Reviewer 3

1) Page 6 line 161-163: Chloroform is unlikely to be ionized by benzene dimer cation given its higher ionization energy. Where would the chloroform fragment come from, i.e. how is the parent chloroform ion generated?

We expect that the chloroform fragment is generated from trace O_2^+ in the instrument. The sensitivity is extremely small (ca. 100 Hz for 180 ppm).

2) Page 9 line 237-241: For the unclear benzene cation reaction mechanism with isoprene, can you approach it through relationship between sharing pi electrons and reaction enthalpy? Presumably, the isoprene molecule shares its pi electrons with the benzene cation. For bigger benzene cation clusters, they have bigger pi system and more pi electrons, and isoprene needs to share "less" of its pi electrons with the benzene cation. It seems reasonable this trend with increasing benzene concentrations was observed.

This is possible. We decided not to speculate on the dependence of the isoprene sensitivity on the concentration of neutral benzene in the manuscript. We expect, although do not have evidence, that the benzene clusters are larger for higher neutral benzene concentrations. It is possible that for larger benzene clusters a larger fraction of the charge is on isoprene at the point of collisional declustering as the reviewer suggests. This would translate to a larger sensitivity at higher benzene concentration. We are working on a subsequent paper that focuses on quantum calculations of these benzene adducts and elect not to speculate on the cause in this manuscript.

3) Page 10 line 268-271: The cited work by Ibrahim et al. (2005) does not contain any IR spectrum. It is also hard to imagine a 3-body deprotonation process that involves benzene, water cluster and isoprene, as proposed by the paper. Could m/z 73 be an isobaric ion of water tetramer ion? Does the ToF have the resolution to determine the exact mass and identify the chemical formula? Also, given this high intensity of protonated water clusters (~9E4 Hz water ion in Figure 6, comparable to 2E5 Hz benzene ion in Figure 5), could BVOC also undergo proton transfer reaction in the IMR?

We thank the reviewer for catching this citation error. As the reviewer notes, the Ibrahim paper did not contain the IR spectra; it only presented the hydration path of ionized benzene via the arrival time distributions of $C_6H_6\text{-}(H_2O)_n^+$ clusters and supporting quantum calculations. The publication the authors should have also cited is Miyazaki et al. (2004). Miyazaki et al. presents IR spectra of $C_6H_6\text{-}(H_2O)_n^+$ clusters up to n=23. Figures 1 & 3 show that the IR spectra of $C_6H_6\text{-}(H_2O)_n^+$ clusters resemble $H^+(H_2O)_n$ starting at $n \geq 4$. Figure 2 of Miyazaki et al. shows the hydrogen bonded H_2O networks required to deprotonate a $C_6H_6^+$. We are speculating that we see the effects of a proton-transfer from a $C_6H_6 \cdot C_5H_8^+$ cluster to a network of H_2O. At this time we cannot definitively comment on what the structure of that network is exactly but the end product is that of a protonated water tetramer. Our own computational studies have so far shown that a key component of sensitivity in benzene CIMS is through charge migration within a given benzene adduct. The influence of a water environment on that charge migration varies depending on the species in that adduct. We have performed quantum mechanical calculations of charged benzene adducts in the presence of varying $(H_2O)_n$ with water network structures of both those in Ibrahim et al. and Miyazaki et al. and have found that in the case of a $C_6H_6\text{-}C_5H_8^+$ adduct, the positive charge starts to migrate towards a $(H_2O)_5$ cluster. Our group is working on more calculations to prepare a separate paper explaining charge distribution with respect to detection *via* benzene CIMS so we chose not to comment further on this at this time.

We cannot rule out an isobaric ion at m/z 73 with the mass resolution of our ToFMS. However, the sensitivity to the isobaric ion would need to be dependent on water and stem from the isoprene source (to be consistent with Fig. 5 and 6). It is possible that this is due to a proton transfer as total water cluster intensity will increase with SH, but total water cluster signal even at 14 g kg^{-1} SH is only 3.7E4 Hz, compared with 9.8E5 Hz for benzene clusters. In addition, this would not explain the observed anti-correlation in signal intensity at 73 and 146 m/Q which would be explained by our proposed mechanism.

The reference on line 267 has been changed from Ibrahim et al. (2005) to Miyazaki et al. (2004). We think this sufficiently addresses the reviewer's concerns.

Reference: Miyazaki et al., Infrared Spectroscopy of Size-Selected Benzene-Water Cluster Cations [C6H6-(H2O)*n*]+(*n*) 1-23): Hydrogen Bond Network Evolution and Microscopic Hydrophobicity, *J. Phys. Chem. A* 2004, *108,* 10656-10660

4) Page 10 line 280: It is not self-explanatory how instrument operational configuration (benzene concentration and electric field) would cause the inconsistency between current work and Kim et al. (2016). More clarifications are needed here.

The inconsistency between Kim et al and this paper is in the SH dependence of the α-pinene sensitivity. In Kim et al., we observed an increase in sensitivity with SH. Here, we observe a very slight decrease. We think the difference in benzene neutral concentration is key here. The increase in sensitivity with SH (Kim et al) was observed using three different mass spectrometers for both laboratory calibrations and in field standard additions. All operating with 10 ppm neutral C_6H_6 concentrations. The slight decrease in sensitivity with SH was replicated over a comprehensive 6 month evaluation of monoterpene sensitivity (this study), at high benzene concentration (>300 ppm).

In Kim et al., we operated at low C_6H_6 concentrations due to contaminants in the benzene compressed gas source. Unfortunately, this led to an increase in the percentage of protonated water clusters as SH increases. This has a few implications. The most notable is that proper normalization to the primary ion becomes challenging at high SH as the observed signal of benzene cluster cations is small. In Kim et al., we normalized only to the sum of the benzene cluster cations, which may have overestimated the dependence of sensitivity on SH when compared to the current study where the sum of the benzene cluster cation signal is small. We note that this does not impact the conclusions drawn from the analyses of Kim et al. 2016 or 2017, as the normalization method was consistent. However, we strongly recommend that future studies use higher benzene neutral concentrations to avoid these issues.

The manuscript has been revised to state:

Line 279: "This is attributed to the different instrument operational configuration used here (e.g., high concentration and purity benzene reagent ion precursor). More specifically, high neutral benzene concentrations (300 ppmv) suppress the formation of protonated water clusters at high specific humidity. As a result, the benzene cluster cations account for greater than 90% of total ion current under all conditions. This reduces complications surrounding the normalization of analyte signals."

5) Page 10 line 292-294: If limonene is ionized through charge transfer followed by isomerization, how to rationalize the fact the stronger C-H bond is broken, instead of the weaker C-C bond? What hydride abstraction reactions for alkenes have been reported in literature that can be related to this work?

A suggested path would require oxidation of an $[M+1]^+$ ion to form a hydroperoxide followed by HOOH elimination. The presence of water clusters in our system should suggest some proton transfer reactions to limonene to make an $[M+1]^+$. It is known that the autoxidation of *d*-limonene results in the allergens *cis-* and *trans*-limonene-2-hydroperoxides. A hydrogen abstraction can occur following the departure of the hydroperoxyl radical from one of these peroxides. Given the abundance of limonene hydroperoxides from autoxidation in nature, the absence of $[M+1]^+$, and our sensitivity to the $[M+32]^+$ ion, an oxidation product ion, this would make the most sense. This value may decrease with increasing specific humidity due to the change in water cluster size distribution to larger water networks, inhibiting proton donation.

The manuscript has been revised to state:

Line 291: "The peak at 135 *m/Q* $(C_{10}H_{15})^+$ represents the $[M-1]^+$ product, perhaps due to oxidation of an $[M+1]^+$ ion followed by departure of HOOH (Karlberg et al., 1994)."

Reference: Karlberg et al., *Hydroperoxides in oxidized d-limonene identified as potent contact allergens*, Arch Dermatol Res (1994) 286:97 103

6) Figure 3 caption line 370-371: "...using a liquid reagent ion delivery..." should be "liquid reagent ion precursor delivery". "...the first RF-only octupole..." I assume it is RF-only quadrupole here. Also in both panels in figure 3, the peak at m/z 156 should be (C6H6)+(C6H6), not the trimer.

This has been changed.

7) Table 2 and Table 3: The manuscript does not have clear reference to what f(H2O) and f(C6H6) are.

Line 304 and 323 have been edited to include these definitions: "The reported sensitivities, product ions, and dependence on ambient water concentrations, $f(H_2O)$, and neutral benzene concentration, $f(C_6H_6)$, for select monoterpenes are shown in Table 2."

8) Table 3: The first two ratios under SH=6.9 look like typos.

Thank you, this has been updated.