The authors would like to thank the editor for managing the peer review process and all the reviewers for reviewing our manuscript and for providing incisive and constructive feedback to help us improve the quality of this paper and to address some issues that required further clarification and discussion. We have made revisions to our original manuscript accordingly. The colorings of text in the reviewer response are:

- Light blue: Original reviewer comments
- Dark blue: Original text in the submitted version of the manuscript. **Bolded sentences** are the text added in the revision while ~~strikethrough words~~ are the text deleted in the revised manuscript.
- Black: Authors' response to the comments and others.

Note that the line number in the response is based on the revised clean-version manuscript.

Anonymous Referee #1

Summary: The authors describe a new instrument consisting of an aerosol impactor, thermal desorption unit, GC, and split column effluent to an FID detector and an iodide adduct chemical ionization mass spectrometer. The separate components of this instrument have been described previously; the combination of the simultaneous FID and CIMS measurement is novel. The goals of this instrument are to (1) isomerically resolve chemical compounds in an aerosol sample, and (2) determine the sensitivity of the CIMS detector to each chemical species. A second novel instrument technique is also described, in which a combination of air and iodide are used as reagent ions in the CIMS. The purpose of this is to ionize both high- and low-polarity compounds.

Major comments: The manuscript is generally well-written and well-organized. The use of chromatography to interpret CIMS spectra is not especially inventive, and because it is so complicated, this instrument will likely not see widespread use in its current form. However, this is a particularly useful instrument because it addresses two major problems with CIMS in atmospheric science: the spectra may be complicated to interpret, and the sensitivities to individual species are difficult to determine. Used under carefully-controlled conditions in a small number of laboratories, this instrument could provide important reference information to interpret iodide-CIMS measurements from field studies.

The analysis of the number of detected isomers was done very well and it is very useful to see the comparison to other studies.

Response: We sincerely appreciate the reviewer's suggestions and feedback for the manuscript. In the general summary, the reviewer expressed some concerns about the instrument being too complicated to be widely used in its current form. We agree with the reviewer that the TAG-CIMS/FID is very complex, and we will simplify the design of the instrument in the future. However, we believe that the current form of the instrument, although complicated, is a reasonable starting point to demonstrate the values and capability of the simultaneous coupling of CIMS and FID to a TAG. The detailed responses of each comment can be found in the sections below.

Comment 1: The inclusion of the air/iodide mixed-reagent-ion technique is interesting, but does not seem to really belong here. It is not even indicated in the title of paper and does not address the motivations mentioned in the introduction. This is better suited to a separate manuscript. If this is

retained, it needs to be better explained how the mixed-reagention approach relates to the other capabilities of the instrument. An additional figure or other concrete example should be shown to demonstrate how chemical information can be derived from this technique.

Response: We thank the reviewer for thinking that it is interesting. Both reviewers highlight multi-reagent chemistry as both interesting and perhaps not fully developed. The intention of including this approach is not necessarily to understand in great detail this specific reagent chemistry, as we agree that an in-depth exploration of such an approach would likely require a separate full manuscript (note, for example, that the core of understanding of iodide chemistry was only achieved over multiple separate manuscripts). Instead, the motivation of this work is to overcome the technical hurdles in coupling a GC with a CIMS (and an FID) and explore the benefits of such an instrument.

We have chosen to include multi-reagent chemistry within this manuscript because it is specifically a feature made possible by coupling these instruments. Adding the GC enhances the ability for CIMS to explore new or simultaneous ionization chemistry by separating analytes with the retention time, yielding "clean" interpretations of complex spectra. Just as the separation provided by the GC allows known chemistries to be explored, it also enables the extension to new approaches such as multi-reagent ionization. We demonstrate that the multi-reagent ionization extends the range of chemical species that can be identified in the form of their elemental formulas, while the FID can serve as the detector for quantification. In the manuscript, we provide an example of the implementation of the multi-reagent ionization using a mixture of known chemical standards and liquid fragrance with unknown components on Line 360. In the example, we have shown that the elemental formulas of the extra compounds that can be detected in multi-reagent ionization mode. To emphasize the example of chemical identification using multi-reagent ionization, we have put the descriptions of the example in a separate paragraph of the manuscript:

"**An example of the benefit of this approach is demonstrated by the detection of compounds not accessible through iodide adduct formation; 4 times as many compounds are observed in multi-reagent ionization mode (with formulas assigned to at least half of them). For example, a known component in the sample of complex fragrance mixtures, eugenol (Peak 2 in Figure 4c), is identified in the multi-reagent ionization mode yet not detected in iodide mode. In Figure 4c, 6 other peaks are labeled that are not detected as iodide adducts, but for which formulas can be assigned using $[M\text{-}H]^-$ and $[M+O_2]^-$ as identifiers, 1: $C_{15}H_{24}O$, 3: $C_9H_{10}O_3$, 4: $C_{12}H_{24}O_2$, 5: $C_{16}H_{32}O_2$, 6: $C_{18}H_{34}O_2$, and 7: $C_{18}H_{36}O_2$. A reasonable objection to multi-reagent ionization is that the complexity of adding up signals in multiple ionization chemistry with variable sensitivities may prohibit reasonable CIMS quantification. However, using CIMS for identification of unknowns by formula or other chemical information is valuable on its own, and quantification of many components is achievable using the FID channel of this instrument. This technique is likely only useful when analytes are individually resolved (i.e., isomer resolution), as the resulting mass spectrum of the complete complex mixture would be otherwise too difficult to interpret."**

Additionally, we have revised the title of this section 3.3 to clarify that this is an example of what the TAG-CIMS/FID can do:

"**3.3 Exploring new chemistries: multi-reagent ionization** ~~Iodide ionization versus multi-reagent ionization~~"

Comment 2: Instead of the mixed-reagent ion description, it would be better to include an assessment of the FID-enabled determination of CIMS sensitivities. This is stated several times as the major benefit of the FID. However there are no data shown to demonstrate this utility. This is a significant weakness of the manuscript. The manuscript could be published with some minor revisions, but would have a much larger impact if the use of the FID to determine sensitivity is demonstrated.

Response: We completely agree with the reviewer that the FID-enable determination of CIMS sensitivities is a major benefit of coupling an FID and should be discussed in detail. However, quantification of iodide CIMS is a complex topic (again, note current quantification schemes have been built up over multiple manuscripts), and a proper treatment of it here would significantly expand the scope and complexity of the present manuscript. We choose instead to focus here on the technical hurdles and the array of potential value/benefits of the coupled instrument. A forthcoming manuscript is nearly ready for submission that addresses in detail the FID-determined CIMS sensitivities, and a wide range of related topics, including an examination of the voltage scan calibration method and the correlation between GC retention time and CIMS sensitivities. We have provided the information on splitting the work as described on Line 226:

"Implementation of this calibration approach including detailed methods of quantification and determination of isomer sensitivity is complex and will be addressed in future work. **This manuscript focuses instead on the descriptions of technical hurdles overcome by TAG-CIMS/FID and its potential value in understanding existing and new ionization chemistries, as well as atmospheric systems.** ~~This manuscript focuses instead on the description of TAG-CIMS/FID, isomer-counting, and evaluation of multi-reagent CIMS.~~"

Comment 3: Specific/minor comments: Section 2.3. It would be helpful to summarize the major technical challenges of CIMS/FID split flow at the top of this section.

Response: We agree with the reviewer that summarizing the major challenges of splitting the flow at the beginning of section 2.3 would help readers to understand the section better. We have added the summary at the top of this section:

"The design of the TAG-CIMS/FID interface needs to allow the efficient transfer of analytes from GC effluent to CIMS and FID. This interface is subject to three technical challenges:1) the connections between capillary columns and fittings need to be leak-tight; 2) all components in the interfaces require proper heating to avoid cold spots and dead volume; and 3) the relative flow rates to CIMS and FID need to be controlled to maintain roughly equal split of flow. ~~The interface between the GC and detectors controls the relative transfer flow toward each detector and must avoid any degradation to the chromatography (i.e., cold spots or dead volume).~~**"**

Comment 4: Page 6 line 166- 170. I don't understand the purpose of the EI-MS experiment. Please explain.

Response: We apologize for the lack of explanation on the EI-MS experiment. The EI-MS experiment was used as a secondary way to verify the stability of the flow split in addition to the flow rate measurement. Since the split flow rate ratio is critical for quantifying analytes in this instrument, we examined the flow split using two methods. The first method is to directly monitor the flow rate at the FID side during a

chromatographic run. Since the total flow rate is known and controlled by TAG, the remainder flow to the CIMS can be calculated. Details of the description can be found on Line 166:

"With these dimensions and temperatures, the flow rate to FID is approximately one-third of total GC flow (0.3 sccm, measured using Sensidyne Gilibrator-2 at the inlet of FID) with the remainder to the CIMS (0.7 sccm). To further evaluate the stability of the split ratio of flow, test runs were conducted prior to the experiments to monitor the flow rate at the inlet of FID, variability in the flow split was found to be less than 10% variation throughout a run cycle, stable enough to be quantitative."

Additionally, we examined the split ratio through the injection of a mixture of alkane standards (C8-C40). Suppose that the split flow ratio is constant throughout a chromatographic run. In this case, the ratio of chromatographic peak area between the two detectors should be the same for a series of n-alkanes, which elute at different retention times depending on their carbon number. However, this cannot be done with an iodide CIMS because it cannot detect alkanes. Since both CIMS and EI-MS is at near-vacuum, swapping CIMS to EI-MS, which can measure alkanes, does not impact the flow split ratio. We therefore replaced CIMS with the EI-MS to evaluate whether the flow split ratio between CIMS and FID is stable in a GC run cycle. We found that the ratios of EI-MS to FID peak area for observed alkanes, which linearly correlate with the flow split ratios at a given retention time, were found to vary by less than 10%.

The EI-MS experiment was conducted for validating the TAG-CIMS/FID interface design before actually coupling the FID to the CIMS. We thought there is no harm to provide more information on the ways of validating the flow split. However, based on the reviewer's comment, adding the extra EI-MS verification method may confuse the reader. Since the measurements of FID flow are sufficient to demonstrate a stable flow rate split, we have deleted the description on the EI-MS method used to validate the flow split:

~~"Additionally, the CIMS was swapped with an EI-MS while maintaining the TAG-MS/FID interface so that liquid injections of alkanes standards (i.e., alkanes mix C8-C40, AccuStandard) can be measured by both EI-MS and FID. The ratios of EI-MS to FID peak area for observed alkanes, which linearly correlate with the flow split ratios at a given retention time, were similarly found to vary by less than 10%."~~

Comment 5: Page 10 Line 235: Wouldn't decomposition during TD change the parent formula as well?

Response: We are not quite clear to the reviewer's question since the sentence has already discussed the decomposition of parent analyte during thermal desorption. In response to what we think the reviewer refers to, we have revised the sentence on Line 236 to mention that thermal desorption may change the parent formula:

"**Overestimation may occur when large parent molecules decompose to isomers of a smaller formula during thermal desorption.** ~~Overestimation may occur because peaks observed might be formed in part by thermal decomposition of analytes during thermal desorption.~~"

Comment 6: Page 11 Line 260: This statement should be qualified with the volatility- or carbon number-range analyzed.

Response: We agree with the reviewer that the conclusion needs to be further constrained on specific samples or the range of compounds. The data in the literature is collected using off-line filters.

Therefore, the compounds in the literature and our study are primarily particle-phase compounds (or some adsorbing low-volatility gases, which are known to be present on some filter samples), with ten or less carbon number. We have added this description in the manuscript on Line 260:

"Together, the published data and that collected by TAG-CIMS/FID support the conclusion that isomers are abundant **for molecular formulas with ten or less carbon number in particle-phase samples**~~atmospheric samples~~."

Comment 7: Page 11 lines 264-266: Could you not use the EI-MS and identify the isomers via matching to a NIST library?

Response: As noted in our response above, while it is possible to include all three EI, CIMS, and FID detectors, doing so was not a focus of this work; EI data was not analyzed for the samples shown here. As addressed in Comment 4, we apologize for misleading the reviewer to believe that the EI-MS was used to measure analytes in this study.

Although not described in the manuscript, we indeed tried using the EI-MS as the 3rd detector to achieve a simultaneous coupling between the TAG and three detectors (iodide CIMS, EI-Tof-MS, and FID) for some test runs during the limonene-O_3 experiments. Unfortunately, even for that data, most of the oxidation products do not have reference mass spectra in the NIST library. This is a common problem for atmospheric GC/EI-MS samples. For example, the EI mass spectra of some primary limonene oxidation products (Witkowski and Gierczak, 2017) such as ketolimononic acid and 7-hydroxy limononic acid are not reported in the NIST library. A common practice of EI-MS users is to build a customized EI-MS library for specific compound categories of their interests (Yee et al., 2018), but such customized libraries can be labor-intensive and it is often the case that the analytes can only be related to a parent molecule, so it is not clear such a task would advance the scope of the present manuscript.

Comment 8: Page 14 lines 330-358: Can you provide an example of how this can be used? This seems to subvert the main benefits of CIMS, which are a 1:1 correspondence between molecule and product ion, and the retention of the parent ion (low fragmentation). If the only benefit is that it allows detection of some other compounds with the CIMS, why not just use the FID, which detects everything and with roughly equal sensitivity? The spectra are probably too complicated to interpret without GC-preseparation. Maybe there is some information about the structure of the isomer, given the observed mixed I-/O2- product ions. If so, can you provide some examples? Please comment on the use of this method to interpret the non-adduct ions typically observable in I- CIMS spectra. Can you state anything concrete about the identity of these ions, given the results of your experiments?

Response: We agree with the reviewer that the multi-reagent chemical ionization is not practical to be used in direct-air-sampling CIMS. As discussed above, multi-reagent ionization is discussed in this manuscript precisely because it is an approach that has some benefits (extending the potential chemical range of the instrument) but is only made possible with GC pre-separation. It is certainly true that the spectra are probably too complicated to interpret without GC pre-separation. The multi-reagent ionization method proposed in this study should be used mostly in the setup of the TAG-CIMS/FID (or some other GC-CIMS) where CIMS serves as an instrument for elemental formula identification and FID quantifies the well-resolved analytes.

The reviewer asked that if the only benefit is that it allows detection of some other compounds with the CIMS, why not just use the FID, which detects everything and with roughly equal sensitivity. It is because the information provided by the FID is very limited. Since FID is a single-channel detector, simply using GC-FID alone does not provide any information on the analyte molecule except its FID abundance. Additionally, the range of FID sensitivities for oxygenated organics still vary by a factor of two (Scanlon and Willis, 1985) while it can be corrected to within 20% if the elemental formulas of the analyte are known (i.e., corrections using O/C and carbon number) (Hurley et al., 2020). As mentioned in Comment 2, this FID-assisted calibration technique will be discussed in detail in a forthcoming manuscript. Simultaneous coupling of the CIMS in multi-reagent ionization mode can identify elemental formulas of chemicals generated in the atmospheric oxidation products. Those identified formulas can serve as correction factors for the FID calibration and also provide an additional dimension of the information (i.e., formula-level information) on the molecule. In this case, increasing the number of detected compounds using multi-reagent ionization in CIMS is beneficial so that more compounds can be identified and quantified.

The example on the identification of the ions was provided on Line 357 :"For example, a known component in the sample of complex fragrance mixtures, eugenol (Peak 2 in Figure 4c), is identified in the multi-reagent ionization mode yet not detected in iodide mode. In Figure 4c, 6 other peaks are labeled that are not detected as iodide adducts, but for which formulas can be assigned using $[M\text{-}H]^-$ and $[M+O_2]^-$ as identifiers, 1: $C_{15}H_{24}O$, 3: $C_9H_{10}O_3$, 4: $C_{12}H_{24}O_2$, 5: $C_{16}H_{32}O_2$, 6: $C_{18}H_{34}O_2$, and 7: $C_{18}H_{36}O_2$."

To better clarify the applicability of the multi-reagent ionization, we have revised the section by moving the example to a separate paragraph demonstrating the more formulas can be identified.

"**An example of the benefit of this approach is demonstrated by the detection of compounds not accessible through iodide adduct formation; 4 times as many compounds are observed in multi-reagent ionization mode (with formulas assigned to at least half of them). For example, a known component in the sample of complex fragrance mixtures, eugenol (Peak 2 in Figure 4c), is identified in the multi-reagent ionization mode yet not detected in iodide mode. In Figure 4c, 6 other peaks are labeled that are not detected as iodide adducts, but for which formulas can be assigned using $[M\text{-}H]^-$ and $[M+O_2]^-$ as identifiers, 1: $C_{15}H_{24}O$, 3: $C_9H_{10}O_3$, 4: $C_{12}H_{24}O_2$, 5: $C_{16}H_{32}O_2$, 6: $C_{18}H_{34}O_2$, and 7: $C_{18}H_{36}O_2$. A reasonable objection to multi-reagent ionization is that the complexity of adding up signals in multiple ionization chemistry with variable sensitivities may prohibit reasonable CIMS quantification. However, using CIMS for identification of unknowns by formula or other chemical information is valuable on its own, and quantification of many components is achievable using the FID channel of this instrument. This technique is likely only useful when analytes are individually resolved (i.e., isomer resolution), as the resulting mass spectrum of the complete complex mixture would be otherwise too difficult to interpret."**

Comment 9: Technical corrections: Line 221: "magnitudes" -> "magnitude"

Response: We have revised the work on Line 220:

"However, comparing to the near-universal response of FID signals, the signals of iodide CIMS per unit mole of analytes may vary up to five orders of **magnitude**~~magnitudes~~ and highly depend on their enthalpies of binding with iodide"

Anonymous Referee #2

Received and published: 3 October 2020 Review of Bi et al., "Coupling a gas chromatograph simultaneously to a flame ionization detector and chemical ionization mass spectrometer for isomer-resolved measurements of particle-phase organic compounds"

Summary: The authors describe a new instrument configuration using a TAG column upstream of both an FID and a ToF-CIMS. The goal was to address several current measurement issues by 1) using the GC to separate isomers in the CIMS spectrum, and 2) using the FID as a means of quantifying unknown compounds in the CIMS spectrum. They also show the simultaneous use of I- and O2- as reagent ions, with the goal of expanding CIMS sensitivity to generally less oxidized compounds. Generally, this is an interesting and well written paper that attempts to address several of the critical issues with CIMS spectrum interpretation of ambient or complex data. Separation of isomers seems be useful (at least for compounds that can make it through a GC column, which will be a subset of what I- usually can measure). This technique may well be very useful (especially for simplified systems), however I don't think the authors have fully illustrated this yet. I have a major issue with some of the methods and interpretations thereof that require major revisions. Mainly, the data shown for iodide ionization shows that the ionization process is different than in typical iodide ionization CIMS setups (at least for some compounds including vanillin). This will diminish the ability to use this instrument to guide interpretation of other typical iodide CIMS measurements. I believe the authors need to address this issue (likely by showing more measurements) before making some of the conclusions drawn here. I also have questions about decomposition, and the utility of interpreting multiple reagent ion spectra.

Response: We sincerely appreciate the reviewer for carefully reviewing this manuscript and providing insights and suggestions on the weakness of the manuscript. The main issue mentioned by the reviewer is the difference of ionization chemistry between this instrument and a direct-air-sampling CIMS. We certainly recognize this concern, but believe that much of this apparent discrepancy is due not to true differences in ionization chemistry, but rather some of the details and features of ionization are made more obvious because this instrument sees the clean spectra of individual analytes due to the pre-separation of the GC as opposed to direct-air-sampling, in which all analytes are measured simultaneously. For detailed discussions and revisions in response to the reviewer's concerns, please see our response in Comment 3 and 4. The reviewer also mentions other issues on thermal decomposition of analytes, which are addressed in the responses of Comment 1 and 2; some of these concerns are due primarily to a lack of clarity in our original manuscript around operating conditions and temperatures, which we apologize for and have tried to correct in the revision. The question on the quantification using multi-reagent ionization is addressed in the response of Comment 5.

Some of the reviewer's comments involve questions of the capability of this instrument to do quantification of analytes. We would like to note that the main objective in this study is to demonstrate the detailed instrumental design for isomer-resolved measurements of particle-phase organics. Such an instrument could be useful to investigate several different issues, include quantification and novel ionization chemistries. In many cases, investigating any one of these questions in detail is likely complex, and we feel that it is best examined in separate manuscripts to give a proper full treatment. In fact, we are preparing another manuscript on the quantification and sensitivity of this instrument. The forth-coming manuscript will discuss the quantification of CIMS sensitivities, the variance of isomer

sensitivities within a formula, examination of the voltage scan calibration method, and correlation between GC retention time and CIMS sensitivities. Including such information in this manuscript would substantially expand the complexity and scope of this manuscript, which we feel would not serve readers well either in terms of understanding the present work, or understanding issues related to quantification and sensivitity. We have provided the information on splitting the work as described on Line 226:

Implementation of this calibration approach including detailed methods of quantification and determination of isomer sensitivity is complex and will be addressed in future work. **This manuscript focuses instead on the descriptions of technical hurdles overcome by TAG-CIMS/FID and its potential value in understanding existing and new ionization chemistries, as well as atmospheric systems.** ~~This manuscript focuses instead on the description of TAG-CIMS/FID, isomer-counting, and evaluation of multi-reagent CIMS.~~"

What we would like to highlight in this manuscript is that this instrumental design provides options to investigate known and new ionization chemistries, which includes in-depth issues such as quantifying sensitivies of iodide CIMS and expanding the range of identified chemical species using multi-reagent ionization. We have added a sentence to highlight the needs of future work on Line 365:

"We demonstrate here an example of exploring new reagent chemistries: simultaneously using multiple reagent ions is only made possible by the GC separation of analytes, but expands the information provided by this instrument. An in-depth understanding of the competition between reagent chemistries in a multi-reagent system is beyond the scope of this manuscript."

Comment 1: Main comments:

Line 112: Is there a risk of decomposition of organic analyte molecules at this 225C temperature in the IMR, especially on metal surfaces? I would also be worried about fragmentation at the 300C temps upstream. Previous FIGAERO CIMS research has suggested decomposition of oligomers and/or highly functionalized molecules when heating at even lower temperatures than 300C. Please add some references to this previously observed issue, and also add some discussion somewhere in the manuscript of how decomposition would affect your measurements.

Response: We agree with the reviewer's concern about the potential for high temperatures to produce decomposition of target analytes, and we seek to address those concerns throughout our responses here and in the revised manuscript. The specific issue raised in this comment is actually simply a misunderstanding due to a lack of clarity in the original manuscript suggesting that the IMR temperature was held at 225 °C in our study. In reality, the IMR was not heated, but instead was kept at room temperature (~20 °C). The transfer line between the passivated flow splitting manifold and the IMR consisted of inert silica tubing (GC guard column) that was maintained at 225 °C using a heated metal sheath and interface. A transfer line using the same materials was also used to connect the flow splitting manifold to the FID in order to ensure that both detectors "see" the same analytes. To clarify the misunderstanding, we have revised the manuscript on Line 114:

"The inlet is a heated metal **interface**~~cartridge~~ which is kept at 225°C and has a 1/32" inner diameter bore-through center hole to allow insertion of fused-silica guard column into the ion-molecule region (IMR) **which is kept at room temperature (~20 °C)**."

Because the heated inlet was directly connected with the IMR, the outer IMR surface facing the inlet had a slightly higher temperature (~50 °C) due to the heat transfer. However, the temperature inside the IMR was room temperature and the surface temperature (50 °C) was not substantially higher than the typical CIMS operating temperature. Additionally, the room temperature reagent ion flow rate (2 slpm) was three orders of magnitudes higher than the heated GC column flow rate (~0.7 sccm @ 225 °C), so the temperature of the mixed flow in the IMR is not expected to be significantly elevated.

Although IMR temperature is a misunderstanding due to unclear aspects of the description, we acknowledge that the thermal-decomposition of analytes can impact the interpretation of the collected data. This decomposition is expected to occur primarily during the heating of TAG sampling cell where compounds may decompose to volatilize, and in the GC column and flow splitting manifold, where compounds are exposed to higher temperatures to mobilize them. As the reviewer notes, we agree it is a concern with any instrument that uses thermal desorption that some artifacts or misinterpretation may occur due to the decomposition of thermally unstable products. Some of those limitations are discussed in the manuscript on Line 285:"thermal desorption may fragment larger accretion products to form analytes not present in the original sample (Isaacman-VanWertz et al., 2016; Lopez-Hilfiker et al., 2016b), or may reverse particle-phase oligomerization reactions (Claflin and Ziemann, 2019)."

Critically, the transfer lines to both detectors are held at temperatures at or below that of the flow splitting manifold to avoid any further decomposition. This is meant to ensure that any thermal decomposition occurs upstream of the flow split and both detectors see the same effluent mixture. In other words, while the eluting analytes may not be identical to the sampled analytes, both detectors see the same eluting analytes. We agree that scientific interpretation of these atmospheric data consequently needs to consider the possibility of decomposition adequately and be interpreted within this context, but decomposition is not expected to influence the comparison of signals between CIMS and FID. To this end, we strive to be transparent and clear about the potential impacts of decomposition on the isomer analyses. As suggested by the reviewer, we have added more references to show that compounds are subject to decomposition in the thermal desorption process and elaborated the discussion of the impacts of such decomposition on the results on Line 273:

"Conversely, thermal desorption **within TAG** may fragment larger accretion products to form analytes not present in the original sample **(Buchholz et al., 2019; Isaacman-VanWertz et al., 2016; Lopez-Hilfiker et al., 2016b; Stark et al., 2017)**~~(Isaacman-VanWertz et al., 2016; Lopez-Hilfiker et al., 2016b)~~, or may reverse particle-phase oligomerization reactions (Claflin and Ziemann, 2019). **These fragments may not represent the actual molecular composition of SOA, though they nevertheless may provide insight into the formation mechanisms of SOA (Isaacman-VanWertz et al. 2016). Consequently, the potential multiple fragments from one parent compound may result in an overestimation of the number of isomers.**~~These fragments may be identified as oxidation products in this analysis and consequently overestimate the number of isomers.~~ We note, however, that similar numbers of isomers are observed when using liquid chromatography (Figure 3b), which does not involve thermal desorption. Given these uncertainties, we believe that the results presented are not a floor or a ceiling on the number of isomers in the atmosphere, but a step toward understanding a poorly constrained problem."

Comment 2: Line 211: Related to my previous comment, how much of these early eluting compounds might be fragmentation products as an artifact of the sampling technique? Fig 4: Regarding decomposition again, one way to investigate would be to show the FID signal for Fig 4 and maybe for

more examples where you are injecting single known compounds. How much signal is in the FID but not the CIMS, i.e., how much fragmentation occurs throughout the sampling process? I think this would be important information for a reader to judge the utility of the technique.

Response: We interpret this comment to raise two possible and related issues on the subject of decomposition. Firstly, decomposition of sampled analytes in the TAG instrument ("upstream decomposition") may mean that detected analytes are actually transformed products of the true sampled analytes. Secondly, if decomposition impacts each detector differently ("downstream decomposition"), comparisons between chromatograms or detectors may be biased or incorrect. We discuss both here in order to address the reviewer's concerns.

Firstly, we agree that decomposition occurring during sampling or transfer of the sample to and/or through the GC column would impact the scientific interpretation of collected data. Critically, we note that decomposition upstream of the flow splitting manifold should not impact the comparison of CIMS and FID data, which would see the same (transformed) analytes. In the context of this work, the impact of upstream decomposition within TAG primarily would impact the counting of isomers, as fragmentation may lead to overestimation of isomer counts, which we have sought to make clear in the revised manuscript on Line 236 as excerpted below. In any work that uses this or any GC-based instrument, similar considerations will need to be taken in the context of any conclusions drawn. These instruments consequently always offer/suffer some tradeoffs between molecular specificity and potential for in-instrument transformations, but their ability to measure specific tracer molecules indicative of sources and chemical pathways (whether or not those tracers are actually decomposition products) has nevertheless provided a range of important atmospheric conclusions, such as the body of work from other TAG instrumentation (Isaacman-VanWertz et al., 2016; Williams et al., 2006; Zhao et al., 2013).

Line 236: "**Overestimation may occur when large parent molecules decompose to isomers of a smaller formula during thermal desorption.** ~~Overestimation may occur because peaks observed might be formed in part by thermal decomposition of analytes during thermal desorption.~~"

Secondly, we consider the possibility for downstream decomposition, such that that the early eluting compounds appeared in FID yet missing in CIMS in Figure 2 is due to the thermal decomposition of analytes in CIMS or FID. Some of this concern may again be due to the implication in the original manuscript that the IMR was heated. Instead, we have sought to design this instrument such that any decomposition occurs upstream of the flow split, as described above, so we believe decomposition is far more likely upstream of the flow splitting manifold than downstream. Specifically, we note that decomposition in transfer lines downstream of the flow splitting manifold should be minimal because the transfer lines are kept at or below the temperatures of the interface, and downstream decomposition is probably not a significant process. The compounds coming out of the TAG, which may be the fragments of a parent molecule, are therefore being measured by the CIMS and FID simultaneously.

Given these considerations, we believe the differences between FID and CIMS chromatograms can be best explained by the wide ranges in CIMS sensitivity previously reported in the literature, as described in the manuscript. While an FID provides a mass-based, near-universal response to hydrocarbons and oxygenated organics, the range of the iodide CIMS sensitivities can vary up to 6 orders of magnitudes (Iyer et al., 2016), with a general tendency to be more sensitive to polar or hydroxyl-containing

compounds. Many oxidation products of monoterpenes are less-polar compounds (e.g., limona ketone (Donahue et al., 2007)) and even compounds having a single hydroxyl group is not necessarily sensitive in an iodide CIMS. Since less-polar compounds tend to elute early on a polar GC column (i.e., MXT-WAX used in this study), those early elutes are expected to be not detected or have low abundance in the iodide CIMS. In contrast, polar compounds tend to elute late in the chromatogram and can provide orders of magnitude stronger signals in CIMS.

Overall, therefore, it is not clear that decomposition could account for the observed differences in CIMS and FID chromatograms, while known trends in sensitivity provide a reasonable explanation. Some early eluting compounds may be present in the CIMS chromatogram at low signal but not visible because displaying them in a single chromatogram is difficult with a linear Y-axis due to the wide range of sensitivity.

To explain the two reasons that result in the differences between CIMS and FID chromatograms, we have added more descriptions on Line 206:

"Since the TAG-CIMS/FID interface and the capillary to the FID is held at 50 °C above the maximum column temperature, differences in the transfer of analytes to these two detectors should be negligible. Instead, these differences are due to the selectivity of the two detectors. FID is a near-universal detector, able to detect almost all organic compounds with relatively similar and predictable responses (Scanlon and Willis, 1985). **The sensitivity of the iodide-CIMS may differ by orders of magnitude and is highest for compounds that contain multiple OH groups and can therefore more readily form an adduct with the iodide ion (Iyer et al., 2016). Since the TAG here used a polar (MXT-WAX) GC column that more preferably retains polar compounds, the early-eluting compounds are likely less-polar, and consequently less sensitive or not detected in the iodide-CIMS. Some early-eluting compounds may be present but have peaks too small to be visible due to the linear display of signal in Figure 2.** ~~The sensitivity of the iodide-CIMS is highest for compounds that are more polar and can therefore more readily form an adduct with the iodide ion (Iyer et al., 2016). The wax GC column used here more readily retains polar compounds, suggesting that the early-eluting analytes are more likely to be lower-polarity compounds that exhibit low sensitivity in the iodide-CIMS.~~"

In the context of the reviewer's concerns, we understand their suggestion to add the FID chromatogram for Figure 4 in the manuscript to probe the decomposed fragments by comparing chromatograms between CIMS and FID. As above, the reviewer suggests that what is shown in the FID chromatogram yet missing in CIMS chromatograms may be decomposition fragments due to heating of the sampling process. We appreciate the reviewer for suggesting options to identify the thermal decomposition compounds in the instrument. For the reasons discussed above, we do not think decomposition is a likely explanation for the observed differences between chromatograms. In Figure R1, we have included the FID chromatogram for Figure 4. The sample injected is a mixture of know chemical standards and unknown fragrance liquids. As in the case of Figure 2, there are clearly more peaks in the FID, as some compounds in the fragrance are expected to be hydrocarbons or lightly-oxygenated compounds that an iodide CIMS cannot detect (e.g., monoterpenes, $C_{10}H_{16}$, a major component of fragrances (Steinemann et al., 2011)). However, it is not clear to us that including this chromatogram provides any additional information or insight than what is already evident from Figure 2, so we have chosen not to add this chromatogram to Figure 4 in the revised manuscript. Furthermore, compounds that are sufficiently stable to be introduced to the instrument are generally less likely to decompose upon thermal

desorption, so the introduction of individual standards does not provide a clear path forward to explore the possibility of upstream decomposition

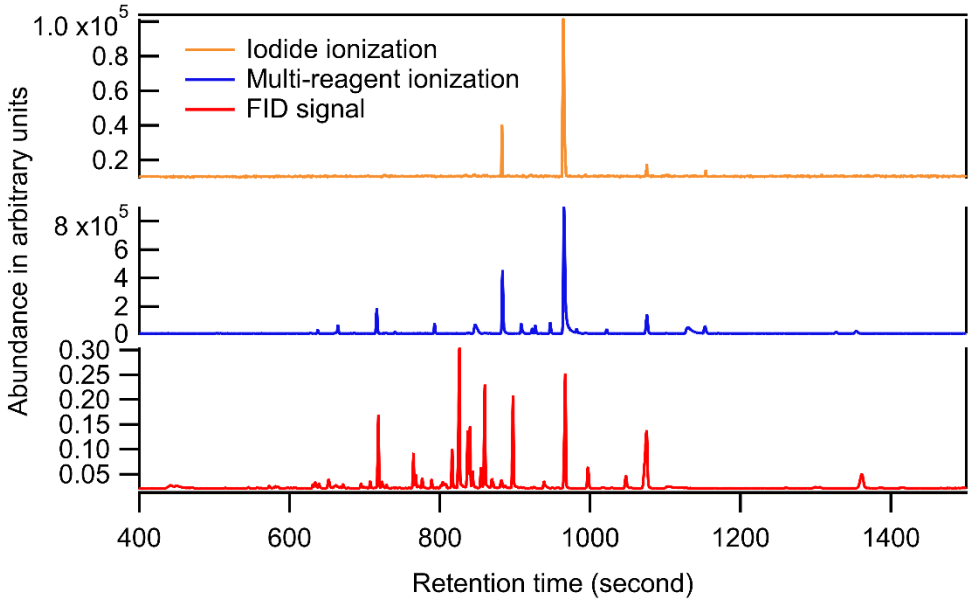

Figure R1: Comparison of chromatograms of analyte total ion counts between CIMS using iodide ionization, CIMS using multi-reagent ionization, and FID. Top two panels are recreated from Figure 4 of the manuscript.

Comment 3: Line 297: This inset in Fig 4a indicates a major issue. In a typical iodide CIMS setup, vanillin would be sampled almost completely at the [M+I]- cluster with iodide, but you're showing that in your instrument it is predominantly sampled at the deprotonated [M-H]- . Therefore, the ionization process is different from a normal iodide CIMS. I think this is a major problem that you need to address before publishing under the pretext that your instrument can be used to help generally interpret iodide CIMS measurements. The most likely answer that I see could be that holding the IMR at 225C is causing the changes? Perhaps at those temperatures (and with metal surfaces?), vanillin becomes a gas phase acid and C8H8O3 + I- –> C8H7O3- + HI proceeds? At line 300, you try to address the [M-H]- by stating that vanillin "produces a large number of detectable ions through reactions with other reagents in the IMR." But, there are no other reagent ions there (except NO2- maybe, but that is often present in typical iodide CIMS spectra and is therefore not the cause), so this statement is probably not accurate. So, please address this issue thoroughly. A first step could be to do the same vanillin injection but hold the IMR at room temp. The vanillin signal may smear, but does is show up at [M+I]-? Again, this seems like a major issue since you're trying to say (eg lines 372- 374) that you can use this method to investigate non-iodide clusters separated by the 'iodide valley', but you're apparently also drastically changing the ionization method.

Response: The reviewer raises several concerns, which are generally related to the ionization occurring within this instrument, and whether it resembles that of other iodide CIMS in use in the field, with a specific discussion of vanillin as an example. A critical difference between this instrument and direct-air-sampling instrumentation is the ability to collect "clean" mass spectra of individual analytes, which leads to some subtleties in how to compare to direct-air-sampling instruments. Consequently, while the reviewer raises very reasonable concerns, we believe that a lot of the apparent discrepancy comes from the fact that this instrument specifically provides an ability to see and explore the non-adduct ions, while a typical CIMS does not straightforwardly relate adduct ions to potential non-adduct counterparts. While iodide CIMS is indeed used in large part specifically for its ability to selectively study molecular ions, non-adduct ions (i.e., ions formed through pathways other than the formation of an iodide adduct) are commonly also generated in iodide CIMS instrumentation. This issue has been previously reported, with iodide adduct ions separated from non-adduct ions by a gap in mass defect by the so-called "iodide valley" shown in Figure R2 (Lee et al., 2014). It is not unexpected that any given analyte (e.g., vanillin) could produce non-adduct ions through side reactions with small impurities in flow streams (discussed further below).

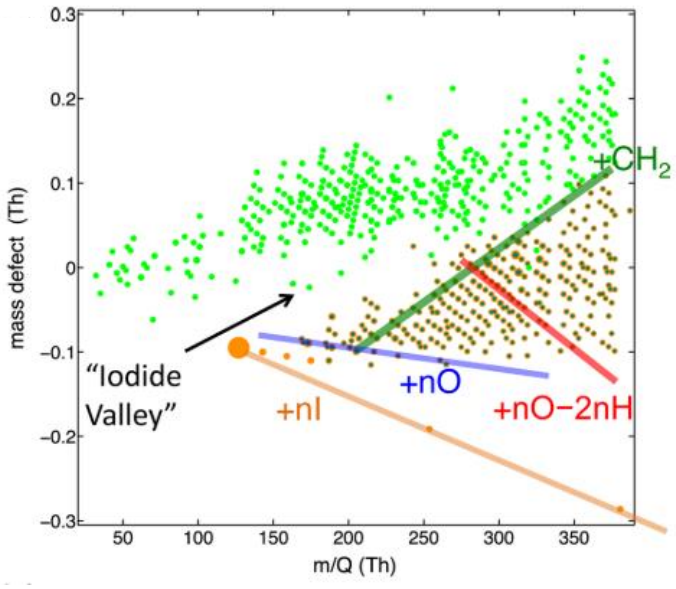

Figure R2: High-resolution mass defect spectrum obtained during ozonolysis of α-pinene (adopted from Lee et al. (2014))

One of the significant values of the described instrument is that it specifically provides an opportunity to study ions at the other side of the iodide valley (i.e., non-adduct ions) shown as the green dots in Figure R2 and their potential relationship to adduct ions. In a direct-air-sampling iodide CIMS, all analytes generate ions simultaneously, so parent ions and non-adduct ions cannot be independently studied. Consequently, researchers frequently discount the non-adduct ions when analyzing the iodide CIMS data. With the pre-separation of the GC, we can explore those non-adduct ions that are simply ignored in a direct-air-sampling CIMS. One of the reviewer's concern is that the 225 ^{o}C IMR temperature may cause the different ionization chemistry, which is, again, confusion due to lack of clarity in our origical description of the instrument as addressed in Comment 1; in fact, the IMR was set at room temperature so it should have minor impacts on the ionization chemistry and we apologize for the confusion and have tried to clarify as described above.

To address the reviewer's specific concern with regards to vanillin, we discuss here possible reasons for observed differences, and comparison to other previously studied analytes. The reviewer suggests that in a typical iodide CIMS setup, vanillin would be sampled almost completely at the [M+I]- cluster. We agree that it is certainly possible for an instrument to be operated in such a way, but in many typical applications of CIMS, the spectra of vanillin would be sampled simultaneously with other analytes (i.e., without the pre-separation provided by GC); given the ubiquity of non-adduct ions in CIMS spectra, in such cases, the spectrum of vanillin and/or its tendency to form non-adduct ions would often not be specifically known, so direct comparisons of our individual-analyte spectra to that of a typical CIMS are primarily limited to cases where individual analytes are introduced. More broadly, we note that while a specific iodide CIMS may be tuned to optimize measurements of a specific analyte, the mass spectrum of any given instrument may be impacted by the tuning and/or the pressure of the IMR. Spectra are therefore heavily dependent on instrumental settings such as voltage settings of the atmospheric pressure inlet (API) and operating pressure, and to our knowledge, there is no consensus on a standardized operating condition of an iodide CIMS. For example, while our IMR pressure was set at 100 mbar, we are aware of other studies using 200 mbar (e.g., Isaacman-Vanwertz et al., (2018)). Indeed, even the voltage setting of the small transfer quadrupole *rf* amplitude can impart fragmenting energy into the analyte molecules and clusters.

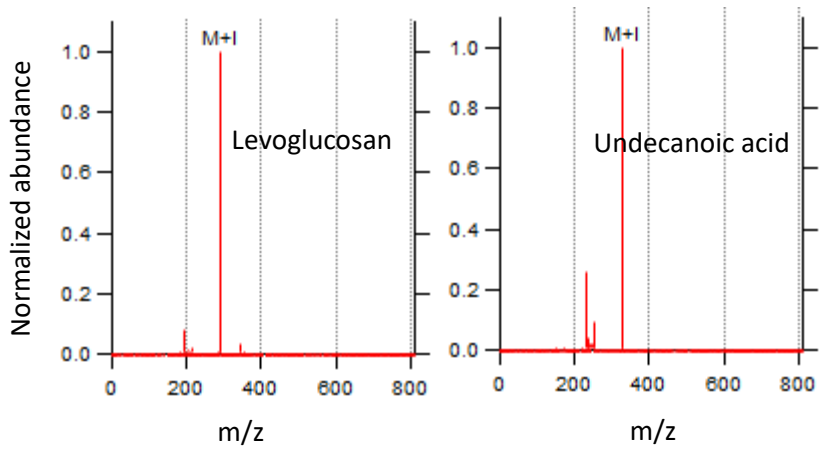

Figure R3. Iodide subtracted mass spectra for liquid standards of levoglucosan, undecanoic acid, and hexdecanoic acid in this study.

To provide the reviewer with further information on the ionization scheme of this instrument, we provide the mass spectra for liquid standards of levoglucosan and undecanoic acid in this study in Figure R3. Those compounds have [M+I]- as the most abundant ion in the "clean" mass spectrum. Levoglucosan, which was reported having the near collision-limited sensitivity in Lopez-Hilfiker et al., (2016a), is also found to form mostly iodide-adduct in this study. The results suggest that the ionization chemistry varies significantly for different compounds, and that more polar (more sensitive) compounds do tend to have more dominant adduct ions. We have revised some description on the ranking of the detectable ions in the manuscript on Line 305:

"**Although the abundance ranking of the produced ions may differ on a compound-by-compound basis, we constantly observe ions other than [M+I]$^-$ in the clean mass spectrum of injected liquid standards such as undecanoic acid, hexadecanoic acid, and 1,12-dodecanediol, as well as more polar**

and low volatility aerosol constituents produced in the oxidation experiments. ~~Similar trends are observed for other compounds injected as authentic standards, including undecanoic acid and 1,12-dodecanediol. In contrast, the iodide-adduct ions ([M+I]$^-$] of more polar and lower-volatility aerosol constituents produced in oxidation experiments are the dominant ions in their analyte mass spectra.~~"

Overall, the TAG-CIMS has a unique advantage of exploring ionization chemistry due to the pre-separation of a GC, but, for the same reason, there are not a lot of published spectra in the literature against which to compare to other CIMS. However, the target of this study is not to investigate the ionization chemistry for specific compounds, but to propose a proof-of-concept instrument for future studies on those specific science questions.

A second question in the comment: "At line 300, you try to address the [M-H]- by stating that vanillin "produces a large number of detectable ions through reactions with other reagents in the IMR." But, there are no other reagent ions there (except NO2- maybe, but that is often present in typical iodide CIMS spectra and is therefore not the cause), so this statement is probably not accurate."

We agree with the reviewer that the statement is not accurately explained and the "other reagent ions" were not clearly defined in this sentence. In fact, there are other reagent ions with their abundance too small to be observed in the figure. Although the abundance of O2- in the iodide ionization mode is very small, 0.03% compared with I-, it may be still competitive to react with the analytes thus produced [M-H]-. The O2- is likely produced by the impurity of UHP N2 (99.999%). Since reagent ions can have dramatically different sensitivity to the analyte, the low abundance of O2- can probably not be ignored in the ionization process. We suspect that the [M-H]- is generated mainly through the reaction between the analyte molecule and the O_2^- because the abundance of [M-H]- ions of most analytes were boosted five to ten times after mixing 5% of the zero-air in the ultra-high purity (UHP) N_2 reagent ion flow. Additionally, previous studies have reported such ionization pathway of O2- as described on Line 317:"It is reported that the presence of O_2^-, which is commonly found in atmospheric pressure ion sources such as electrospray ionization (ESI) (Hassan et al., 2017), atmospheric pressure chemical ionization (APCI) (McEwen and Larsen, 2009), atmospheric pressure photoionization (APPI) (Song et al., 2007), and direct analysis in real-time (DART) (Cody et al., 2005), may result in the deprotonated molecules through oxidative ionization."

Mentioned the reaction with other reagent ions before introducing the reaction mechanism probably lead to the confusion of the reviewer. To avoid such confusion, we have deleted the description on "other reagent ions" on Line 303:

"In other words, this compound, which is generally measurable by iodide-CIMS (Gaston et al., 2016), produces a large number of detectable ions other than the iodide-adduct ions ~~**through reactions with other reagents in the IMR."**~~

Comment 4: Line 303: Interesting that the lower volatility compounds or more polar compounds appear to have different ionization processes relative to the more volatile or less polar compounds like vanillin. Since one of the advantages of I- ionization has been a more consistent (and single) ionization process for the majority of compounds, do you have any thoughts on how this affects interpretation of the spectra?

Response: We agree with the reviewer that one of the main benefits of the iodide CIMS is the simple ionization chemistry. The simple adduct formation makes the quantification using an iodide CIMS straightforward by only tracking the abundance of the iodide-adduct. The findings in our study do not change this fact. However, not all analyte molecules form an adduct with iodide. Previous studies have reported some iodide-adducts, such as simple monocarboxylic acids or diols, may be rapidly disassociated when increasing the voltage differences in specific components of the API (Lopez-Hilfiker et al., 2016a). Additionally, the use of multi-reagent ionization in our study demonstrates that other reagent ions can compete with iodide and produce non-adduct ions. The finding here suggests that there is not only iodide chemistry in the IMR, but also other potential ionization pathways producing the ions at the other side of the iodide valley. As noted above, we believe this to be one of the major advantages of a coupled GC-CIMS system - to better understand ionization chemistries and examine features that are otherwise difficult to study (such as non-adduct ions). To avoid the misunderstanding that iodide ionization chemistry may change with the polarity of compounds, we have revised the manuscript on Line 305:

"**Although the abundance ranking of the produced ions may differ on a compound-by-compound basis, we constantly observe ions other than $[M+I]^-$ in the clean mass spectrum of injected liquid standards such as undecanoic acid, hexadecanoic acid , and 1,12-dodecanediol, as well as more polar and low volatility aerosol constituents produced in the oxidation experiments.** ~~Similar trends are observed for other compounds injected as authentic standards, including undecanoic acid and 1,12-dodecanediol. In contrast, the iodide-adduct ions ($[M+I]^-$) of more polar and lower-volatility aerosol constituents produced in oxidation experiments are the dominant ions in their analyte mass spectra.~~"

Comment 5: Line 318: Since you're seeing the deprotonated ions using both ionization methods (just I-, and both I- and O2-), it seems like it would be really hard to convert the signal in multiple reagent ion mode to mixing ratios as the sum of two ionization processes with variable sensitivities. Especially this would be hard if you have are sampling a complex mixture. It makes me wonder if it's feasible to use both reagent ions at the same time, or if you should instead use them one at a time in series. No doubt that O2- ionization gives you a lot of extra information about the less oxidized/polar compounds that Ican't see. Please discuss this to give the reader confidence that using two reagent ions simultaneously is actually a practical scientific improvement. Best would be to show a quantitative example of a calibration curve using both reagents, but possibly this will be the subject of a future manuscript.

Response: We fully agree with the reviewer that it is complicated to calculate the mixing ratio of an analyte by summing up concentrations/abundance in the two ionization processes of CIMS without building a deeper understanding of the O2- pathway. However, this is not what we intend to do. In the multi-reagent ionization mode, the CIMS is primarily valuable for examing elemental formulas while the quantification could be achieved by FID. We agree that alternating different modes might be helpful, but note that due to the inherent semi-continous nature of GC, that would come with its own tradeoffs in terms of time resolution and the fact that each analysis might not be examining exactly the same sampled air. We have revised the sentences on Line 360 to clarify the issue:

"A reasonable objection to multi-reagent ionization is that ~~the complexity and/or novelty of the chemistry may prohibit reasonable quantification~~**the complexity of adding up signals in multiple ionization chemistry with variable sensitivities may prohibit reasonable CIMS quantification.** However,

using CIMS for identification of unknowns by formula or other chemical information is valuable on its own, and quantification of many components is achievable using the FID channel of this instrument."

Comment 6: Technical comments: Fig. 3 Caption: extra 's' after SOA

Response: We have deleted the "s" in the caption of Figure 3:

"Figure 1. …… combined datasets from **SOA**~~SOAs~~ formation ……"

Comment 7: Line 324: This sentence just needs some clarification. You're either adding zero air to the ionizer alongside methyl iodide, or adding O2- to the ionization region (aka IMR) alongside iodide. Also "ionization region" is ambiguous because that could be the ionizer or the IMR.

Response: We agree with the reviewer that the description on Line 324 is ambiguous. We have revised the sentence on Line 328 for clarifications :

"the CIMS was operated in a multi-reagent ionization mode by adding ~~5%~~**100 sccm flow (i.e., 5%) of ultra-zero air to the 2 slpm flow of N_2 for the gas supply of the methyl iodide permeation tube**~~the ionization region alongside iodide~~**.**"

Comment 8: Line 326: This was confusing to me because you list the numbers with multi-reagent ion first and iodide second, right after referring to Figs. 4b (iodide) and 4d (multi) in the reversed order. Please reverse the order of listing the numbers in order to stay consistent with the Fig.

Response: We thank the reviewer for pointing out the reversed order of ionization mode. We have revised the manuscript on Line 330:

" the total ion counts are ~~1.4~~**2.4**×10^6 and ~~2.4~~**1.4**×10^6 ions/s and the I^- ion counts are ~~0.7~~**1.8**×10^6 and ~~1.8~~**0.7**×10^6 ions/s for ~~multi-reagent~~**iodide** ionization and ~~iodide~~**multi-reagent** ionization, respectively."

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