

Stereochemical transfer to atmospheric aerosol particles accompanying the oxidation of biogenic volatile organic compounds

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Received 20 June 2011; revised 13 July 2011; accepted 20 July 2011; published 26 August 2011.

[1] Asymmetric emission profiles of the stereoisomers of plant-derived volatile organic compounds vary with season, geography, plant type, and stress factors. After oxidation of these compounds in the atmosphere, the low-vapor pressure products ultimately contribute strongly to the particle-phase material of the atmosphere. In order to explore the possibility of stereochemical transfer to atmospheric aerosol particles during the oxidation of biogenic volatile organic compounds, second-order coherent vibrational spectra were recorded of the particle-phase organic material produced by the oxidation of different stereoisomeric mixes of α -pinene. The spectra show that the stereochemical configurations are not scrambled but instead are transferred from the gas-phase molecular precursors to the particle-phase molecules. The spectra also show that oligomers formed in the particle phase have a handed superstructure that depends strongly and nonlinearly on the initial stereochemical composition of the precursors. Because the stereochemical mix of the precursors for a material can influence the physical and chemical properties of that material, our findings suggest that chirality is also important for such properties of plant-derived aerosol particles. **Citation:** Ebben, C. J., S. R. Zorn, S.-B. Lee, P. Artaxo, S. T. Martin, and F. M. Geiger (2011), Stereochemical transfer to atmospheric aerosol particles accompanying the oxidation of biogenic volatile organic compounds, *Geophys. Res. Lett.*, 38, L16807, doi:10.1029/2011GL048599.

1. Introduction

[2] The emission profiles of the stereoisomers of plant-derived volatile organic compounds vary with season, geography, plant type, and stress factors [Yassaa *et al.*, 2001; Phillips *et al.*, 2003; Kanakidou *et al.*, 2005; Stephanou, 2007; Williams *et al.*, 2007]. (Here, we use the term stereoisomer instead of enantiomers in order to avoid having to distinguish between enantiomers and diastereomers). After oxidation of these compounds in the atmosphere, the low-vapor pressure products ultimately contribute strongly to the particle-phase material of the atmosphere [Seinfeld and Pandis, 1998]. Given that many biogenic volatile organic

compounds are chiral, and given that atmospheric processing towards the formation of aerosol particle material involves chemical pathways, we ask here whether it is possible for stereochemical transfer to occur from the molecular precursors to the particles via chemical reactions. We answer this question by collecting, analyzing, and interpreting second-order coherent vibrational spectra that were recorded of the particle-phase produced in an environmental chamber by the oxidation of different stereoisomeric mixes of α -pinene. The spectra show that the stereochemical configurations of the carbon atoms comprising the aerosol particle phase are not scrambled but instead transferred from the gas-phase molecular precursors to the particle-phase molecules. The data are consistent with the presence of oligomers possessing a handed superstructure in the aerosol particle phase. The nonlinear optical chiral response obtained from the particle phase depends nonlinearly on the initial stereochemical composition of the gaseous precursors. Because the stereochemical mix of molecular precursors can influence the rigidity, the extent of crystallinity, the molecular order, the long-range disorder, and the melting points and solubilities of enantiomers and materials formed from them [Eliel, 1962; Mackay *et al.*, 2001; Lemmerer *et al.*, 2008], our findings open the door to a possible biosphere-atmosphere-climate feedback process involving plant-derived aerosol particles and their chiral hydrocarbon precursors.

[3] Chiral molecules are important constituents of self-replicating systems, involved in biological recognition events, and critical for signaling within animal and plant populations [Phillips *et al.*, 2003]. Of particular interest in molecular sciences are stereoisomers, which are chiral compounds that have the same chemical formula and atom connectivity but different spatial orientation of their atoms. This attribute determines their physical and chemical properties, with a prominent example being the characteristic smells of spearmint and caraway that are due to the stereoisomers R-(+)- and S-(-)-carvone, respectively [Friedman and Miller, 1971]. Plants rarely produce pure terpene stereoisomers but instead mixtures of stereoisomers whose ratios are controlled by the biosynthetic pathways that produce them [Phillips *et al.*, 2003]. For instance, the ratio of emissions of (+)- to (-)- α -pinene, an important monoterpene representing 10–50% of the fraction of BVOCs [Kanakidou *et al.*, 2005], can be 1:2 in tropical forests compared to 3:1 for some boreal forests [Yassaa *et al.*, 2001; Stephanou, 2007; Williams *et al.*, 2007]. As shown in Figure 1a, the ozonolysis of α -pinene initially produces less-volatile organic compounds such as pinonaldehyde and pinonic acid, followed by the formation of other oxidation products such as pinic acid and

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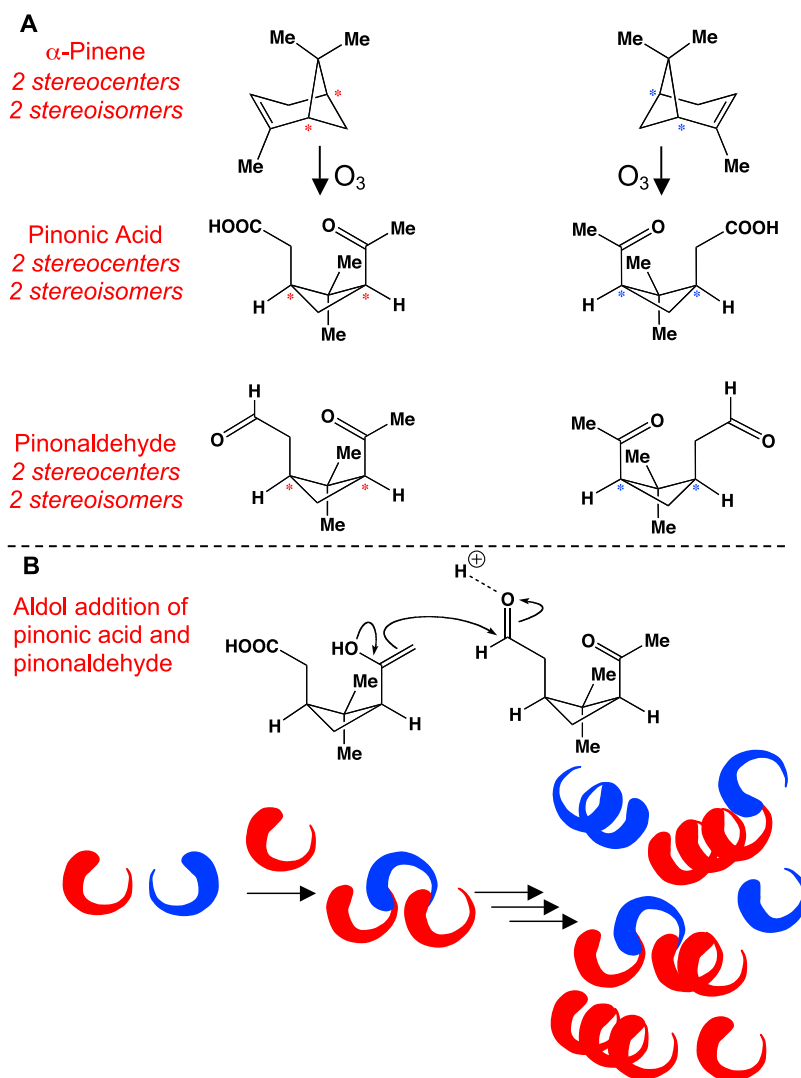


Figure 1. (a) Stereochemistry of pinonaldehyde and pinonic acid, which are important α -pinene ozonolysis products. Subsequent aldol reactions provide one example of a pathway by which oligomers can be formed with new stereocenters. (b) Cartoon representation of stereochemical transfer to atmospheric aerosol particles accompanying the oxidation of biogenic volatile organic compounds.

terpenylic acid [Claeys *et al.*, 2009]. Compared to the precursor, these products and others like them in the oxidation family have additional oxygen-bearing functional groups yet retain the four-membered ring that contains the stereogenic carbon atoms [Tolocka *et al.*, 2004; Docherty *et al.*, 2005; Kroll and Seinfeld, 2008; Heaton *et al.*, 2009]. If products such as these dominate the chemical composition of the particle, the initial stereoisomeric mix of the BVOC reactant should determine the chiral balance of the particle. Furthermore, as shown in Figure 1b, an absence of scrambling of the stereocenters would indicate the possibility of an ongoing stereochemical influence in guiding further particle-phase accretion reactions, such as dimerization and oligomerization, that are emerging as an enigmatic but important atmospheric process [Kalberer *et al.*, 2004; Mueller *et al.*, 2008; Gao *et al.*, 2010; Yasmeen *et al.*, 2010]. Analogous arguments apply to prochiral unsaturated compounds, such as isoprene. Here, we evaluate the chemical pathways discussed above by using vibrational sum frequency gener-

ation linear dichroism (SFG-LD) [Oh-e *et al.*, 2004; Stokes *et al.*, 2007], which is uniquely sensitive to the presence of molecular chirality.

2. Materials and Methods

[4] In the experiments, secondary organic material was produced in an environmental chamber [Shilling *et al.*, 2008] from the oxidation of 23 ± 2 ppb α -pinene stereoisomers and 300 ± 15 ppb of ozone at $25.0 \pm 0.1^\circ\text{C}$, $40 \pm 1\%$ relative humidity, and low NO_x (<1 ppb). The surfaces of ammonium sulfate seed particles were used to collect the condensing oxidation products. The seed particles, initially of 50 nm, grew to 93 nm (see auxiliary material) before exiting the chamber, which was operated in a continuous-flow steady-state mode for several days.¹ After collecting parti-

¹Auxiliary materials are available in the HTML. doi:10.1029/2011GL048599.

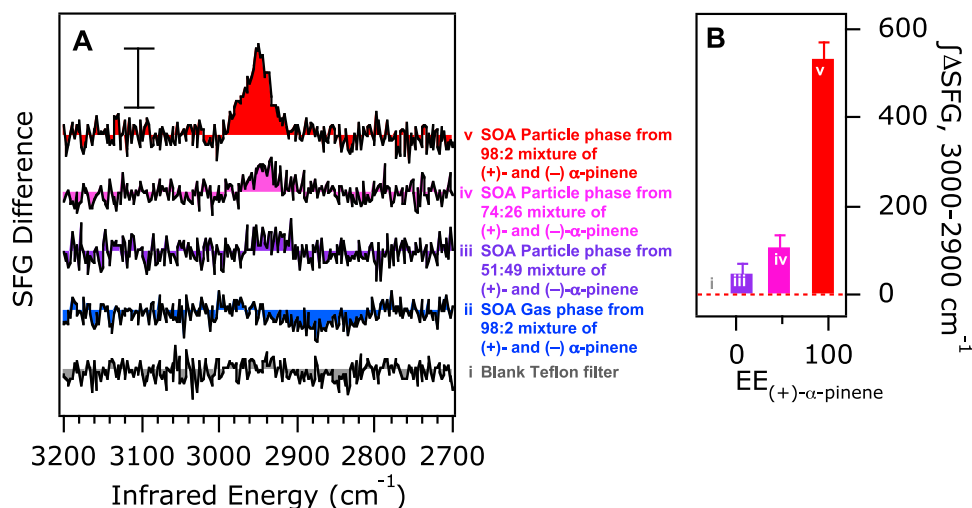


Figure 2. Vibrational sum frequency generation linear dichroism (SFG-LD) spectra of (a) blank Teflon filter (curve i), the aerosol gas phase (curve ii), and the aerosol particle phase produced from α -pinene ozonolysis at a 51:49 (curve iii), 76:24 (curve iv), and a 98:2 ratio of (+)-:(-)- α -pinene (curve v). Spectra were recorded at 290 K and 1 atm of air and run in triplicate. Scale bar indicates 20 counts per second. (b) Total SFG-LD response between 2900 and 3000 cm^{-1} as a function of enantiomeric excess of (+)- α -pinene in the gas phase during aerosol formation, with the background SFG-LD response from a Teflon filter (no particle phase present) indicated by the horizontal dashed line. Data are scaled for total particle mass on the filters.

cles for 48 hr on Teflon filters from the continuous outflow of the chamber, vibrational sum frequency generation linear dichroism (SFG-LD) spectra were recorded of the material on the filters [Oh-e *et al.*, 2004; Stokes *et al.*, 2007]. For C_{∞} symmetry, spectral response is zero if the χ_{xyz} tensor element of the nonlinear susceptibility tensor $\chi^{(2)}$, which is unique to all chiral species, is zero [Boyd, 2008]. The tensor was accessed by upconverting the *p*-polarized infrared light at the filter surface using visible light polarized either $+45^\circ$ or -45° away from the surface normal and recording the *p*-polarized component of the vibrational SFG response [Oh-e *et al.*, 2004]. Under this configuration, achiral and racemic systems exhibit no signal difference whereas systems consisting of mixtures of unequal amounts of stereoisomers respond strongly [Belkin *et al.*, 2000; Stokes *et al.*, 2007].

3. Results

[5] As a first control measurement, Figure 2a (curve i) shows negligible SFG-LD intensity in the CH stretching region of a Teflon filter. As a second control, with particles removed from the chamber outflow by the use of a HEPA filter, no appreciable SFG-LD signals were obtained (Figure 2a, curve ii). This finding indicates that the secondary organic species in the gas phase were too volatile to stick on the Teflon filter. Removal of the HEPA filter led to the collection of the particles onto the Teflon filter. Weak to negligible responses in the SFG-LD spectra were obtained for particles formed from $51 \pm 5\%$ of the (+)- and $49 \pm 5\%$ of the (-)-stereoisomer (Figure 2a, curve iii). For particles produced from a 74:26 mix, however, chiral vibrational responses were obtained (Figure 2a, curve iv). These signals occurred in the CH stretching region and increased considerably for particles produced from a 98:2 mix (Figure 2a, curve v). Figure 2b shows that the relation

between the intensity of the signal response between 2900 and 3000 cm^{-1} and enantiomeric excess (Figure 2b) is non-linear (see auxiliary material for details).

4. Discussion

[6] The 2940–2960 cm^{-1} peak position of the spectral response shown in Figure 2a for the 98:2 mix of (+) and (-) stereoisomers is up-shifted by 20–30 cm^{-1} from that of the asymmetric CH_3 stretches observed for fused silica windows exposed to the equilibrium room temperature vapor pressure of neat (+)- α -pinene in air (see auxiliary material). These CH_3 groups would be achiral if it were not for the induction of chirality – a common phenomenon found in supramolecular systems [Franke *et al.*, 2006] – by a chiral environment. The data in Figure 2a then suggest that the organic material produced by α -pinene ozonolysis contains methyl groups that are present within a chiral superstructure (Figure 1b). Such a superstructure may be formed from diesters and non-covalent hydrogen-bonding complexes formed between monomers, which have been reported in the literature from mass spectrometric analysis [Kalberer *et al.*, 2004; Mueller *et al.*, 2008; Claeys *et al.*, 2009; Zhao *et al.*, 2009; Gao *et al.*, 2010; Yasmeen *et al.*, 2010], or it may be provided in the form of helical oligomers as are commonly found in products of stereoselective polymerization chemistry [Chisholm *et al.*, 2005]. The spectral shift between the molecular α -pinene monomers and the particle material (Figure 2a) and the nonlinear response apparent in the data of Figure 2b indicate that molecular interactions – including those that result in chemical bond formation – are taking place and that these interactions are subject to induced chirality. In contrast, physical processes resulting in mixtures of non-interacting stereoisomers would have produced a linear dependence [Byers *et al.*, 1994] like the one observed in the well-known

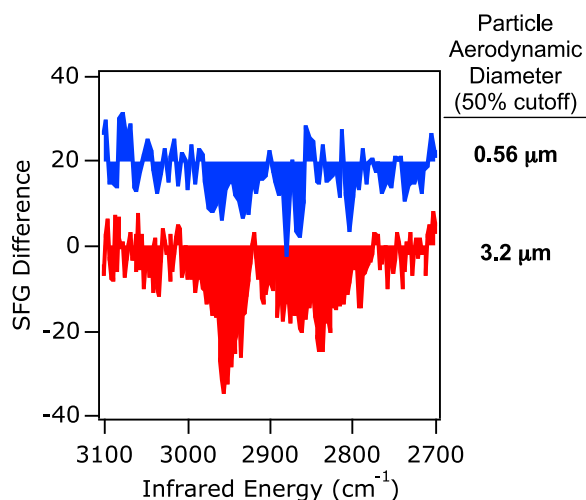


Figure 3. Representative vibrational sum frequency generation linear dichroism (SFG-LD) spectra of aerosol particle material collected during AMAZE-08 in the central Amazon Basin in the (top) submicron and (bottom) supermicron size range.

optical rotation of mixed sugar solutions, which is directly proportional to concentration.

[7] If the chemical environment within the oligomers were helical, as is indeed common in polymer chemistry [Tabei *et al.*, 2003; Chisholm *et al.*, 2005], the particulate material prepared from the racemic 51:49 mix of molecular α -pinene monomers might consist of an equal mix of right- and left-handed helices that are possibly organized into domains of like handedness within the organic material. Alternatively, the material may consist of oligomers having a sequence of left- and right-handed monomer units. The chiral signals obtained from the particle material prepared from the 74:26 mix indicate that it consists of oligomers in which there are more monomer units with one handedness than the other, or that there are more oligomers with one handedness than the other. Reminiscent of chain end control [Chisholm *et al.*, 2005] and the well-known nonlinearities in the yield of chiral reactions [Soai, 2010], this bias is nonlinear and increases greatly for higher mixtures, such as the 98:2 mix, because the stereogenic centers of one handedness dominate the molecular organization within the oligomers (Figure 1b). We note that a definitive proof for the transfer of chirality from the gas-phase terpenes into chiral oligomers can only be made by isolating these oligomers and investigating their chirality, which is the subject of ongoing research on this topic.

5. Atmospheric Implications

[8] Given that the enantiomeric excess of emissions of (+)- to (-)- α -pinene was reported to be 33% in tropical forests and 50% in boreal forests [Yassaa *et al.*, 2001; Stephanou, 2007; Williams *et al.*, 2007], the data shown in Figure 2 cover enantiomeric excess values that are atmospherically relevant. Therefore, we expect stereochemical transfer to be active in the natural environment as well. As one example, we evaluated molecular chirality in atmospheric aerosol particles rich in secondary organic material that were collected under the pristine conditions of the

central Amazon Basin [Pöschl *et al.*, 2010] at tower TT34 during the wet season of February and March 2008 [Martin *et al.*, 2010a]. Close to 90% of detected particles consist of secondary organic aerosol (SOA) droplets that were formed by atmospheric oxidation and gas-to-particle conversion of biogenic volatile organic compounds. The secondary organic material in this particular environment has a multitude of BVOC precursors, as well as multiple oxidants and photochemistry, all of which combine to produce secondary organic material that deposits across the entire size range of particles [Martin *et al.*, 2010b]. Primary biological aerosol particles in the supermicron size mode can be expected to dominate the SFG-LD response when the laser spot is focused on them, whereas the more numerous submicron particles consisting mainly of secondary organic material, for which the chemical pathway discussed here might be important, are more uniformly distributed across the filter. Alongside the chemical pathways are physical processes that can enrich achiral aerosol particles with chiral material, such as carbohydrates or nucleic and amino acids [Salma *et al.*, 2010]. To distinguish between these two cases, we recorded the SFG-LD responses from two fractions of highly size-resolved aerosol particles collected during AMAZE '08 (Figure 3). The two size fractions are characterized by aerodynamic diameters of 3.2 μm and 0.56 μm at the 50% cut-points, respectively, which were chosen to differentiate primary biological particles, if present, from secondary organic material. The presence of chirality in the asymmetric and symmetric CH stretches seen in the SFG-LD spectra of the coarse and fine modes particles shows that the chemical pathways discussed here are in fact important not only for model systems but also naturally occurring aerosol particles rich in secondary organic material.

6. Conclusions

[9] The coherent nonlinear vibrational spectra of organic material constituting the particle-phase that is produced by the oxidation of different stereoisomeric mixes of α -pinene indicate that stereochemical configurations are not scrambled but instead are transferred from the gas-phase molecular precursors to the particle-phase molecules. The products are likely to be present in the form of handed superstructures whose chirality depends strongly and nonlinearly on the initial stereochemical composition of the precursors. The discovery of chirality in super- and submicron-sized aerosol particles collected under pristine conditions in the central Amazon Basin indicates that the chemical pathways discussed here are important not only for model systems but also for secondary organic aerosol particles having climate-relevant sizes. According to the results presented here, biogenic volatile organic stereoisomers emitted in one part of the world might produce particle-phase organic material with chiral properties that are different from material produced by different stereoisomeric compositions emitted in other parts of the world. Given that chirality determines the physical and chemical properties of a given material [Elie, 1962; Mackay *et al.*, 2001; Lemmerer *et al.*, 2008], the physical and chemical properties of the atmospheric aerosol particles can be likewise variable [Stokes *et al.*, 2009; Salma *et al.*, 2010]. The results presented here therefore open the possibility for investigating whether stereochemical reactions have the potential to drive biosphere-atmosphere-climate

feedbacks in which local climate stresses, BVOC emissions, and aerosol properties are coupled through molecular chirality. Future work will address the details of this feedback loop, the role of molecular chirality in it, and the utility of chirality in aerosol particles as an atmospheric marker to distinguish anthropogenic from biogenic emissions.

[10] **Acknowledgments.** FMG thanks the National Science Foundation Atmospheric Chemistry division for support under grant NSF ATM-0533436. STM thanks the Office of Science (BES), U.S. Department of Energy, for support under grant DE-FG02-08ER64529. We also thank R. J. Thomson and K. A. Scheidt for discussions regarding the topic of chirality in heterogeneous reactions, and anonymous reviewers who provided very helpful comments on the work presented here.

[11] The Editor thanks two anonymous reviewers for their assistance in evaluating this paper.

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