Response to Reviewer #2

In this work, Zhang et al. presented a new framework to describe complex organic mixture within aerosols. The authors first introduced the 2-dimensional cross section-m/z framework and methods for calculating ion-neutral collisional cross sections. They demonstrated the applicability using a range of standard compounds, and showed unique behaviors in the 2-D space. The authors also showed how molecular identification can be performed using collision-induced dissociation. This framework is novel and unique, and addresses an important knowledge gap in accounting for molecular structures/functional groups in the organic aerosols. The work is thorough and the manuscript is very well presented. I have some very minor concerns about how to apply this framework broadly, which are more about framing the work in a broader context. This manuscript should be published in Atmospheric Chemistry and Physics after addressing these minor comments.

We thank reviewer #2 for the constructive and insightful comments. Our point-by-point responses can be found below, with reviewer comments in ***black****, our responses in* ***blue****, alongside the relevant revisions to the manuscript in* ***red****.*

Major comments:

1. I am not quite sure how this framework would work with real atmospheric mixtures, which likely contain many multifunctional organic compounds. A very unique feature of this technique is the cross section decreases with increasing oxygenation. However, there are different types of oxygenated functional groups. For example, from Figure 2 it appears that ketone group lowers cross section the same amount as a 2nd carboxylic group does. One might not be able to identifying uniquely the structure of the molecules based solely on the location in this plane. Rather it is possible to identify the general trend (e.g. shifts in location as a function of time/oxidation) during oxidation or atmospheric processes. This is not a critique of the framework itself, but I would like to see a discussion of the limitations and/or applicability to better assess its useful for different purposes.

[Responses] The reviewer has raised a very important issue on utilizing the $\Omega - m/z$ space to resolve complex aerosol mixture, and we agree that it is rather difficult to identify uniquely the structure of the molecules based solely on the location of unknowns on the $\Omega - m/z$ space. Therefore, we highlight the use of Collision Induced Dissociation (CID) in *Section 4.4 'Molecular Structure Elucidation of multi-Functional Species'* as an additional dimension of separation. We also emphasize that the CID method becomes crucial if the locations of two unknown species cannot be well resolved on the space under the current IMS resolution (*t*/*dt* ~ 100). The key message we would like to deliver in this manuscript is that a combined knowledge on the mass to charge ratio of the unknowns, the location of the unknowns on the 2-D space, as well as the fragmentation patterns of unknowns, could provide information on the chemical classes to which the unknowns belong as well as the functional groups the unknowns contain. We have refined the major conclusions in the revised manuscript, also given below:

[Changes] Line 318-328: The demonstrated $\Omega_{N_2} - m/z$ trend lines provide a useful tool for categorization of structurally related compounds. Mapping out the locations and distribution patterns for various functionalities on the 2-D space would therefore facilitate classification of chemical classes for unknown compounds. It is likely that trend lines extracted from a complex organic mixture overlap and, as a result, the distribution pattern of unknowns on the space alone would not provide sufficient information on their molecular identities. In this case, the fragmentation pattern of unknowns upon collision induced dissociation (CID) needs to be explored for the functionality identification, as discussed in detail in Section 4.4. As it is highly unlikely that two distinct molecules will produce identical IMS, MS, as well as CID-based MS spectra, the 2-D framework therefore virtually ensures reliable identification of species of atmospheric interest.

[Responses] Another important issue raised by the reviewer is the complexity of atmospheric aerosol mixtures. In this manuscript, we have characterized alcohols, amines, aldehydes, carbonyls, carboxylic acids, esters, and organic sulfates. We note that we have devoted our recent efforts to the characterization of more chemical classes that are atmospheric interest, including two families that are representative of rural and urban atmospheres, respectively, i.e., organic peroxides and nitrates. The goal is to fill more information on the space to facilitate the investigation of complex organic aerosol mixture.

[Responses] Work in progress has been evaluating the application of the IMS-MS technique to laboratory generated SOA mixtures. The application of IMS-MS to a rather simple SOA system that is generated from the reactive uptake of IEPOX onto acidified ammonium sulfate seed particles, for example, has been demonstrated by our recent study (Krechmer et al. AMT, 2016). Figure 5c in Krechmer et al. (2016) shows the distribution of IEPOX derived organosulfate, along with its dimers and trimers, on the 2-D space. A trend line for the major IEPOX monomers, dimers, and trimmers is clearly visible. The characteristic fragment upon CID, i.e., sulfate (m/z 97), adds further confirmation on the chemical identities of the IEPOX derived products in the particle phase.

2. Along the same lines of limitations/applicability, lines 349-350 seem to suggest that aromatic compounds may exhibit significant deviations. In atmospheric mixtures, there will be a larger mix of aliphatic/aromatic compounds. Would that imply this framework will work well for laboratory experiments to constrain oxidation, but not for atmospheric mixtures?

[Responses] Figure 3(C) in the manuscript shows that benzoic acid deviates by ~ 8% from the predicted trend lines for alkanoic acids. If this deviation is attributed to the presence of the planar aromatic ring, one would expect that all aromatics exhibit deviations in the measured Ω_{N_2} from the aliphatic ones, even if they contain the same type and number of functional groups. For example, within the narrow band of *mono*-carboxylic acids, there would be two sub-lines that characterize the aromatic series and aliphatic series, respectively. We think the reviewer raises a good point and we need further studies to refine these trend lines for aromatics. Collected filter samples for SOA generated from the photooxidation of aromatic precursors will be a good start to provide relevant information.

3. In this work, the authors used electrospray ionization, and there are a number of problems with ESI. First the ionization chemistry is very complex. In fact, the authors dedicated a whole paragraph (lines 363 – 374) to explain the chemistry, and the complexity can also be seen in Table 1. While ESI is a universal technique and is able to ionize almost all molecules one would encounter in SOA, it will be difficult (or, at the very least, tedious) to work backwards and deduce the original molecules from the large set of ion formulas observed. The second problem is that ESI is not a quantitative technique, especially with direct infusion shown here without prior separation. ESI suffers from matrix effects, and it is difficult to use surrogate standards for quantification. Perhaps the authors should point out to readers that more quantitative ionization techniques should be used to fully exploit the usefulness of the 2D framework.

[Responses] We acknowledge the major ESI disadvantage in terms of quantification of analytes, and as suggested, we have added corresponding discussions to clarify the capability and proper applications of the ESI scheme, also given below. We would like to note that we use ESI due to its great compatibility with the high-voltage inlet of the drift tube as it can handle voltages higher than 10 kV so that the ESI emitter can be directly placed at the entrance of the drift tube dissolvation region. Also note that developing alternative ionization schemes that are compatible with the IMS drift tube is actually one of our main research focuses now.

[Changes] Line 364-367: For species investigated in this study, their integral molecular structures are maintained during electrospray ionization. Quantification of these species requires prior chromatographic separation to avoid matrix suppression on the analyte of interest (Zhang et al., 2016) or alternative ionization scheme that is compatible with the high-voltage IMS inlet and does not induce matrix effects.

[Responses] We agree with the reviewer that it is not quite straightforward to elucidate the molecular structure of the analytes based on their ionic formula from ESI. This is also why we spent a long paragraph to try to give readers more generalized information on the applicability of ESI scheme to most common functional groups in the atmosphere.

[Changes] Line 349-353: For species investigated in this study, their integral molecular structures are maintained during electrospray ionization. An exhibition of molecular formulas of ionic species is given in Table 1. Depending on the proton susceptibility of functional groups, amines, esters, and aromatic aldehydes are sensitive to the ESI(+) mode, whereas carboxylic acids and organic sulfates yield high signal-to-noise ratios in the ESI(–) spectra.

4. Resolving isomeric structures: leucine and isoleucine are biological molecules and there are many other techniques that are capable for resolving those compounds. I find the use of leucine and isoleucine to demonstrate the capability of isomer separation to be not too effective. Perhaps the authors can consider showing the capability of the IMS to separate molecules of atmospheric interest?

[Responses] We agree that using species of atmospheric interest to demonstrate the IMS capability of isomer separation would be more appropriate for the scope of this study, although chemical standards for most isomeric structures that have been proposed in the atmosphere are commercially unavailable. Nevertheless, our recent study (Krechmer et al., AMT, 2016) has demonstrated the mobility separation of IEPOX derived sulfate isomers that are produced from the reactive uptake of synthesized *trans/cis*-IEPOX onto the acidified ammonium sulfate seeds in chamber experiments. Figure 4 in Krechmer et al. (2016) shows three isomers with proposed chemical structures and their drift times.

In the revised manuscript, we have added the following sentences to point to the IMS data for the atmospheric relevant isomers. We think the leucine data carry merits in a way that isomer separation in both ESI positive (+) and negative (–) modes can be demonstrated due to the presence of both amine and carboxyl functional groups. Moreover, we show that the Ω_{N_2} values for the same isomer are different in these two ESI modes, depending on the functional group (NH_2 vs. COOH) that carries the charge. This is also consistent with the predictions by the trajectory method.

[Changes] Line 407-411: Here we demonstrate the separation of isomers on the $\Omega_{N_2} - m/z$ space using the mixture of L-leucine and D-isoleucine as an illustration, as they can be directly ionized by electrospray in both positive and negative modes due to the presence of amino and carboxyl groups. We refer the reader to Krechmer et al. (2016) for the mobility separation of atmospheric relevant isomeric species.

Minor:

Figure 2: it seems to me that citric acid and the tricarboxylic acid are not quite the same (differs by an –OH group, the other homologue series differs by one or more –CH2- groups) so the trend line should not be drawn the same way as in the other series.

[Responses] Corrected.

Figure 4: I don't understand the fragmentation pattern in the amine (di-tert-butyl pyridine). Why is there a loss of –CH3 group? (It will form an unstable ion with an unpaired electron.)

[Responses] As shown in the figure below, the unpaired electron on the carbon atom resulted from the neutral loss $-CH_3$ group can be stabilized by conjugation with the pyridine ring. The Time-of-Flight (TOF) extraction period is 69 µs. Thus we think it is a reasonable assumption that such a radical could survive within the order of micro-seconds before being detected.