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Atmospheric β -Caryophyllene-Derived Ozonolysis Products at Interfaces

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Supporting Information

ABSTRACT: By integrating organic synthesis, secondary organic aerosol synthesis and collection, density functional theory (DFT) calculations, and vibrational sum frequency generation (SFG) spectroscopy, we identify close spectral matches between the surface vibrational spectra of β -caryophyllene-derived secondary organic material (SOM) and those of β -caryophyllene aldehyde and β -caryophyllonic acid at various interfaces. Combined with the record high surface tension depression described previously for these same oxidation products, we discuss possibilities for an intrinsically chemical origin for cloud activation by terpene-derived surfactants. Although the present study does not unequivocally identify the synthesized and analyzed oxidation products on the β -caryophyllene-derived SOM surfaces, these two compounds appear to be the most surface active out of the series and have also been



foci of previous β -caryophyllene field and laboratory studies. An orientation analysis by phase-resolved SFG spectroscopy reveals a "pincer-like" configuration of the β -caryophyllene oxidation products, albeit on a model quartz surface, that somewhat resembles the orientation of inverse double-tailed surfactants at the surfaces of biological systems. The structural information suggests that the less polar moiety of a surface-localized oxidation product, such as those studied here, may be the first site-of-contact for a gas-phase molecule approaching an SOA particle containing surface-active β -caryophyllene oxidation products.

KEYWORDS: Sum frequency generation (SFG) spectroscopy, β -caryophyllene ozonolysis, sesquiterpene chemistry, secondary organic material (SOM), phase-resolved SFG, density functional theory (DFT) calculations

1. INTRODUCTION

The atmospheric oxidation of biogenic volatile organic compounds (BVOCs) results in the production of naturally produced secondary organic aerosol (SOA) particles,¹⁻¹⁴ a principal, yet elusive, class of airborne particulate matter that impacts the Earth's radiative budget.^{15–18} Given that the particle surface is the first point of contact for surrounding species, interfacial phenomena likely influence key SOA processes.^{19–22} Therefore, chemical information regarding the aerosol particle interface is of interest for understanding particle growth,^{23–26} heterogeneous chemistry,²⁷ optical properties,^{28,29} and cloud activation.^{23,30–41} Surface-active terpene oxidation products

have now been observed at the gas/particle interface for the specific cases of deposited isoprene (C_5)- and α -pinene (C_{10})-derived secondary organic material (SOM).^{21,23,28,35,40}

Here, we report a spectroscopic and structural study on the comparatively more complex species derived from sesquiterpene oxidation,⁵ specifically that of β -caryophyllene, the most abundant sesquiterpene BVOC emitted into the atmos-

Received:October 15, 2018Revised:December 7, 2018Accepted:December 10, 2018Published:December 10, 2018

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phere.^{42–48} We are motivated by the fact that reaction products produced from β -caryophyllene ozonolysis have been foci in recent field^{49–52} and laboratory^{44,53–55} studies examining atmospheric oxidation of sesquiterpenes. Recently, we synthesized several β -caryophyllene oxidation products for use in Yee et al. as tracer standards to identify several of these species in the gas and particle phases within SOM collected in the Central Amazon region using semivolatile thermal desorption aerosol gas chromatography (SV-TAG).⁵² Additionally, we recently reported record cloud activation potentials for these β caryophyllene oxidation products (Figure 1) from measure-



Figure 1. β -Caryophyllene-derived oxidation products synthesized and analyzed in this work.

ments of surface tension that exceed those of SDS^{56} at equivalent concentrations.⁵ In this present work, we take the first steps toward elucidating the interfacial structure and orientation of these molecules benchmarked to the surface of an SOA model synthesized from the ozonolysis of β -caryophyllene.

Probing the interfacial molecular composition of SOM remains challenging, as few techniques are appropriate for nondestructive interfacial analysis while also providing chemical bond specificity. These include mass spectrometry configured to ablate external vs internal portions of particles⁵⁷ and X-ray based methods⁵⁷ under ultrahigh vacuum conditions, as well as scanning probes⁵⁸ and Raman and infrared spectroscopy under ambient conditions. 59-64 In these cases, the relative signal contribution from the particle surface vs the particle bulk is small.⁶⁵ An additional challenge in the analysis of aerosol particles is that concrete elucidation of proposed oxidation products within SOM mixtures remains indeterminate without the chemical synthesis of molecular standards that otherwise may be difficult to isolate in sufficient amounts or separate from the complex mixtures in field or laboratory collected materi-al.^{5,14,20,22,49,50,55,66-70} While mass spectrometry has long remained the widespread method of choice employed in the aerosol science community,^{22,71-78} surface-selective vibrational spectroscopy^{21,59,79-82} offers the prospect of complementing such studies by selectively probing SOM interfacial chemistry under ambient conditions, nondestructively, and with capabilities for observing constituents present on the surfaces of SOM as well as obtaining molecular orientation information. Previous work in this area reported on the observation of organic molecules at the interface of aerosol particles deposited on or in contact with solid substrates $^{21,22,24,61,65,79,83-85}$ and, more recently, suspended in air.^{28,86} Now, we combine vibrational sum frequency generation (SFG) spectroscopy, density functional theory (DFT) calculations, and organic synthesis to probe

the surface composition of β -caryophyllene-derived SOM and to obtain detailed structural and orientational information on individual molecular constituents on the particle surfaces. By comparing the spectra from the synthesized reference compounds with those observed from the β -caryophyllenederived SOM in both the C–H and C=O stretching frequency regions, we identify β -caryophyllene aldehyde (1), along with β caryophyllonic acid (3), as the most likely surface-localized species. These same species were also found to exhibit the highest and second highest surface activities (and thus estimated cloud activation potentials), respectively, of the oxidation products we previously studied by dynamic surface tension measurements.^{5,20}

2. EXPERIMENTAL AND COMPUTATIONAL METHODS

2.1. Synthesis of Molecular Standards of Putative β -Caryophyllene-Derived Oxidation Products. The syntheses of all compounds studied here are described in our previous work.⁵ In summary, aldehyde and monoacid oxidation products 1-4 are prepared from ozonolysis of β -caryophyllene under varied reaction times and ozone generator voltage, followed by either oxidative or reductive workup conditions to access the desired product carbonyl functionality. Diacid oxidation products 5 and 6 can be synthesized from β -caryophyllonic acid (3) as follows: iodolactonization of monoacid 3 simultaneously protects the carboxylic acid and alkene moieties, silyl enol ether formation and a subsequent ozonolysis convert the methyl ketone to a carboxylic acid, and iodolactone removal reveals the desired acid product, β -caryophyllinic acid (5). β -Nocaryophyllinic acid (6) can be accessed through a final ozonolysis of β -caryophyllinic acid (5) with reductive workup conditions.

2.2. Collection of Synthetic Secondary Organic Material (SOM) Derived from β -Caryophyllene. A comprehensive description of the Harvard flow tube reactor used in this work can be found in our previously published work.^{24,87} Briefly, β -caryophyllene was introduced into the flow tube as a solution of β -caryophyllene (\geq 98.5%, Sigma-Aldrich Inc.) diluted in 1butanol $(1:625 \text{ v/v})^{24,88,89}$ at selected injection rates that altered the gas-phase concentration in the range of 300-500 ppb, which subsequently changed the organic particle mass loading in the flow tube. 1-Butanol was used as an OH scavenger to ensure that ozonolysis products were generated. Excess ozone (53 ppm) was passed through the reactor with a flow rate of 4 SLPM to ensure β -caryophyllene was fully reacted. Aerosol particle samples were nucleated in the absence of seed particles and collected on Teflon filters (PTFE-47 membrane, pore size 0.45 μ m, Z269425, Sigma-Aldrich Inc.) for 7-10 h, or until saturated, for subsequent SFG analysis. From the flow rate, collection time, collection efficiency, and particle mass concentration (obtained from a scanning mobility particle sizer), the mass of the particles collected on the filters was estimated in the range of 5-14 mg. The SOM generated had mode diameters of 66-80 nm during the course of the flow tube experiment, with an average mass loading of 7 mg m⁻³. See Table S6 for more details on the SOM collection. Previous chamber and flow tube studies of sesquiterpene (β -caryophyllene) and monoterpene SOM suggest that the chemical composition of the β -caryophyllene SOM in this study is likely to be similar to those performed under low volatile organic compound (VOC) concentrations, due to a low effective saturation concentration of β -caryophyllene SOM.^{87,89–91} All filter samples were sealed using Teflon tape and parafilm, stored in a -20 °C freezer,

and warmed to room temperature before breaking the sealant for SFG measurements. No spectral changes were observed over the course of approximately 1.5 years, suggesting the high stability of the SOM once formed, at least as detected by SFG spectroscopy.

2.3. Vibrational Sum Frequency Generation. 2.3.1. Sample Configurations and SFG Experimental Setup. The synthesized standards, along with β -caryophyllene $(\geq 98.5\%)$, Sigma-Aldrich Inc.), were measured in both the condensed and vapor phases in contact with solid fused silica or calcium fluoride substrates at laboratory ambient temperature and relative humidity in near total internal reflection geometry. Vapor phase spectra were taken by exposing an optical window with the equilibrium vapor pressure of the compound being measured, and condensed phase spectra were obtained by measuring a window containing a spin-coated sample. Samples were prepared for measurement by spin-coating the compound, dissolved in a deuterated solvent (CDCl₃ and/or CD₃OD), at 3000 rpm onto an optical window. Synthetic SOM was analyzed by pressing an optical window against a Teflon filter containing the collected material. Spectra were measured with ssp and ppp polarization combinations. The ssp polarization combination probes the components of the vibrational transition dipole moments that are oriented perpendicular to the solid substrate,²² whereas the *ppp* polarization combination needed for detailed orientational analysis⁹² probes off-diagonal elements of the second-order susceptibility tensor.

The standard (Northwestern University, 10–15 cm⁻¹)^{79,93,94} and high (Pacific Northwestern National Laboratory, 0.6 cm^{-1})^{80,95-97} spectral resolution broadband SFG laser systems used herein for obtaining C-H spectra have been detailed in previous work. For the standard resolution SFG laser system, vapor phase spectra of the synthesized compounds were taken by adding 1-2 drops of viscous liquid compound to the bottom of a fused silica window, which was then sealed with a Viton Oring to a home-built Teflon cell and placed on a sample stage. The vapor was allowed to equilibrate for $\sim 10-45$ min before spectral acquisition. The visible and IR beams were aligned above the sample droplet to probe the vapor/solid (as opposed to liquid/solid) interface. Windows containing spin-coated sample were sealed with a Viton O-ring to the Teflon cell and clamped onto the sample stage prior to measuring condensed phase compound spectra. All optical windows were plasma cleaned for 10-15 min prior to sample exposure. The spectra reported here are an average of 4-7 individual spectra each taken for 2 min each. Spectra were referenced to the ppppolarized nonresonant SFG response of gold deposited on fused silica to account for the incident IR energy distribution, and frequencies were calibrated using a polystyrene film.^{22,87,98,99} The IR beam and the upconverter pulse were directed onto the sample at 60° and 45° from the surface normal, respectively. The beams are refracted in the substrate and therefore incident at the substrate/sample surface at $\sim 38^{\circ}$ and $\sim 30^{\circ}$ for the IR and visible, respectively. For the high resolution SFG system, vapor phase compound spectra were acquired by placing 1-2 drops of liquid sample at the edge of a shallow Teflon beaker that was then capped with a fused silica optical window. The vapor was allowed to equilibrate for ~10-45 min before spectral data acquisition. For spectra of spin-coated compounds, samples were prepared using the same procedure as stated above. All fused silica windows were placed in an ozone cleaner (Novascan Technologies) for ~10 min, and plasma cleaned (PDC-001-HP, Harrick Plasma) for ~15 min before depositing sample. The incident angles of the visible and IR beams were 45 and 55° from

surface normal, respectively. The spectra reported are an average of 2–3 individual acquisitions each recorded for 5–10 min. Although the data was experimentally obtained using 0.6 cm⁻¹ resolution, we note that the spectra were subsequently binned to improve signal-to-noise. The data points in the high-resolution SFG spectra were binned by 5 points, or by 1.73 cm⁻¹, in Igor Pro Version 6.11 (WaveMetrics, Lake Oswego, OR, USA). SFG intensities were normalized to the *ppp*-polarized nonresonant SFG profile of clean z-cut α -quartz, and frequencies were calibrated to a polystyrene film.

SFG spectra collected in the C=O region were measured using a TOPAS (TOPAS-C, Light Conversion) tunable optical parametric amplifier setup that has been described in detail previously.¹⁰⁰ Å schematic of the SFG setup is provided in the Supporting Information (Figure S1). Sample preparation and data collection for obtaining condensed phase C=O spectra were carried out under the same protocol as described above for the standard resolution SFG laser system used for obtaining C-H spectra. All C=O spectra were measured using calcium fluoride optical windows. Spectra were recorded using a Python script to measure the IR center wavelengths (5500-6300 nm with 695 nm as the spectrograph center wavelength) that cover the frequency range of interest (~1590–1820 cm^{-1}). Spectra were normalized to the incident IR energy profile by recording a ppp-polarized nonresonant spectrum from a gold film deposited on calcium fluoride, and frequencies were calibrated to a polystyrene film measured in the C-H region.¹⁰¹ The incident angles were 45° for the visible beam and 60° for IR beam. We also note that large nonlinear bulk responses from β nocaryophyllinic acid (6) were observed upon slow crystallization of the sample (see Figure S4.1), which is consistent with our earlier reports on molecular chirality in field-collected and synthetic atmospheric aerosol particles.^{21,102,103}

2.3.2. Phase-Resolved Spectra on Quartz. We employ a recently established^{80,104–106} internal heterodyne method to obtain phase-resolved SFG spectra of, and thus structural information on, the β -caryophyllene oxidation products spin-coated on z-cut α -quartz. Phase-resolved SFG responses are obtained directly, and without the need of an additional external local oscillator as seen in conventional heterodyne SFG setups.^{107–109} Briefly, when measuring an SFG spectrum of a sample deposited onto z-cut α -quartz, the resulting SFG response contains contributions from (1) the bulk quartz and (2) the molecules adsorbed on the quartz. The nonlinear susceptibility contribution from the adsorbed layer contains both real and imaginary components. The intensity of the SFG spectrum, *I*, that is directly measured is given by eq 1:

$$I \propto |\chi_{S,\text{eff}}^{(2)}|^2 = |\chi_{S,Re}^{(2)} + i\chi_{S,\text{Im}}^{(2)} + i\chi_{quartz}^{(2)}|^2$$
(1)

Here, $\chi_{S,\text{eff}}^{(2)}$ is the effective nonlinear susceptibility from the surface, $\vec{\chi}_{S,\text{Re}}^{(2)}$ is the real part of the nonlinear susceptibility from the adlayer, $\vec{\chi}_{S,\text{Im}}^{(2)}$ is the imaginary component of the nonlinear susceptibility, and $\vec{\chi}_{quartz}^{(2)}$ is the nonlinear response from the quartz bulk. The $\vec{\chi}_{quartz}^{(2)}$ term is assumed to be off-resonance, therefore remaining a constant throughout the experiment, and $\chi_{S}^{(2)}$ is assumed to contribute much less than $\vec{\chi}_{quartz}^{(2)}$. Therefore, eq 1 can be reduced down to eqs 2 and 3.

$$I = |\vec{\chi}_{\text{quartz}}^{(2)}|^2 + 2\vec{\chi}_{\text{quartz}}^{(2)} \cdot \vec{\chi}_{\text{S,Im}}^{(2)} + |\vec{\chi}_{\text{S}}^{(2)}|^2$$
(2)



Figure 2. High-resolution (A) *ssp*- and (B) *ppp*-polarized SFG C–H spectra of synthetic β -caryophyllene-derived SOM pressed against fused silica (black trace) compared to β -caryophyllene and synthesized β -caryophyllene oxidation products (1–6) spin-coated onto fused silica. All maximum SFG intensities have been normalized to 1 and offset for clarity.

$$\approx |\vec{\chi}_{quartz}^{(2)}|^2 + 2\vec{\chi}_{quartz}^{(2)} \cdot \vec{\chi}_{S,Im}^{(2)}$$
(3)

Thus, as long as the azimuthal angle (φ) of the quartz substrate is known, the sign of $\vec{\chi}_{S,Im}^{(2)}$ is readily obtained directly.

A brief experimental description for phase-resolved measurements using quartz follows. Synthetic standards 1–4 were selected as representatives within our available molecular suite for phase-resolved measurements, and all samples were spincoated onto z-cut α -quartz (right-handed, size 12.7 × 12.7 × 5 mm, Conex System Technology) analogous to what is described in section 2.3.1. The incident visible and IR beams were focused onto the top side of the quartz piece. Spectra reported herein are an average of five individual spectra each acquired for 5 min. *ssp*-Polarized spectra of the quartz were obtained at azimuthal angles of $\Phi = 0^{\circ}$ and $\Phi = 180^{\circ}$. The individual spectra were normalized to the spectrum of clean α -quartz at the same azimuthal angle.

2.4. Computational Methods. Density functional theory (DFT) calculations were employed to aid in spectral interpretation. Similar to our previous work,^{110,111} geometries for a number of different conformers of each oxidation product were optimized by using B3LYP^{112–114}/6-311G(d,p)¹¹⁵ via the Gaussian09 software package located at Yale University.¹¹⁶ Upon optimization, the harmonic and anharmonic frequencies were calculated in addition to the dipole and polarizability derivatives with respect to each normal mode. We identified Fermi resonances through a previously described proce-

dure^{110,111,117} that employs a multimode Fermi resonance Hamiltonian with a frequency cutoff of 10 cm⁻¹. According to this model, if an overtone or combination band is within 10 cm⁻¹ of a fundamental vibrational mode, the modes couple and result in a shift in frequencies and intensities dependent on the coupling constant. Additional frequency cutoffs were tested; however, a 10 cm⁻¹ cutoff appeared to result in the closest spectral matches across all of the oxidation products.

3. RESULTS AND DISCUSSION

3.1. Comparison of SFG Spectra of β -Caryophyllene-Derived SOM and Oxidation Products: C-H Stretches. Polarization-resolved SFG spectra were recorded in the C-H stretching region for the β -caryophyllene oxidation products in both the condensed and vapor phases and the β -caryophyllenederived SOM surfaces in contact with fused silica. The phase state of SOA particles remains difficult to experimentally probe, and little is known about molecular environment changes that may lead to phase behavior differences at the surface vs in the bulk. Indeed, surface-induced melting has been observed in a range of systems, from metal nanoparticles to ice for instance.^{118,119} Therefore, we provide both the vapor and condensed phase spectra for compounds 1-6, though we expect the condensed phase spectra to more accurately reflect the phase states of the compounds present in the collected particle-phase SOM (see Figures S3.2 and S3.4 for vapor phase spectra).²² ²We first compare the condensed phase C-H spectra of the β - caryophyllene oxidation products and the β -caryophyllenederived SOM surfaces in the ssp versus ppp polarization combinations. The *ssp*-polarized SFG spectrum of β -caryophyllene-derived SOM contains two distinct peaks around 2943 and 2860 cm^{-1} (Figure 2). Comparison to the *ssp*-polarized spectra of the oxidation products reveals that all compound spectra also display these two peaks at approximately 2940 ± 5 and 2860 ± 5 cm⁻¹. An additional peak centered between 2902 and 2912 cm^{-1} , which is not present in the SOM spectrum, is observed in the spectra of β -caryophyllene, β -nocaryophyllone aldehyde (2), β -nocaryophyllonic acid (4), and both diacid compounds 5 and 6. The spectra of β -nocaryophyllone aldehyde (2) and β nocaryophyllinic acid (6) also contain a 2963 cm^{-1} peak not observed in the other spectra. In contrast to the other compounds, the *ssp*-polarized SFG spectra of β -caryophyllene aldehyde (1) and β -caryophyllonic acid (3) contain only two prominent peaks near 2943 and 2860 cm⁻¹, though β caryophyllonic acid (3) shows a small peak around 2902 cm⁻¹. The *ppp*-polarized SFG spectrum of β -caryophyllenederived SOM contains one distinct peak centered at 2947 cm⁻¹, while the *ppp*-polarized SFG spectra of compounds 2 and 6 contain an additional prominent peak around 2964 cm⁻¹. The *ppp*-polarized spectra of compounds 1, 3, 4, and 5 as well as β caryophyllene, however, also contain one identifiable peak, though the spectra of β -caryophyllene and compound 4 contain a possible shoulder near 2920 cm^{-1} . As in the *ppp*-polarized SFG spectrum of β -caryophyllene-derived SOM, one prominent peak centered at 2947 cm⁻¹ is observed in the ppp-polarized SFG spectra of compounds 1 and 3.

The *ssp*- and *ppp*-polarized SFG spectra in the C–H stretching region show a best match for β -caryophyllene aldehyde (1), as it most closely resembles the *ssp*- and *ppp*-polarized SFG spectra of the β -caryophyllene-derived SOM. β -Caryophyllonic acid (3) is an additional close spectral match. As discussed earlier, we recently found that β -caryophyllene aldehyde (1) exhibits the highest surface activity in aqueous droplets within the synthesized suite of β -caryophyllene oxidation products, with β -caryophyllonic acid (3) as the second most surface active compound in the series.⁵ While surface-specific measurements of aqueous media are not directly comparable to those in organic SOM, it may be speculated, based on our SFG results, that compounds 1 and 3 exhibit a higher propensity to populate the surface of SOM than the other compounds studied.

3.2. Comparison of SFG Spectra of β -Caryophyllene-**Derived SOM and Oxidation Products: Carbonyl** Stretches. Applying our spectral analysis in the C=O stretching region, albeit on calcium fluoride (given its transparency in this infrared region), we find (Figure 3) the following: The SFG spectrum of the β -caryophyllene-derived SOM is remarkably simple, as it contains only one broad peak centered at ~1730 cm⁻¹. Few spectral differences are observed in the oxidation product spectra compared to that of the β caryophyllene-derived SOM, with the exception of a slight mismatch between the spectral shape and center peak frequency in the SOM and compound 4 spectra in the C=O region. Additionally, the SFG spectrum of diacid compound 6 contains a possible shoulder around 1690 cm^{-1} , which is in contrast to the other spectra. These spectral differences suggest that compounds 4 and 6 may not populate the surface of β caryophyllene-derived SOM, lending further support to our conclusions from the interfacial tension measurements and the



Figure 3. Standard resolution *ssp*-polarized SFG C==O spectra of synthetic β -caryophyllene-derived SOM on calcium fluoride (black trace) compared to β -caryophyllene and synthesized β -caryophyllene oxidation products (1–6) spin-coated onto calcium fluoride. All maximum SFG intensities have been normalized to 1 and offset for clarity.

ssp- and *ppp*-polarized SFG spectra we collected in the C–H stretching region (*vide supra*).

The SFG spectra of compounds 1, 2, 3, and 5 all contain a broad peak centered near 1730 cm⁻¹, which matches closely to the SFG spectrum of β -caryophyllene-derived SOM. The absence of prominent spectral differences in the C=O region suggests the insensitivity of this region for identifying carbonyl groups on SOM derived from β -caryophyllene with chemical specificity. Yet, this same insensitivity offers the opportunity to test generically for the presence of carbonyl groups at the interface by SFG spectroscopy. While the C=O data alone cannot help to distinguish which oxidation products may populate the surface of the SOM, the C-H spectra reveal more notable spectral variances in the oxidation products compared to the SOM.

A thorough analysis of spectral assignments in the C=O region that is based on comparison to carbonyl standards is forthcoming. β -Caryophyllene was also measured as a control and showed no C=O signal by SFG, as expected. We note that the oxidation products gave negligible signal in the *ppp* polarization combination in the C=O region. We caution that the *ppp* signal may have an incident angle dependence,¹²⁰ and indeed in forward scattering geometries, for instance,

nonzero *ppp* signal intensities may be detected, though such additional orientational analyses are beyond the scope of this study. Taken together, the C–H and C==O data reveal that the spectrum of β -caryophyllene aldehyde (1), as well as that of β -caryophyllonic acid (3), spectrally resemble the β -caryophyllene-derived SOM surface to the largest degree out of the suite of compounds studied herein.

3.3. Analysis of Phase-Resolved Spectra and Intensity Spectra Using DFT Calculations. Accounting for Fermi resonances as determined by our DFT calculations, we obtain similar mode assignments for the dominant peaks in the experimental SFG spectra of the compounds studied here (Table 1). These assignments resemble those of α -pinene, a

Table 1. General Vibrational Mode Assignment for Oxidation Products of β -Caryophyllene with Largest Signal Intensities as-Calculated by Fermi Resonance-Corrected DFT

scaled vibrational frequency [cm ⁻¹]	vibrational mode
~2940	CH ₂ -symmetric (ring)
~2860	CH ₃ -symmetric (ring)

molecule that has some similar structural motifs (geminal methyl groups on a four-membered ring) to the compounds studied here.^{117,121} Specifically, by SFG and DFT, it was found that a majority of the peak intensity in the SFG spectrum of α -pinene was due to contributions of the methylene group within the four-membered ring, which also exhibited the longest vibrational decoherence lifetimes.⁹⁶ There are likely some lower intensity vibrational modes present in the spectrum, but this general assignment holds for the compounds studied here for the dominant peaks.

The phase-resolved SFG spectra are rather similar across oxidation products 1–4; therefore, we include a representative *ssp*-polarized phase-resolved SFG spectrum of β -caryophyllene aldehyde (1) on α -quartz at an azimuthal angle of 0° in Figure 4A. The interference (difference) SFG spectrum shows a positive peak at 2950–2960 cm⁻¹, a negative peak from 2910–2940 cm⁻¹, and a small negative peak near 2850–2880 cm⁻¹. Based on the vibrational mode assignments and the azimuthal angle of quartz, we identify the sign of $\vec{\chi}_{S,Im}^{(2)}$ and therefore deduce the orientation of the four-membered ring on β -caryophyllene aldehyde (1) (and, by extension, that of the other oxidation products) at the quartz surface (please see Supporting Information section S.5.3). From our analysis, the negative interference peaks indicate that both the CH₂ and CH₃ groups on the cyclobutane ring face away from the surface.

In addition to an "up" vs "down" determination of the discussed stretches on the cyclobutane ring given by the phase-resolved SFG results, a hybrid experimental/DFT method previously published for simulating SFG spectra and carrying out conformational analysis^{110,111} was used to determine the molecular orientation that gives the best matched SFG spectrum (Figure 4B) to the high resolution C–H spectrum of compound 1 spin-coated on fused silica. With this information in mind, the probable orientation of β -caryophyllene aldehyde (1), and by extension, the remaining oxidation products studied, is given in Figure 4C. This orientation is reasonable for a somewhat amphiphilic molecule as it enables hydrogen bonding of the oxygenated groups to the Si–OH groups on the quartz surface. We were unable to obtain phase-resolved spectra within the C= O stretching region; however, the negligible *ppp*-polarized signal



Α

Δا_{SFG} [a.u.]

Figure 4. (A) Phase-resolved *ssp*-polarized SFG spectrum of β -caryophyllene aldehyde (1) on α -quartz with quartz oriented at $\Phi = 0^{\circ}$. (B) Best matched SFG simulation (purple trace) overlaid to experimental high resolution spectrum (black trace) of compound 1 (spin-coated on fused silica). (C) Proposed orientation of β -caryophyllene aldehyde (1) on the α -quartz surface based on phase-resolved data and comparison of calculated vs experimental SFG spectra (tilt and twist angles of the assigned *Z*-axis with respect to surface normal (black arrow) are 70° and 110°, respectively).

intensities suggest that the C=O functional groups within the molecule are aligned nearly perpendicular to the surface, resulting in strong *ssp*-polarized signal intensities. Note that polarization intensity ratio analyses⁹² using the *ssp*- and *ppp*-polarized C–H spectra in Figure 2 were unsuccessful due to minimal *ppp* signal for the isolated 2860 cm⁻¹ CH₃-symmetric (ring) stretch (see Figure S3.1 in the Supporting Information). Altogether, the orientation analysis of complex molecules on a model surface enabled here by phase-resolved SFG measurements opens the possibility to carry out such analyses on the surfaces of synthetic and field-derived SOM.

4. ATMOSPHERIC IMPLICATIONS AND CONCLUSIONS

This work integrates organic synthesis, aerosol synthesis and collection, DFT calculations, and SFG spectroscopy to search for the presence of sesquiterpene-derived oxidation products, specifically those derived from β -caryophyllene, on the surfaces of synthetic SOM. Polarization-resolved SFG spectra of β -caryophyllene aldehyde (1), along with β -caryophyllene-derived SOM, both in the C–H and the C=O stretching regions, but especially the former. These two compounds also appear to be the most surface active out of the series based on our previously reported dynamic surface tension measurements, as they lead to the largest depressions of interfacial tension in aqueous droplets.⁵

The present study cannot unequivocally identify the oxidation products on the β -caryophyllene-derived SOM surface, though a comprehensive compositional analysis of the SOM examined herein is forthcoming. Nevertheless, β -caryophyllene aldehyde (1) and β -caryophyllonic acid (3) have previously been positively identified in several nonsurface-specific ambient field $SOM^{52,55}$ and laboratory β -caryophyllene ozonolysis^{53,54,122} studies. Considering thermal methods such as GC/ MS^{53,55} and SV-TAG⁵² may cause decomposition,¹²³ one possible caveat is that compounds 1 and 3 actually could have formed as analytical artifacts in such studies. Yet, these compounds have also been detected using ESI-MS coupled with liquid chromatography,^{54,122} which does not rely on high temperature conditions, supporting their existence as β caryophyllene oxidation products detected in SOM. Furthermore, we note that compounds 1 and 3 bear an intact alkene adjacent to the cyclobutane ring, allowing them to potentially further react in the presence of atmospheric ozone. Yet, the rate constant of the endocyclic alkene is \sim 100 times greater than that of the exocyclic double bond.⁵⁴ Therefore, we presume that β caryophyllene aldehyde (1) and β -caryophyllonic acid (3) may still serve as important SOM constituents given their high surface activities, even considering their possibly limited lifetimes as first generation products in the atmosphere. We note that the potential presence of highly oxidized multifunctional compounds (HOMs), an important yet elusive class of SOA constituents,^{1,70,78,124,125} was not considered because of (1) the likelihood of decomposition of HOMs in the SOM upon shipping, handling, and spectroscopic analysis, and (2) the significant challenges that would arise in the synthesis of such standards given their reported instabilities and relatively short lifetimes. $^{126-128}$

Our current and recent studies⁵ provide concrete lines of evidence supporting that SOM surfaces may be disproportionately populated by a minority subset of compounds that exhibit amphiphilic or surfactant-like properties. We caution that mismatches between the spectra of the other compounds and that of the SOM may be due to a lack of surface activity of these molecules and therefore a propensity to sit in the bulk of the particles. Although mismatches presumably could be due to surface oscillator orientation changes within the SOM, we do not expect diffusion that may cause molecular orientation changes within the β -caryophyllene-derived particles to be likely at the ambient laboratory relative humidity (RH) conditions (~40% RH) used in this study.¹²⁹ Additionally, orientation analysis by phase-resolved SFG spectroscopy reveals a "pincerlike" configuration of the β -caryophyllene oxidation products, albeit on a model quartz surface, that somewhat resembles the orientation of double-tailed surfactants at the surfaces of biological systems. This configuration orients the cyclobutane moiety away from the surface, enabling hydrogen bonding of the terminal oxygenated functional groups to the quartz substrate. Though quartz serves as a distant model system for an actual aerosol particle surface, an analogous orientation at a particle surface may be promoted by the presence of water, inorganic salts, highly oxidized molecules, or any other plausible constituents that could induce polarity, charge density, or hydrogen bonding capabilities at the particle surface. Moreover, the "pincer-like" configuration adopted by the β -caryophyllene oxidation products suggests that the less polar moiety of a surface-localized oxidation product, such as those studied here, may be the first site-of-contact for a gas-phase molecule approaching an aerosol particle. Yet, similar investigations of additional SOM constituents are needed in order to fully realize the implications of understanding interfacial structure and orientation on the heterogeneous chemistry leading to particle

growth, cloud activation, and other aerosol processes in the atmosphere.

The observed close spectral matches between β -caryophyllene-derived SOM surfaces, β - caryophyllene aldehyde (1), and β -caryophyllonic acid (3) presented herein, and the high surface tension depression described previously⁵ for these same oxidation products open the possibility for revealing an intrinsically chemical origin for cloud activation. Indeed, the considerable surface activity points to a high likelihood that these molecules may occupy the surfaces of SOA particles formed from β -caryophyllene oxidation in the atmosphere. Taken together, the discussed interfacial tension and SFG results also suggest that the terpene-derived surfactant pool at SOA particle surfaces may be far less chemically complex than that present in the particle bulk. Such findings on the structure and orientation of terpene-derived oxidation products and their corresponding SOM at interfaces may improve our understanding of the drivers of heterogeneous processes at SOM surfaces containing such species and the influence they have on estimated cloud activation potentials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsearthspace-chem.8b00156.

Schematic of NU Solstice/TOPAS laser setup; IR and Raman spectra of synthesized oxidation products; supplementary C–H and C=O SFG spectra; nonlinear bulk responses from β -nocaryophyllinic acid upon crystallization; supplementary data for phase-resolved SFG experiments; details of SOM collection (PDF)

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Notes

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ACKNOWLEDGMENTS

A.G.B., H.M.C., and M.A.U. gratefully acknowledge NSF Graduate Research fellowships. M.A.U. also acknowledges a National Aeronautics and Space Administration Earth and Space (NASA ESS) fellowship and support from a P.E.O. Scholar Award. A.T. acknowledges support by the US Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Division of Materials Science and Engineering. F.M.G. gratefully acknowledges a Friedrich Wilhelm Bessel Prize from the Alexander von Humboldt Foundation. This work was supported by the National Science Foundation (NSF) under Grant No. CHE-1607640 and the Environmental Molecular Sciences Laboratory (EMSL) at Pacific Northwest National Laboratory (PNNL) under user project 49291.

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