Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2016-481-RC1, 2016

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "A Novel Framework for Molecular Characterization of Atmospheric Organic Aerosol Based on Collision Cross Section and Mass-to-Charge Ratio" *by* X. Zhang et al.

Anonymous Referee #2

Received and published: 31 July 2016

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.

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.

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?

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.

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?

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.

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.)

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-481, 2016.