

Interactive comment on “Evaluation of NO⁺ reagent ion chemistry for on-line measurements of atmospheric volatile organic compounds” by Abigail R. Koss et al.

Anonymous Referee #1

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This is a well-written and detailed description of the conversion of an H₃O⁺ ToF-CIMS into an NO⁺ ToF-CIMS, and a solid discussion of instrument sensitivities and challenges in measuring a suite of volatile organic compounds in the atmosphere. The Supplemental contains relevant and useful information. This manuscript is appropriate for publication in this journal. While the paper is comprehensive and well-written, I have two major comments that the authors should address.

Major comments. 1. The authors describe differences in sensitivity between NO⁺ and H₃O⁺ ionization. However, it is unclear how this parameter of sensitivity was determined. Typically sensitivity is taken as the slope of a calibration curve (i.e. different signals of a VOC as measured by an instrument as a function of different concen-

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trations). From the manuscript, I think that the authors instead only used a single concentration (they write "each VOC was sampled twice, once with H₃O⁺ and once with NO⁺"). This is unfortunately not representative of instrument sensitivity, as this approach assumes linearity - which is often not the case for CIMS measurements. Did the authors do a proper multi-point calibration, or just take a single point? In either case, to what extent is the instrument linear for the selected analytes across an atmospherically relevant range? Finally, to what extent is the instrument response linear for the selected analytes across an atmospherically relevant range of relative humidity? As the charging mechanisms clearly change as a function of RH, I would not be surprised if the changes in charging mechanisms shifted at higher RH leading to non-linearities in sensitivity. In my opinion, linearity (or a clear understanding of non-linearity!) is an essential parameter to demonstrate when proving a new instrument is valuable for atmospheric measurements.

2. The discussion of NO⁺ mechanisms would benefit from more detail. In lines 220-224, the authors describe charging mechanisms for the NO⁺ reagent ion. Are these statements based on previous work (in which case, references are required), or this work (in which case, more evidence is required). The authors present two particularly useful pieces of information: Table 2, in which dominant peaks observed by NO⁺ CIMS are described along with sensitivities, and Figure 4, in which the theoretical basis of the charging mechanisms are quantified. While the observed signals for most components (e.g. methanol and benzene) appear to clearly fit the theory, it looks like some molecules may not. If I'm reading the figure and tables correctly, toluene (molecule 41) looks like it should be charged approximately equally by a charge transfer and hydride reaction. However, Table 2 suggests that toluene is charged almost entirely via a charge transfer from the NO⁺. As the instrument should be in an equilibrium-dominated regime for ion-molecule interactions, as opposed to a kinetically-limited regime, this is surprising. To what extent are the observed ions consistent with the predicted distribution? Can differences be attributed to changes in transmission efficiency as a function of m/z, or the breaking of adducts downstream in the mass spectrometer?

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Minor comments.

line 155-156. Replace "10e6" with proper scientific notation

Figure 2E: Figure caption should note the RH at which experiments were performed, as the signals for the NOH₂O⁺ cluster, H₃O⁺ and H₂OH₃O⁺ cluster should depend on that.

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