

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

Anonymous Referee #2

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Overview

The manuscript by Lavi et al investigates the sensitivity of benzene cluster cation chemical ionization for the detection of a variety of biogenic volatile organic compounds. Importantly, the paper investigates how the sensitivity of this CIMS method depends on the concentration of neutral reagent ion precursor and on water vapor. The work builds on previous work done by the same group using benzene cluster cation CIMS for the detection. Given the growing popularity of CIMS within the atmospheric measurement community, calibration is an area of significant interest. It is important to pursue and publish technical investigations such as this one in order to develop a community

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understanding of best practices and limitations of the wide variety of ionization mechanisms being used. I think that this manuscript will be of interest to the community and is appropriate for AMT, however, I feel that there are a few issues that need to be addressed prior to publication.

Major Comment

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.

Minor Comments

Sections 3.1 & 3.2: How does the abundance and ratio between $C_6H_6^+$ and

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(C₆H₆)⁺(C₆H₆) change as the concentration of neutral benzene is increased? Does this provide any insight into the isoprene results?

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.

Technical

Line 14: replace alpha with the correct symbol

Line 57-58: The references for NO⁺ and H₃O⁺ 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).

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.”

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?

Line 330-331: The wording here makes it appear like a recommendation to only use C₁₀H₁₆⁺ for quantification of monoterpenes. However, the average sensitivity appears to be that obtained using the M⁺, [M-1]⁺, and [M+32]⁺ ions (Figure 10) and not just the M⁺ ion (Figure 7). What recommendation do the authors provide for quantification of monoterpenes?

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

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

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not suggesting that such an explanation be incorporated; I do not think it would be appropriate given the extent of the data.

Figure 3: The peak at m/z 156 should be labeled (C₆H₆)⁺ (C₆H₆)

References

Brophy, P. and Farmer, D. K.: Clustering, methodology, and mechanistic insights into acetate chemical ionization using high-resolution time-of-flight mass spectrometry, *Atmos Meas Tech*, 9(8), 3969–3986, doi:10.5194/amt-9-3969-2016, 2016.

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Lopez-Hilfiker, F. D., Iyer, S., Mohr, C., Lee, B. H., D'Ambro, E. L., Kurtén, T. and Thornton, J. A.: Constraining the sensitivity of iodide adduct chemical ionization mass spectrometry to multifunctional organic molecules using the collision limit and thermodynamic stability of iodide ion adducts, *Atmos Meas Tech*, 9(4), 1505–1512, doi:10.5194/amt-9-1505-2016, 2016.

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