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Title: Evaluation of NO⁺ reagent ion chemistry for on-line measurements of atmospheric volatile organic compounds

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Response to reviewer 1

Reviewer comments are in black text.

Our response is in blue text.

Changes to the manuscript are highlighted in bold text.

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.

We thank the reviewer for their positive and insightful comments. Responses to specific questions are below.

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 concentrations). 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.

First, we will respond to the reviewer's concerns about non-linearity of sensitivity with concentration. We can assume linear sensitivity over the investigated concentration range in this situation for the following reasons:

- First, we did multi-point calibrations across an atmospherically relevant concentration range to generate the quantitative sensitivities for the 11 compounds reported in Table 2A. All 11 species, which include a range of functional groups, had linear sensitivity through the entire range (0-10 ppb). We added an extra figure to the supplement (Fig. S10) to show this. (The addition of Fig. S10 is noted in the "changes to manuscript", below.)

- Second, H₃O⁺ CIMS (PTRMS) instruments consistently have linear sensitivity over a very wide range of concentrations (de Gouw and Warneke, 2007; Sulzer et al., 2014) and we have demonstrated

linearity in our H₃O⁺ CIMS system in a separate publication (Yuan et al., 2016). We are therefore not concerned about non-linearity in the H₃O⁺ data used to generate Figure 3.

- Third, we compared NO⁺ ToF-CIMS measurements of ambient air to independent GC-MS measurement, and there is good agreement (R² typically >0.9, Table 3, Section 3.2.2).

The data used to generate Figure 3 (comparison of NO⁺ and H₃O⁺ sensitivity) were collected using a single concentration data point each for NO⁺ and for H₃O⁺. There is an example calculation shown in Figure S5. The calculation involves integrating the area under a GC peak, which inherently accounts for the instrument background. Essentially, we assumed a linear sensitivity extrapolated from two points: the instrument response under the GC peak, and the instrument response off the GC peak.

The ideal way to create Figure 3 would have been to quantitatively introduce each of the 87 species shown in Figure 3 into the NO⁺ ToF-CIMS, do a multiple-point calibration, then repeat each multiple-point calibration with H₃O⁺ settings for a total of 174 individual calibrations. This is just too time consuming for the point we want to make in Figure 3. We note that finding methods to quickly and inexpensively calibrate hundreds of species detected by CIMS instruments is a broad current challenge in the CIMS community.

Next, we will respond to the reviewer's concerns about non-linearity of sensitivity with changing humidity. This is a very valid concern. Determining a thorough, robust, and easily applicable treatment of humidity effects in NO⁺ CIMS will require much careful work and we anticipate that it will be the subject of a separate manuscript, just as humidity effects in PTRMS were discussed in earlier focused investigations (e.g. Španěl and Smith (2000)). We would like to highlight that there is good agreement between the NO⁺ ToF-CIMS and GCMS measurements of ambient air (Table 3). The good agreement between the two independent techniques, despite the use of NO⁺ ToF CIMS data that is not humidity corrected, is a very promising result when evaluating the NO⁺ technique for atmospheric measurements. This indicates that the humidity effect is likely not severe for most species.

We have incorporated this discussion into the manuscript in the following ways:

We have added Figure S10 to the supplemental information. This figure shows the periodic zeros taken during ambient air measurements (see response to Reviewer 3) and a linear sensitivity from multiple-point calibrations for several VOCs.

At line 194 in the edited manuscript, we have added,

“Because only one concentration was sampled, this metric relies on sensitivity being linear with concentration. Linear sensitivity is assumed for the NO⁺ and H₃O⁺ ToF-CIMS because separate multiple-point calibrations for select VOCs showed a linear response (Section 3.1.4), H₃O⁺ CIMS has demonstrated linear sensitivity over a wide range of concentrations (de Gouw and Warneke, 2007; Sulzer et al., 2014; Yuan et al., 2016), and the NO⁺ CIMS agrees well with an independent technique over a range of atmospheric concentrations (Section 3.2.2).”

At line 415 in the edited manuscript, we have added,

“The good agreement also indicates that humidity-dependence of sensitivity is likely not a severe effect for most species; however, addressing and quantifying this effect should be a priority for future work.”

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?

We included Figure 4 to provide a framework to explain why certain groups of VOCs undergo particular ionization mechanisms, and to suggest a likely mechanism for VOCs not explicitly studied in this work. We do not want to suggest that Figure 4 is an absolute predictor of ionization mechanism. The reaction enthalpies of charge transfer and hydride abstraction need to be such that the reactions are thermodynamically allowed, but they do not predict the relative rate coefficients for the two processes. Similar behavior is observed in PTRMS (H_3O^+ CIMS), where the product ions are not in equilibrium with the primary ions, and the number of product ions are controlled by the rate constants of the proton-transfer reactions and the average time the ions spend in the drift tube (Lindinger et al., 1998). A more complete understanding of all ionization mechanisms is well beyond the scope of this work.

The statements in this paragraph (220-224, lines 228-242 in edited manuscript) are a description of the patterns shown in Figure 4. The thermodynamic information is available in reference tables from Lias et al. (1988). The mechanistic information is taken from this work and from a large collection of SIFT studies. Our understanding of NO^+ ionization mechanisms relies heavily on excellent and extensive work done by especially Smith, Španěl, and colleagues using SIFT techniques and we provide more citations in the revised manuscript.

The product ion distribution depends also on instrumental conditions. There are differences in measured product ion distributions between our work and previous work and these are likely due to a combination of E/N settings in the ion-molecule reaction region and the presence of impurity ions such as O_2^+ . Mass-dependent transmission is an unlikely explanation, as transmission is nearly mass-independent above m/z 30 (Yuan et al., 2016).

Regarding the reviewer's questions about toluene (as an example), we realize that the 1:1 line in Figure 4 seems to suggest that molecules on this line should equally participate in charge transfer and hydride abstraction reactions. However, the actual ionization mechanism depends on more than simple thermodynamics, as stated above. To avoid further confusion **we have removed the 1:1 line from Figure 4.**

We have revised section 3.1.2 to address the limitations of Figure 4 and added several relevant citations. The revised Section 3.1.2 now reads:

"It is somewhat more difficult to predict the ionized VOC products of NO^+ CIMS compared to H_3O^+ CIMS, because NO^+ has three common reaction mechanisms: charge transfer, hydride abstraction, and cluster formation. Groups of VOCs that have similar charge transfer and hydride abstraction enthalpies tend to react with similar ionization mechanisms (Figure 4). Figure 4 uses thermodynamic information from Lias et al. (1988), and mechanistic information from this work (see table S1 for a list of species) and from SIFT studies (Španěl and Smith, 1996, 1998a, b, 1999; Španěl et al., 1997; Arnold et al., 1998; Francis et al., 2007a; Francis et al., 2007b). Charge transfer occurs if the reaction enthalpy is

favorable, regardless of the hydride transfer enthalpy. If the charge transfer enthalpy is close to zero, then NO^+ clustering occurs; and if charge transfer is not favorable but hydride transfer is, then hydride transfer will occur. In terms of VOC families, this means that carbonyls participate in two mechanisms: ketones cluster with NO^+ , and aldehydes hydride transfer. Branched alkanes exclusively undergo hydride transfer. Aromatics undergo charge transfer and benzene also clusters; alcohols undergo hydride transfer, and alkenes charge transfer, cluster, or hydride transfer depending on the size of the molecule and the location of the double bond within the molecule.

Although Figure 4 provides a general way to predict the possible mechanisms for a particular VOC, it provides no information about the distribution of the signal between different mechanisms or the degree of fragmentation. The distribution depends strongly on instrumental conditions, which include E/N settings in the ion-molecule reaction region, which is by far the most important effect, fragmentation and clustering in the ion optics, presence of impurity ions such as O_2^+ from the converted hollow cathode ion source, and relative humidity (Section 3.1.5).

In Figure 5 the product ion distributions of several VOCs determined in this work are compared to three others using NO^+ . Studies by the University of Leicester used a much higher E/N ratio in the drift tube, leading to higher fragmentation and lower NO^+ adduct formation compared to this work (Wyche et al., 2005; Blake et al., 2006). Investigation of higher-mass alkanes by Yamada et al. (2015) used similar E/N, but achieved lower contaminant O_2^+ , which is a likely explanation for the higher degree of fragmentation of tridecane seen in this work. In SIFT-MS studies, without an electric field, fragmentation is minimized and preselection of NO^+ primary ions eliminates contaminant H_3O^+ and O_2^+ and therefore SIFT product ion distributions are generally simpler. These differences highlight the importance of selection of drift tube operating conditions and instrument characterization.”

We have edited the caption of Figure 4 to read “Ion thermodynamic information is available for several species whose reaction mechanism was not experimentally verified in this or previous work ...”

We have added Figure 5, which compares product ion distributions from several laboratory studies of NO^+ CIMS. To reduce the number of figures in the manuscript, we have moved the original Figure 5 (example aliphatic product ion distributions) to the supplementary material (now Figure S4).

Minor comments.

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

Fixed

Figure 2E: Figure caption should note the RH at which experiments were performed, as the signals for the NOH_2O^+ cluster, H_3O^+ and $\text{H}_2\text{OH}_3\text{O}^+$ cluster should depend on that.

This is addressed in our response to the other reviewer.

Citations

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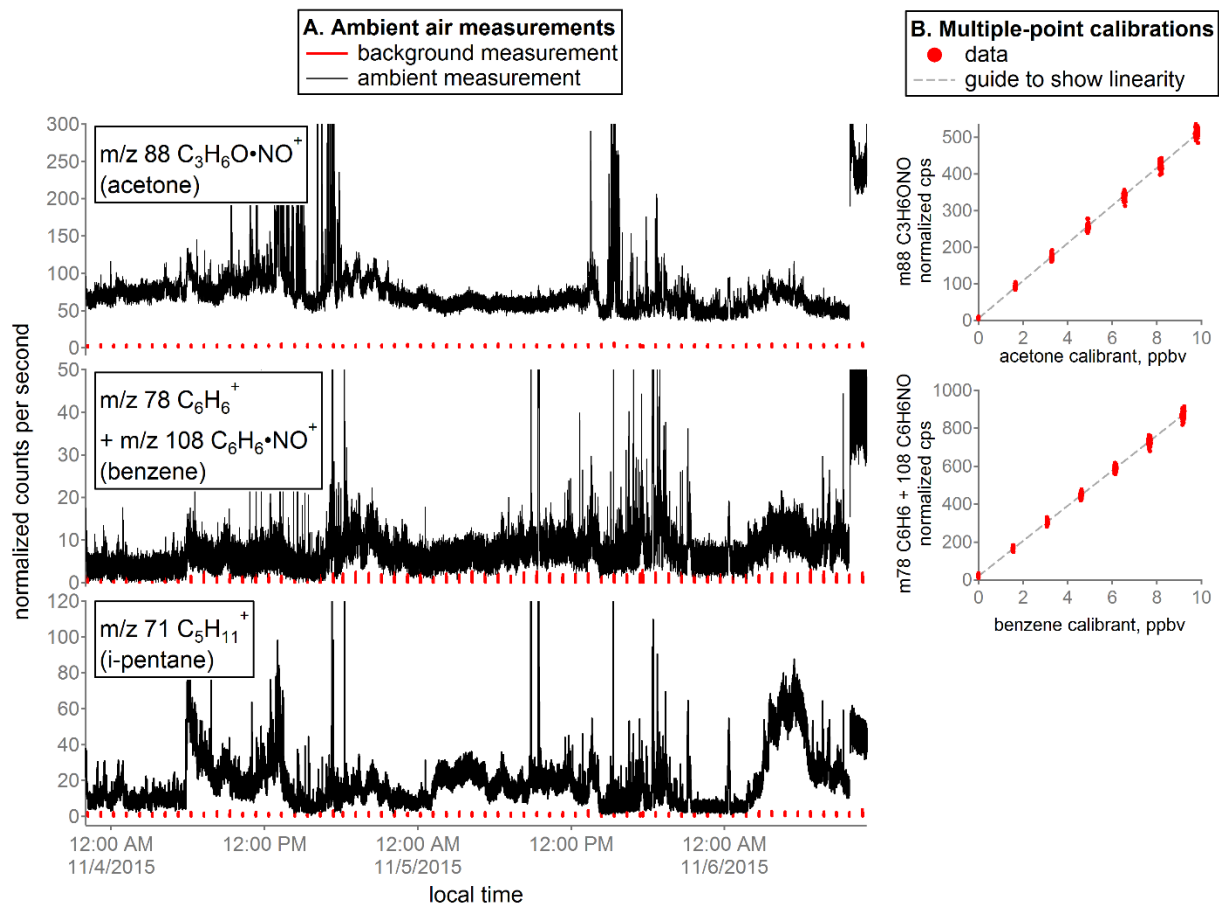


Figure S10. A. Background and ambient measurements taken during urban air sampling with the NO^+ ToF-CIMS. B. Example multiple-point calibrations of the NO^+ ToF-CIMS showing sensitivity linear with concentration.

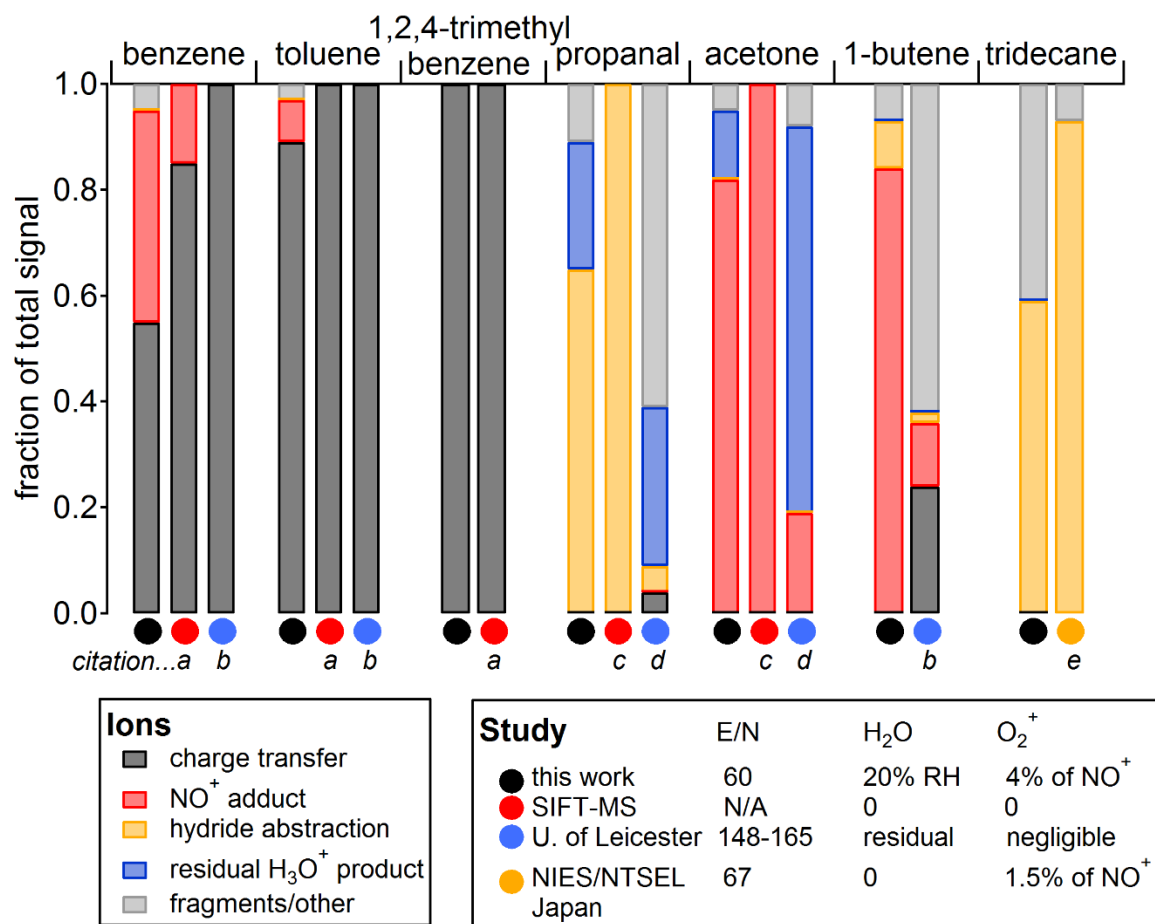


Figure 5. Comparison of product ion distributions between four sets of instrumental and environmental conditions.

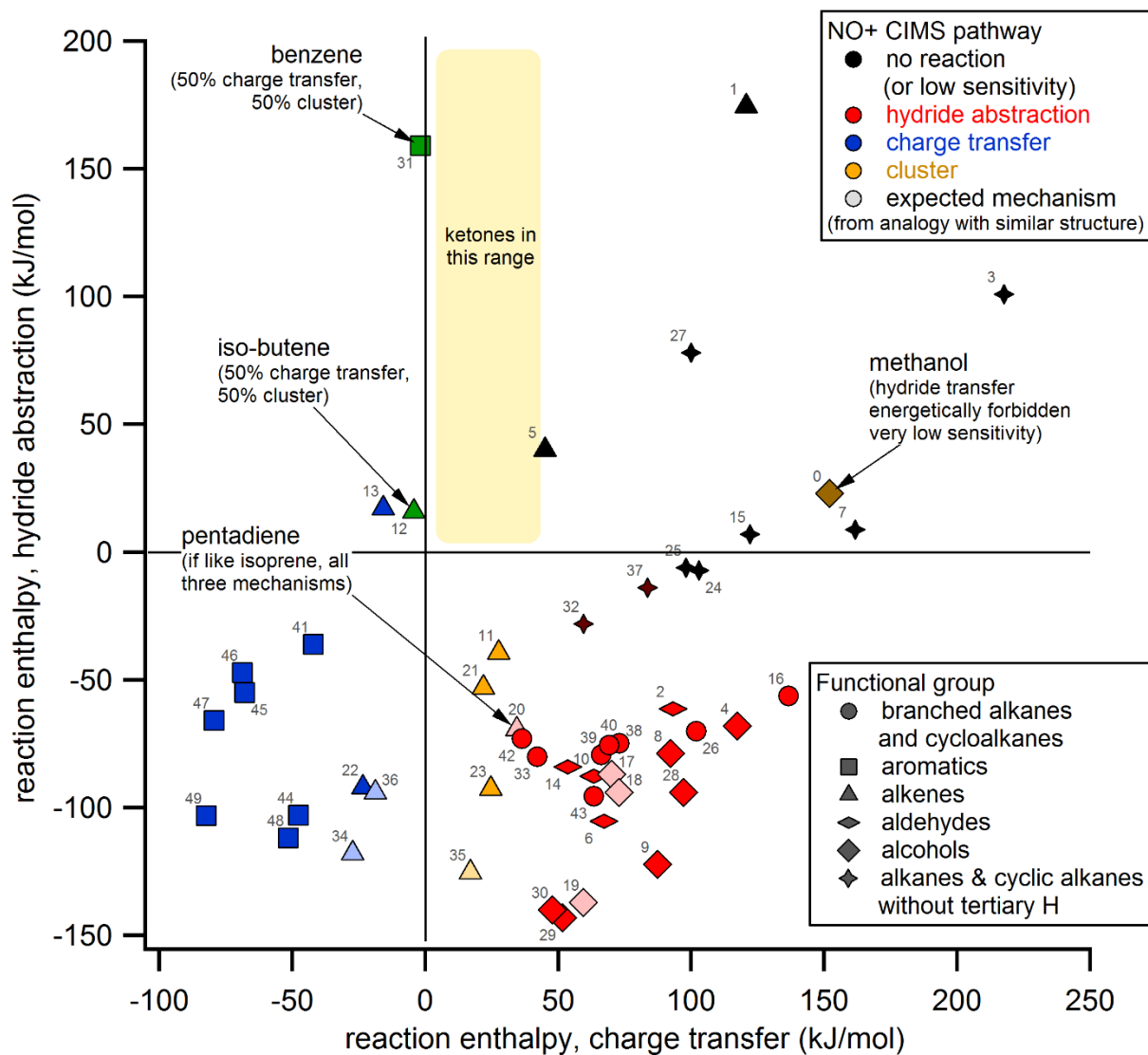
a. Španěl and Smith (1998a)

b. Blake et al. (2006)

c. Španěl et al. (1997)

d. Wyche et al. (2005)

e. Yamada et al. (2015)



Revised Figure 4