We thank the reviewer for constructive comments which have improved the paper. The reviewer comments are shown below in black. Our responses are shown in blue, and changes to the manuscript are shown in red.

This paper, *Temperature dependent sensitivity of iodide chemical ionization mass spectrometers*, describes observations of instrument performance made during laboratory experiments and previous field campaigns to understand unexpected instrumental behavior. Iodide Chemical Ionization Mass Spectrometers (I-CIMS) are used by numerous groups worldwide to measure a variety of species including halogens, NOZ constituents and oxidized organic compounds. This makes this paper highly relevant to the community.

On its face, it seems obvious that higher temperatures would results in less strongly bound clusters falling apart but it is not something you typically see considered in these types of measurements. Since cluster chemistry is important to other ionization schemes beyond iodide, the significance of this work extends to other ion chemistries as well (eg. NH4+, Br-, Fluoride transfer). One part I feel should be made clearer is which experiments were done with which IMR. I realize the IMR heating experiments were performed with the Aerodyne IMR, but what about the cooling experiments or the room temperature sweep experiments? This is not clear to me and left me confused as to which IMR was used where. I suspect I would not be the only one. I am wondering if the authors could also provide a few more details about the closed loop humidity control. This should be added to the SI. It would give the reader a better understanding of how this system works and the variability of the amount of humidified nitrogen added. Since the I(H2O)- cluster is both a product ion and also a reagent ion the temperature dependence of it has important direct and indirect implications on the instrument sensitivity. The manuscript is well written and falls within the scope of AMT. It should be published once the few minor comments are addressed.

We have added the following sentences to sections 2 and 3.3 in order to clarify which IMR was used for each experiment.

L146:

"The NOAA IMR design was deployed during SUNVEx and the ARI IMR design was used to investigate the influence of IMR temperature in the laboratory."

L169:
"Three types of experiments were performed using the ARI IMR design to examine temperature control strategies that could be implemented to stabilize sensitivity if ambient temperatures change substantially."

L180:
"This experiment replicates conditions during prior field deployments and reveals the sensitivity changes that can occur in the absence of IMR temperature control and was conducted on both IMR designs."

L266:
"The impact on HCOOH sensitivity due to IMR temperature changes during the SUNVEx field campaign (NOAA IMR) are shown in Figure 5."

L282:
"The variations in sensitivity with temperature in lab experiments and field observations are similar, however absolute sensitivities may differ between the two IMR designs (SUNVEx, NOAA IMR, shown in gray in Fig 6b; Lab experiments, ARI IMR, red, salmon and blue points, Fig 6b)."

L291:
"Several ToF body experiments were conducted on the ARI IMR to determine effective methods for stabilizing sensitivity when environmental temperatures change (Figure 6)."

Additionally we have added a section to the supplemental material to describe our IH2O control strategy more clearly L134:

"A detailed description of the CR closed loop control system can be found in the supplemental section 1."

1 Ion molecule reactor cluster ratio closed loop control system

The NOAA I- chemical ionization mass spectrometer (CIMS) utilizes a closed loop control system to achieve fixed cluster ratio ($I–•H2O:I–$) (CR) in the ion molecule reactor (IMR) with varying sample gas humidity. This closed loop control system is comprised of a water bubbler, N_2 mass flow controller (MFC), saturated gas transfer line and computer control software. This system is outlined in supplemental figure 1. Real time signal measured at nominal mass 127 ($I–$) and 145 ($I–•H2O$) is transferred from TofDAQ to the National Instruments Labview instrument control software. The apparent CR is determined at 0.1 Hz and compared to the user defined reference CR set point (typically 0.5), an error is determined and the saturated N_2 flow (0 – 100 sccm) MFC set point is adjusted accordingly. This system dynamically adjusts the amount of saturated N_2 flow delivered to the IMR as inlet sample gas humidity changes with altitude (on an aircraft) or time of day (at a ground site).
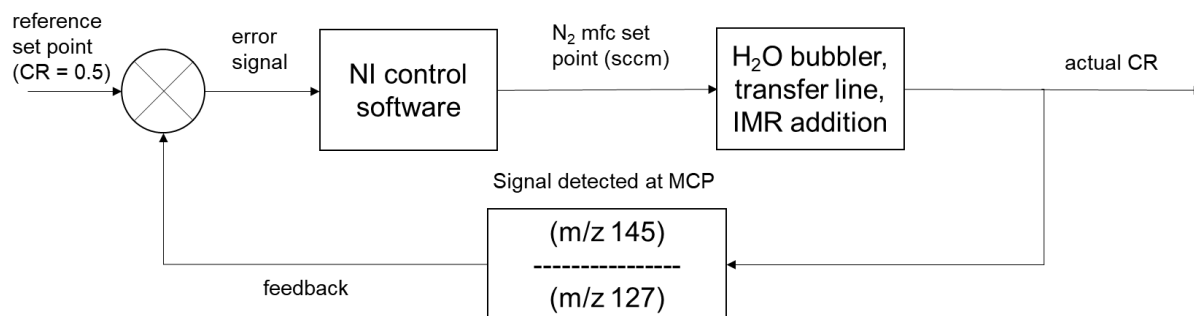
Supplemental Figure 1: Block diagram of closed looped control of IMR cluster ratio.

Specific Comments

P1 L 23: Sentence should be reworded. If gives the reader the impression that only cooling reduces the sensitivity drift.

"Finally, we recommend two approaches to minimizing this effect in the field, namely heating or cooling the IMR; the latter has the added benefit of improving absolute sensitivity and reducing drift in harsh field environments."

Now reads

"Finally, we recommend two approaches to minimizing this effect in the field, namely heating or cooling the IMR; the latter has the added benefit of improving absolute sensitivity."

P1 L26: Atmospheric trace….
Corrected.

P3 L73: This is a very good point. I am struggling to think any temperature dependent studies beyond some of the initial kinetics papers in 90's.
We agree.

P4 L103: The authors should provide a couple of example analytes not merely the reference.
This sentence now reads:
"Temperature affects the abundance of product ions, and hence the sensitivity of iodide adduct CIMS, as has been shown for some analytes studied in the laboratory, such as the iodide carboxylate anion reaction (R3) and the Br–(HO2) cluster (Villalta and Howard, 1996; Sanchez et al., 2016)."

P4 L114: The stabilization of sensitivity assumes the clusters make it the detector without falling apart, also dependent on the operating pressure of SSQ there is potential for chemistry to continue into this region which is never temperature controlled on any of these instruments.

We agree with the reviewer that declustering in the SSQ should have an impact on sensitivity, however temperature controlling the entire instrument was deemed out of scope for this work. We believe that most users can benefit by temperature controlling their IMR system, greatly improving the repeatability of in-field calibrations. We have reworded L114:

"Consequently, we compare our experiments to field observations and recommend temperature control strategies to improve sensitivity stability."

P5 Figure 1: It seems odd to me that the nylon liner on the NOAA IMR does not provide some form of temperature isolation from the outside temperature of the stainless steel fittings. Clearly, it's just not enough isolation

Experiments were done before the SUNVEx campaign in attempt to isolate the issue, and we determined the nylon sleeve does not have a significant impact on HCOOH sensitivity dependence on temperature. We have chosen to not include these experiments in this manuscript.

P5 L131: How much N2 do you have to flow through the bubbler? Is it the same flow to maintain the same cluster I-:I(H2O)- cluster distribution in the two IMR's? I am curious because dependent on IMR geometry I have seen this vary greatly in our instrument.

We flow 0 to 100 sccm of N_2 flow through our bubbler to maintain cluster ratio. We have updated L131 to read:

"These experiments (unless stated otherwise) were done with water dynamically added to the IMR (via a saturated small N2 flow (0 – 100 sccm)) to maintain a cluster ratio (I–•H2O:I–) (CR) of 0.50 ± 0.002, as is typical in field operation of the instrument."

We see similar cluster distribution effects due to IMR geometry in our instrument. During a ToF Temperature experiment, the NOAA IMR design requires 15 sccm of saturated N_2 flow to maintain a CR = 0.5 at 28 °C and 19 sccm of saturated N_2 flow to maintain that same CR at 30 °C. The same experiment conducted with the ARI IMR design requires 5 sccm of saturated N_2 flow to maintain a CR = 0.5 at 28 °C and 7 sccm of saturated N_2 flow to maintain the same CR at 30 °C.

We have included an additional figure in the SI (Supplemental Figure 3) to show this difference in designs:
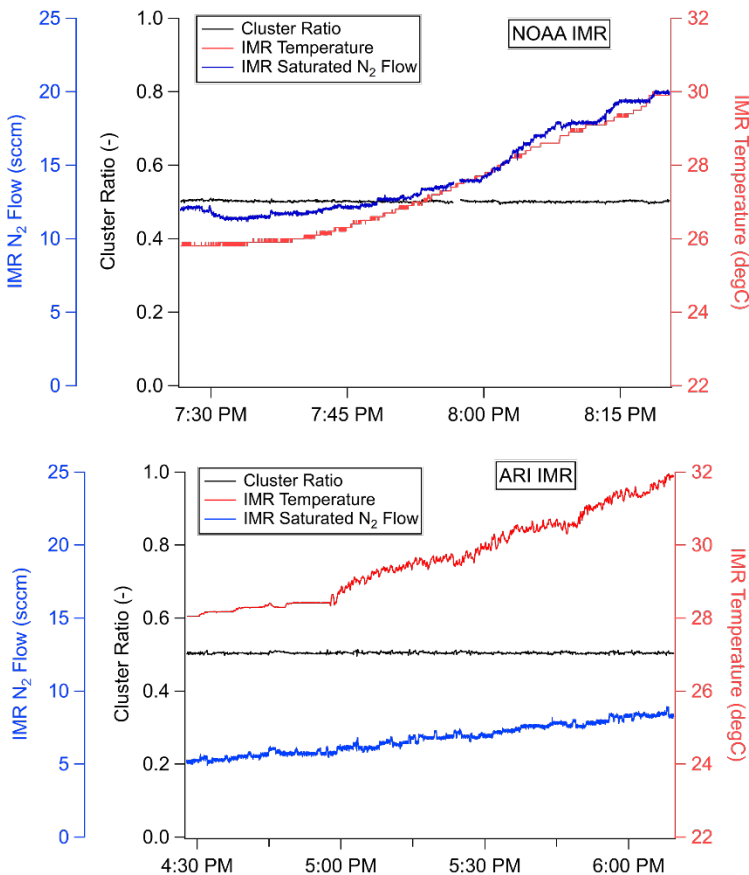
Supplemental Figure 3: Comparison of NOAA IMR and ARI IMR during ToF body temperature experiments.

And have added L179:

"A comparison of IMR saturated N2 flow rates during the ToF body temperature experiment between the two investigated IMR designs is provided in Supplemental Figure 3. The changes observed in added IMR saturated N2 flow is likely due to geometry differences between designs and the impact on mixing in the IMR."

P5 L 138: I'm curious why the authors chose only to normalize by the I(H2O)- cluster. Granted it should account for any variation in reagent signal it is merely that often in the literature the reagent is taken as the sum of the two.

The primary reason is that for many species of interest to us (PAN, HNO3, formic, halogens) the reaction proceeds almost entirely with I(H2O)- as the regent ion. Therefore normalization using IH2O- most accurately accounts for changes in the primary ions. However, for species that react strongly with I- as the primary reagent ion (HCN for example), normalization to I- is the more appropriate choice. Further as we show in this work several species react with both IH2O- and I- so the sum may be more appropriate. Ultimately the choice of normalization is somewhat arbitrary as long as it is held consistent throughout calibration and analysis. However,

normalization using IH2O- of a species that reacts predominantly with I- (again HCN for example) can impart an apparent 'humidity dependence' and should be considered. It is our not so satisfactory conclusion is that normalization should be a compound specific decision, but careful processing of data and laboratory calibration can minimize the potential for error. It is worth stating that as we show in this work a given CR may not be identical across instruments so caution should be used even when comparing normalized sensitivities between instruments.

P6 L157: From the looks of the temperature profile these experiments, they were not done as ramp and soak type experiments. I'm curious as why this decision was made as opposed to trying to assess the issue at discrete temperatures. Granted this mimics what typically occurs in most measurement trailers or aircraft.

These experiments were designed to mimic SUNVEx trailer temperature profiles fit into several hours rather than the 24 hrs.

P7 L172: Do you have any idea as to the actual gas temperature in the IMR's? I am guessing even with heating or cooling they would be very different when the instrument is operated as a PAN CIMS.

We have conducted experiments which indicate the IMR excess flow temperature is very similar to the IMR wall temperature (~1.5 °C offset) both in PAN CIMS mode and normal operation. We have not conducted these experiments for heating or cooling the IMR yet, but plan to once we have designed and fabricated a new IMR.

P7 L179: are shown

Corrected.

P8 Table 1: I am curious why you did not calculate the sensitivities for 2-nitrophenol and phenol if you know what mixing ratio added to the inlet is?

These experiments do not require us to know the inlet mixing ratio, only that the inlet mixing ratio is stable during the experiment. At the time of these experiments, we did not have the ability to calibrate for 2-nitrophenol or phenol.

P8 L204: It is not exactly fair to compare the PAN chemistry (particularly the anion chemistry) when the ionization chemistry is a different mechanism than the rest. The authors should specify which channel or drop it and merely discuss the halogens.

The authors agree that the anion PAN chemistry differs from the other analyte clustering chemistries discussed here. However, we believe it is still interesting to the reader and useful to PAN CIMS users, to put PAN temperature dependence into context of other iodide CIMS

analytes. We believe we have made the mechanism clear by indicating a reaction number on L204:

"Notably the sensitivity of several halogens remain nearly constant with temperature and the PAN carboxylate anion (R3) sensitivity does not decrease with temperature."

P9 L212: Again, I am not sure grouping the PAN anion channel with the others is appropriate.

In order to make the grouping clearer, we have reworded L212 as follows:

"The analytes studied here can be grouped into two classes, strongly bound clusters with weak IMR temperature dependence (such as Br_2, N_2O_5, and $ClNO_2$) and weakly bound clusters with strong IMR temperature dependence (HCl, HONO, HCOOH, HCN and PAN via peroxy radical cluster). The carboxylate anion detection of PAN behaves similarly to strongly bound clusters, but is not clustering ion-molecule chemistry and cannot be classified."

P9 L215: Why were the sensitivities not determined?

At the time of these experiments, we did not have the ability to calibrate for 2-nitrophenol or phenol.

P9 L227: How much nitrogen needs to be added/removed for the humidity control? Are we talking about 10's of sscm on a couple of litres or is it more? I am curious if there is any possibility of dilution in the IMR and without that information, it is not clear to the reader.

During normal operation 10s of sccm are added to the IMR to control cluster ratio. As we have found here, this increases with increasing temperature due to declustering of the IH2O cluster. We have corrected for this possible dilution artifact, and the figures and slopes presented in Table 1 have not changed appreciably. We have added the text L131:

"The added saturated N_2 flow can dilute the sample in the IMR and is typically a negligible effect under stable temperature operating conditions, but due to the nature of these experiments (large N_2 flow at high IMR temperatures) we have corrected for dilution."

P10 L230: I(H2O)- is also a reagent ion. If it is falling apart in the IMR as a results of increasing temperature that would have a direct effect on sensitivity beyond clusters falling apart downstream.

We agree with the reviewer on this topic and have reworded this sentence to emphasize the importance of controlling cluster distribution and IMR temperature, as they can both impact sensitivity in concert L235:

"This thermodynamically controlled behavior of the I–•(H2O) product ion, which is also a critical reagent ion in our IMR, emphasizes the importance of temperature and CR control to maintain a constant reagent ion distribution and stable sensitivity."

P12 L280: This is definitely true.
We have adjusted the text to read L286:

"The variations in sensitivity with temperature in lab experiments and field observations are similar, however absolute sensitivities differ between the two IMR designs (SUNVEx, NOAA IMR, shown in gray in Fig 6b; Lab experiments, ARI IMR, red, salmon and blue points, Fig 6b)."

P12 L283: At what pressure do you operate the NOAA I-CIMS SSQ? 2 mBar or lower?

We have adjusted the text on L119 to indicate our SSQ operating pressure:

"The NOAA CIMS notably operates at lower IMR pressure (40 mbar, rather than 100 mbar used in many) and small segmented quadrupole (SSQ) pressure (1.64 mbar, rather than 2 mbar) in order to reduce the impact of secondary chemistry in the IMR and SSQ instruments (Bertram et al., 2011; Lee et al., 2014)."

P13 L294: Are the sensitivities the same using both NOAA IMR and the Aerodyne one? There are definitely geometry differences between the two. Were the cooling experiments only done with the NOAA IMR and heating experiments only done with the Aerodyne IMR?

We point the reviewer to Figure 6b, where absolute sensitivities are reported for HCOOH for both IMR designs. We have adjusted the text in the figure caption to make this comparison more clear L294:

"**Figure 6: Comparison of absolute HCOOH sensitivity between laboratory IMR temperature experiments (ARI IMR design) with SUNVEx field standard additions (NOAA IMR design).**"