

Reviewer #1

Lopez-Hilfiker et al. presented the laboratory experimental results of fragmentation and sensitivity behaviors of oxidation products of alpha-pinene, which can be applicable other terpenoid species, using a ToF-CIMS system with I<sup>-</sup> ion chemistry. The main goal of this research seems pretty clear that the evaluating sensitivities of alpha pinene oxidation products as the preparations of the standard samples are extremely difficult. The N<sub>2</sub>O<sub>5</sub> sensitivity towards I<sup>-</sup> ion chemistry, which is known as a collisional limit, is used for the evaluation. The authors applied the concepts of fundamental ion – neutral molecule interactions to the ToF-CIMS analytical system with an expanding user basis to reasonably assess actual concentrations of all the identified peaks in complex ToFCIMS spectra. The authors achieved the goal by assessing fragmentation patterns and transmission efficiency for a wide range of ion masses. As I<sup>-</sup> ion chemistry has been highlighted for its sensitivity towards highly oxidized organic compounds, this study will be highly beneficial to the user base. I think that the manuscript is well written and aligned well with the purpose of Atmospheric Measurement Technique. I would recommend the publication of this manuscript after addressing the following concern. The ion transmission efficiency as a function of mass is a critical parameter to assess sensitivity of analytes along with ion-neutral reaction rates in the CIMS analytical system. The authors followed the evaluation method for transmission efficiency presented in Huey et al. which utilized a quadrupole mass spectrometer system. Therefore, I urge for authors to justify whether the identical method can be utilized to the ToF system.

***We thank the reviewer for these comments. We agree that the ion transmission efficiency as a function of mass is a critical parameter to assess sensitivity. While this importance was briefly addressed in the manuscript, we have added a stronger statement to the discussion section that emphasizes the importance of the mass transmission function, including a reference to an independent manuscript on the topic (Heinritzi et al., 2015). The main mass discriminating optics in the APi-TOF-MS are the quadrupole ion guides which can be tuned for the range of mass of interest by adjusting the RF frequency as well as RF amplitude and gradient along the segmented rods. As the declustering approach we use involves only potential differences between to static (DC) optics, we do not expect mass discrimination and the total ion current remaining approximately constant provides some support for that expectation. The method of assessing relative mass transmission efficiency attributed to Huey et al. , and which we use herein to constrain the total ion production from N<sub>2</sub>O<sub>5</sub> reactions with Iodide, has been used more generally by the mass spectrometry community (e.g. PTR-MS and APi-TOF), including the above referenced paper.***

Reviewer #2

This paper describes sensitivity determination for the UW iodide HrTOF-CIMS with FIGAERO inlet. The results of this study can be used to provide the upper limit of the instrument sensitivity for a class of highly oxidized organic compounds, which are not known in molecular structures or even in functional groups. The authors conducted calibration of N<sub>2</sub>O<sub>5</sub> detection with iodide-adduct HrTOF-CIMS to derive the highest sensitivity – collision limited, using independent absorption method. Then by changing the electric field between two electronic lenses, they monitored the declustering of adduct ions from relevant product ion distributions. By applying this method to other organic compounds, they conclude that N<sub>2</sub>O<sub>5</sub> and all these organic compounds react with iodide at collision-limited ion-molecule reactions. But some of the adduct products are declustering. The electric field applied for declustering is related to the binding energies of adducts, which determines CIMS sensitivities, by affecting transmission efficiencies.. The statement that organic compounds tested in this study all react with iodide at collision-limit quite trivial. It is well known that ion-molecule reactions take place in collision limited reaction rates, which are all close to 1-2e-9 cm<sup>3</sup> s<sup>-1</sup>, very little dependent on molecules (size and shape; only has 30% changes in reaction rate), as also discussed in [Erupe et al., 2011]. That means, by simply using this 2e-9 cm<sup>3</sup> s<sup>-1</sup> reaction coefficient, one can estimate CIMS's highest sensitivity of 20 Hz per ppt reactant per million Hz reagent ions using the ion-molecule reaction time used in this specific CIMS in this study. Similarly, we can also apply this method to other CIMS, including CI-Api-TOF, with known ion-molecule reaction times. This application, however, is only valid with extremely low background ion signals of reactants. Therefore, experimentally demonstrating that these large highly oxidized organic compounds can be estimated with this upper limit of sensitivity is an important contribution to ELVOC and HrTOF-CIMS community.

*We thank the reviewer for these comments. We agree that it isn't too surprising that an assumption of collision-limited reaction rates between a suite of oxygenated organics and Iodide is reasonably supported by comparison to a bulk organic aerosol measurement by the AMS. However, there is a paucity of empirical support for that assertion, and given the potentially wide distribution of adduct binding energies, the effective adduct formation rate can still be substantially different from the collision limit (as demonstrated herein). Indeed, the selectivity in Iodide adduct ionization appears to be driven not by the adduct formation rate but the stability of the resulting adduct during transit through the mass spectrometer. Thus, our conclusion is that the collision limit sensitivity likely applies to a large fraction of atmospheric oxygenated organic compounds found in aerosol particles, but there could be molecular ions detected by this method at orders of magnitude lower sensitivity, and thus care must be taken reporting the distribution of mass across different ion compositions detected.*

Minor comments:

Page 10876: Line 26, please include You et al. ACP 2014 and Yu and Lee EC 2012 [You et al., 2014; Yu and Lee, 2012] – they are quite relevant to this study in terms of discussing the deviation of actual sensitivities from the collision-limited sensitivity.

*We thank the reviewer for pointing out these references, they have been added.*

Page 10877: Lines 9-10: Good selectivity is an advantage, for most CIMS, except CI-API-TOF and the current UW CIMS that measures hundreds of different compounds together.

*We agree with the reviewer that different reagent ions have different selectivity rules which is what we meant by that statement. Indeed, utilizing a quadrupole mass selector with CIMS motivates using a highly selective reagent ion in order to avoid potential interferences. However, we note that even reagent ions which were initially thought to be quite selective (e.g. nitrate ions) have proven to detect hundreds of molecules when combined with the ToFwerk H-TOF. And, this capability isn't detrimental for the most part given the ability to resolve many of these ions into unique molecular ions. Ultimately, "selectivity" is a relative term, and in the case of Iodide adduct ionization, it is nearly insensitive, or completely so, to simple alkanes, alkenes, aromatics, ketones, aldehydes, amines, etc. Thus, it is in that way selective to multi-functional organic compounds and some inorganics (such as halogens) which interact strongly with Iodide.*

Line 10-13: Not measuring molecular structure is not unique to CIMS. This is a general issue for all mass spec techniques, unless tandem analysis is used.

*We agree and have changed the language accordingly.*

Line 26-29: Experimentally determine "the relative strength of bindings of clusters" (rather than effective binding energies) . . .  $dV_{50}$  (volts) is an electric potential difference and is not energy (J or cal).

*We have changed this sentence accordingly: "the relative binding strength of clusters..."*

Page 10884: Line 20: What is needed for DFT calculations is cartesian geometries, rather than functional groups and molecular structures. Although, the half of the statement is correct.

*We have made this clearer.*

Figure 5 results: please show the detailed list of specific  $C_xH_yO_zN_0-II-$  compounds. Did you include C5 and C9+C10 together? Can you discuss more relative difference C5 vs. C9+10 and in Alabama vs Hytiala? What can you say with the comparison of sub-micron size of organic aerosol (derived from AMS) with your measurements – are they really related to each other – physically? I would remove AMS data here which does not bring any new information regarding the main conclusion of the paper but rather more confusing with that.

*We included all molecular formulas with  $C_xH_yO_zN_0-11$ . This includes C5, C9, C10 and many others. Fundamentally the AMS measurements and FIGAERO particle desorptions are linked because the FIGAERO detects the molecules that make up the aerosol and the AMS can measure the total, therefore the comparison itself is of scientific value and they should be directly related. We therefore feel that the AMS comparison is important as it provides an independently calibrated perspective on the extent to which the Iodide adduct FIGAERO-CIMS explains organic aerosol from a molecular perspective. Further scientific insights from this type of comparison, such as which molecular tracers make up most of the mass, etc, is the subject of other papers, and therefore beyond the scope of this paper.*

#### References:

Heinritzi, M., Simon, M., Steiner, G., Wagner, A. C., Kürten, A., Hansel, A. and Curtius, J.: Characterization of the mass dependent transmission efficiency of a CIMS, Atmos. Meas. Tech. Discuss., 8(11), 11369–11399, doi:10.5194/amtd-8-11369-2015, 2015.