FINAL AUTHOR COMMENTS on acp-2013-813

Anonymous Referee #1

Received and published: 6 January 2014

General comments:

This manuscript presents a novel method of investigating the presence and phase state of isoprene-derived secondary organic aerosol (SOA) constituents. After synthesizing a number of isoprene epoxydiols (IEPOX) and tetraols, the authors characterize the compounds by polarization-resolved sum frequency generation (SFG), and compare these spectra to those of isoprene-derived synthetic and authentic SOA particles. Their results indicate that the synthetic SOA is well represented only by trans-B-IEPOX, while ambient aerosol from the Amazon Basin does not match any of the epoxides or tetraols synthesized, suggesting that if such species are present, they may be found primarily on the interior of the particles rather than at the surface. While the experimental techniques described here may provide a new method for probing the phase state of SOA constituents, the results offered in this manuscript allow only for limited conclusions, as it appears a compound's existence in an SOA sample can neither be confirmed, discounted, nor quantified by SFG spectroscopy. However, the unique ability to probe the phase states of SOA constituents, particularly when used in conjunction with additional instrumentation to confirm the presence of compounds in SOA material, may open valuable new doors for investigating chemistry at the aerosol-gas interface. I would suggest the authors focus more attention on this novel aspect of their experiments, and on the possible atmospheric implications of a molecule's specific orientation at the gas-particle interface.

Specific comments:

The references need some revision. A large number of cited papers appear to address topics irrelevant to the manuscript (e.g., references #2, 6, 11, 12, 14, 17-20, 26, 27, 41, 42, 49, 51, and 55 discuss CdSe solar cells, nanocrystals, and other unrelated subjects), and journal abbreviations (e.g. ACP and ES&T) are inconsistent.
We thank the review for noting these inconsistencies but wish to point out that the reviewer apparently had a different manuscript version from the one that was published online at ACPD. The reference numbers noted by the reviewer do not match the version published online; however we have noted several references which are not those intended. We apologize for the errors and have now corrected them, as follows:
Page 29812, line 12; Page 29814, line 10 and 12: (Sun et al., 2003) has been replaced with (Paulot et al., 2009)

Page 29812, line 13; Page 29814, line 11: (Hudson et al., 2008) has been replaced with (Poeschl et al., 2010)

Page 29812, line 13; Page 29814, line 11 and 12: (Yasmeen et al., 2010) has been replaced with (Claeys et al., 2004)

Page 29813, line 4: (Murray et al., 2000) has been replaced with (Carlton et al., 2009)

Page 29813, line 7: (Weiss et al., 2008a) has been replaced with (Riipinen et al., 2011)

Page 29813, lines 8-12:
(Weiss et al., 2008b; Kleiber et al., 2009; Wang et al., 2005b; Mena-Carrasco et al., 2009; Huynh et al., 2003; Palaniappan et al., 2009; Greenham et al., 1996; Sharma et al., 2003; Grassian, 2009)
have been removed and replaced with
(Claeys et al., 2009; Constantinescu et al., 2007; Kalberer et al., 2004; Kroll and Seinfeld, 2008; Lin et al., 2012; Mueller et al., 2008; Streets et al., 2006; Wilczak et al., 2006)

Page 29814, line 14: (Lewis et al., 2005) has been replaced with (Jimenez et al., 2009)

Page 29815, lines 17 and 25: (Zhang et al., 2012) has been replaced with (Surratt et al., 2010)

Page 29818, lines 17-18; Page 29828, line 20: (Nelson et al., 2001; Huang et al., 2008) have been replaced with (Renbaum-Wolff et al., 2013; Virtanen et al., 2010)

Page 29821, line 1: (Weiss et al., 2007) has been replaced with (Kawaguchi et al., 2012)

Page 29821, line 9: (Watson, 2010) has been replaced with (Buchbinder et al., 2011)

p. 29813 line 14: The compounds studied in this manuscript result not from reactions of BVOC oxidation products "with each other," but from their reaction with atmospheric oxidants. This section would benefit from a clearer explanation of how IEPOX and the tetraols form, and therefore in what locations and phase states they may be expected to arise.
p. 29814 lines 1, 12: The oxidation pathways leading to SOA are not entirely "unknown," and the epoxides and tetraols are not merely "proposed" but observed constituents of isoprene-derived SOA. Both the introduction and the discussion of results would benefit from greater description of how this manuscript fits with previous observations of IEPOX and tetraol particle uptake and/or gas-phase chemistry.

We appreciate these two comments, which are closely related.
First, the following clarification has been made to page 29813, lines 13-15: We changed
"…the products formed from the gas phase oxidization of biogenic volatile organic compounds react with one another to form species with lower and lower vapor pressures, ultimately leading to SOA particle formation."
to
"…the products formed from the gas phase oxidization of biogenic volatile organic compounds can react with one another or undergo further oxidation to form species with lower and lower vapor pressures, ultimately leading to SOA particle formation."

Second, we have added the following text to page 29814, line 14: "Under low NO_x conditions, isoprene photooxidation by OH radicals is expected to yield hydroxyhydroperoxides. Further gas phase oxidation results in the formation of second-generation epoxydiols of isoprene, or IEPOX compounds (Paulot et al., 2009). Formation of 2-methyltetraols occurs primarily through the reactive uptake of IEPOX into aerosols by acid-catalyzed epoxide ring opening followed by nucleophilic addition (Surratt et al., 2010)."

p. 29816, section 2.2: It is important to note that IEPOX and the tetraols are presumed to be products of isoprene oxidation under low-NO conditions. Were the synthetic samples prepared in such conditions?
We thank the reviewer for this comment. As described in Chen et al., 2011, [NO_x] at the HEC is below the 1 ppbv minimum detection limit of the Teledyne 200E NO_x analyzer used there. We have clarified this aspect of the oxidation chemistry by making the following change to page 29816, lines 3-4:
"photochemical reaction of isoprene and OH radicals at the Harvard Environmental Chamber"
has been changed to
"photochemical reaction of isoprene and OH radicals under low NO conditions at the Harvard Environmental Chamber."

Are NO levels known for the time and place where the AMAZE08 samples were collected?
Yes, as described by Martin et al. in *Atmos. Chem. Phys.* **2010**, *10*, 11415 and summarized by Ebben et al. in J. Phys. Chem. A, 116, 8271-8290 (2012), [NO] during AMAZE-08 was 0.1 ppb.

p. 29817, line 5-6: Does the 8 cm-1 variability refer to variations among spectra of the same compound, or between the various epoxides and tetraols?
This variability refers to individual SFG spectra of the same compound that are averaged together to generate the spectra shown in this manuscript. Individual spectra are shown in supporting information. To clarify, we changed
"In general, we find that the frequency positions of the spectral features vary by less than 8 cm^{-1} among the individual spectra."
to
"In general, we find that the frequency positions of the spectral features vary by less than 8 cm^{-1} among the individual spectra for each compound."

p. 29821, lines 3-14: Are there no previous IR studies of epoxidic methylene groups to which IEPOX can be compared?
We thank the reviewer for this request for clarification. Similar shifts to what we report here have been observed for epoxide-containing molecules, and we have added a sentence to this effect to line 13 on page 29821:
"Similar frequency shifts have been observed for epoxide-containing molecules, both due to the strain of the three-membered ring and the proximity to the oxygen atom (Henbest et al., 1957)."

p. 29824, line 7: Trans- and cis-B-IEPOX switch between compounds #1 and #2 in figures 1 & 2; they appear to be consistent in the text, but should be double-checked.
We appreciate this comment, but there does not appear to be a problem with the labeling of the compounds in the discussion paper published online.

p. 29826, line 16: "Title" should be "tilt."

We thank the reviewer for noting this error. The word “title” has been changed to “tilt.” We apologize for the oversight.

p. 29826, lines 21-25: It seems unsurprising that the synthetic isoprene-derived SOA (itself in the condensed phase) is better matched by condensed-phase epoxides than gas-phase epoxides. Should the gas-phase epoxides even be compared to condensed-phase SOA samples? What is gained by this comparison?
This point is interesting to consider in the context of the well-known phenomenon of surface premelting in molecular (ice) and metallic (lead) solids. There may be a distribution of surface-localized species on the isoprene-derived SOA particles that are in a molecular environment closer to that of the gas phase than that of the bulk SOA particle phase. In order to demonstrate the capability of distinguishing, at least in principle, surface-localized species in these two environments, we feel it is appropriate to include the comparison between vapor phase epoxides and SOA samples. Therefore, no change has been made.

Anonymous Referee #2

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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”.

We very much appreciate the reviewer’s comments and fully agree that improvement as suggested below will be highly beneficial.

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.

We appreciate the reviewer's comment; however, the intention of this paper is to describe how the combination of synthesis and surface-specific vibrational spectroscopy may be utilized to gain insight into the surface molecular environment of SOA particles. O/C ratios for the particles studied here are provided in the papers we reference. Other physical properties of the molecules synthesized here will be the subject of future work.

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.

We appreciate the reviewer's comment and understand the need for further clarification. We have changed the title of this manuscript from
"Synthesis and Coherent Vibrational Laser Spectroscopy of Putative Molecular Constituents in Isoprene-Derived Secondary Organic Aerosol Particles"
to
"Synthesis and Coherent Vibrational Laser Spectroscopy of Putative Molecular Constituents Associated with the Surfaces of Isoprene-Derived Secondary Organic Aerosol Particles"

We don't agree, however, that there is a need for continuous emphasis on surface-specificity. We use surface-specific language throughout the results/discussion sections, e.g. (please note italics) Section 3.2.1. Epoxides: "Figure 2A shows that a peak at 2955 cm^{-1} dominates the SFG spectra *of fused silica windows in contact with* the vapor-phase epoxides."

b) In order to understand the information gained from the experiments it would be 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.
We very much appreciate this comment and agree it is necessary to elaborate somewhat in that section. We felt it most appropriate to add the following statements to the end of Section 3.2:
"We recently described the origin of the SFG response for well-characterized α-pinene-derived SOA particle material (Shrestha et al., 2013). In that work, we point out that the ssp-polarized SFG signals produced by the C–H oscillators originate from a non-centrosymmetric environment, i.e. a surface or interface. Moreover, the molecular orientation distribution of the oscillators needs to be non-zero, i.e. net ordered. Matches and mismatches of the SFG signals

obtained from the reference compounds and the SOA particle material studied here are to be understood within that precise framework."

- 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.
We appreciate the reviewer's comment. We point out that Section 4 of the manuscript addresses this point. The beginning of this section reads, "One benefit of SFG is an exquisite sensitivity to molecular orientation at interfaces. However, the orientation of the oscillators that produce SFG signals may change based on what phase state they are in (Wei et al., 2001)."
In order to further clarify this aspect of the SFG analysis, and to address it an earlier point in the manuscript, we have changed the first paragraph of Section 3.1 to read (we reproduce here the sentences that were not changes as well, for the sake of completeness):
"There exists a keen interest in determining the phase state of SOA particles (Renbaum-Wolff et al., 2013; Virtanen et al., 2010), as reactive processing inside the particle bulk may be turned off upon particle solidification and may compete with surface reactions if the particles are not solid. SFG spectroscopy can be sensitive to interfaces undergoing phase changes (Miranda and Shen, 1999; Wei et al., 2002), due to the appropriateness of this technique to detect changes in molecular orientation and conformation, which often accompany phase changes. We report here which of the model compounds are liquid vs. solid at temperatures relevant to the upper and lower troposphere. In the following section, we also discuss differences in the vibrational SFG responses obtained from vapor phase vs. condensed phase model compounds in contact with the fused silica windows employed here."

- 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.
We certainly appreciate this comment. We felt it most appropriate to address this point in section 3.2, with the new paragraph we added in response to the reviewer's previous comment.

- 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, 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.
The reviewer is exactly correct and has understood the possibilities and limits of SFG very well. It is true that SFG is not "molecularly specific" to the extent that the technique cannot be used to identify the specific molecules present in complex SOA samples. By synthesizing known terpene oxidation products that may serve as SOA forming constituents and analyzing these molecules with SFG, we are, however, able to begin to understand the molecular environment present at the surfaces of SOA particles. The approach we chose is analogous to that used in mass spectrometry, where a mass peak at 128 amu, for example, may be seen but only understood when compared to the mass spectral signatures of known reference compounds.

Regarding the second aspect of this comment: throughout the manuscript, we use what we feel is very careful language. As an example, addressing specifically the reviewer's comment in the second part of the paragraph above, we state, in the original manuscript version (at the end of Section 4): "…mismatches between the spectra of these compounds and that of isoprene-derived SOA particles may result from a lack of surface activity of these molecules. However, we cannot rule out that these mismatches may result from differences in orientation of the surface oscillators of these molecules under the phase conditions studied here."
Again, many such conditionals are pointed out by us, and we feel that we have appropriately addressed this aspect of the reviewer's comment.

- 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?
We agree that pressing the SOA particle material against an optical window is likely to change the particle surfaces to some extent. The question is whether this change will be picked up by SFG. The sample geometry utilized with the silica window in these experiments results in conditions that approach total internal reflection for the incident and output light fields. These experimental conditions result in amplification of the SFG signal intensity. Control experiments on α-pinene-derived SOA particle material collected on Teflon filters published by us recently (Shrestha et al., 2013) show that lower SFG signal intensities are obtained when probing the particle-containing Teflon filters in an external reflection geometry. However, the spectral lineshapes and frequencies of peak positions are identical in both internal and external reflection geometries. This result indicates that pressing the samples against an optical window has negligible impact on the SFG response from α-pinene-derived SOA particle material. We assume the same to be true here.

- 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?
The reviewer raises an interesting point. We have now addressed it by adding the following sentence to the end of the first paragraph in Section 5:
"There are many reasons why the SFG spectra of the SOA particle material collected during AMAZE-08 would not match any of the synthetic samples probed here, including the possibility that functional groups such as sulfates or nitrates may impact the orientation distribution of the C–H oscillators probed here."

As an aside, the reference for IEPOX in SOA (Sun et al. 2003 in nanoletters), seems erroneous.
The reviewer is correct about the erroneous reference, and we apologize for the oversight. Sun et al., 2003 has been replaced with (Paulot et al., 2009).
The reference used in this section for tetraol formation (Yasmeen et al. 2010) is also incorrect and has been changed to (Claeys et al., 2004).

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.
SFG was not used at this temperature; the phase state was assessed by visual inspection.

It 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.
We appreciate this comment, but including the information is justified as stated in the introduction to Section 3.1.

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.

We agree with the reviewer that this portion of the manuscript is speculative and may not contribute to the rest of the paper. We have removed the final paragraph of the manuscript and replaced it with the concluding statement:
"Synthesis of these homogenous first and second-generation oxidation products has allowed for analysis of these compounds by vibrational SFG. The results from this surface specific technique were compared to spectra obtained from SFG studies carried out on SOA particles derived both naturally and synthetically, providing insight towards the chemical composition of SOA particles at the surface. Given that our present study shows that trans-β-IEPOX appears to be of significant importance at the SOA particle surface, this compound is likely to be of importance for the chemical and physical processes underlying the condensational growth of

aerosol particle material under model conditions (Ebben et al., 2011b). Investigating the atmospherically relevant properties of trans-β-IEPOX and the other compounds investigated herein may potentially yield insight into SOA particle formation and growth. These experiments are ongoing and will be reported in due course."
Since the remaining comments address aspects of the manuscript that have been removed, it is no longer necessary to address these comments.

- "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 pressures 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."

New references that have been added to the manuscript:

Buchbinder, A. M., Gibbs-Davis, J. M., Stokes, G. Y., Peterson, M. D., Weitz, E., and Geiger, F. M.: Method for Evaluating Vibrational Mode Assignments in Surface-Bound Cyclic Hydrocarbons Using Sum-Frequency Generation, J. Phys. Chem. C, 115, 18284-18294, 2011.
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