Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2016-481-RC2, 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 #1

Received and published: 2 August 2016

In this manuscript, the authors present a new framework with which to identify and characterize atmospherically relevant organic compounds based on a combination of ion mobility and molecular mass. Though a wide variety of such two-dimensional frameworks have been employed to parameterize and simplify descriptions of atmospheric mixtures, the technique proposed by the authors is unique and valuable in its ability to characterize compounds based on structural features and to separate isomeric species. The authors have done an excellent and detailed job of exploring intrinsic spatial relationships in this parameter space. Continued application of the tools and techniques described in this manuscript will likely provide more molecular and chemical information than has previously been available.

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Discussion paper

General comments:

While this manuscript builds a strong foundation for the application of these techniques to atmospheric samples, no attempt is made to apply these techniques to complex mixtures of unknowns. The title, abstract, and some portions of the introduction should be re-framed to highlight what is actually in this manuscript and focus less on what the authors hope to do with these tools in the future. It is implied or, in the case of the title stated explicitly, that this paper is about the "Characterization of Atmospheric Organic Aerosol." Given the home institutions of the authors, I have no doubt this is the goal and am excited to see it applied to ambient mixtures. However, without more detailed attempts to apply this technique to atmospheric mixtures or at least detailed discussion, the language and title of this manuscript should be changed to focus more on "atmospherically relevant organic compounds," or "highly oxidized small organic compounds," or "characterizing functionality of organic compounds."

The detailed description of the framework also needs some added clarity – see detailed comments below.

Minor comments:

Line 40: "scatter plots" is not a verb

Line 64: Re-word, perhaps use "and subsequent interactions" in place of "as well as"

Line 169: This phrase is awkwardly broken up and should be re-worded: "the instrument standard (the reduced mobility of such a standard is not affected by contaminants in the buffer gas) is needed"

Lines 184-200 describe the apparent crux of this framework, but some points could be made clearer. In particular, explicitly relating the measured parameters to the calculated parameters would be very helpful. For instance, in Eq. 6, it would be useful to re-frame in terms of t_d since that is what is actually being measured, instead of K_0 and v_d. What is the functional form of this relationship, considering all of the terms in

the equation? Is it collision cross section generally linear with drift time? Relatedly: âĂć Line 187: Is z=1 assumed for all ions? In contrast to other ionization techniques, ESI can under some conditions yield a distribution of charges – is this an issue and to what extent would it change the results? âĂć Line 190: Is thermal velocity calculated as a function of molecular mass? âĂć Line 193: How are the mass fractions calculated? How might this work for a mixture of unknowns with poorly defined sensitivities?

Line 214: Define or clarify "(12,4) potential"

Sections 3.1 and 3.2 could perhaps be switched, as they are discussed in Section 3 and in Section 4 in the opposite order.

Line 301: It is not clear to me that "functionalization and fragmentation can be represented by an intrinsic directionality" as claimed by the authors. As the authors note, the connected markers shown in Figure 2 represent addition of non-functionalized carbon atoms, but this is not the form that atmospheric functionalization takes. Instead, addition of carbon moves up and to the right, but addition of functional groups appears to move down. What would a vector of functionalization or fragmentation look like in this space? This question is particularly important if the authors intend to keep their focus on using this approach to characterize complex mixtures.

Line 345: While the trend lines described in the Section 4.2 provide an important characterization of this framework, and a useful test of the core model, it's not completely clear they would be particularly help in identifying unknown species, as implied in this sentence. As demonstrated by Figure S5, there is substantial overlap between the regions of all of the trend lines – if one were handed an unknown, its location in this space alone would not provide much information on its family. These lines are perhaps useful for identifying family of species, and demonstrate the utility of the core model for helping to understand its location in the space, but as written this sentence is a bit of an overstatement without some explanation or support. Section 4.3, on the other hand, does indeed seem very promising for identifying unknowns. . .

Line 386: A dominant peak at 108 is mentioned but not shown in Figure 4.

Line 398: The there is no O-O bond in dioctyl phathalate. Do the authors mean the carbonyl-oxygen bond? Interestingly (and relatedly), this 149 peak is the dominant peak in EI spectra.

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