Review of manuscript acpd-11-31983-2011: “Atmospheric sulphuric acid and neutral cluster measurements using CI-APi-TOF”

(submitted for publication in Atmospheric Chemistry and Physics)

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Referee report (anonymous)

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1 Overall evaluation

I recommend the editor to accept the manuscript for publication in ACP after minor revision.

2 General comments

The paper contributes to an important subject of atmospheric chemistry and physics, namely the elucidation of evolutionary formation pathways of ultrafine particles and their precursors in the planetary boundary layer. Having in mind the ongoing discussion regarding this subject, it seems that it is still impossible to “close the book” with the story about the evolutionary steps from the primordial vapour phase to the embryonic phase (in the atmosphere). One reason for this is the missing information about the chemical composition of newly formed particles of nanometric sizes (near the critical size), the knowledge of which would allow us to safely identify the key precursors. Until this problem is solved in a satisfying manner, one relies on atmospheric measurements of possible atmospheric precursors with refined detection methods (lowered limits of detection, measurements of higher aggregation states of monomers and ions of precursor gases such as sulphuric acid).

Sulphuric acid, safely identified as a key precursor gas, occurs in different degrees of hydration and merisation and in ionised form. The authors presented "the first ambient measurements using nitrate ion based Chemical Ionisation with the Atmospheric Pressure Interface Time-of-Flight mass spectrometer CI-APi-TOF) for sulphuric acid and neutral cluster detection" and aimed "to investigate the initial steps of neutral nucleation and [to] enlighten the role of sulphuric acid, ions and stabilising compounds in atmospheric aerosol nucleation." Thus, the paper focusses on both the more "technical problem" of measurements and on the mechanistic explanation of new particle formation. In view of the enormous effort (inclusively tricky problems in application of mass spectrometry) required to ensure high-quality data on atmospheric sulfuric acid, this paper provides a necessary and significant contribution to the community. The paper is scientifically relevant and satisfies ACP standards for publication.

In my specific comments I will raise some questions, which can hopefully help to make some points more clearly in a revised version of the manuscript.

3 Specific comments

1. The abstract is clear.

2. The introduction gives a meaningful overview about the problem and state of the current discussion, especially about seemingly contradictory findings on the contribution of ions to new particle formation. A key problem of mass spectrometry is the "manipulation" of the object of investigation (neutral composite clusters) by the method itself. Inherent in mass spectrometry is the necessity to "artificially" charge neutral clusters and to destroy their natural structure (as a collateral damage). The application of selective ionisation methods to generate artificial ions and adducts is associated with the problem that the proton affinities of neutral composite clusters (sulphuric acid plus stabilising compound) and pure sulphuric acid molecules may differ. Thus, neutral-cluster charging upon collision with charger ions might be hampered, or in case of success, can decrease the cluster stability and lead to a loss of constituting components. The authors concluced: "Therefore, direct measurement of the true molecular composition of neutral clusters is

not possible by means of a chemical ionisation mass spectrometer as some information will be lost upon charging." The key idea of the CI-APi-TOF instrument is the ionisation of neutral sulphuric acid molecules and clusters via proton transfer involving nitrate ions. In this way the ionisation product $HSO_4^-{\cdot}HNO_3$ becomes a marker for the H_2SO_4 molecule to be measured.

3. While Reaction (R1) is clear to me, Eq. (1) is not. Denoting the second-order forward reaction coefficient with $k_{\mathrm{f}}^{(\mathrm{II})}$ and the second-order backward coefficient with $k_{\mathrm{b}}^{(\mathrm{II})}$, I would write the differential equation for (R1) as follows:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{HSO_4^-{\cdot}HNO_3}] &= k_{\mathrm{f}}^{(\mathrm{II})} \times [\mathrm{H_2SO_4}] \times [\mathrm{NO_3^-{\cdot}(HNO_3)_{n,n=0-2}}] \\ &\quad - k_{\mathrm{b}}^{(\mathrm{II})} \times [\mathrm{HSO_4^-{\cdot}HNO_3}] \times [\mathrm{(HNO_3)_{n,n=0-2}}]\,.\end{aligned}$$

In dynamic equilibrium (setting the left-hand side equal to zero), we obtain:

$$\begin{aligned}[\mathrm{H_2SO_4}]_{\mathrm{eq}} &= \frac{k_{\mathrm{b}}^{(\mathrm{II})}}{k_{\mathrm{f}}^{(\mathrm{II})}} \times \frac{[\mathrm{HSO_4^-{\cdot}HNO_3}] \times [\mathrm{(HNO_3)_{n,n=0-2}}]}{[\mathrm{NO_3^-{\cdot}(HNO_3)_{n,n=0-2}}]} \\ &= \underbrace{\frac{k_{\mathrm{b}}^{(\mathrm{II})}}{k_{\mathrm{f}}^{(\mathrm{II})}}}_{=C} \times \frac{[\mathrm{HSO_4^-{\cdot}HNO_3}] \times \sum_{\mathrm{n=0}}^{2} [\mathrm{(HNO_3)_n}]}{\sum_{\mathrm{n=0}}^{2} [\mathrm{NO_3^-{\cdot}(HNO_3)_n}]}\,.\end{aligned}$$

In this case, the ratio of backbard/forward-rate constants define the dimensionless calibration constant C. The concentration units at both sides of the equation are consistent (in your Eq.(1) it is not). I suspect the plus sign in the numerator at the rhs of Eq. (1) must be replaced with a multiplication sign. Please explain the origin of $H_2SO_4{\cdot}NO_3^-$ in your Eq. (1) (it is per m/z ratio identical to $HSO_4^-{\cdot}HNO_3$, but is this chemically meant?).

4. P. 31988: From Fig. 1 I see that the final calibration coefficient is not constant over the whole concentration range (down to the detection limit (LOD)). Thus standard calibration coefficient is obviously valid only down to $10^6\,\mathrm{cm}^{-3}$. Below there is large(r) scatter.

5. On page 31990 you have evaluated deprotonated sulphuric acid monomer HSO_4^-, dimer $H_2SO_4{\cdot}HSO_4^-$, trimer $(H_2SO_4)_2{\cdot}HSO_4^-$, tetramer $(H_2SO_4)_3{\cdot}HSO_4^-$.

What is the “true nature” in these objects and what is induced by “artificial” ionisation due to the measurement method? I suspect, the degree of merisation is a natural (true) signal, but the ionic form originates from the ionisation in the device, or? For non-specialists it is difficult to recognise, what originates from natural (atmospheric) charging and what from chemical ionisation. Please add a sentence.

6. In Fig. 2 there are several peaks: the dashed purple lines correspond to the sulphuric acid monomer signal (m/z=97), the blue ones to higher mers (as described). Are the blue curves superpositions of the green ones? Can the green peaks be attributed to specific compounds in the sulphuric acid mers or is it simple mathematical assistance? Are the green peaks linked to the fluorinated compounds described later?
7. Figure 3[1]: Please check the order of figures and/or annotations (408 - 97 - 195 - 293 - 391; are the figures unsorted or the annotations or both?). Check the unit of the ion concentration at the ordinate (it must be $\mathrm{molec\,cm^{-3}}$). Does the green line (integer mass) represent the total mass of all ingredients in the detected in the vapour mixture? Does the blue line include all sulfuric clusters (i. e., monomers, dimers, trimers etc.)? As an unguided observer I would conclude that the number concentrations of sulphuric acid clusters (blue) are always significantly larger than the natural ion concentrations (red) (except for 293 Th data at 29:40 and 30:30 hour were charged particles dominate).
8. Figure 4: From this figure I can understand that the CI-APi-TOF derived concentration of sulphuric acid monomers (blue) is significantly higher than the API-TOF derived concentration of naturally charged ions (green), i. e., artificially charged monomers exceed the naturally ones. This makes the application of CI-APi-TOF for sulphuric-acid monomer measurements reasonable. In contrast to this, the CI-APi-TOF concentrations of artificially charged 195 Th, 293 Th, 391 Th, 408 Th clusters (among them dimers) were found to be in the same order of magnitude as APi-TOF concentrations of the corresponding naturally charged clusters. Hence, does the CI-APi-TOF method not allow a reliable detection of neutral higher mers? Is your message that (a) dimers, trimers, and tetramers cannot be doubtless detected by

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[1] The size of this figure is direful, not readable without PC display.

your method (in contrast to the reported findings of the Chinese colleagues for sulphuric acid tetramers), or (b) that higher mers do not exist?

9. I agree with the conclusion that the CI-APi-TOF field observations do not support Petäjä's laboratory findings on collision-limited formation of sulphuric acid dimers, i. e., "kinetically limited neutral sulphuric acid nucleation seems implausible." However, the estimated steady-state dimer concentrations at Hyytiälä (Eq. (2)) can also not rule out neutral dimer formation under laboratory conditions, or? The authors wrote that "the variation in observed rates *can partly* result also from changing concentrations of ternary species" or *can* originate from "rapid condensation of oxidised organics on dimers forming compounds that cannot be detected using nitrate ion based chemical ionisation." Do you expect that condensed organics are able to "hide" dimeric clusters (if they would exist)? What about previous empirical findings from Hyytiälä (and many other places) supporting a power of two dependence of sub-3 nm particle formation rates on sulphuric acid concentration (some data revealing exponents of less than two, others of more than two)? Is a linear dependence (power of one according to activation theory) the general accepted view on this problem? Can the authors propose a way by which the "unknown" third species (e.g., amine) can be identified in ambient samples? It would be nice to get to know authors position on these issues.

10. Technical:

    - P. 31987: In the literature the annotation m/z is more frequently used than m/Q for the mass-to-charge ratio. A hint to the unit "Thomson" for Th might be helpful (1 Th=1 Da/e; note, "Thomson" is non-SI unit).
    - P. 31989, line 12: add meaning of ^{241}Am source (from the context: ammonia source?);
    - P. 31898, line 23: the meaning of the "resolving power" and its unit (3600 Th/Th) is not clear to me; maybe you can add a sentence;
    - P. 31992, line 22: write "cannot" (also on p. 31993, line 18);
    - P. 31992, line 24: avoid "that ... that ..." construct in this sentence;
    - P. 31993, line 17: maybe "oxidised organics";

- P. 31999, Figure 1: add concentration units (cm^{-3}) at least to the text in the caption.

Anonymous