Reviewer #1 (Blue)

Dear authors,

The clear amount of work put into improving the manuscript is highly appreciated. I do have a small amount of comments/technical corrections:

Comments:
line 207: why is 60% chosen? For example, in a PTR-MS a decay of the primary reagent ion of more than 10% already breaks linearity for mixtures. Also in the revised Figure 2B, showing a very simple mixture of compounds of very similar collisional rate constants and simultaneous concentration steps, true linearity is not entirely given even at clearly lower decays of [Bz]+.

The 60% reagent ion remaining threshold is based on previous work by Aggarwal et al. with flow tube CIMS to avoid non-linear responses. Beyond this threshold, non-linear responses have been observed. In Figure 2B we demonstrate linear responses with $R^2>0.99$ which we deem to be a highly linear response. As noted in the manuscript, this is mainly a challenge of positive ion chemistries which are more general than negative ion chemistries. Standard additions may be performed periodically to ensure that linearity is maintained if experimental conditions are near a titration threshold.

Prior acceptance of the manuscript I need to suggest a simple experimental test to verify this number: inject a stable concentration of toluene (e.g. 0.5 ppbv would be atmospherically relevant). Vary a-pinene in steps from 0 to 20 ppbv (or until 60% of the [Bz]+ signal is reached). Plot toluene in ncps for each concentration step of a-pinene. Once a-pinene deviates by more than 10-20% of the initial ncps, the linearity limit is reached. a-pinene has an IE of 8.07 eV, toluene of 8.83 eV; the variable $C_{10}H_{16}^+$ ions will not be able to ionize toluene. Hence, and this is my apprehension, a significant amount of reagent ions will be missing and can not ionize toluene - the sensitivity will drop based on the gas-matrix. This is something that can easily and even more severely happen in complex atmospheric mixtures.

This publication is not introducing a new, novel ionization strategy, but rather using a well-established ionization strategy at medium pressure. Similar experiments have been done in published literature at similar pressure and reaction times in Lee et al. (2014) with the use of iodide reagent ions and tracks the relationship of formic acid signal while adding a constant amount of nitric acid in Fig. S7 of the supplementary information. A very similar experiment to what the reviewer proposes is the basis of the titration experiment described in the supplemental where a solvent was used to titrate benzene reagent ions with constant a-pinene introduced to the inlet. Deviations of a-pinene during the titration event are shown in normalized space directly showing the normalization error(s) as a function of reagent ion remaining.

Technical Corrections:
Figure S1: please add a unit to the y-axis

I have added a note about the units in the caption.

Figure S3: please explain the normalized unit of the y-axis

Figure S3: Relationship between resulting analyte signal and fraction of reagent ion remaining for the detection of α-pinene using a [Bz]+ ionization strategy following the introduction of a high concentration of solvent to the inlet to force reagent ion depletion. The resulting normalized analyte signal remains roughly constant until a remaining fraction of 0.5-0.6 remaining after which normalization errors rapidly increase.

The normalized analyte signal is the signal of the constantly introduced calibrant normalized to reagent ion, and then normalized for the figure to 1 when the calibrant is measured without significant reagent ion consumption (i.e. a clean environment).