Response to reviewers for the paper, "Ion Mobility Spectrometry-Mass Spectrometry (IMS-MS) for on and off-line analysis of atmospheric gas and aerosol species"

We thank the referees for supporting publication of our manuscript in AMT and for the helpful suggestions to improve it. To facilitate the review process we have copied the reviewer comments in black text. Our responses are in regular blue font. We have responded to all the referee comments and made alterations to our paper (**in bold text**) or in new figures copied in this document.

Interactive comment on "Ion Mobility Spectrometry-Mass Spectrometry (IMS-MS) for on and off-line analysis of atmospheric gas and aerosol species" by J. E. Krechmer et al.

Anonymous Referee #1:

The paper introduces the application of ion mobility spectrometry-mass spectrometry (IMS-MS) to gas and particle analysis in atmospheric science. Two methods are presented. In one case the gas phase is aspired, ionized and measured during a field campaign as well as in the laboratory behind a PAM chamber to characterize highly oxidized species. In a second approach aerosols were collected on filters, extracted and directly injected via an ESI source. The authors demonstrate the great analytical potential of IMS-MS. Using ESI-IMS-MS it is possible to separate efficiently complex mixtures and analyze polar compounds without derivatization. This method has clear advantages compared to LC-MS and also avoids thermal decomposition as expected in thermal-desorption techniques. The instrument has a high mobility resolution and is able to separate isobars and even isomers. With a few examples the authors present these features. They demonstrate that different chemical oxidation pathways of precursors can be identified even in an ambient sample. With the help of collisional induced dissociation it is confirmed that highly oxidized C20 molecules from a-pinene ozonolysis are covalently bound molecules and not clusters. The paper is well written. The various features of the instrument and the exemplary experiments are well presented and explained. This paper shows that IMS-MS has a great potential in the chemical analysis of gas and particle phase. I recommend publication of this paper after some minor revisions.

R1.1 Line 224: "can be readily separated from each other with IMS-MS". What do you mean here. The peaks 133/155 and 183/199 are not separated on the mobility scale. How are you sure that the lower mass is not a fragment? Please elaborate.

A1.1 We agree with the reviewer that this statement is not clear enough. We note that the CID voltage used for these measurements was too low to allow for fragmentation by breaking of

chemical bonds. Thus, the limited separation of the 133/155 and 183/199 ions pointed out by the reviewer likely reflects that these pairs of molecules have similar collision cross sections. The following text has been added to address the reviewers comments:

P7 L229: "On the other hand, as shown in Figure 3b, some of these WSOC ions can be distinguished from each other by their ion mobility drift times: *m/z* 215 has a drift time that is clearly larger than the others, *m/z* 199 and 183 have intermediate drift times, and *m/z* 155 and 133 have the lowest drift times. The drift times of m/z 155 and m/z 133 differ from each other slightly. Further ion mobility separation of m/z 199 and m/z 183, however, appears to be limited by similarity in their CCS."

And added clarifying text to the Figure caption:

P27 L753 "The ion mobility spectra for the MS peaks highlighted in (a) are shown in (b). The IM spectra were extracted from separate mass spectra and then placed together in the graph above for clarity."

R.1.2 Line 260ff: The peak at 41.82ms is attributed to both cis-b and trans-b-IEPOX. Considering the resolution of the instrument I would expect a double peak, although not fully resolved. The HWHM of this peak is not much wider than those of the pure compounds. Could it be that the mobility scale was shifted in the SOAS filter experiment? Please comment.

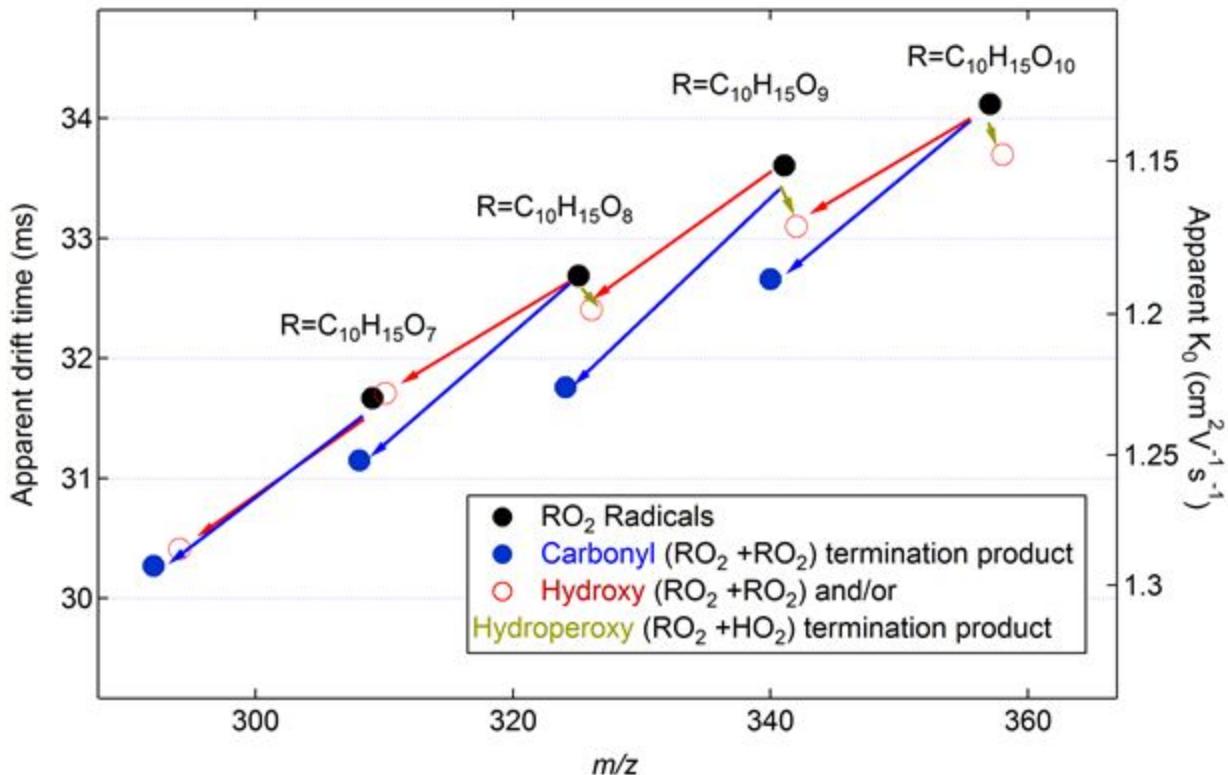
A1.2 The SOAS ambient filter measurements and the chamber filter measurements were performed under the same conditions and contained the same reference standard (sodium dodecyl sulfate, or SDS) as mentioned in the manuscript (P8 L245). Thus, it is unlikely that the SOAS ion mobility scale could be biased significantly from that of the chamber filters.

R1.3 Line 412ff: It is claimed that the hydroxy termination product from C10H15O9 and the hydroperoxy termination product of C10H15O8 overlap at C10H16O8. Given the potential of IMS-MS, why are these two different products not mobility separated? What indication do the authors have that there are two products overlapping? Could this not indicate that only one of these is formed?

A1.3 The referee raises a good point: we can not definitively say that the two (hydroxy and hydroperoxy) products are both formed. The collision cross sections of the products containing hydroperoxy and hydroxy groups may be similar enough that they cannot be separated under the ambient analysis conditions under which the IMS acquired the data.

We added the following text to qualify this:

P13 L410 "Termination products for each of the identified peroxy radicals are shown in Fig. 9 with arrows denoting their peroxy radical precursors. The hydroxy and hydroperoxy termination products were not separated in the IM spectra, however. We suspect this may be due to less-than-ideal operating ambient operating conditions, or because the two products have such similar CCS that they cannot be separated by this instrument."

We also modify the figure caption to read **"Hydroxy (RO$_2$ + RO$_2$) and/or Hydroperoxy…"**

R1.4 Line 419: What kind of ring-closure reactions do you expect?

A1.4 These reactions have been reported in the literature, in the references cited at the end of this sentence. Further investigation of such reactions is well beyond the scope of this instrument demonstration paper,and any additional statements on our part would be unsupported speculation. As such, we prefer to leave this question for future work.

R1.5 Figure 10: The dimer region m/z 500-600 in Figure 6 corresponds to a drift time of about 45-50 ms. In the Figure legend it says 52-55 ms. Is this a different experiment taken under different instrument settings?

A1.5 That is correct. The data in Figure 10 was acquired under different IMS operating conditions and therefore the dimers have a different drift time. We have added the following text to clarify that is indeed the case:

"P34 L797 A 20V CID-MS of laboratory α-pinene ozonolysis products averaged over the drift time region of the HOMs dimers (52-55 ms) in the 2D IMS-MS plot. Note that these data were acquired under different operating conditions than those in Figure 6, leading to slightly different IMS drift times."

Anonymous Referee #2:

The paper "Ion Mobility Spectrometry-Mass Spectrometry (IMS-MS) for on- and off-line analysis of atmospheric gas and aerosol species" by J. Krechmer et al. is a very good manuscript that introduces a very interesting meaurement technique. It is well written, the Figures are informative and the scientific relevance is high. Thus I recommend to accept the paper after some minor revisions which are mostly of technical nature:

R2.1 Equations 2 and 3: The relationship between Equ. 2 and 3 is not clear to me. Why and to what degree gives Equ. 3 better results than Equ. 2? Also I suggest to arrange Equ. 3 similar to Equ. 2. How is the effective temperature in Equ. 2 calculated? Please explain why T_eff is not used in Equ. 3 and how v_d is calculated. Are the alpha and beta terms known well enough to be sure that Equ. 3 is more precise?

A2.1 We acknowledge the reviewer's point that this section was confusing, especially the use of Equ. 3. Unfortunately, the derivation of Equ. 3 and difference in results between 2 and 3 are complex topics and beyond the scope of this manuscript, which is focused on the demonstration of IMS applications to current atmospheric chemistry topics. Indeed those questions are so complex that their answers comprise the entirety of the referenced *Analytical Chemistry* paper (Siems et al, 2012).

In response to this point, we have modified the manuscript text in several ways. We rearranged equation 3 to make the connection between Equ. 2 and Equ. 3 more intuitive, as the referee suggested. We also added definitions of the α and β terms in equation form and clarified the terms within:

P5 L137: "Collision cross sections can more accurately be calculated using a momentum transfer scan law that includes field-dependent corrections for both collisional momentum

transfer and collision frequency (α and β terms, respectively) (Siems et al., 2012).

$$\Omega = \frac{1}{K_0}\frac{3qz}{16N}\left(\frac{2\pi}{\mu kT}\right)^{\frac{1}{2}}\left[1+\left(\frac{\beta_{MT}}{\alpha_{MT}}\right)^2\left(\frac{v_d}{v_T}\right)^2\right]^{-\frac{1}{2}}$$

(3)

in which K_0 is mobility, q is the elementary charge, z is the charge number, N is the neutral gas number density, μ is the reduced mass of the analyte-buffer gas pair, k is the Boltzmann constant, T is the standard temperature, v_d is the drift velocity, and v_T is the thermal velocity (Siems et al., 2012). α_{MT} and β_{MT} are calculated as follows:

$$\alpha_{MT} = \frac{2}{3}\left[1+\hat{m}\hat{c}+\widehat{M}\hat{h}\right]$$

$$\beta_{MT} = \left[\frac{2}{\hat{m}(1+\hat{m})}\right]^{\frac{1}{2}}$$

where $\hat{m}$ is the reduced mass of the colliding pair, $\hat{c}$ is the fraction of collisions that cool the ion, and $\hat{h}$ is the fraction of collisions that heat the ion (Siems et al., 2012)."

References:

Siems, W. F.; Viehland, L. A.; Hill, H. H. Improved Momentum-Transfer Theory for Ion Mobility. 1. Derivation of the Fundamental Equation. *Anal. Chem.* 2012, 84, 9782–9791.

R2.2 Line 156 "mixure" -> "mixture". Should "diasteromers" read "diastereomers"? Line 241: Fig. S2 depicts only three HSE isomers.

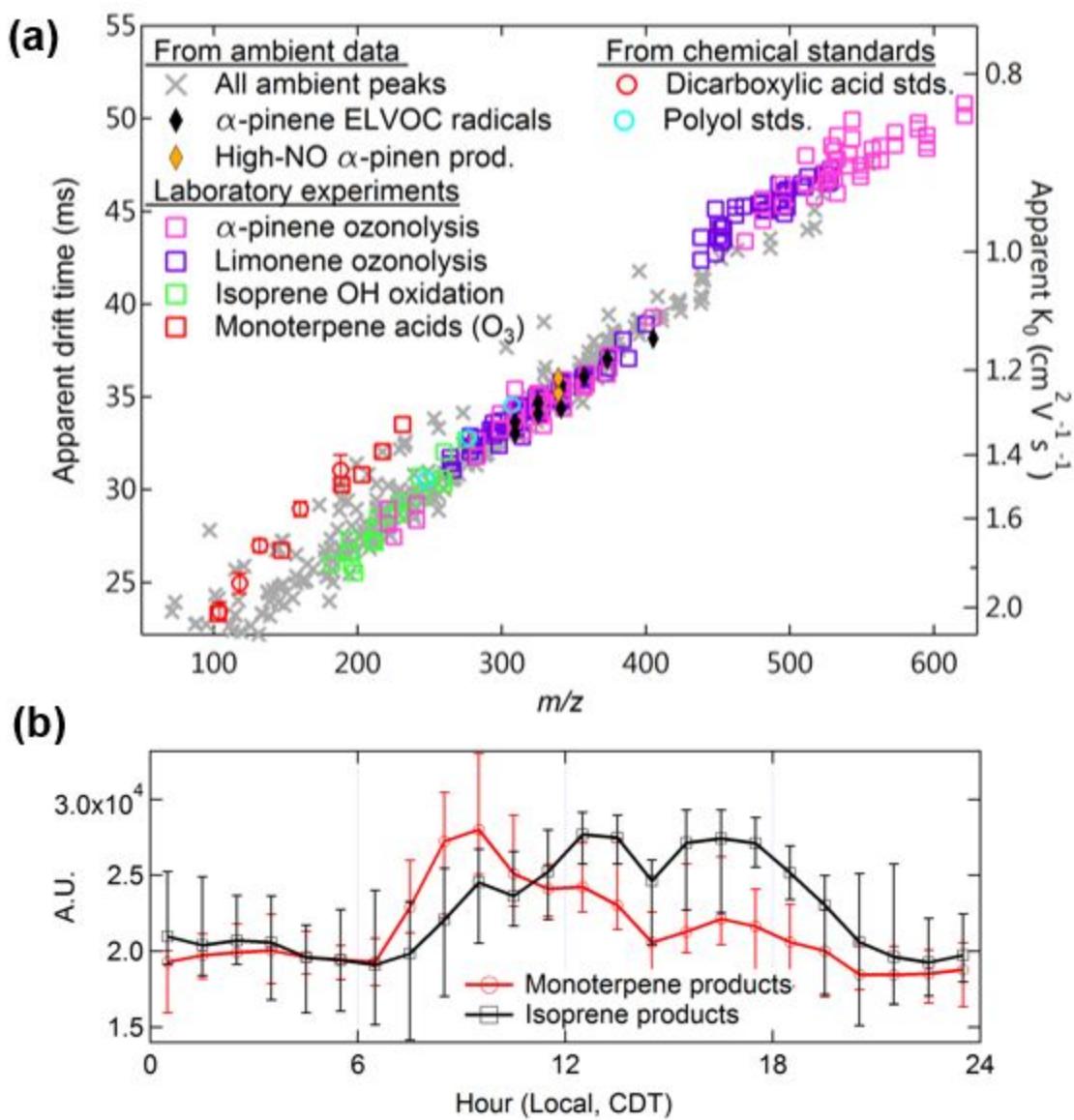
A2.2 We thank the referee for pointing out the typos. We also clarified the text in Line 241:

"Its molecular structure, however, has up to eight possible isomers (Hettiyadura et al., 2015), three of which are thought to be major ones... "

R2.3 Line 287: Where in Fig 1 is the potential of 28 V applied? Is that a typical value? What would be the typical range? See also comment to line 428 below.

A2.3 We have added the following text to P4 L124: **"For the examples reported in this work, we utilized a typical CID potential difference between the exit of the first quadrupole and the entrance of the second quadrupole ranging from 1 to 30 V."**

R2.4 Fig. 6a: the symbols for alpha-pinene ELVOC radicals are hard to see -> please use different color

A2.4 We have changed the symbols representing the ELVOC radicals to black and include a revised Figure 6a as follows:

R2.5a Fig. 8c is not discussed at all in the text.

A2.5a: We modify the text on P12 L381 as follows:

"This elemental formula was identified in previous NO$_3^-$-CIMS literature as a HOM produced from α-pinene ozonolysis (Ehn et al., 2012). In Figure 8c, we provide extracted IM spectra from the identified MS peak at three different points in the time series."

R2.5b I understand that it shows the drift times measured at the times indicated by the vertical lines in Fig. 8a (three, not four as stated in the caption!). However, the green line denotes a time where DT 37.12 is not zero. Thus I had expected a small signal at 37.12 in the green curve in Fig. 8c.

A2.5b The ion mobility spectra shown in the figure are obtained after using post-processing routines that deconvolute the multiplexed raw ion mobility data. These routines include smoothing and noise analysis of the raw ion mobility data. In this example, the small signal belonging to 37.12 was on the order of the noise in the ion mobility traces and was therefore suppressed during the post-processing.

We add text in the caption to address both the reviewer's points:

"(c) shows the ion mobility spectrum for C$_7$H$_{10}$O$_4$ at three different points in the time series. IM spectra shown are obtained after post-processing of the raw multiplexed ion mobility data.."

R2.6 Line 428: Here a voltage range for CID experiments is given. I suggest to mention the typical range of voltages that is used for CID in the instrument description

A2.6 Please see our response to A2.3, which includes our textual changes to address this referee comment.