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Interactive comment on “Contrasting organic aerosol particles from boreal and tropical forests during HUMPPA-COPEC-2010 and AMAZE-08 using coherent vibrational spectroscopy” by C. J. Ebben et al.

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Referee #2: Comments: The authors present a new analysis of biogenically derived atmospheric organic aerosol using vibrational sum frequency generation (SFG). The paper is largely a proof of concept study showing that SFG can be used to differentiate between samples which are expected to primarily originate from isoprene, and those which are expected to form via monoterpene oxidation (based on the emissions profiles in the field sampling regions). Some further insight into particle formation and growth is obtained by analyzing the size dependence of the SFG signal in each location. The

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information provided by SFG is similar to that provided by FTIR spectroscopy of aerosol particles, but this technique is sensitive to sub-nanogram levels of material. The paper is interesting and should be published in ACP after the following issues are addressed.

- I agree with Anonymous Referee #1 that some more discussion of whether just the top surface layer of the collected particles is being sampled by SFG, and what this means for the interpretation of the data in this and future studies, is in order.

We very much appreciate the reviewer's comment regarding a need for clarification. As outlined in our response to the comments by Referee #1, we have addressed this issue as follows: We have added the following sentence to the first paragraph of the section I: "SFG is forbidden in centrosymmetric media, which means that it is a surface-specific technique for achiral systems." and, in the SFG theory section: "SFG responses obtained from such molecules therefore originate from the aerosol particle surface. Chiral molecules do not possess a center of inversion, and their SFG responses can originate from the surface and the bulk of the aerosol particle, depending on symmetry. Details regarding the role of chirality in SOA particles are discussed in our recently published work. We emphasize that the present work is carried out using the SSP-polarization combination, which is insensitive to molecular chirality and yields SFG signals from the CH oscillators that are located at the surface of the aerosol particles as opposed to those that are located in the bulk." Finally, in the conclusions section, we now emphasize the following: "Given that the SSP-polarized SFG spectra report on CH oscillators located at the surface of the aerosol particles as opposed to those that are located in the bulk, we conclude that these growth processes introduce little or no changes in the chemical composition of the particles' surface region."

- Some more discussion should be provided regarding the chemical identity of the lab generated SOA, and what differences are expected compared to the ambient SOA. The reference to "reaction cascades" leading to SOA formation from isoprene on page 8 is too vague. Was the relative humidity similar in the chamber experiments and the field? 40% RH is below the deliquescence RH of ammonium sulfate – isoprene SOA

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formation on deliquesced aerosols vs. “dry” aerosols is expected to be mechanistically different since most isoprene oxidation products are volatile but water-soluble. Could this have contributed to the observed differences in the spectra of the submicron Amazon aerosols as compared to the lab aerosols?

The reviewer is correct that the use of the words ‘reaction cascade’ is vague. At one point, we considered the wording ‘the process resulted in the formation of organic material on the seed particles’, which, in our opinion, is as informative but longer. We trust that the reviewer will concur with us that a detailing of the published putative reaction mechanisms goes beyond the scope of this manuscript. We do not yet know what the differences are for the SFG responses of synthetic SOA prepared at the Harvard Environmental Chamber if one uses various RH levels during growth, but our ongoing work is geared towards elucidating this complex parameter space in a stepwise fashion, and we certainly appreciate the reviewer’s comment. We have now added the following sentence to paragraph on page 16949: “Given that the formation of isoprene SOA particles on deliquesced vs. “dry” seeds is expected to be mechanistically different since most isoprene oxidation products are volatile but water-soluble, the different RH conditions could contribute to the observed differences in the SFG spectra of the submicron Amazon aerosols as compared to the lab aerosols.”

- One of the stated findings of this work is that the organic composition of submicron aerosols formed by monoterpenes is similar, but for larger particles it is not. The authors need to provide some insight as to why that might be. Are the larger particles associated with primary biogenic emissions?

We thank the reviewer for this comment and would like to state that the reviewer’s intuition is exactly correct. We have clarified our argument by adding a statement to the discussion section to address this point: “The new spectral features obtained from the supermicron particles, when compared to the SFG spectra obtained from the submicron particles, are attributed to the presence of chemically complex primary biological material in the supermicron size range.”

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Specific comments: - Page 8: As far as I am aware the use of an ozone monitor to track H₂O₂ concentrations is not common practice so more explanation is needed in this passage.

We appreciate the reviewer's comment and have changed the text as follows. "An ozone monitor was used to estimate the H₂O₂ concentration. H₂O₂ shows a small absorption at the operation wavelength of the ozone monitor (254nm). By using the absorption cross-section of H₂O₂ ($\sigma_{\text{H}_2\text{O}_2}=6.7\text{e-}20$; 254nm, 298K; Sander et al., 2011) the H₂O₂ concentration can be calculated. For an apparent ozone concentration of 76.4 ppb +/- 13.9 ppb (standard deviation) the resulting H₂O₂ concentration is around 13.1 ppm. Under the experimental conditions, the fraction of ozone produced as a byproduct in the chamber is small compared to the H₂O₂ concentration in the gas phase."

- Page 13: How was plasma cleaning carried out? If a commercially available instrument was used please provide some specifics.

This section has been updated to include the instrument used (Harrick Plasma, Plasma Cleaner PDC-32G).

- Page 21: The sentence "Consistent with work by Riipinen et al. . ." needs to be clarified (as is it essentially reads: growth is associated with increase in aerodynamic size). Also, that reference to Riipinen et al. is incomplete.

This sentence has been updated as follows: "Consistent with work by Riipinen et al. (Riipinen et al, 2011), this finding suggests that the condensable vapors associated with the growth of the nucleation and Aitken modes, rather than continued aerosol phase chemical reactions, are involved in processes that lead to the mass increase of the particles that goes along with the increases in aerodynamic size. Given that the SSP-polarized SFG spectra report on CH oscillators located at the surface of the aerosol particles as opposed to those that are located in the bulk, we conclude that these growth processes introduce little or no changes in the chemical composition of

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the particles' surface region." We also apologize for the oversight in the reference. The year 2011 has been added.

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