

## ***Interactive comment on “Atmospheric sulphuric acid and neutral cluster measurements using CI-API-TOF” by T. Jokinen et al.***

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Referee #1 We wish to thank the referee for all the useful comments which are addressed below:

Specific comments:

- 1) Thank you.
- 2) We agree on this matter.
- 3) The referee is correct that the equation 1 and R1 are not consistent in their nomenclature. We corrected the Eq1 to reveal that the proton is associated with the nitrate. An important point to realize with our CI-API-TOF instrument in contrast to CIMS instru-

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ment (Eisele and Tanner, 1991) is in a fundamental manner different. In CI-API-TOF we do not have a collision cell and thus the clusters are not reduced to core-ions after chemical ionization. Thus, we need to consider the sum of sulfuric acid monomer and the associated nitrate while converting our raw counts to concentration.

The referee is correct to point out a mistake in units. We added molec cm<sup>-3</sup> as the unit of our calibration coefficient.

4) It is true that there is more scatter in low concentrations of sulfuric acid apparent in Figure 1. This is due to two things. First, the reference CIMS instrument has a nominal detection limit is 5e4 for 30-min average (Mauldin et al. 2001), and secondly, there are not too many one hour average concentrations in the lower concentration regime.

5) The referee is enquiring about the true nature of the sulfuric acid clusters that we have measured whether they are naturally charged or neutral objects that are charged in the CI source. The whole point of our work is to elucidate this point. Our main result is shown in Figure 4. It shows that the sulfuric acid monomer is clearly charged by the CI source and the signal attributed to the other –mers are originating from naturally charged sulfuric acid ions.

6) We did not keep the colour coding the same throughout the paper. This might be the distracting fact for the referee. In Figure 2 we show high resolution mass spectra corresponding to sulfuric acid a) monomer, b) dimer, c) trimer, and d) tetramer. The sulfuric acid –mer is depicted in purple dashed line as indicated in the figure caption. The green trace presents the other compounds found in the high resolution mass spectra. The referee is correct that in the case of 195 amu range (dimer), the impurity corresponds to fluorinated contaminant.

7) The annotation is done for a reason. Titles are correct, first we wanted to depict the general evolution of the new particle formation (panel DMPS). Furthermore, we wanted to show side by side sulfuric acid monomer and dimer (97 and 195), and trimer and tetramer (293 and 391). The 408 panel, which corresponds to sulfuric acid tetramer

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associated with ammonia. The ion concentration in the ordinate is counts per second, since we cannot convert the raw signal to concentration in the case of multimers.

We wanted to show, what would a unit-mass resolution CIMS detect as a signal for multimers. This is depicted as green lines in the figures. This was done to underline the crucial fact that one needs a high resolution time of flight instrument to detect reliably the multimers as the signal is obscured by contaminant components. Each multimer of sulfuric acid is presented in a separate panel.

The referee points out that during some period of time the neutral signal seems to dominate over the ion signal. This could be attributed to the fact that the ion APiTOF was during the campaign more sensitive.

8) Our method is quite similar to the one of our “Chinese” colleagues (If referring to Zhao et al., ), and our system should detect neutral clusters the same way as theirs. We, however, have found that using the mass resolution insufficient for separating compounds having a same integer mass might yield to serious measurement artifacts. Higher  $n$ -mers can still exist.

9) We expect that organics can “hide” the clusters, as discussed in the introduction-chapter of the paper.

To connect our observations to nucleation rates and to a specific nucleation mechanism is out of the focus of the present study.

This study cannot be interpreted to be supporting or not supporting Petäjä et al. results. But results of Petäjä et al. do not describe our observations in Hyytiälä conditions for yet unknown reason.

We wished that our experiment yielded information on the ternary species participating in nucleation, but as we had no indication of neutral clusters that wish was not fulfilled.

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Interactive comment on Atmos. Chem. Phys. Discuss., 11, 31983, 2011.

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