

## ***Interactive comment on “The sensitivity of benzene cluster cation chemical ionization mass spectrometry to select biogenic terpenes” by Avi Lavi et al.***

### **Anonymous Referee #3**

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This paper reported laboratory evaluation of the sensitivities in measuring biogenic volatile organic compounds (BVOC) for chemical ionization mass spectrometry (CIMS) using benzene-derived cations, and discussed the influence of reagent gas concentration, electronic field setting, and water vapor concentration on the instrument's sensitivity. The wide range of tested BVOC, including isoprene, monoterpenes and sesquiterpenes, gave a more comprehensive assessment of the capabilities of this CIMS method to detect BVOC. The ionization and fragmentation pattern of the BVOC were described, including the presence of the  $[M-1]^+$  ionization product. The authors showed that after accounting for fragmentation ions, the benzene cluster cation CIMS had comparable sensitivities toward isomers of monoterpenes and sesquiterpenes

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across typical boreal forest summer humidity, making the instrument suitable for field quantification of BVOC. This paper contributes to application of CIMS method to BVOC measurement and CIMS ionization methodology, and is recommended for publication in Atmospheric Measurement Techniques after the following comments are addressed.

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?

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.

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 ( $\sim 9E4$  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?

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.

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

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in literature that can be related to this work?

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  $(C_6H_6)_+(C_6H_6)$ , not the trimer.

Table 2 and Table 3: The manuscript does not have clear reference to what  $f(H_2O)$  and  $f(C_6H_6)$  are.

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

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