

Referee 3

We thank the referee for a positive assessment of our manuscript. The comments (in black), our response (in blue) and changes to the manuscript (in red) are listed below.

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 were motivated by observations from airborne 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 is made throughout the manuscript, as rather unserious and problematic. On this account, I would strongly hesitate to consider the paper for acceptance.

We posted the SI in response to this comment. As we state, the retraction of the SI was not intentional. If we had not intended to show the SI we would not have cited it in the manuscript.

General comments to the paper.

While the introduction is well written and easily accessible, the sections “experimental details” and “Laboratory characterization” could well be worked 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.

We posted the SI in response to this comment.

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.

In the atmospheric chemistry community the acronym PAN is more readily recognised than its correct, full name (peroxy acetyl nitric anhydride) so we prefer to keep it as PAN in the title. However, we have now defined PAN in the abstract:

....in the presence of peroxy acetyl nitric anhydride (PAN) or peroxyacetic acid (PAA).... and subsequently refer to the acronyms....

The loss of CH_3CO_2^- via conversion to NO_3^- in the presence of HNO_3 may represent a significant bias in I-CIMS measurements of PAN and PAA in which continuous calibration (e.g. via addition of isotopically labelled PAN) is not carried out.

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.

We now list two citations:

In a very well-known series of reactions (Lightfoot et al., 1992; Atkinson et al., 2004), NO is oxidised (R1, R2) by reaction with O_3 or peroxy radicals (RO_2) to NO_2

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

We now write:

Both HNO_3 and N_2O_5 have important, non-gas-phase loss processes (Crowley et al., 2010) such as uptake to particles and other surfaces.

The statement on rapid photolysis of NO_3 should also be quantified with a reference and an actual number for the photolysis rate.

It is not possible to quote a single number for a photolysis rate without defining the solar zenith angle and cloud-cover. We prefer to state its approximate daytime lifetime and provide a citation.

The chain of reactions to form N_2O_5 is broken during the day as NO_3 is generally photolysed within a few seconds (Wayne et al., 1991)...

Comment 3: Page 3, line 81. I believe a rate of 380 s^{-1} would correspond to $\sim 3 \text{ ms}$ rather than $\sim 2 \text{ ms}$ 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.

As we quote only approximate temperatures, we prefer not to give an accurate lifetime w.r.t. thermal decomposition. We now provide citations and write:

At this inlet temperature and pressure, the lifetime of PAN with respect to thermal decomposition $< 3 \text{ ms}$ (IUPAC, 2021). For N_2O_5 , the lifetime with respect to its thermal dissociation to NO_2 and NO_3 is $\sim 0.5 \text{ ms}$ (IUPAC, 2021)).

To appreciate the importance of these timescales, the authors should also specify the transport time of the various ions through 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.

As this point of the manuscript we are dealing with the likelihood that PAN and N_2O_5 are thermally decomposed in the heated inlet. The residence time for PAN and N_2O_5 in the heated inlet is already stated on the preceding line of text. Adding text about residence times in the IMR is not appropriate here.

Comment 4: page 3, line 86. Give reference to the origin of the stated reaction rate constants.

A citation (to IUPAC) has been added:

As NO reacts more rapidly with NO_3 than with $\text{CH}_3\text{C}(\text{O})\text{O}_2$ at $170 \text{ }^\circ\text{C}$ ($k_{\text{NO}+\text{NO}_3} = 2.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{\text{NO}+\text{CH}_3\text{C}(\text{O})\text{O}_2} = 1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2021))

What was the actual concentration of added NO ?

The concentration of NO is now listed:

...we periodically add NO ($\sim 5 \times 10^{12}$ molecule cm^{-3}) to the inlet to remove $\text{CH}_3\text{C}(\text{O})\text{O}_2$ and thus eliminate sensitivity to PAN.

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 $[\text{I}(\text{H}_2\text{O})]/[\text{I}]$ ratio changes dramatically (approximately a factor of 7 (stated as 6, line 116)), so a least humidity must be important here. The loss of intensity at m/z 127 is because water is present at much larger concentrations (percent in the boundary layer) than the trace-gases we try to detect (usually in the ppb range or lower). This is why the normalised signals are further corrected for relative humidity, as we describe. This is standard practice. We extend and clarify this:

Throughout the paper, when presenting raw data, we generally normalise the I-CIMS signal by dividing by the primary ion signal at m/z 127. This is standard practise and corrects for drifts in the CH_3I flow which may occur over several hours after the instrument was switched from standby mode to operational mode. It also accounts for longer term drifts caused by the weakening activity of the ^{210}Po source over the duration of a measurement campaign (months) or since the last calibration and for loss of detector sensitivity over similar time periods. We show later, that when adding large concentrations of reactants that significantly deplete the primary ion signal at m/z 127 this procedure may lead to bias in some measurements. For this reason, when detecting HNO_3 at m/z 190, we normalise to an interpolated signal at m/z 127 that was measured when the air was scrubbed.

We have also added a new Figure (8) and text (new section 3.2) related to the loss of I- (and thus sensitivity to HNO_3) at m/z 190 when adding large concentrations of O_3 to the IMR.

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 O_3 . 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.

Our apologies: The reference should have been to R7 and not to R6. We now write:

The weak signal in the absence of O_3 (blue data points) confirms the conclusions of previous studies that derive a low rate coefficient for reaction (R7)

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 O_3 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)

We use “could” not in the sense of “might have been able to” but as the past tense of “can” i.e. “were able to”. To remove any ambiguity we now write:

This was confirmed by adding NO.....

Comment 8: page 5, R10. On the right hand side, IO2- should be IO3-

Correction made

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.

We considered this, but there are too many uncertainties including the reaction time, the greatly different rate coefficients presented in the two studies (Teiwes and Bhujel), the lack of information about the influence of water clusters, the potential impact of non-thermal reactions in these low-pressure studies and the possibility that we do not detect all IO_x- anions with the same efficiency. The goal of the present study was not to elucidate details of the reactions of IO_x anions but to show that 1) they are formed when O₃ is present and 2) that they are likely candidates for the observed detection of HNO₃.

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 IO_x- components may affect the actual relative intensity ratios between them. The authors need to clarify this issue.

We state that:

“However, the relative ion-abundance we observe at the detector does not necessarily reflect the relative concentration of the ions in the IMR and we cannot assign the individual contribution of any single IO_x⁻ anion to HNO₃ detection.”

This states clearly that we know neither the absolute numbers nor the relative abundance of IO_x- in the IMR. Given the uncertainties listed in the reply to the comment above, it is not obvious how we can further clarify this. We now weaken this statement by writing:

We note that the increase in signal at *m/z* 62 is about a factor of 100 greater than the reduction in the signal from IO_x⁻, IMPLYING that the detection of IO₃⁻ in our instrument is inefficient.

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 sort 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].

The amount of IO_x anions formed depends exponentially on the rate coefficient (*k*), the concentration [O₃] of ozone in the IMR and the reaction time (*t*): [IO_x]*t* = [I]₀(1-exp[-*k*[O₃]*t*]).

This is why we chose this form of equation.

After equation 2 we have added:

Which reflects the expected exponential dependence of the concentration of IO_x⁻ in the IMR on the O₃ concentration.