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## ***Interactive comment on “Molecular corridors represent the multiphase chemical evolution of secondary organic aerosol” by M. Shiraiwa et al.***

### **Anonymous Referee #2**

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#### Overall Comment and Recommendation:

This paper presents the novel framework of molecular corridors (based on volatility and molar mass) as a way to capture aspects of SOA formation and aging. This is more of a theory paper that is not directly applied to simulate smog chamber data. The authors mostly use the smog chamber data that exists in the literature to propose this idea. The authors conclude that the molecular corridor theory could serve as a basis for compact representation of SOA formation and aging in models. The manuscript is well written, but I feel lacks many details needed for readers to better understand how this theory was developed from existing smog chamber data. Furthermore, in order to keep my comments concise and not create repetition of what has already been raised by the other reviewer, I want to state here that I completely agree with the other reviewer's

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concerns and recommend that these be adequately addressed before publication is considered. Besides not applying this theory to simulate SOA formation from existing chamber data at Caltech, my other biggest concern with this paper is how previous chemical data were exactly utilized for estimating volatility. This is not clear at all and I feel should be added in the appendix. The authors say they use prior identified compounds, but it is completely unclear which ones are selected and why others may or may not have been left out. Since I'm an analytical atmospheric chemist, I also warrant caution to the authors about soft ionization mass spectrometry methods. The authors cite the Kalberer et al. (2006, ES&T) study a lot and even use it to determine the average MW of the SOA in Table A1 for isoprene and alpha-pinene systems. With the Kalberer et al. (2006) study, the authors should be aware that MALDI-MS is prone to substantial artifacts. This is also true for other soft ionization methods like ESI-MS. Specifically, cluster ions may form in the ion sources, leading to much higher MW products than might actually exist. In my opinion, the use of chromatography and synthetic standards are the gold standards now and are typically needed to confirm the identity of certain compounds found in SOA systems. I'm surprised that the authors used the Kalberer et al. (2006) study for Table A1 when they say in the text they developed the 2D plots using Surratt et al. (2006; 2010) studies. For isoprene, I would argue that the Surratt et al. studies are more useful since much work was put in to derive the functionality of oligomers under both low- and high-NO<sub>x</sub> conditions. In addition, I'm unclear (and I'm sure other readers would be as well), how exactly aerosol acidity would be utilized in this framework since this is especially important in the isoprene and alpha-pinene SOA systems (Kleindienst et al., 2006, ES&T; Offenberg et al., 2009, ES&T). Lastly, in addition to these major comments above, I would like to request the authors consider my specific comments below.

#### Specific Comments:

1.) I wonder if the Editor and authors would agree if this should really be considered a Technical Note, especially since this theory is not applied to simulate laboratory data?

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I think many readers would wonder how applicable and useful is this theory in actually simulating SOA formation in the lab. Naturally, I think we would all agree this isn't ready for prime time in regional or global modeling of SOA until it is validated with laboratory data.

2.) Fig 1: I think we have to be careful here. Specifically, I think the authors need to EXACTLY clarify for readers how the different SOA types were generated. For example, is the isoprene SOA in Figure 1 a from photooxidation or ozonolysis? The way these plots read is that these would represent the behaviors for SOA generated under all oxidant, NO<sub>x</sub>, and seed aerosol conditions. Is that true? Do we even know that these plots would hold up under all conditions? In isoprene SOA, NO<sub>x</sub> and seed aerosol type will affect the type (i.e., functionality) and size of oligomers that form (Surratt et al., 2006; 2010).

3.) Section 3 - Kinetic regimes for SOA Formation:

The authors walk us very clearly through the different limiting cases of kinetic behavior for particle- and gas-phase reactions. Specifically, for the particle-phase reactions, the authors propose there could be 8 limiting cases of kinetic behavior, where as for the gas-phase reactions, the authors propose there to be 4 limiting cases. From prior work on the SOA systems you discuss here in this paper, I wonder if the authors can already rule out any of these limiting cases? I realize they may want to leave these all in to provide flexibility in the future development of the model, especially as more laboratory studies become available.

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