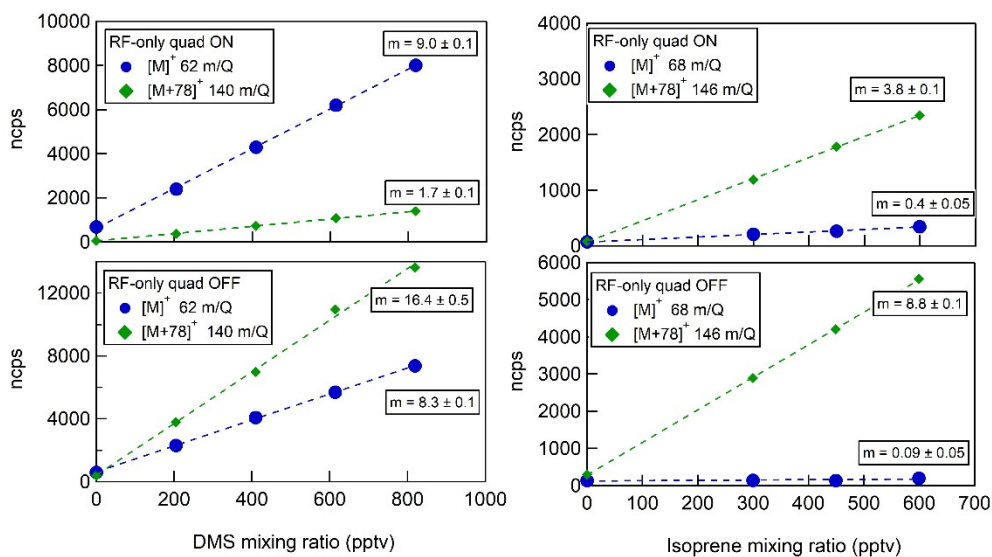


Reviewer 2

1) The manuscript states that a “new set of applied voltages with softer de-clustering power” (line 118) is used here, however there is no information given on what the voltages are or how the voltages compare to those used by the group previously (other than the above vague remark). For instance, there is no discussion about how the relative intensity of the $C_6H_6^+$ and $(C_6H_6)^+(C_6H_6)$ compare. Given the current emphasis on voltage scanning within the community (Brophy and Farmer, 2016; Lopez-Hilfiker et al., 2016), I am surprised that such experiments were not carried out here. I think that the inclusion of such experiments would be an asset to the manuscript as it may help provide (at least a basic) explanation of some of the peculiarities that are occurring with isoprene. I am not suggesting that the declustering experiments be performed for all the compounds investigated here; however, the inclusion of a select few would improve the impact of the manuscript. Currently, the only change in the declustering voltages is by turning off the voltages in the first RF-only quadrupole and these results are only shown for sampling zero air (no analyte; Figure 3). While this provides some insight, it is limited given the large drop in ion transmission and the lack of measurement of an analyte. It would be interesting to see how the distribution of $[M-1]^+$, M^+ , and $[M+32]^+$ changed as a function of voltage scanning for the monoterpenes and sesquiterpenes. I think it is also an overstatement to say in the abstract (lines 19 & 22) and conclusion (line 328) that the effect of declustering voltages was studied given the limited investigation into this effect.

The reviewer raises an important point that highlights we need to further clarify our intent regarding voltage settings. In Bertram et al. [2011], we described the utility of voltage tuning of the exit lenses of the RF-only octupoles to vary cluster distributions while maintaining high transmission. The operational voltages used here have essentially the same field strengths at the “weak field” described in Bertram et al. [2011]. The only deviation is that we start from 0V on the front end of the IMR for practical considerations.

To reduce field strengths even further, in an attempt to probe the cluster distributions of the IMR, we turned off the RF-only quadrupoles completely. This is not meant as an operational configuration, as ion transmission is sacrificed (as the reviewer notes). However, it gives us the best insight into the cluster distribution in the IMR and hence the ion-molecule reaction mechanism. Below, we show the impact of the RF-only quadrupole on analyte-cluster distributions for DMS and isoprene.



As shown above, reduction in the field strength favors the $M+78$ cluster in the case of DMS, as expected. In the case of isoprene, with the focusing RF quad on, we observe a small percentage of isoprene as the

bare ion (ca. 10%). We expect that this is due to declustering of the isoprene-benzene cluster at a point when a sufficient amount of positive charge is on the isoprene in the cluster. Following declustering, there are few collisions of the bare isoprene ion with benzene and the molecular ion is transferred to the mass analyzer. With the RF-only quad off, we do not observe statistically significant amounts of the bare ion. This suggests that the isoprene is found exclusively as the cluster in the IMR.

The manuscript has been edited in the following locations to address these points:

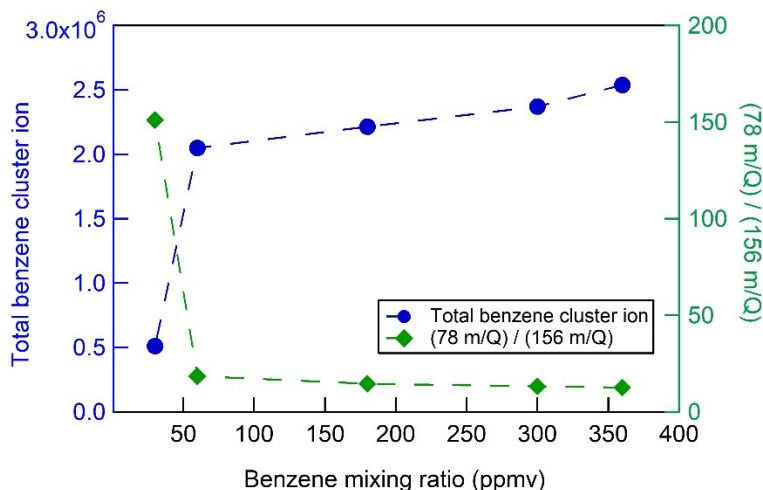
Line 18: In addition, we determine the dependence of CI-ToFMS sensitivity on the reagent ion neutral delivery concentration and water vapor concentration.

We have also removed the phrase “declustering voltages” from line 328 as the reviewer is correct that we adjusted the field strength to learn about the ionization mechanism, but not to develop new operational configurations for sampling.

Line 118: This line has been edited to now read: “We also examine the de-clustering power of the RF only quadrupole to better determine the cluster distribution present in the ion molecule reaction chamber.”

2) Sections 3.1 & 3.2: How does the abundance and ratio between $C_6H_6^+$ and $(C_6H_6)^+(C_6H_6)$ change as the concentration of neutral benzene is increased? Does this provide any insight into the isoprene results?

We expect that at higher benzene neutral concentrations, larger benzene cluster cations ($(C_6H_6)^+(C_6H_6)_n$, $n>1$) are favored. However, we do not have evidence for this as clusters larger than $n=1$ have very weak binding enthalpies, prohibiting their efficient transmission in the mass spectrometer. As noted in the manuscript, even with the RF-only quadrupole off, we do not observe clusters larger than $n=1$. As a result, there is only a small change in the cluster distribution observed in the mass spectra. The effect of benzene neutral concentration on the observed cluster distribution and the total benzene cluster ion concentration are shown below. We note that at low benzene neutral concentrations, a significant fraction of total ion current can be found as protonated water clusters or O_2^+ . We caution over interpretation of the reduction in total benzene cluster ion signal intensity at low benzene neutral concentrations (< 50 ppm) shown here as this experiment was not designed to assess the low concentration regime.



3) I do not see where the text references the tables. Including a reference to the table in the text would be beneficial since the tables show that the M^+ , $[M-1]^+$, and $[M+32]^+$ ions were investigated for all the compounds and not just those discussed in depth in the text.

We have added references to the tables in the text.

The manuscript has been edited in the following locations to address these points:

Table 1 is now referenced in line 113: “We discuss the sensitivity of benzene cluster cation chemistry to a select number of terpenes (Table 1) at atmospherically relevant mixing ratios (<500 pptv).”

Table 1 is now referenced in line 304: “The reported sensitivities, product ions, and dependence on ambient water concentrations and neutral benzene concentration for select monoterpenes are shown in Table 2.”

Table 1 is now referenced in line 323: “The reported sensitivities, product ions, and dependence on ambient water concentrations and neutral benzene concentration for select sesquiterpenes are shown in Table 3.”

4) Line 14: replace alpha with the correct symbol

This has been corrected.

5) Line 57-58: The references for NO^+ and H_3O^+ seem a bit strange as the references refer only to early work and not more recent work, while the references for other ionization mechanisms contains more recent work. For instance, the absence of Koss et al. (2016).

References to Karl et al., 2012, Mochalski et al., 2014, and Koss et al., 2016 have been added.

6) Line 185: “error bars are the standard deviation of repeated triplicate measurements” but caption of figure 2 “error bars represent the standard deviation of the 1 Hz measurements.”

The figure caption has been revised. The error bars represent the standard deviation of the triplicate calibrations.

7) Line 209: “Without the first RF-only quadrupole” Is it removed or just the voltages turned off. If the voltages was it all the voltages or just the RF component?

The manuscript has been revised to read: “ ... but without the RF and voltage bias applied to the first quadrupole ion guide.”

8) Line 330-331: The wording here makes it appear like a recommendation to only use $\text{C}_{10}\text{H}_{16}^+$ for quantification of monoterpenes. However, the average sensitivity appears to be that obtained using the M^+ , $[\text{M}-1]^+$, and $[\text{M}+32]^+$ ions (Figure 10) and not just the M^+ ion (Figure 7). What recommendation do the authors provide for quantification of monoterpenes?

As shown in Table 2 (and 3), for most monoterpenes and sesquiterpenes measured, the majority of the measured signal is as the molecular ion. However, select monoterpenes (and sesquiterpenes) such as D-limonene have a significant amount of signal at $[\text{M}-1]$ and $[\text{M}+32]$. For these reasons, we would recommend including signal intensity at these masses in the overall measurement of monoterpenes (and sesquiterpenes).

The manuscript has been revised (line 337) to read: “Given that signal intensity was observed at $([\text{M}-1]^+$ and $([\text{M}+32]^+$, for a few select terpenes (e.g., D-limonene) we recommend that future measurements of total monoterpenes utilize all three product ions.”

9) Lines 333-334: Same comment as above expect for sesquiterpenes.

See response to comment #8.

10) Table 1: I don't find this particularly useful since there is no in depth exploration of how structure might relate to the different observed sensitivities. To be clear, I am not suggesting that such an explanation be incorporated; I do not think it would be appropriate given the extent of the data.

While we did not make tangible connections between terpene structure and sensitivity, we think the table is helpful to the reader that may not be directly familiar with terpene structure.

11) Figure 3: The peak at m/z 156 should be labeled $(C_6H_6)^+$ (C_6H_6)

Thank you for catching this error. The figure has been revised.