>4</sub> would cluster with amine and be by far not quantitatively detected by CIMS. Here again, the authors admit themselves (p. 30553) that the validity of the equilibrium assumption is not given. It would be of interest, instead, to estimate the reaction rate constant of H<sub>2</sub>SO<sub>4</sub>-water clusters with amine to form a stable cluster and thus estimate the fraction of H<sub>2</sub>SO<sub>4</sub> lost to amine clusters and compare it to the loss to existing aerosol surfaces. Also atmospheric budgets of H<sub>2</sub>SO<sub>4</sub> generally indicate a missing source or an overestimated sink (e.g. Eisele and Tanner, 1993, Petäjä et al., 2009) and give no indication for a missing H<sub>2</sub>SO<sub>4</sub> sink, like the cluster forming reaction with amines.

4. In the section 3.4, the authors tentatively conclude implications for different CIMS instruments for their different ability to measure the various clusters and thus come up with different results. However, since the CIMS charging probability is a kinetically limited process, the charging depends on the concentration of the nitrate ion (and its clusters with nitric acid) and the respective rate constants. Because the calibration is generally based on sulfuric acid and the NO<sub>3</sub>-(HNO<sub>3</sub>) cluster is the by far predominant reaction ion in CIMS systems, differences between different CIMS systems are not expected to be substantial. The authors should revise their discussion here, and should think of a specific estimate of how much deviation is expected between two specific CIMS systems.

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Similar to the concerns from Referee #1, I'd encourage the authors to first address the question of the most probable H<sub>2</sub>SO<sub>4</sub> clusters formed in atmosphere, starting from H<sub>2</sub>SO<sub>4</sub>-water clusters which then react with other compounds and form more complex clusters. This should be done as a kinetic process, as life time of H<sub>2</sub>SO<sub>4</sub> is limited to a few minutes. If significant fractions of H<sub>2</sub>SO<sub>4</sub> exist in such clusters, these should then be checked for their charging probability in CIMS.

#### Minor Comments

p. 30541, l. 12: Contrary to what is stated here, in continental atmosphere often ambient malonic acid observed by nitrate ion CIMS, and in marine environment methane sulfonic acid (e.g. Eisele and Tanner, 1993; Berresheim et al., 2002)

p. 30549, l. 20-26: There are quite a few repetitions here which should be omitted.

p. 30552, l. 26: Reference Tanner and Eisele (1995) is missing.

#### References

Berresheim, H., T. Elste, H. G. Tremmel, A. G. Allen, H.-C. Hansson, K. Rosman, M. Dal Maso, J. M. Mäkelä, M. Kulmala, and C. D. O'Dowd, Gas-aerosol relationships of H<sub>2</sub>SO<sub>4</sub>, MSA, and OH: Observations in the coastal marine boundary layer at Mace Head, Ireland, *J. Geophys. Res.*, 107(D19), 8100, doi:10.1029/2000JD000229, 2002.

Eisele, F., and D. Tanner, Measurement of the gas phase concentration of H<sub>2</sub>SO<sub>4</sub> and Methane Sulfonic Acid and estimates of H<sub>2</sub>SO<sub>4</sub> production and loss in the atmosphere, *J. Geophys. Res.*, 98(D5), 9001-9010, 1993.

Petäjä, T., Mauldin, III, R. L., Kosciuch, E., McGrath, J., Nieminen, T., Paasonen, P., Boy, M., Adamov, A., Kotiaho, T., and Kulmala, M.: Sulfuric acid and OH concentrations in a boreal forest site, *Atmos. Chem. Phys.*, 9, 7435-7448, doi:10.5194/acp-9-7435-2009, 2009.

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