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Towards the identification of molecular constituents associated with the surfaces of isoprene-derived secondary organic aerosol (SOA) particles

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Abstract. Secondary organic aerosol (SOA) particle formation ranks among the least understood chemical processes in the atmosphere, rooted in part in the lack of knowledge about chemical composition and structure at the particle surface, and little availability of reference compounds needed for benchmarking and chemical identification in pure and homogenous form. Here, we synthesize and characterize SOA particle constituents consisting of the isoprene oxidation products α-, δ-, and *cis-* and *trans-β*-IEPOX (isoprene epoxide), as well as syn- and anti-2-methyltetraol. Paying particular attention to their phase state (condensed vs. vapor), we carry out a surface-specific and orientationally selective chemical analysis by vibrational sum frequency generation (SFG) spectroscopy of these compounds in contact with a fused silica window. Comparison to the vibrational SFG spectra of synthetic isoprene-derived SOA particle material prepared at the Harvard Environmental Chamber yields a plausible match with *trans-β*-IEPOX, suggesting it is an abundant species on their surfaces, while the other species studied here, if present, appear to be SFG inactive and thus likely to be localized in a centrosymmetric environment, e.g., the particle bulk. No match is found for authentic SOA particle material collected at the site of the Amazonian Aerosol Characterization Experiment (AMAZE-08) with the surface SFG spectra of the compounds surveyed here, yet we cannot rule out this mismatch being attributable to differences in molecular orientation. The implications of our findings for SOA formation are discussed in the context of condensational particle growth and reactivity.

1 Introduction

Secondary organic aerosol (SOA) particles are important in the climate system as they can lead to significant negative radiative forcing, especially over the world's large forest ecosystems (Carlton et al., 2009; Kanakidou et al., 2005; Williams et al., 2011). Despite this prominent role, SOA particle formation ranks among the least understood processes in the atmosphere (Galbally et al., 2007; Goldstein and Galbally, 2007; Hallquist et al., 2009; Kanakidou et al., 2005; Riipinen et al., 2011), rooted in part in the limited knowledge about SOA chemical composition. Molecular studies (Claeys et al., 2009; Constantinescu et al., 2007; Docherty et al., 2005; Gao et al., 2010; Heaton et al., 2009; Kalberer et al., 2004; Kroll and Seinfeld, 2008; Lin et al., 2012; Müller et al., 2008; Tolocka et al., 2004; Yasmeen et al., 2010) aimed at bridging this knowledge gap support the hypothesis that the products formed from the gas-phase oxidization of biogenic volatile organic compounds react with one another or undergo further oxidation to form species with lower and lower vapor pressures, ultimately leading to SOA particle formation. Heterogeneous processes such as physisorption and surface reactions are important for conditions of condensational particle growth. The formation of larger particles through coagulative growth may also be largely influenced by processes occurring at the surfaces of the particles, especially under conditions of low relative humidity for which SOA particle material has been shown to be solid.

One key challenge in understanding SOA particle growth which is addressed in this present work is that little concrete evidence for chemical structures is available. Moreover, most

reference compounds needed for benchmarking and chemical identification in, for instance, mass spectrometric studies of SOA particles (Heaton et al., 2007, 2009) are not available in pure and homogenous form from commercial sources. A third challenge is that laboratory model studies typically begin with hydrocarbon precursors, such as isoprene or α-pinene, to form SOA particles, while field studies sample SOA particles at various stages along their formation pathway, which is currently unknown. Finally, few molecularly specific techniques exist that are appropriate for probing the particle–gas interface or the surfaces of samples of putative SOA particle constituents directly.

Here, we address these challenges by synthesizing and subjecting to physical and chemical analysis putative isoprene-derived SOA particle constituents. Our surface-selective spectroscopic analysis of these compounds is followed by comparison to synthetic SOA particles prepared at the Harvard Environmental Chamber (HEC) and to authentic SOA particles collected in a tropical forest environment, namely the Amazon Basin (Martin et al., 2010a), where isoprene oxidation by OH radicals has been reported to dominate SOA particle formation (Claeys et al., 2004; Martin et al., 2010b; Paulot et al., 2009; Pöschl et al., 2010). 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). As part of this work, we focus on the epoxides (Paulot et al., 2009) and tetraols (Claeys et al., 2004) that have been proposed to be present in the SOA particles and that are characterized by oxygen-to-carbon (O/C) ratios (Jimenez et al., 2009) that fall into the 0.4 ± 0.1 range typical for SOA particles in tropical forests (Ebben et al., 2012). Following a brief description of the synthesis and the analytical methods, we characterize the compounds prepared here by a variety of physical measurements and surface-selective spectroscopic probes. We collect polarization-resolved vibrational sum frequency generation (SFG) spectra of condensed-phase and vapor-phase samples of four epoxides and two tetraols in contact with a fused silica window. We compare the spectral responses from the tetraol and epoxide model compounds with those obtained from the natural and synthetic SOA particle samples that were collected on filter substrates and pressed against a fused silica window, and we discuss a possible match for the SFG response of one of the epoxides with that of the synthetic SOA particle material. We conclude our work by discussing how the approach described here will allow for the study of the SOA particle formation pathways from first- and second-generation oxidation products by effectively "fast-forwarding" through the initial reaction steps of particle nucleation via a chemically resolved approach aimed at testing
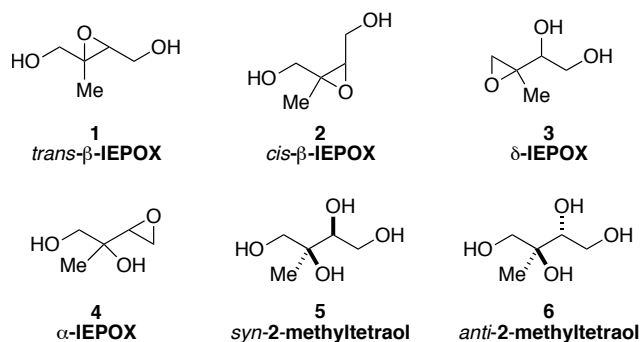
Fig. 1. Chemical structures of the isoprene-derived oxidation products synthesized and analyzed in this work.

the underlying chemical mechanisms of SOA particle formation.

2 Experimental

2.1 Synthesis of putative isoprene-derived SOA particle precursors

During the isolation and structural determination of naturally occurring molecules, concrete evidence for tentative structural assignments is often obtained by synthesizing the proposed structures in the laboratory. This need for de novo synthesis of putative structures is especially important when the compounds in question exist naturally in such small quantities that isolation of enough material for thorough spectroscopic analysis is not practical or even possible. In this respect, the numerous organic molecules formed in the atmosphere from naturally occurring isoprene represent a challenge due to difficulties associated with their collection in meaningful amounts (µg or mg amounts for offline analytical studies) and the complexity of the thus obtained mixtures. In order to perform physical studies on these putative species that are relevant to atmospheric processes, we sought to obtain a suite of pure chemical standards. To this end, we have accomplished the synthesis of six putative hydroxyl radical-mediated, isoprene-derived oxidation products (Fig. 1).

Epoxides 1–4 were synthesized in an analogous fashion to the procedures reported by Surratt and coworkers (Surratt et al., 2010). While all samples reported herein are racemic, efforts were made to prepare diastereomerically pure samples where possible.

The internal epoxides 1 and 2 were prepared in diastereomerically pure form starting from 3-methyl-2-buten-1-ol and 3-methyl furan-2(5*H*)-one, respectively. The terminal epoxides 3 and 4 were synthesized as 1:1 mixtures of inseparable diastereomers starting from 2-methyl-2-vinyloxirane. Tetraols 5 and 6 were prepared in diastereomerically pure form starting from protected *trans*- and *cis*-2-methylbut-2-ene-1,4-diols, respectively (Fontana et al., 2000; Surratt et

al., 2010). The procedures employed in these syntheses are described in further detail in the Supplement.

2.2 Synthetic and field-collected SOA particle material derived from isoprene

We compare the SFG spectra obtained from the epoxides and tetraols prepared here to those obtained from aerosol particles synthesized as a model system from the photochemical reaction of isoprene and OH radicals under low-NO conditions at the HEC (Chen et al., 2011; Ebben et al., 2011a), as well as from submicron-sized SOA particles collected in the central Amazon Basin during the Amazonian Aerosol Characterization Experiment (AMAZE-08) campaign (Martin et al., 2010a), chosen as an example of a tropical forest whose air is typically rich in isoprene. We thus expect the SFG spectra obtained from the surfaces of the synthetic and field-derived particles to be due to products of isoprene oxidation pathways. The approach for our analysis of SOA particle material prepared at the HEC and collected at the AMAZE-08 field site by SFG has been described in detail in our prior work (Ebben et al., 2012).

2.3 Vibrational sum frequency generation

The surface-specific probe employed here is based on a SFG setup that has been previously described (Buchbinder et al., 2009; Stokes et al., 2009a, c; Voges et al., 2005, 2007). Briefly, we utilize a Ti : S femtosecond laser system operating at 1 kHz repetition rate (Spectra Physics, Spitfire Pro). Half of the 800 nm output is used to pump an optical parametric amplifier (Spectra Physics, OPA 800C) for generating tunable broadband (full width at half maximum, or FWHM, of ~150 cm^{-1}) infrared (IR) light appropriate for covering the aromatic and aliphatic C–H stretching regions. At the sample surface, the IR light field is upconverted using a visible pump beam filtered with a narrow bandpass filter yielding an 800 nm pump pulse with a bandwidth of 1.57 nm. To avoid optical damage, the incident pulse energies and foci are limited to 2 μJ and 50 μm in diameter, respectively. Internal reflection geometry, in which the incident light fields pass through the fused silica window to reach the sample interface, is utilized in all experiments. The ssp polarization combination that is employed in these experiments probes those components of the vibrational transition dipole moments that are oriented perpendicular to the solid substrate. SFG experiments are repeated several times from at least two different sample spots for spin-coated samples, or from vapor samples prepared separately. Spectra shown in this work are averages of the individual spectra. The Supplement shows the individual spectra for the various compounds under investigation in this work. 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. The full C–H stretching frequency region is analyzed with a hybrid scan-

ning/broadband method pioneered by Walker and coworkers (Esenturk and Walker, 2004). Spectra are collected for 7 acquisitions lasting 2 min each, in order to increase the signal-to-noise ratio. SFG spectra are referenced to the SFG response from a gold substrate to account for the energy distribution in the incident IR pulse, and the frequencies are calibrated using a polystyrene standard (ICL Crystal Laboratories).

2.4 Sample configurations

The synthetic epoxide and tetraol samples were analyzed at room temperature by SFG by contacting a fused silica window with (a) their equilibrium vapor pressure (Lide, 1997) and (b) their condensed phase following spin coating of the sample dissolved in deuterated methanol. Synthetic SOA particle material, condensed over the course of several days onto 50 nm-sized ammonium sulfate seed particles during the reaction of isoprene and OH radicals at the HEC and subsequently collected on Teflon filters as described in our earlier work (Ebben et al., 2011a), was probed by SFG by pressing a fused silica window against a Teflon filter containing SOA particle material (Ebben et al., 2011b, 2012). Finally, field-derived SOA particle material, collected on nucleopore impactor substrates sampled using a micro-orifice uniform-deposit impactor (MOUDI) (Marple et al., 1991) in the central Amazon Basin from 9 April 2008 to 17 April 2008 at the site of the AMAZE-08 campaign (Martin et al., 2010a), was probed by SFG in the same way as the synthetic SOA particle material prepared at the HEC. Before collecting an SFG spectrum, all fused silica substrates were rinsed and sonicated in methanol and Millipore water, nitrogen- and oven-dried, and plasma-cleaned prior to exposure to samples. Substrates not exposed to sample compounds showed no evidence of C–H stretches.

In the window–vapor experiments of the epoxides, a volume of approximately 30 μL of sample was injected through a syringe into the void space of a custom-built Teflon sample cell having an opening against which a fused silica window was sealed using an O-ring. Vapor experiments with the gel-like tetraol samples were carried out by spreading a gel drop of the sample at the bottom of a fused silica window. Following the introduction of the sample to the sample cell and window, the vapor of the condensed-phase samples was allowed to equilibrate in the void space of the cell. In this configuration, the incident laser fields did not illuminate the condensed-phase sample.

In addition to window–vapor experiments, all of the compounds were dissolved to 100 mM in deuterated methanol and then spin-coated directly onto fused silica windows, which were then placed against the sample cell with an O-ring. In this configuration, the incident laser fields did illuminate the spin-coated film.
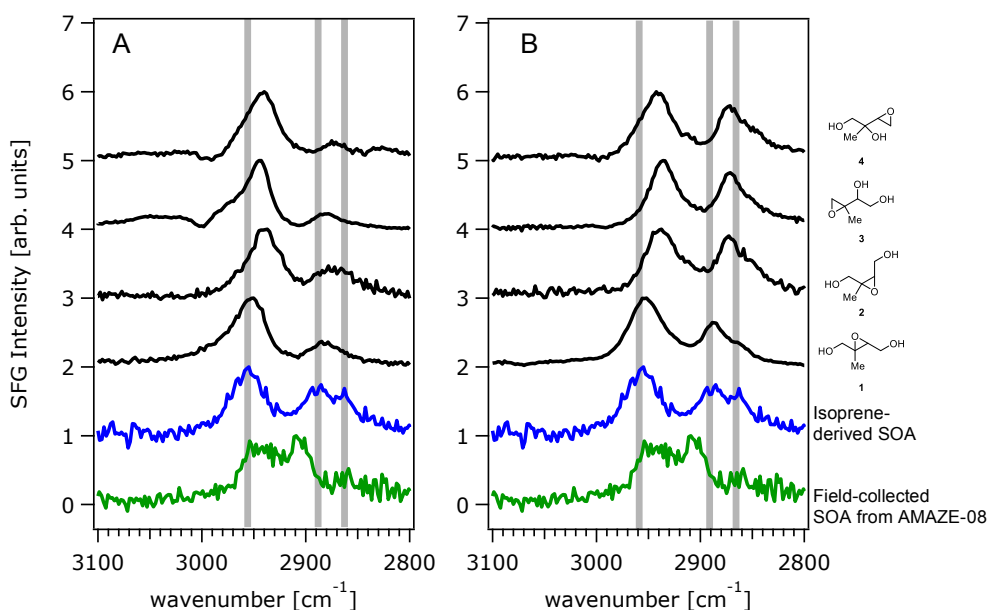
Fig. 2. ssp-Polarized SFG spectra of vapor-phase (left) and spin-coated (right) epoxides in contact with fused silica and comparison to synthetic isoprene-derived SOA particles (blue) and SOA particles collected in the central Amazon Basin (green). From top: α-IEPOX (4), δ-IEPOX (3), cis-β-IEPOX (2), trans-β-IEPOX (1), synthetic isoprene-derived SOA, and natural SOA from the central Amazon Basin. Gray vertical lines indicate (from left) CH$_3$ asymmetric, CH$_3$ symmetric, and CH$_2$ symmetric stretches. Spectra are offset for clarity.

3 Results and discussion

3.1 Phase states

There exists a keen interest in determining the phase state of SOA particles, 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 (Renbaum-Wolff et al., 2013; Virtanen et al., 2010). 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.

We find that each of the epoxides is a liquid at room temperature, becoming increasingly viscous (but not solid) with lower and lower temperatures down to −40 °C. The two tetraol compounds described in this work are also not solid at room temperature. However, in contrast to the epoxides that form them, they are gel-like down to −40 °C. The gel state made it difficult to handle the tetraols with a syringe. As described in the prior section, the vapor experiments with the tetraol samples were therefore carried out by spreading a gel drop of the sample at the bottom of a fused silica window,

followed by equilibration of the vapor in the space between the window and the cell. Room-temperature vapor pressures over the epoxides and tetraols – and their binding constants for interaction with the solid fused silica substrate – are evidently high enough to produce the sizable SFG responses at the vapor–solid interface reported here.

3.2 Vibrational sum frequency generation spectra

Figures 2a, b and 3a, b summarize our findings from carrying out ssp-polarized vibrational SFG spectroscopic analyses of the epoxides and tetraols in the two phase states studied here (vapor and condensed phase), of isoprene-derived synthetic SOA particle material, and of field-derived SOA particles in the 1.0 μm size fraction. The latter was chosen as a representative spectrum of PM1-sized (i.e., below 1 μm in diameter) SOA particles collected during AMAZE-08 (Ebben et al., 2012). Using our sample storage procedures, SFG spectra of the isoprene-derived synthetic SOA particle material do not change over the duration of three years, as shown in the Supplement. The following two sections discuss the results obtained from the epoxides and the tetraols, and the last section compares the results to those obtained from the synthetic and field-derived SOA particle samples. 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 nonzero, 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.

3.3 Epoxides

Figure 2a shows that a peak at $2955 \, \text{cm}^{-1}$ dominates the SFG spectra of fused silica windows in contact with the vapor-phase epoxides. The spectra also exhibit smaller signal contributions around $2880 \, \text{cm}^{-1}$. SFG responses from methyl groups of long-chain hydrocarbons usually occur at $2960 \, \text{cm}^{-1}$ and $2940 \, \text{cm}^{-1}$, attributable to the Fermi resonance of the CH_3 asymmetric stretch with a CH_3 bending overtone and the CH_3 asymmetric stretch (Chen et al., 2002; Miranda and Shen, 1999; Opdahl et al., 2002), and at $2880 \, \text{cm}^{-1}$, which is attributable to the CH_3 symmetric stretch (Conboy et al., 1997, 1998; Miranda and Shen, 1999). These SFG responses are typically the dominant and most intense features in the SFG spectra of hydrocarbons. We therefore attribute the strong peak near $2955 \, \text{cm}^{-1}$ to the asymmetric methyl stretch and/or its Fermi resonance and the smaller peak near $2880 \, \text{cm}^{-1}$ to the symmetric methyl stretch. However, the molecules studied here also contain one or two hydroxyl-substituted methylene groups. SFG spectra of analogous ethanolic methylene groups within a series of alcohols have been reported in one study by Wang and coworkers to exhibit a symmetric stretch at $2886 \, \text{cm}^{-1}$ and a Fermi resonance at $2974 \, \text{cm}^{-1}$ (Lu et al., 2004), located where the SFG spectra of the epoxides studied here also show some intensity. Epoxides 3 and 4 also contain a vicinal diol moiety having one methylene group. The SFG responses from this methylene group may be compared to those reported by the Wang group for the two methylene groups at the glycol–vapor interface (Lu et al., 2004), for which symmetric and asymmetric stretches occur at $2870 \, \text{cm}^{-1}$ with strong intensity and at $2900 \, \text{cm}^{-1}$ with quite low intensity, respectively, along with a Fermi resonance having medium signal intensity at $2938 \, \text{cm}^{-1}$. The SFG spectra reported here exhibit SFG signal intensity at these frequencies, but the contributions are either not well resolved spectroscopically or overlap with the strong SFG responses produced by the methyl group.

The SFG spectra of epoxides 3 and 4 show some intensity between 3050 and $3020 \, \text{cm}^{-1}$. In SFG spectroscopy, this frequency region is typically associated with aromatic C–H groups (Hommel and Allen, 2003; Kawaguchi et al., 2012), or vinylic groups (Buchbinder et al., 2009; Stokes et al., 2008, 2009a, b), which are not present in these two species. While the SFG responses observed from epoxides 3 and 4 between 3050 and $3020 \, \text{cm}^{-1}$ are weak, they are likely to indicate the presence of the single methylene group attached to the strained epoxide ring structure in these compounds:

previous SFG studies have shown that as the number of carbon atoms in a cyclic hydrocarbon decreases, and the C–C single bonds become increasingly strained, the vibrational frequencies of the methylene symmetric stretches shift beyond $3000 \, \text{cm}^{-1}$ (Buchbinder et al., 2011). Furthermore, the IR spectra of bromocyclopropane (Diallo and Waters, 1988), cyclopropane-d_1 (Diallo and Waters, 1988), cyclopropane-1,1-d_2 (Keeports and Eggers, 1984), cyclopropane 1,1,2,2-d_4 (Keeports and Eggers, 1984), and cyclopropane (Diallo and Waters, 1988; Spiekermann et al., 1980) all show vibrational responses beyond $3000 \, \text{cm}^{-1}$. 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). Based on these literature reports, we assign the peak at $\sim 3020 \, \text{cm}^{-1}$ that is exhibited by epoxides 3 and 4 to the symmetric stretching mode of the single methylene group in the epoxide motif of these molecules.

Finally, the epoxides studied here all contain one methine group, which is generally observed by SFG at a frequency of approximately $2900 \, \text{cm}^{-1}$ (Buck and Himmelhaus, 2001; Lu et al., 2005). The SFG spectra shown in Fig. 2a and b exhibit little intensity at those frequencies, indicating that the contributions from the methine group in the epoxides are quite weak.

From our spectral analysis, we conclude that the epoxides studied here produce SFG signals that are mainly due to their CH_3 asymmetric stretch and/or Fermi resonance, with minor contributions from the CH_3 symmetric stretch and some contribution from the methylene groups, depending on whether the epoxide ring is internally or terminally located.

As described in the experimental section, the SFG experiments were also carried out by spin-coating the same IEPOX samples in deuterated methanol onto fused silica windows. Figure 2b shows increased SFG signal intensity in the symmetric stretching region (i.e., below $2900 \, \text{cm}^{-1}$) for all compounds analyzed when compared to Fig. 2a. Generally, the ratio of the SFG signal intensities from the symmetric and the asymmetric stretching modes of a methyl group informs on that group's molecular tilt angle (Yang et al., 2002). The increased SFG signal intensity obtained from the methyl symmetric stretching mode suggests that the C_{3v} symmetry axes of the methyl groups of the four epoxides studied here are tilted much more towards the surface normal for the spin-coated samples than for the vapor-phase samples. The ratio of the SFG signal intensities from the symmetric and the asymmetric stretching modes may thus be used as a marker for distinguishing vapor samples from condensed-phase samples in contact with the fused silica windows. Finally, the contributions from the strained methylene group in epoxides 3 and 4 that we observed above $3000 \, \text{cm}^{-1}$ in the window–vapor experiments are much weaker, if present at all, in the condensed-phase samples. Moreover, well-resolved spectral features at the frequencies associated with ethanolic or glycolic methylene groups are not observed in Fig. 2b. Taken
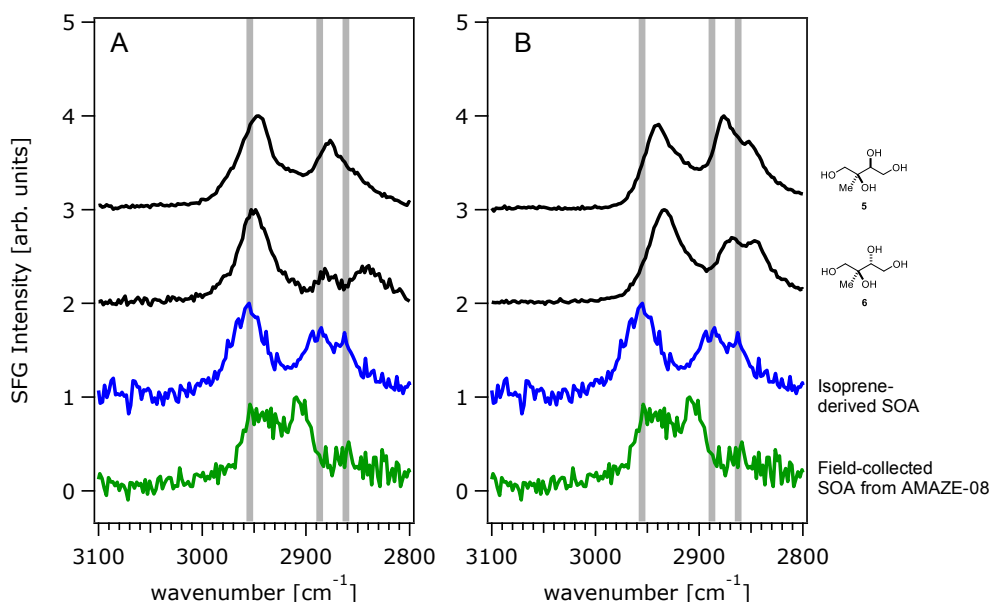
Fig. 3. ssp-Polarized SFG spectra of vapor-phase (left) and spin-coated (right) 2-methyltetraols in contact with fused silica and comparison to synthetic isoprene-derived SOA particles (blue) and SOA particles collected in the central Amazon Basin (green). From top: *syn*-2-methyltetraol (5), *anti*-2-methyltetraol (6), synthetic isoprene-derived SOA, and natural SOA from the central Amazon Basin. Gray vertical lines indicate CH$_3$ asymmetric, CH$_3$ symmetric, and CH$_2$ symmetric stretches. Spectra are offset for clarity.

together, our findings indicate significant restructuring of the epoxides at the fused silica windows employed here depending on whether they are in the condensed or vapor phase.

3.4 Tetraols

As mentioned in the Introduction, ongoing reactions with hydroxyl radicals under acidic low-NO$_x$ conditions can lead to the formation of 2-methyltetraols from IEPOX precursors, which may be part of SOA particle material. We therefore analyzed two tetraols, 5 and 6, which are *syn*- and *anti*-diastereomers of one another. Just like in the case of the epoxides, we carried out our analysis for vapor and spin-coated tetraol compounds in contact with fused silica windows (Fig. 3a, b).

As expected, neither tetraol shows appreciable SFG signal intensity at frequencies exceeding 3000 cm^{-1}, which is consistent with the absence of aromatic, vinylic, or strained methylene groups in these tetraols. Similar to the epoxides, the SFG spectra of the vapor of tetraols 5 and 6 display a dominant feature at 2946 and 2953 cm^{-1}, respectively, which we attribute to the methyl asymmetric stretch and/or Fermi resonance of the methyl group in the tetraols for the reasons outlined above. As in the case of the epoxides, the methyl symmetric stretching contribution to the SFG spectra increases – quite substantially in fact – when the samples are spin-coated as opposed to present in the vapor phase. Furthermore, while *syn*-2-methyltetraol (5) features only one peak in this region at 2880 cm^{-1}, *anti*-2-methyltetraol (6) shows an additional fairly well resolved

contribution at 2840 cm^{-1}, which we attribute here to contributions from the symmetric methylene C–H stretches for the reasons outlined above. Just like the epoxides, the two tetraols studied here contain one methine group. Unlike for the epoxides, however, the SFG spectra of the tetraols in contact with the fused silica windows (except for the tetraol 6 vapor) exhibit significant SFG signal intensity at 2900 cm^{-1}, which is where methine stretches have been reported to occur (Buck and Himmelhaus, 2001; Lu et al., 2005). Finally, we find that the SFG spectra obtained from the fused silica surface in contact with the room-temperature equilibrium vapor pressure above a drop of tetraol 5 are about two to three times higher in intensity than those obtained from tetraol 6. This finding could be due to a less ordered interfacial structure in terms of the methyl and methylene oscillators, or due to a lower vapor pressure of the *syn*-(5) vs. the *anti*-tetraol (6).

3.5 Comparison to synthetic and field-derived SOA particle material

In this section, we compare the SFG spectra obtained from epoxides (1–4) and tetraols (5 and 6) to those obtained from synthetic and field-derived SOA particle material. We report and discuss a possible match in the SFG spectra obtained from one of the model compounds and the synthetic SOA particle samples, which allows for an improved understanding of what functional groups may be present at the surfaces of the SOA particles. Furthermore, comparing the particle spectra with those obtained from the gas- and

condensed-phase samples yields information on the molecular environment of the functional groups that may be present on the particle surfaces.

Our previously published work reported that the SFG spectra obtained from fused silica windows in contact with the equilibrium room-temperature vapor pressures of α-pinene, β-pinene, limonene, isoprene, *cis*-2-pentene, *n*-hexene, *n*-pentene, cyclohexene, and cyclopentene did not agree with those obtained from the AMAZE-08 particle samples or the synthetic isoprene-derived SOA particle samples prepared at the HEC (Ebben et al., 2011a). In the context of our current work, Figures 2 and 3 show that the vibrational SFG spectra of the epoxides and tetraols studied here do not match those obtained from the surfaces of field-derived SOA particles collected during AMAZE-08 either. Figure 2a, however, shows some reasonable agreement between the SFG spectra obtained from the vapor-phase–window interface of epoxide 1 and the synthetic SOA particle material–window interface. Most importantly, this compound is the only one whose $2952\,\mathrm{cm}^{-1}$ peak position matches that of the synthetic SOA particle material, which occurs at $2955\,\mathrm{cm}^{-1}$, and whose methyl and methylene symmetric C–H stretches at 2880 and $2850\,\mathrm{cm}^{-1}$, respectively, are also reasonably well matched. An even better match is found for the SFG spectrum of the spin-coated *trans*-β-IEPOX–window interface and the synthetic SOA particle material–window interface. In contrast to the results obtained from epoxide 1, epoxides 2, 3, and 4 at the vapor–window interfaces exhibit SFG peak positions at 2941, 2945, and $2940\,\mathrm{cm}^{-1}$, respectively, and these frequency positions do not agree with those obtained from the synthetic or the natural isoprene-derived SOA material. This result suggests that the surface of spin-coated epoxide 1 is a reasonable representation of the surfaces of the isoprene-derived SOA particles, at least as probed by SFG in the C–H stretching region.

Figure 3 shows that the analogous comparison between the SFG spectra obtained from tetraols 5 and 6 and the synthetic and field-derived SOA particle samples does not result in a reasonable match in the asymmetric C–H stretching region near $2955\,\mathrm{cm}^{-1}$ except for perhaps the case of the vapor–window interface of tetraol 6. The symmetric C–H stretching region, however, is not well matched. We conclude that the SFG spectra of the fused silica windows containing the condensed-phase – i.e., spin-coated – tetraols do not match those obtained from the synthetic or field-derived SOA material.

4 Spectral fitting and molecular orientation analysis

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). By utilizing the ssp and ppp polarization combinations via the polarization intensity ratio method (Buchbinder et al., 2011; Moad and Simpson, 2004; Wang et al., 2005), the tilt angle of the C_{3v} symmetry axis and the associated distribution width of the methyl group of *trans*-β-IEPOX (epoxide 1) with respect to the surface normal were predicted. This molecule was chosen because the spectra of this molecule provide the best match to isoprene-derived SOA under both vapor and spin-coated conditions. Briefly, each spectrum was fit with a combination of in-phase and out-of-phase Lorentzian peaks, representing the symmetric and asymmetric C–H stretching vibrational modes of the one methyl and the two methylene groups, as well as Fermi resonances that may be present (see details of the fitting procedures and outcomes in the Supplement). The fits show that the SFG responses are due to the asymmetric and symmetric methyl stretches and a methyl Fermi resonance and not due to the asymmetric and symmetric methylene stretches (or their Fermi resonance).

As shown in the Supplement, spectral fitting yielded a point estimate and standard error for the amplitudes of the methyl symmetric stretch, located near $2880\,\mathrm{cm}^{-1}$, for each polarization combination. Based on the spectral fits to the experimental SFG spectra, we determined a point estimate and standard error, in parentheses, of the ppp/ssp amplitude ratio of 0.31(5). In a separate step, theoretical values of χ_{ppp}/χ_{ssp}, where χ is the second-order susceptibility of the system under investigation for each of the two polarization combinations, were computed for a range of molecular tilt angles based on the optical properties of the system and assuming monomodal Gaussian distributions ranging from 1 to $40°$ (at FWHM). These theoretical ratios are plotted as a function of tilt angle (Fig. 4). The set of angles for which the theoretical values for each orientation distribution overlap with the experimentally determined values is then the range of molecular tilt angles of the methyl group with respect to the surface normal. Further information on this method of analysis is provided in the Supplement.

Assuming a $1°$ distribution, which corresponds to all of the methyl C_{3v} axes being aligned to within $1°$ of one another, the tilt angle would be $40°$ from the surface normal (Fig. 5). Including the range of amplitude ratios within standard error opens up this cone of tilt angles to a range of 27–$52°$ for vapor phase epoxide, and tilt angles from 0 to $90°$ are possible when the Gaussian distribution width is broadened to $40°$ FWHM.

The second radial plot indicates possible tilt angles for the C_{3v} axis of the methyl group in spin-coated epoxide 1. Based on the spectral fits to the experimental SFG spectra, we determined a point estimate and standard error of the ppp/ssp amplitude ratio of 0.39(9). The standard error for this point estimate encompasses all theoretically possible tilt angles, but the point estimate itself results in tilt angles ranging from 53 to $65°$. The tilt angles obtained for the methyl group of epoxide 1 in the condensed phase are comparable, albeit somewhat larger, to those obtained for the vapor–fused silica case. This result indicates that the tilt angle of the methyl group in
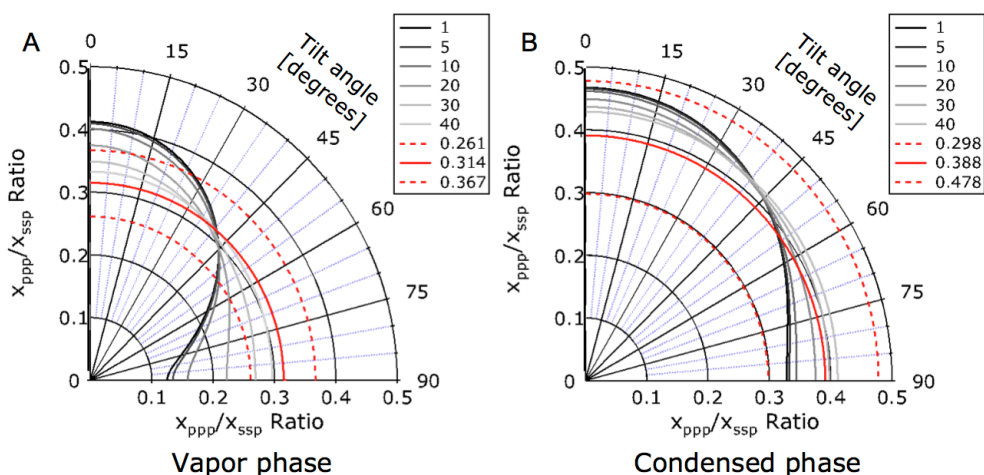
Fig. 4. Radial plots indicating methyl C_{3v} tilt angle as a function of χ_{ppp} / χ_{ssp} amplitude ratio of the methyl symmetric stretching mode for vapor (left) and spin-coated (right) *trans-β*-IEPOX (1) calculated as described in the text. Solid red curves indicate the experimentally determined ratio point estimates, and dashed red curves indicate the standard errors of these ratios. Gray curves indicate theoretically calculated monomodal Gaussian orientation distributions of widths ranging from 1 to 40°.
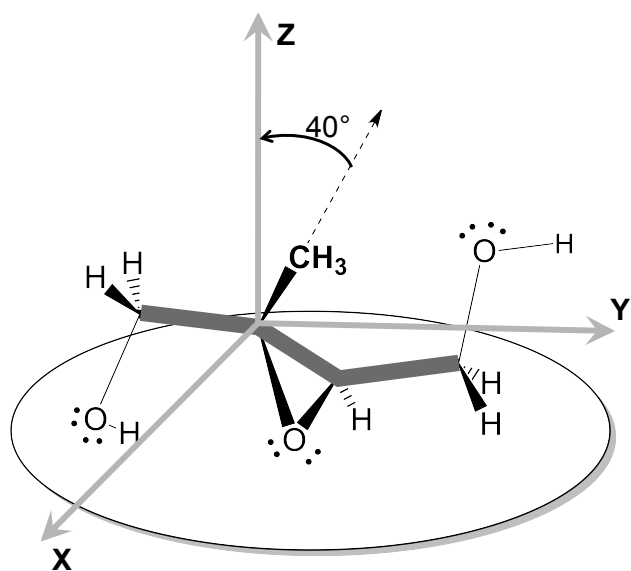
Fig. 5. Proposed model of *trans-β*-IEPOX (1) molecular orientation on a surface. The surface normal is located along the *z* axis, with a 40° methyl tilt angle. The rigid backbone of the molecule due to the epoxide ring is indicated by a thick gray line.

trans-β-IEPOX (1) depends only weakly on the phase state. We conclude from this result that the phase state which *trans-β*-IEPOX (1) is in might influence the SFG spectra by influencing the orientation distribution of oscillators other than the methyl symmetric stretch. Such an influence of phase state on the SFG spectra is indeed observed for the molecules probed here, including *trans-β*-IEPOX (1). We then conclude that the spectral, as opposed to orientational, analysis discussed in section 3.2.3 suggests that, if synthetic isoprene-

derived SOA particle material is in fact well represented by *trans-β*-IEPOX (1), its methyl group is likely to be in an environment resembling a condensed phase, rather than a vapor phase.

Based on the radial plots and on observations from the spectral fits of our SFG data, we gain additional insight into the orientation of *trans-β*-IEPOX (1) at the fused silica surface. The absence of symmetric and asymmetric methylene contributions in the spectral fits (vide supra and the Supplement) may indicate that the two methylene groups are trans-configured to one another, so that their SFG responses cancel out through destructive interference. The rigid carbon backbone of this molecule, shown in Fig. 5, would allow for the existence of a strong coupling mechanism for the vibrational coherences probed by SFG. Similar long-range coupling and phase interference was recently reported for a nonlinearly active chromophore selectively placed at various positions along a DNA helix (Doughty et al., 2013). It is also possible that the symmetric stretching modes are oriented parallel to the surface, so as not to be probed using the ssp polarization combination, and that the resulting asymmetric stretches of the two methylene groups in trans-β-IEPOX (1) are out of phase from one another (Fig. 5).

Based on this discussion, we hypothesize that the epoxide oxygen atom is oriented toward the silica surface, allowing for hydrogen-bonding interactions between the epoxide and SiOH groups present on the silica surface. As shown in Fig. 5, this arrangement is consistent with a 40° tilt angle of the methyl group with respect to the surface normal.

Given that the carbon atoms forming the backbone of this molecule are held rigidly in place by the presence of the epoxide ring, only the alcohol groups and their associated methylene groups can rotate freely. We propose that

the hydroxyl group located on the carbon atom further away from the methyl group (viz. Fig. 5) is rotated toward the surface, so as to reduce steric hindrance between the methylene and the methyl groups. This arrangement would also allow for hydrogen-bonding interactions between the SiOH groups and the oxygen from the OH group, in addition to that of the epoxide. If the hydroxyl group on the carbon atom adjacent to the methyl group were to be oriented toward the surface as well, the methylene groups would be trans-configured (consistent with the absence of methylene stretches in the SFG spectra), and H-bonding interactions of the molecule with the surface SiOH groups would be maximized.

A thorough structural and orientational analysis was not carried out for epoxides 2, 3, and 4 or for tetraols 5 and 6. As noted in Sects. 3.3 and 3.4, we propose that 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.

5 Implications for atmospheric chemistry and conclusions

While it is impossible from our study to definitely determine whether the epoxide or tetraol compounds prepared and studied here are part of isoprene-derived SOA particles, our results can be summarized as follows: the SFG spectra obtained from synthetic isoprene-derived SOA particle material are reasonably well reproduced by spin-coated trans-β-IEPOX (1) and to a lesser degree by the vapor phase of trans-β-IEPOX (1) and also *anti*-2-methyltetraol (6) in contact with a fused silica window. The obvious mismatch of the SFG spectra obtained from the synthetic SOA particle material and the *cis*-β-IEPOX (2), δ-IEPOX (3), α-IEPOX (4), and *syn*-2-methyltetraol (5) samples, in vapor or spin-coated form, indicates that, if these species are in fact present in the SOA material, they are not SFG active (SFG signal intensities vanish in centrosymmetric environments under conditions where molecular orientation distributions average to zero) (Boyd, 2003; Shen, 1984). We therefore conclude that *cis*-β-IEPOX (2), δ-IEPOX (3), α-IEPOX (4), and *syn*-2-methyltetraol (5), and possibly *anti*-2-methyltetraol (6), if indeed part of the synthetic SOA material prepared at the HEC or collected during AMAZE-08, are likely to be located in the bulk of the particles and not at their surfaces. Under low relative humidity conditions, for which SOA particle material has been reported to be solid (Renbaum-Wolff et al., 2013; Virtanen et al., 2010), these bulk-localized species may therefore not be available for chemical reactions. However, in the absence of a complete orientation analysis of the molecules studied here, we cannot rule out completely that the mismatches between the SFG spectra of the molecules

other than trans-β-IEPOX and isoprene-derived SOA material are due to changes in molecular orientation. 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.

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., 2011a). 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.

Supplementary material related to this article is available online at http://www.atmos-chem-phys.net/14/2303/2014/acp-14-2303-2014-supplement.pdf.

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