Atmospheric Measurement Techniques Discussions

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Comment on amt-2021-57

Anonymous Referee #3

Referee comment on "Iodide CIMS and *m/z* 62: the detection of HNO_3 as NO_3^- in the presence of PAN, peroxyacetic acid and ozone" by Raphael Dörich et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2021-57-RC3, 2021

The paper reports an investigation of the influence of the presence of HNO3 on the detection of NO3- and N2O5 when using chemical ionization mass spectrometry with I- as the reactant ion. Investigations are reported for especially the effect of ozone and humidity (that may affect the reactions through direct association of water molecules to ions). Additionally, the effect of PAN or PAA, that can release acetate anions causing extra reactions with HNO3, are reported. Finally, examples of field data, where the significance of the HNO3 trace gas is important for data interpretations of I-CIMS data, is given. The reported investigations wer motivated by observations from air borne measurements using an I-CIMS where the magnitude and variation of the signal at mass 62 (NO3-) seemed to contradict previous beliefs on the measurement sensitivity to trace amounts of HNO3.

The theme of systematic sources of inaccuracies in CIMS measurements is of high relevance in general to atmospheric measurements and the presented results give important information on this aspect for the particular case of HNO3 trace gases in I-CIMS. As such the paper is of high relevance.

The supplementary information is not available, and as I learned from the editors, this information was actively removed by the authors prior to the review process. The supplementary information is in fact heavily needed to critically address the content of the paper, in particular

- Page 2 - Fig. S1 – should illustrate the data that motivated the re-investigation of the sensitivity of the I-CIMS detection of N2O5 to presence of the HNO3 trace gas
- Page 4 - Fig. S2 – should show details of the experimental calibration
- Page 9 - Fig. S3 – should give more information on the data corresponding in fig. 7
- Page 12 - Fig. S4 + Fig. S5 – should show data from The CAFE-Europa flights

I consider the removal of the supplementary information, where essential information is given and to which reference in made throughout the manuscript, as rather unserious and problematic. On this account, I would strongly hesitate to consider the paper for acceptance.

General comments to the paper.

While the introduction is well written and easily accessible, the sections "experimental details" and "Laboratory characterization" could well be work over again for logic argumentation and clarity in the presentation.

I have the following specific comments, if the editors at all find the paper relevant for publication after the removal of the supplementary information.

Comment 1: Title and Abstract(e.g. line 11,14)

The meaning of PAN is not given. Should be mentioned the same way as PAA. In line 14 either use PAN and PAA or give the chemical formulas for both – a least be consistent.

Comment 2: Page 2, Line 34-45 – several references to literature is missing . The statement "In very well known series of reactions …" must be backed up with a reference where one can find the reaction rate constants for these reactions.

The statement on the "non-gas loss process" should also be backed by references

The statement on rapid photolysis of NO3 should also be quantified with a reference and an actual number for the photolysis rate.

Comment 3: Page 3, line 81.

I believe a rate of 380 s-1 would correspond to ~3 ms rather than ~2 ms as stated, or simply state 2.63 ms to keep the number of significant digits ?. I am also missing the reference that tells where the stated reaction rates comes from, i.e, where do the numbers 380 s^-1 and 1940 s^-1 come from. To appreciate the importance of these timescales, the authors should also specify the transport time of the various ions though the instruments sectors. I realize that some of this information can (partly) be reconstructed from the description of pages 6-7, but it should be clearly stated in this place, which would also ease the reading of the pages 6-7 a lot.

Comment 4: page 3, line 86.

Give reference to the origin of the stated reaction rate constants.

What was the actual concentration of added NO ?

Comment 5: page 5, line 133.

To appreciate that it is correct to normalize all signals to the primary ions signal, the reader need to be assured that the intensity of this peak (mass 127) is not affected (i.e. only marginally) by the reactions taking place. The authors needs to quantify this more precisely. I am in particular puzzled, since the [I(H2O)]/[I] ratio changes dramatically (approximately a factor of 7 (stated as 6, line 116)), so a least humidity most be important here ?

Comment 6: page 5, line 133-135.

Could you expand on the explanation why reaction R6 (association of water to I-) is affected by the concentration of O3. This may be true in some indirect way, but to understand that, it really requires a more explicit explanation at this place in the paper.

Comment 7: page 5, line 146.

The statement "This could be confirmed … m/z 62" seems to reflect an action that the authors speculate could prove their point that the first mentioned explanation for the sensitivity to O3 is not likely. Is this speculation or did you really do the suggested measurement ? It would be good to see the suggested evidence. (A figure in the missing supplementary information would be fine)

Comment 8: page 5, R10.

On the right hand side, IO2- should be IO3-

Comment 9: page 6-7 - discussion of the observed intensities of IOx-.

Given the rate coefficients of the various reactions, it seems straightforward to calculate the steady state distributions of I-, IO-, IO2-, and IO3- under the various conditions shown in figure 3. Following all the argument that ends on line 200, I believe it would worthwhile to do such a (simple) calculation and compare the result to the data in figure 3.

Moreover, following the discussion one page 7-8, in line 242, the statement is made that " confirming that the detection of IO3- in our experiment is inefficient" (see also line 223-24). I am puzzled if the efficiencies of the various IOx- components may affect the actual relative intensity ratios between them. The authors needs to clarify this issue.

Comment 10: figure 7a and equation 2.

Please explain the idea of suggesting the form in equation 2 to represent the data. I suppose it represents a short of saturation – but please clarify this more explicitly. Also the description in line 251 that "is clearly non-linear" is not really true: except for the lowest curve (18.5ppbv) all displayed curves are in fact linear to a good approximation as also suggested by eqn. 2, which is indeed almost linear at low [O3].