Atmos. Chem. Phys. Discuss., 13, C10904–C10909, 2014
www.atmos-chem-phys-discuss.net/13/C10904/2014/
© Author(s) 2014. This work is distributed under
the Creative Commons Attribute 3.0 License.

Atmospheric Chemistry and Physics Discussions
Open Access

Interactive comment on "Synthesis and coherent vibrational laser spectroscopy of putative molecular constituents in isoprene-derived secondary organic aerosol particles" *by* C. J. Ebben et al.

Anonymous Referee #2

Received and published: 10 January 2014

The manuscript presents a study using surface specific SFG techniques to compare synthesized isoprene derived tetrols and epoxides with SOA from isoprene chamber studies and SOA sampled in the Amazon. The manuscript proposes that the surface of chamber SOA is close to a specific epoxide and maybe a specific tetrol, whereas there is no similarity with the Amazon SOA. The authors also suggest that their approach will allow "fast-forwarding" from first and second generation gas-phase oxidation products though nucleation to SOA formation and will allow testing of SOA formation mechanisms. This would be an extremely important contribution. However, despite the

very high degree of expertise in SFG spectroscopy and thorough analysis, the authors should explain more clearly what is meant by the above goals within the context of their work and how this is or will be achieved with their results/methods. The application of SFG to SOA studies in combination with synthesis is a fairly unique approach, with only a few earlier studies by the authors. Thus, the work is suitable for ACP after the authors delineate more clearly what the method really can provide, also with respect to the mentioned "fast forwarding". Some detailed comments follow:

1. The manuscript outlines challenges for mechanistic and molecular level understanding of SOA in the introduction (p. 29813 L.21 – p. 29814 L 3). The authors address the challenge of providing standards of important molecules very well, and this is a clear strength of the work. However, it would help to summarize more clearly what the presented method can contribute to the other challenges. The conclusion of the analysis here shows that one specific IEPOX shows larger similarity with the surface of ambient SOA than the rest of the molecules. This raises questions, with respect to whether SFG can meet the challenge of molecular specific techniques, explained below:

It would be useful if the authors could clarify what molecular specific aspect is provided by SFG, also with respect to the molecular aspects of greatest interest for SOA, such as O/C ratio, volatility, hygroscopicity:

a) First in the discussion it should always be made clear that SFG is sensitive to the surface, if I understand the manuscript correctly. The abstract mentions that SFG is a surface technique but in the rest of the abstract it would be good to remind readers that the findings discussed pertain to the surface. Otherwise the impression might arise that it is the bulk that is being studied. I would very strongly recommend changing the title from "in" to "on" or "in/on the surface of isoprene..." The requirement for this clarification does not detract from the importance of the work. In fact, it is valuable to have a surface specific technique.

b) In order to understand the information gained from the experiments it would be

ACPD
13, C10904–C10909, 2014

helpful if the following points are considered:

- p.28924 line 19-29 “at least as probed by SFG in the C-H stretching region” is the crux. The authors need to show very clearly what this means with respect to the actual composition and properties of SOA surfaces.

- What causes the difference between the spin-coated and vapor spectra of epoxide 1. As much in the conclusion of the paper hinges on the similarity of the spectra of the spin-coated epoxide 1 with chamber and ambient SOA, the “molecular” aspects differentiating the spectra should be clearly delineated, i.e., what aspects of the molecule is SFG sensitive to.

- Within the same context. The used SFG method, if I understand correctly, is only sensitive to the surface. This means the method does not measure the gas-phase vapor or the bulk compounds but rather molecules on the surface of the fused silica. It would be helpful to state this more clearly, and exactly how many layers of molecules are observed. If it is indeed the case, that the method sees only the adsorbed (vapor-experiments) or first layer of molecules, then a brief discussion of the purpose of the two types of experiments is useful. This is later addressed in the orientation section, but it will be useful to readers to get this background up front.

- From section 3.2.1 and 3.2.2 it appears that the method can distinguish different types of C-H bond types/groups. If this is the case the authors should clarify that when they talk about molecular specific techniques this is meant. From my reading the method is not specific to molecules but only to a very specific type of functional group, but this with great detail. This does not belittle the interesting information that can come out of this but it is not the same as I first thought was meant by molecular specific. It is very interesting that small differences in molecules can make a noticeable difference in the spectra. However, given that many spectra look similar to those not acquainted with SFG, one could also argue that the technique is not that molecular specific, especially when probing a complex mixture of molecules such as that expected for SOA. Similarly,

ACPD

13, C10904–C10909, 2014

in previous work by the authors the spectra of pinene, pinene chamber SOA and ambient SOA from HUMPPA-COPEC look very similar (Ebben et al. Atmos. Chem. Phys., 11, 10317-10329, 2011). All these spectra do in fact have differences, as do the ones here, but as these are small, care should be taken to convince the reader that these differences, which may appear subtle, are significant, and again what the implications of analyzing complex mixtures are.

- To what degree is the original surface of the SOA actually probed by the SFG method? Do the authors have a way of determining whether the pressing of SOA against the window brings only original SOA surface in contact with the window. One could imagine that it partially exposes bulk to the window as well?

- The above point is relevant for the following reason: From previous studies, in particular by the Surratt group at UNC (e.g., Environ. Sci. Technol. 47, 5686−5694, 2013 dx.doi.org/10.1021/es400023n and references therein) it would seem more likely to find tetrols or organosulfates or other IEPOX derived organosulfates in SOA than IEPOX itself. This has two reasons. First, IEPOX is very reactive and hence its lifetime in aerosol is short. Second, as the authors themselves state in the implications section the vapor pressure is high enough for the compounds to partition to the gas-phase and be lost at some point. It is thus reasonable that the Amazon SOA would not retain IEPOX on the surface and hence will not look similar to the synthetic compounds. The perhaps more important point is that the Amazon SOA does not resemble the tetrols, which one could envision in and on Amazon SOA. It is interesting that the chamber SOA surface (if that is what it still is) resembles compound 1 for the reasons just stated and as it is surprising that the surface of SOA would consist of just one specific IEPOX? As an aside, the reference for IEPOX in SOA (Sun et al. 2003 in nanoletters), seems erroneous.

2. P. 29818 L. 20-24 and later: The authors should make clearer what they learn about the phase state and how. They state that they find that the compounds remain liquid down to -40C. Was SFG used for this or did they just look at the samples. It

ACPD

13, C10904–C10909, 2014

is not too surprising that these compounds do not crystallize well/turn solid, as other poly-alcohols such as glycerol or glycol are known to behave similarly. As the relation between the compounds discussed her and the bulk (in contrast to surface) of atmospheric SOA, which is not probed by the surface specific SFG, is unclear from this work, it is not clear how much is gained by this statement.

3. Implication section P. 29828 L. 26-P. 29829 L. 19. This implication section requires improved clarity with suggestions below. I recommend the authors consider cutting this or shortening it as it is quite speculative and wanders far from the actual results of this work.

- "is SOA particle formation possible ... when using the first- and second-generation oxidation products described here as opposed to plain terpenes?" The observation of tetrols and IEPOX derived organosulfates in field and chamber SOA (numerous studies by the Claeys, Surratt and other groups) already has demonstrated that SOA formation from isoprene as opposed to only from terpenes occurs and is important, so the statement "is SOA particle formation possible" should be removed.

- "are the climate-relevant properties of thusly formed SOA particles impacted when using the first- and second-generation oxidation products described here as opposed to plain terpenes?" and "Testing this hypothesis will advance our mechanistic information regarding the formation of SOA particles, specifically during the stages that take the molecular precursors towards the particle phase."

It would help to clarify the two statements. Why can chamber studies starting with isoprene in contrast to the individual synthesized products not better address this question? Likely, the SOA properties are determined by the mix of compounds present as it is not obvious that the properties will simply be the addition of SOA from individual precursors components. How will studies with individual compounds test the hypothesis?

- P. 29829 Line 2-3 "Compounds 1–6 should have sufficiently high enough vapor pres-

ACPD

13, C10904–C10909, 2014

sures for this experiment" and line 6 "this experiment "Please consider clarifying. Compounds with low vapor pressure give more SOA, so this sentence may be misinterpreted and readers might question why IEPOX is on or in SOA if it has such a high vapor pressure. Also, please clarify which experiment is being discussed? I assume the authors are proposing SOA chamber studies starting, e.g., with compound 1, but it makes it hard to follow the next section as it is not clearly described.

- P. 29829 Line 4-Line 11. See previous comment on experiments using isoprene vs. IEPOX above, which could make the described approach challenging.

- P. 29829 "Such experiments will allow us to test whether SOA particle formation that began with a given terpene precursor involves one type of molecular species or if multiple species act in concert." This sentence needs work as it may be read as if the authors are suggesting that SOA formation might involve only one molecular species. I assume they mean that if SOA formation is initiated by oxidation of one terpene (not SOA from the terpene itself) other precursor processing may contribute, e.g., isoprene oxidation.

- P. 29829 Line 14 "The rates of the two pathways just described differ by their order" Please clarify what two pathways you mean and how they differ in their order?

P. 29829 Line 18 It would be helpful to describe a little more what is meant by "fast-forwarding."

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 29811, 2013.