

Referee 2

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.

This is a very nice manuscript that explores a large dynamic signal that occurs at mass to charge ratio 62 (NO_3^-) in the iodide CIMS instruments. This signal has long puzzled users of the iodide ion for detection of trace gases, and this manuscript adds extremely valuable information to that ongoing debate. The manuscript is clearly written and organized and presents a well thought out convincing argument assigning signal at 62 to HNO_3 detection via the IO_x^- anion. This will be a valuable addition to the existing literature on iodide CIMS and I fully support its publication pending minor changes.

It has been my own experience, having run a similar set of experiments, that addition of significant O_3 to the iodide CIMS instrument while holding HNO_3 addition constant will result in observable depletion of IHNO_3^- observed at m/z 190, even when normalizing to iodide. The authors convey nicely that the impact of ozone on signal detection will be highly variable depending on the instrumental conditions used, and that alone could be the difference here.

However, considering the authors present HNO_3 data from the field using observations at m/z 190, the data should exist from the laboratory experiments to validate that this does not occur in their system. It would be beneficial to this manuscript if the authors could include a figure similar to 7a but looking at the signal at m/z 190. This information is important to validate some of the assumption throughout the manuscript such as on page 8, line 232 where it is indicated that “negligible depletion of HNO_3 ” occurs, a fully testable assumption considering the ability to detect HNO_3 at m/z 190. It would also be useful in understanding the comparisons of the m/z 62 and m/z 190 data at the end of the manuscript from the ambient observations.

In summary, the referee asks whether the HNO_3 mixing ratio in the IMR (and thus its detection at m/z 190) is influenced by the addition of O_3 . We have conducted laboratory experiments in which a constant flow of HNO_3 was monitored at m/z 62 and m/z 190 while various amounts of O_3 (up to 800 ppbv) were added. The results are now displayed as a new Figure (8) and described in a new section (3.1);

3.2 Detection of HNO_3 at m/z 190

We now compare the detection of HNO_3 at m/z 62 to its detection at m/z 190, the $\text{I}(\text{HNO}_3)$ adduct, with various amounts of O_3 present. In Fig. 8 we present the results of an experiment in which a constant flow of HNO_3 (12.5 ppbv) was introduced into the inlet and the ozone mixing ratio was varied from zero to 900 ppbv. We observe a great increase in the signal at m/z 62 as expected (from 9 counts to > 6000 counts). At zero ozone, the signal at m/z 190 is about 1000 counts and is largely background free, making this the preferred mass to monitor HNO_3 in the absence of O_3 . The cross-over point (when the signals at m/z 62 and m/z 190 are equal) is at an ozone mixing ratio of 100 ppbv. At an ozone mixing ratio of 800 ppbv, the signal at m/z 62 is a factor 8.5 larger than that at m/z 190.

Apparent from this figure is the depletion of the signal at m/z 190 as the O_3 mixing ratio increases to values of 800 ppbv, as observed e.g. in the lower stratosphere. The solid lines are least-squares fits to the datasets that describe the exponential growth of the m/z 62 signal as O_3 is increased and the exponential decay of m/z 190 over the same range. The reduction in signal at m/z 190 is characterised by an exponential term $\exp(-0.00046 \times [\text{O}_3])$ which means that at 800 ppbv O_3 a ~30% reduction in sensitivity is observed. The loss of sensitivity at m/z 190 is driven by the loss of I^- in the IMR as O_3 is added. At the same time, the depletion of the signal at m/z 127 is weaker, which reflects the fact that only a small fraction of IO_x^- formed in

the IMR are detected, the rest presumably being fragmented in the CDC before being detected as I.

The fact that some I is converted to IO_x in the IMR at high O₃ levels but is not reflected in the I signal at *m/z* 127 has repercussions for normalisation of product ion signals to the primary ion signal whereby the assumption is made that the measured signal at *m/z* 127 stems only from I. In our instrument, the loss of I in the IMR is significant at high levels of O₃ (e.g. 30 % at 800 ppbv O₃). For this reason, we normalise the signals using values of the signal at *m/z* 127 obtained by interpolating between measurements obtained when scrubbing the air. The normalisation problem may occur in other I-CIMS instruments to varying extents, and the degree of bias will depend on the conversion of I⁻ to IO_x⁻ and the extent to which IO_x⁻ is detected as I. The potential bias can be circumvented by the continuous addition of a calibration gas that is detected via reaction with I.

We have modified text in other positions. On page 5 we now write:

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 CH₃I 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 ²¹⁰Po 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 HNO₃ at *m/z* 190 (see later), we normalise to an interpolated signal at *m/z* 127 that was measured when the air was scrubbed.

In the abstract we now write:

At high ozone mixing ratios, we show that the concentration of I ions in our IMR is significantly depleted. This is not reflected by changes in the measured I signal at *m/z* 127 as the IO_x⁻ formed do not survive passage through the instrument, but are likely detected after fragmentation to I. This may result in a bias in measurements of trace gases using I-CIMS in stratospheric air masses unless a calibration gas is continuously added or the impact of O₃ on sensitivity is characterised.

Figure 10 (now 11) has been modified to take the O₃ dependence of the sensitivity to HNO₃ at *m/z* 190 into account.

I am having a difficult time understanding how the authors are able to retrieve an ambient HNO₃ signal from the NO₃⁻ signal. The signal that occurs at that mass is dependent on a changing HNO₃ ambient concentration as well as a changing O₃ concentrations. It would seem rather difficult to retrieve the real concentration unless you make an assumption that at any given point HNO₃ is not changing and only O₃ is changing, or the other way around. The only way this may work is if the authors used a measurement of true O₃ collected during the ambient flights, however it is unclear from the description that this was the case, perhaps those details are just missing. If an ozone measurement was used what instrument provided that data. I would like to see more details of how the concentration profiles in Figures 9 and 10 are determined, and what assumptions were made. If the author agree that one can not retrieve true HNO₃ unless a true ozone measurement is used it would benefit the readers to explicitly state this. It is possible that a reader could interpret the data presented here to mean that by using the Iodide CIMS measure of IO_x⁻ and NO₃⁻ one can quantitatively measure HNO₃.

It is, of course, correct that HNO₃ can only be derived from the signal at *m/z* 62 if O₃ (and H₂O) are simultaneously measured. However, these parameters are essential to analysis of

atmospheric composition and are measured routinely in the HALO aircraft. We now mention this in the manuscript.

During both HALO campaigns, O₃ and H₂O (required for analysis of the signal at m/z 62) were routinely measured.

I am in general surprised by the lack of instrument response to ambient features in the data in figures 9, 10 and S1. HNO₃ should have a significant inlet response time relative to O₃ in the CIMS regardless of the inlet conditions. In figure S1 in particular there appears to not be any lag in the observations. This quality in addition to the exact correlation to O₃ makes me believe that you are really just detecting HNO₃ that is made inside of the instrument. Otherwise, I would expect some deviation between the ambient O₃ and HNO₃ from 12:00 to 15:00 in figure S1. Can the authors comment on the time response of their measurements? What does a laboratory time response on m/z 190 look like relative to m/z 62?

An examination of Figure 9 (blue O₃ curve in panel a and red m/z 62 curve in panel b) shows that features (e.g. in O₃) are matched by those in m/z 62. The “time lag” which the referee refers to presumably relates to the sticky nature of HNO₃ on inlet material and might be expected to occur (to an extent depending on the inlet material and temperature) if the HNO₃ and O₃ were both ambient. We agree with the statement that the dominant contribution to the signal at m/z 62 is from the polonium source, and we clearly show this in Figure 9. We do not try to disguise this fact and state that (because of this) the m/z 62 data is not accurate and should not be overinterpreted. Comparison with the time-response of a laboratory source of HNO₃ is not helpful in this regard as we cannot conduct lab experiments under flight conditions using the HALO-trace-gas-inlet.

Has the data from Figure 10b been corrected for scrubber zeros? Is this actually signal over zero. The way the data correction is explained for 9b where an approximate exponential of the Po HNO₃ source is subtracted out would suggest that there are not real zeros removed from the ambient data, which would include source HNO₃. If real zeros have not been used how do you know any of the features shown in figure 9b or 10b are real ambient signals. If real zeros were used why didn't they account for the Po source background?

The data presented in figure 10b has not been corrected for background HNO₃ from the Polonium source. This is not possible as scrubbing also removes O₃ and thus the signal from HNO₃ generated in the polonium source would also be (falsely) zeroed. We now clarify this and write:

We note that the background signal at m/z 62 that originates from the polonium source cannot be obtained by scrubbing the air of HNO₃ as this also removes O₃ and thus also sensitivity to HNO₃ at this mass.

This ion chemistry is ultimately a three-body reaction as indicated in page 7, line 216. Therefore, the result should be quite dependent on IMR pressure. The iodide CIMS literature is filled with instruments running across a very large range of pressures, sometimes exceeding 100 mbar, do the authors have any data or comments on the impact of pressure on this ionization mechanism.

On page 7, line 16 we listed a NET reaction sequence in which three molecules are involved in sequential, bimolecular reactions. This is not to be confused with a termolecular (3-bodied reaction) in which pressure (i.e. collision rates) plays a role in quenching adducts that are initially formed with some degree of internal excitation. There is no reason to assume that the chemistry we outline is pressure dependent. In any case, as our objective was to understand the signals obtained during the HALO campaigns, we only conducted experiments at our “standard” airborne IMR pressure.

The authors comment on the potential issues with past data sets using iodide CIMS to measure PAN, due to the secondary acetate ion chemistry that is occurring. It is my experience that many if not all of the airborne systems employ a constant standard addition of ^{13}C PAN to the instrument. I believe that this addition would account for any secondary ion loss due to IOx-chemistry. I think the authors should add a comment in their discussion on this point on pages 9/10. While there are likely many dataset that have not used such an internal standard to track sensitivity changes it is not appropriate to question the data set that have used that method. A related question is do the authors believe such a system would indeed correct for these ion chemistry issues? That could be a good couple sentence discussion to add here.

The referee is correct in stating that a continuous, internal ^{13}C standard will avoid this problem (assuming that labelled acetate anions reacts with the same rate coefficient as the unlabelled one). We have amended the text appropriately:

One way to avoid this problem is the continuous addition of isotopically labelled PAN to the inlet (see e.g. Roiger et al. (2011)) as the secondary, reactive losses of ^{12}C and ^{13}C CH_3CO_2^- are expected to be identical.

And also the abstract:

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 $\text{CH}_3\text{C}(\text{O})\text{OOH}$ in which continuous calibration (e.g. via addition of isotopically labelled PAN) is not carried out.

On page 12, line 369 the authors state that 190 does not show any correlation with O_3 . However, in the same figure, #10, it is clear that 190 correlates with m/z 62. It was previously argued in describing figure 9, using panel C that it is expected that HNO_3 should correlate with O_3 even after correction for this unique ion chemistry. Additionally, there are clearly features in 10b that correlate with the ozone signal shown in 10a. Please elaborate on the disagreement between these two statements.

The statement was ambiguous as correlation can be caused both by the expected covariance of stratospheric HNO_3 and O_3 but (for m/z 62) also stems from the strong dependence of the sensitivity to HNO_3 on the O_3 mixing ratio at this mass. We now write:

Similar to the CAFE-Africa data-set, the signal at m/z 62 covaries strongly with the O_3 mixing ratios, which were between ~ 40 and ~ 700 ppbv whereas the raw signals at m/z 62 and m/z 190 (both due to HNO_3) bear little resemblance to each other.

On page 6 there is a discussion on the residence time in the flow tube and comparison to similar work. I encourage the authors to reconsider their calculation of the residence time in their flow tube as presented. With a critical orifice on a cylinder there will be a jetting effect of the air through the region such that your reaction timescale will not be equivalent to the laminar sweeping of the volume. Rather it will be dependent on the velocity and flow dynamics of that jetting effect. This likely results in a significantly shorter reaction time than the volumetric calculation for most of the analyte molecules being sampled. It is not necessarily a discussion that is needed here but should be considered when trying to understand the difference being discussed, and leveraged as a potential answer for some of the disagreement observed.

Agreed. We do not know the flow-dynamic in the IMR and now emphasise that the reaction times are rough approximations. We write:

Note that the IMR reaction times we derive are only approximate as we do not take into account the mixing and flow dynamics in the IMR, which are likely to be complex (and possibly shorter than 25 ms) owing to sampling via a critical orifice. While we can not rule out that our observation of IO^- (and not IO_3^-) being the dominant ion-signal is partially caused by differences in reaction times, slight differences in O_3 concentrations and differences in temperature (our IMR is at $\sim 15^\circ\text{C}$ above ambient temperature owing to the heated inlet) we note that the higher pressure of O_2 (factor $\sim 1-10 \times 10^4$) in our IMR is likely to have a large effect.

Figure 1. I am interested in the flow dynamics in the figure with the initial sampling line. It appears that at some point your inlet could be connected to a pump exhaust line in the far left of the diagram. Even if overflowing the inlet with N₂, depending on the flow characteristics and pressures I could see a scenario where pump exhaust would flow out the inlet past your sampling point. Perhaps something is missing or I am interpreting this diagram incorrectly.

When overflowing with line with N₂ a valve is closed and the connection to the exhaust line is closed. We have added this information to the caption.

When overflowing the inlet line, the valve to the exhaust line is closed. When sampling air, the valve to the N₂ bottle is closed.

Why do the authors believe the HNO₃ to 62 appears nonlinear in the inset figures on Fig 2 and 8?

We are dealing with very small signals when either acetate anion or O₃ are absent. The signal is close to background levels and may be influenced by variations therein. The point of the expanded scale in the insets is just to show that the signal is very low and detection of HNO₃ very inefficient.

Figure 9 and 10. These figures are difficult to interpret because there is not legend given in the figure and the colors are reused for different species. In 9, I believe the label attitude should be black and without reading the caption the reader has no idea what the pink line is for example. Blue is used in 3 places in Fig 9 for three different things.

Figure 9 (now 10) has been redrawn with more legends and corrected colours. Figure 10 (NO₂ 11) has also been redrawn and the lines better defined.

Page 8, line 238 needs a space between the and IOx

Correction made

Page ,8, line 241, suggest adding the word “of” in front of 100 greater.

Correction made

Page 9, line 265, there is a close parenthesis missing.

Correction made

Page 12, line 371, calibrations should be singular

Correction made