Beyond Local Group Modes in Vibrational Sum Frequency Generation

Hilary M. Chase,[†] Brian T. Psciuk,[‡] Benjamin L. Strick,[†] Regan J. Thomson,[†] Victor S. Batista,[‡] and Franz M. Geiger^{*,†}

[†]Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States

[‡]Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520-8107, United States

Supporting Information

ABSTRACT: We combine deuterium labeling, density functional theory calculations, and experimental vibrational sum frequency generation spectroscopy into a form of "counterfactual-enabled molecular spectroscopy" for producing reliable vibrational mode assignments in situations where local group mode approximations are insufficient for spectral interpretation and vibrational mode assignments. We demonstrate the method using *trans-β*-isoprene epoxydiol (*trans-β*-IEPOX), a first-generation product of isoprene relevant to atmospheric aerosol formation, and one of its deuterium-labeled isotopologues at the vapor/silica interface. We use our method to determine that the SFG responses that we obtain from *trans-β*-IEPOX



are almost exclusively due to nonlocal modes involving multiple C–H groups oscillating at the same frequency as one vibrational mode. We verify our assignments using deuterium labeling and use DFT calculations to predict SFG spectra of additional isotopologues that have not yet been synthesized. Finally, we use our new insight to provide a viable alternative to molecular orientation analysis methods that rely on local mode approximations in cases where the local mode approximation is not applicable.

1. INTRODUCTION

Vibrational sum frequency generation (SFG) spectroscopy has proven to be an excellent method for studying molecules at surfaces and interfaces.¹⁻¹⁷ Provided that accurate vibrational mode assignments are available, the coherent nature of the method makes it particularly useful for understanding vibrational mode coupling within and among surface-bound species and for providing quantitative information regarding molecular structure, orientation, or ordering of a particular surface-bound species. Yet, assigning vibrational modes in a reliable fashion can be challenging even when the spectral resolution is adequate, particularly when vibrational modes manifest themselves in congested frequency regions, such as the C-H stretching region, or when the phases of the modes are not known. Compounding the issue is that vibrational modes are often delocalized and involve multiple local group vibrations oscillating simultaneously at a particular frequency, such as in cases of methylene and methyl oscillators. To clarify, we define a local group vibration as a vibration of a given frequency isolated solely in one group in the molecule, that is, a methylene symmetric stretch or a methyl asymmetric stretch. When multiple groups oscillate in the molecule as one mode of a particular frequency, we classify this situation as a *delocalized* coupling of vibrations. This situation is expected to be important especially for the case of hydrocarbons containing aliphatic rings, heterocycles, or C=C double bonds.

There are currently no accurate and reliable methods to interpret SFG spectra in situations where the local group mode approximation breaks down. Instead, most commonly rely on spectral fitting followed by comparison to literature precedents

to assign a local vibrational mode, such as a CH₃ symmetric stretch, to a given SFG band. In addition to not knowing whether the local group mode approximation is valid, a further caveat with this approach is that the spectral line shapes need to be known to high accuracy, which has been difficult to verify until the recent development of sub-1 cm⁻¹ resolution vibrational SFG spectroscopy.^{18,19} Deuteration is a classic method for verifying the reliability of vibrational mode assignments,^{20,21} but this method can be tedious given the number of C–H groups that are of potential interest for a given molecular spectrum. Recently, computational methods have been invoked for aiding in the analysis and mode assignments of SFG spectra. Simulations of SFG spectra based on theoretical models have been used in conjunction with experiment to help interpret nonlinear optical responses of systems ranging from surfaces of liquids and aqueous solutions²²⁻²⁹ to interfaces between immiscible liquids³⁰⁻³³ to small molecules, ^{2,34-40} peptides, ^{17,41,42} proteins, ^{6,16,43-46} and polymers^{47,48} at interfaces and surfaces. Density functional theory (DFT)-based simulation methods, in particular, have been used with much success to simulate SFG spectra, with the added benefit that these methods are computationally affordable and reasonably accurate.^{6,42,48} A key difficulty with this method, however, is that an independent evaluation of the reliability of the computed/simulated spectra, which would be

Received:
 March 6, 2015

 Revised:
 March 15, 2015

 Published:
 March 16, 2015

Here, we combine the best of the three approaches (deuterium labeling, DFT calculations, and experimental SFG spectroscopy) into a form of "counterfactual-enabled molecular spectroscopy". We demonstrate that our new method produces reliable vibrational mode assignments through the study of a small oxygenated species that has become of interest recently in understanding the surfaces of organic atmospheric aerosol particles, namely, *trans-* β -isoprene epoxydiol (*trans-* β -IEPOX (1), Figure 1).^{5,49–53} This compound contains multiple polar



Figure 1. Structures of *trans-\beta*-IEPOX and the isotopologue studied in this work.

groups that facilitate hydrogen bonding to the silica surface, resulting in a narrow range of preferred orientations that we quantify using experiment and computation. Furthermore, this molecule contains only one CH group, two CH₂ groups, and one CH₃ group, while a rigid epoxide restricts the molecule's conformational degrees of freedom. Finally, we expect the various molecular group oscillators in *trans-β*-IEPOX to be strongly delocalized, further motivating the use of this species in our study of how nonlocalized vibrational modes manifest themselves in SFG spectroscopy.

We use our method to determine that the SFG responses that we obtain from *trans-* β -IEPOX (1) are almost exclusively due to vibrational modes involving nonlocal group oscillators associated with the methine, methylene, and methyl groups. Moreover, we verify our assignments using deuterium labeling and use DFT calculations to predict SFG spectra of additional isotopologues that have not been synthesized. Finally, we use our new insight to provide a viable alternative to molecular orientation analysis methods that rely on local group mode approximations in cases where local group mode approximations for interpreting SFG spectra are insufficient.

2. SFG THEORY

The theoretical basis behind SFG has been thoroughly described.^{7,8,15,54–60} Briefly, SFG is a second-order nonlinear process that arises when two light fields combine at a surface or interface, spatially and temporally, producing a third light field that has a frequency that oscillates at the sum of the two input frequencies. The intensity of the sum frequency signal is given by

$$I_{\rm SFG} \propto I_{\rm vis} I_{\rm IR} |\chi_{\rm eff}^{(2)}|^2 \tag{1}$$

Here, $\chi_{\rm eff}^{(2)}$ is the effective second-order nonlinear susceptibility tensor of the interface, and $I_{\rm vis}$ and $I_{\rm IR}$ are the intensities of the visible and IR incident light fields, respectively. In our case, $\chi_{\rm eff}^{(2)}$ is dominated by its resonant contribution as the nonresonant component has been shown to be negligible at oxide surfaces.^{3,10,61} Thus, $\chi_{\rm eff}^{(2)}$ can be rewritten as a resonant term $\chi_{\rm R}^{(2)}$ according to

$$\chi_{\rm R}^{(2)} = N_{\rm ads} \langle \beta_{jk,q} \rangle \tag{2}$$

Here, $N_{\rm ads}$ is the number of adsorbate molecules at the surface or interface, and $\langle \beta_{\nu} \rangle$ is the ensemble orientation average of the molecular hyperpolarizability tensor, which is expressed as the product of the polarizability derivative and dipole derivatives with respect to the normal mode, q, according to

$$\beta_{ijk,q} \propto \frac{\partial \alpha_{ij}}{\partial Q_q} \frac{\partial \mu_k}{\partial Q_q}$$
(3)

The molecular hyperpolarizability is rotated from molecular frame coordinates (i, j, k) to the lab frame coordinates (I, J, K) to obtain the second-order tensor $\chi_{IJK}^{(2)}$ using a z-y-z Euler transformation matrix according to

$$\chi_{IJK,q}^{(2)} = N \sum_{i,j,k} \langle R_{Ii} R_{Jj} R_{Kk} \rangle \beta_{ijk,q}$$
(4)

The molecular orientation is defined by a "tilt" angle, θ , and "twist" angle, ψ . The in-plane rotation is defined as ϕ , and for a rotationally isotropic noninteracting surface, ϕ is averaged by integrating from 0 to 2π . The tensor elements can be accessed through polarization control of the IR, visible, and SFG beams. In our present study, we utilize the ssp polarization combination, defined as

$$\chi_{\rm ssp}^{(2)} = L_{yy}(\omega_{\rm SFG})L_{yy}(\omega_{\rm vis})L_{zz}(\omega_{\rm IR})\sin\alpha_{\rm IR}\chi_{yyz}$$
(5)

to probe vibrational mode components that are oriented perpendicular to the surface. The ssp polarization combination is designated s-polarized SFG, s-polarized visible, and ppolarized IR beams. As a note, "p" designates a light field polarization that is parallel to the plane of incidence, and "s" designates a light field polarization that is perpendicular to the plane of incidence.

3. EXPERIMENTAL AND COMPUTATIONAL METHODS

A. Substrate Synthesis. Synthesis of *trans-* β -IEPOX (1) was carried out according to the literature procedure.^{5,62} The synthesis of *trans-* β -IEPOX- d_2 (2) required development of a novel procedure (Scheme 1), which began with aldehyde 3, an





intermediate used in the synthesis of the parent *trans-β*-IEPOX molecule (i.e., 1). A Corey–Gilman–Ganem oxidation with MnO_2 and NaCN produced methyl ester 4 in 53% yield.^{63,64} Reduction to the primary alcohol with LiAlD₄ followed by epoxidation with mCPBA afforded deuterium-labeled epoxide 5 in 73% yield over the two steps. Finally, removal of the silyl-protecting group with TBAF gave desired *trans-β*-IEPOX- d_2



Figure 2. (A) Best-fit computed ssp-polarized SFG spectrum of *trans-\beta*-IEPOX (red trace) compared to experiment (black trace) determined by computing a normalized sum of the square difference contour map (B), where the dark purple regions indicate the best fit to experiment. Three regions of poor fit are labeled with colored circles, and their corresponding SFG spectra are displayed to the right.

(2) in 81% yield (full experimental details and characterization data are found in the Supporting Information).

B. SFG Spectrometer and Sample Cell Configuration. The broad-band SFG setup used in this study has been described in previous work, 3,5,10,13,65,66 and we refer the reader to those papers for the experimental details. The compounds in this study are highly viscous (see the Supporting Information for details) and were spread at the bottom of a fused silica window that was then sealed with an O-ring against the opening of a custom-built Teflon sample cell. The incident IR and visible beams were centered above the sample spot to probe the vapor/silica interface at internal reflection geometry. The reported spectra in this study are an average of 5-7 individual spectra with 2-5 min spectral acquisition times in order to achieve acceptable signal-to-noise ratios.

C. Computational Methods. In our computations, we employ previously described methods that we modified to compute ssp-polarized SFG spectra.^{6,42} All DFT calculations are performed with the hybrid B3LYP^{67–69} functional and 6-311G(d,p) basis set with the Gaussian 09 package.⁷⁰ Following geometry optimization, we compute harmonic vibrational frequencies along with dipole derivatives and polarizability derivatives with respect to each vibrational mode, which are printed using the keyword "iop(7/33=1)". We assessed additional DFT functionals and basis sets, to be shown in forthcoming work that indicates that this combination of functional and basis set is sufficient for computing SFG spectra for the systems under investigation in this work. Despite the evidence of nonlocal oscillators that we will present below, Fermi resonances are seemingly unimportant in this system, as assessed by computing Fermi resonance splittings with DFT (see the Supporting Information for details).

We simulate SFG spectra by computing $\beta_{lmn,q}$ elements using eq 3 with the molecular coordinates displayed in Figure 3B. We use the z-y-z Euler transformation matrix to project the molecular hyperpolarizabilities from the molecular frame onto the lab frame. Then, we compute the subsequent second-order nonlinear susceptibilities for each normal mode $(\chi_{ijk,q}^{(2)}(\phi,\psi,\theta))$ for a particular set of orientation angles. By averaging $\chi^{(2)}$ over phi (ϕ) angles for every S° from 0 to 360°, we invoke full azimuthal rotational symmetry. This step results in a molecular orientation defined by a tilt (θ) and a twist (ψ) angle. Effective second-order susceptibilities are then computed where a Lorentzian function of 12 cm⁻¹ bandwidth is introduced to account for inhomogeneous broadening. We apply a scaling factor to the computed vibrational frequencies of 0.9671 to the final SFG spectrum in the C–H stretching region, which is similar to other suitable scaling factors used for this level of theory.^{71,72} Fresnel factors used in these computations are reported in the Supporting Information.

4. RESULTS AND DISCUSSION

A. Computations of ssp SFG Spectra of trans-β-IEPOX and Its Isotopologue Match Experiment. Figure 2A shows the ssp-polarized SFG spectrum of *trans-\beta*-IEPOX (1) obtained from both experiment and theory. The latter was obtained for a tilt angle of 70° and a twist angle of 90° (70°, 90°) of the C_{3u} symmetry axis of the methyl group with respect to the surface normal. SFG spectra computed for other tilt and twist angles do not match the experimental spectrum, as shown in the lighter purple regions of the normalized sum of the square difference contour plot in Figure 2B. By determining the normalized sum of square differences between computed and experimental spectra for all possible θ and ψ combinations in 10° increments from 0 to 360°, we find quite narrow regions of best fits (dark purple regions in Figure 2B) that are likely due to the fact that *trans-\beta-IEPOX* (1) possesses multiple hydrogen-bonding sites that can interact with the Si-OH groups on the silica substrate, resulting in a net preferred orientation within $5-20^{\circ}$ for θ and ψ . This distribution is shown by the area of the dark purple best-fit regions in Figure 2B. Figure 3A shows what the simulations indicate to be the molecular orientation of *trans-\beta-*IEPOX (1) at the surface based on the molecular coordinates given in Figure 3B. Stick spectra for are provided in the Supporting Information to show the various mode contributions to the overall SFG spectrum. According to the DFT



Figure 3. Determined orientation of *trans-* β **-**IEPOX at the vapor/silica interface (A) based on the molecular coordinates shown in (B).

Table 1. Tabulated Computed Scaled SFG Frequencies and Normalized SFG Intensities of *trans-\beta*-IEPOX (1) of the Various Delocalized Stretches Based on the Best-Fitting ssp Spectrum at a Molecular Orientation of (70°, 90°) as Well as the IR Intensities and Raman Activities Computed by DFT^{*a*}

scaled frequency [cm ⁻¹]	normalized SFG intensity	IR intensity [km/mol]	Raman activity [Å ⁴ / amu]	mode description
2864	0.0005	19.8	13.0	(C1, C4) CH ₂ – SS out of phase
2866	0.3	90.0	178	(C1, C4) CH ₂ - SS in phase
2928	0.006	36.4	63.1	(C1) CH ₂ –AS, CH
2938	0.1	20.9	85.5	СН₃–SS , (С4) СН ₂ –АS
2943	1.0	29.6	106	CH ₃ –SS, (C4) CH ₂ –AS, CH
2985	0.2	33.7	79.5	СН , (С4) СН ₂ – АЅ
3005	0.06	17.7	74.1	СН₃–АЅ , (С4) СН ₂ –АЅ
3035	0.005	17.3	52.4	CH ₃ -AS

"The group vibrations that display the largest atomic displacements are bolded for any given delocalized vibrational mode. A graphical representation of each vibrational mode is provided in the Supporting Information.

normal-mode analysis (Table 1), the intense band at ~2943 cm⁻¹ corresponds to a mode that consists of a simultaneous symmetric methyl stretch, weaker methylene symmetric stretch from the C4 atom, and methine stretch, while the smaller band at ~2866 cm⁻¹ corresponds to the simultaneous symmetric stretching of both methylene groups, which are also depicted in Table 1. The lower-frequency mode (2864 cm⁻¹) is very low in intensity and is associated with methylene symmetric stretches that are out-of-phase, whereas the mode at ~2866 cm⁻¹ is associated with methylene symmetric stretches that are in-phase.

Figure 4A shows the ssp-polarized SFG spectrum of d_2 -trans- β -IEPOX (2) obtained from both experiment and theory. The corresponding stick spectrum is given in the Supporting Information. We see a clear SFG signal intensity increase of the band at ~2865 cm⁻¹ from the unlabeled IEPOX ssp spectrum. The optimized structure of unlabeled *trans-\beta*-IEPOX shows the methylene groups in a trans configuration, resulting

Table 2. Tabulated Computed Scaled SFG Frequencies and Normalized SFG Intensities of d_2 -trans- β -IEPOX (2) of the Various Delocalized Stretches Based on the Best-Fitting ssp Spectrum at a Molecular Orientation of (80°, 90°) as Well as the IR Intensities and Raman Activities Computed by DFT^a

scaled frequency [cm ⁻¹]	normalized SFG intensity	IR intensity [km/mol]	Raman activity [Å ⁴ / amu]	mode description
2865	1.0	55.7	97.4	CH ₂ -SS
2938	0.17	17.1	83.8	СН₃–SS , СН ₂ –АS, СН
2943	0.56	29.8	104	CH ₃ –SS, CH ₂ –AS, CH
2985	0.11	30.7	72.9	CH, CH ₂ –AS
3005	0.03	17.3	74.0	CH ₃ –AS, CH ₂ –AS, CH
3035	0.002	17.3	52.3	CH ₃ -AS

^{*a*}The group vibrations that display the largest atomic displacements are bolded for any given delocalized vibrational mode. A graphical representation of each vibrational mode is provided in the Supporting Information.

in destructive interference and an overall low-intensity signal at around 2865 cm⁻¹, as shown in Table 2. Deuterating one of the CH₂ groups removes the destructive interference, and an overall increase in the CH₂ symmetric stretching signal intensity is observed, both in the experiment and in the simulation. Table 2 shows that the large intensity peak at 2865 cm^{-1} of the d_2 -IEPOX spectrum is associated with the remaining methylene group. As expected, the tilt and twist angles that correspond to best matches between the experimental and the simulated SFG spectra (Figure 4B) are comparable to those that we determined for the unlabeled compound (Figure 2B). It can be concluded from this analysis that the unlabeled and deuterium-labeled trans- β -IEPOX molecules studied here (i.e., compounds 1 and 2) are subject to comparable orientation distributions and that the simulated SFG spectra are reliable.

Using this thorough computational analysis, we reassess our previously published orientation analysis of *trans-\beta*-IEPOX at the vapor/silica interface using the polarization intensity ratio method.⁵ In that work, which was based on a Lorentzian peak fitting of the experimental ssp spectrum, we assumed



Figure 4. Best-fit computed ssp-polarized SFG spectrum of d_2 -trans- β -IEPOX (green trace) compared to experiment (black trace) (A). The normalized sum of the square difference contour map (B) indicates that the native IEPOX and d_2 -IEPOX compounds have similar orientation distributions.

uncoupled *localized* group vibrations. Moreover, we assumed that the SFG band at 2880 cm⁻¹ was entirely due to the CH₃ symmetric stretching mode. This local group mode approach resulted in a reported tilt angle of ~40° relative to the surface normal for the methyl C_{3v} symmetry axis. Our current analysis, which does account for the presence of nonlocal group modes, results in a CH₃ tilt angle of approximately 70–80° from the surface normal and thereby emphasizes the importance of scrutinizing the validity of the local mode approximation in molecules containing nonlocal oscillators.

B. SFG Predictive Capabilities of the Computational Method for Compounds Not Yet Synthesized. With good agreement between experiment and simulation, we now have the capability to compute ssp SFG spectra for other *trans-\beta*-IEPOX isotopologues that have yet to be synthesized. Using a similar tilt and twist angle combination (80°, 90°) used for computing the SFG spectra of compounds 1 and 2, we computed ssp-polarized SFG spectra for a host of isotopologues (Figure 5) that are helpful in making reliable vibrational mode



Figure 5. Predicted ssp-polarized SFG spectra of IEPOX isotopologues that have not been synthesized. The left-hand column includes *trans-\beta*-IEPOX, *d*₂-*trans-\beta*-IEPOX, and other isotopologues surveyed that contain CH₃ groups. The right-hand column includes all isotopologues surveyed that contain CD₃ groups.

assignments for *trans-* β -IEPOX. The corresponding stick spectra are given in the Supporting Information. All spectra reported here have been normalized to the maximum peak intensity of *trans-* β -IEPOX. It should be noted that the spectra in the left-hand column are of isotopologues with a hydrogenated methyl group, and the spectra in the right-hand column include isotopologues with a deuterated methyl group.

By partitioning the spectra this way, it is evident that the higher-intensity peak at $\sim 2943 \text{ cm}^{-1}$ is dominated by methyl group stretches, with minor contributions from methylene

stretches. We simulated the deuteration on other C–H groups along with the methyl group to see how the remaining C–H oscillators interact, either constructively or destructively. This analysis reveals that the lower-intensity peak centered at around ~2865 cm⁻¹ is solely due to contributions of methylene symmetric stretching modes. When both methylene groups are deuterated, the SFG intensity at 2865 cm⁻¹ is completely eliminated. Additionally, it is found that the high-frequency shoulder at around 3005 cm⁻¹ is due entirely to the methine stretch.

Upon solely deuterating the methyl group, (Figure 5, gray trace, right column), a majority of the SFG intensity is eliminated, specifically at 2943 cm⁻¹. The resulting spectrum exhibits low-intensity peaks at \sim 2980 and 2865 cm⁻¹. The large drop in SFG intensity indicates a strong spectral interference between both methylene groups. Specifically, due to the proposed trans conformation of the methylene groups, it appears that they destructively interfere, thereby reducing the overall SFG intensity. In contrast, the SFG spectrum associated with the IEPOX isotopologue with the deuterated methylene groups (Figure 5, gray trace, left column) shows that there is minimal interference between the remaining hydrogenated methyl and methine groups. Replacing the methine C-H (gray trace) with a C-D group (orange trace) results in little to negligible change in SFG intensity at 2943 cm⁻¹. Due to the apparent anti-positioning of the methyl group relative to the methine group, it could be predicted that their vibrational motions may destructively interfere, resulting in a net decrease in SFG intensity, but based on our SFG simulations, this is not the case. Perhaps these vibrations may not interact as strongly as the methylene groups, whose C-H bonds appear to stretch with displacements of similar magnitude at the same frequency. Alternatively, the methine C-H oscillators may be associated with much smaller IR and/or Raman transition dipole moments when compared to the methylene and methyl groups. Finally, the vibrational mode at 2943 cm⁻¹ includes minimal contributions from the methine stretch, and perhaps the difference in displacement magnitudes does not result in a net destructive interference.

5. CONCLUSION

We have shown that our DFT-based perturbative methodology predicts accurate ssp-polarized SFG spectra for trans- β -IEPOX and one of its isotopologues at the vapor/silica interface. We find that the vibrational modes of both species are delocalized throughout the various molecular groups in the C-H stretching frequency region. As a result, we conclude that commonly used localized group vibrational mode approximations used to interpret SFG spectra are not appropriate in the case of *trans-\beta*-IEPOX. Furthermore, we have shown that DFT calculations can be used to reliably predict SFG spectra for compounds that have yet to be synthesized, including compounds that might be difficult to synthesize or short-lived and/or unstable. The predictive capability of our atomistic calculations is advantageous for elucidating information regarding the structure and orientation of molecules with nonlocal C-H group vibrational modes that defy the capability limitations of more approximate approaches based on simplified point group symmetry assumptions.

ASSOCIATED CONTENT

S Supporting Information

Experimental synthesis, ¹H- and ¹³C-NMR spectra, Fresnel factors used in SFG simulations, Fermi resonance assessment, computed stick spectra, and graphical representation of vibrational modes. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail geigerf@chem.northwestern.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

H.M.C. acknowledges support from a National Science Foundation (NSF) graduate research fellowship and the Institute for Sustainability and Energy at Northwestern (ISEN). F.M.G. and R.J.T. acknowledge support from the National Science Foundation (NSF CHE1212692 and SP0017343). V.S.B. acknowledges supercomputer time from NERSC and support from NSF Grant CHE-1213742.

REFERENCES

(1) Achtyl, J. L.; Buchbinder, A. M.; Geiger, F. M. Hydrocarbon on Carbon: Coherent Vibrational Spectroscopy of Toluene on Graphite. *J. Phys. Chem. Lett.* **2012**, *3*, 280–282.

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

(3) Buchbinder, A. M.; Weitz, E.; Geiger, F. M. Pentane, Hexane, Cyclopentane, Cyclohexane, 1-Hexene, 1-Pentene, *cis*-2-Pentene, Cylohexene, and Cyclopentene at Vapor/ α -Alumina and Liquid/ α -Alumina Interfaces Studied by Broadband Sum Frequency Generation. *J. Phys. Chem. C* 2009, *114*, 554–566.

(4) Ebben, C. J.; Shrestha, M.; Martinez, I. S.; Corrigan, A. L.; Frossard, A. A.; Song, W. W.; Worton, D. R.; Petaja, T.; Williams, J.; Russell, L. M.; et al. Organic Constituents on the Surface of Aerosol Particles from Southern Finland, Amazonia, and California Studied by Vibrational Sum Frequency Generation. *J. Phys. Chem. A* **2012**, *116*, 8271–8290.

(5) Ebben, C. J.; Strick, B. F.; Upshur, M. A.; Chase, H. M.; Achtyl, J. L.; Thomson, R. J.; Geiger, F. M. Towards the Identification of Molecular Constituents Associated with the Surfaces of Isoprene-Derived Secondary Organic Aerosol (SOA) Particles. *Atmos. Chem. Phys.* **2014**, *14*, 2303–2314.

(6) Fu, L.; Xiao, D.; Wang, Z.; Batista, V. S.; Yan, E. C. Y. Chiral Sum Frequency Generation for In Situ Probing Proton Antiparallel β -Sheets at Interfaces. *J. Am. Chem. Soc.* **2013**, *135*, 3592–3598.

(7) Moad, A. J.; Simpson, G. J. A Unified Treatment of Selection Rules and Symmetry Relations for Sum-Frequency and Second Harmonic Spectroscopies. J. Phys. Chem. B 2004, 108, 3548–3562.

(8) Shen, Y. R. The Principles of Nonlinear Optics; Wiley-Interscience: New York, 1984.

(9) Shen, Y. R. Surface Properties Probed by 2nd Harmonic and Sum Frequency Generation. *Nature* **1989**, *337*, 519–525.

(10) Stokes, G. Y.; Buchbinder, A. M.; Gibbs-Davis, J. M.; Scheidt, K. A.; Geiger, F. M. Heterogenous Ozone Oxidation Reactions of 1-Pentene, Cyclopentene, Cyclohexene, and Menthenol Derivative Studied by Sum Frequency Generation. *J. Phys. Chem. A* 2008, *112*, 11688–11698.

(11) Stokes, G. Y.; Buchbinder, A. M.; Gibbs-Davis, J. M.; Scheidt, K. A.; Geiger, F. M. Chemically Diverse Environmental Interfaces and

Their Reactions with Ozone Studied by Sum Frequency Generation. *Vib. Spectrosc.* **2009**, *50*, 86–98.

(12) Stokes, G. Y.; Gibbs-Davis, J. M.; Boman, F. C.; Stepp, B. R.; Condie, A. G.; Nguyen, S. T.; Geiger, F. M. Making "Sense" of DNA. *J. Am. Chem. Soc.* **2007**, *129*, 7492–7493.

(13) Voges, A. B.; Al-Abadleh, H. A.; Geiger, F. M. *Environmental Catalysis*; CRC Press: Boca Raton, FL, 2005; pp 83–128.

(14) Walter, S. R.; Geiger, F. M. DNA on Stage: Showcasing Oligonucleotides at Surfaces and Interfaces with Second Harmonic and Vibrational Sum Frequency Generation. *J. Phys. Chem. Lett.* **2009**, *1*, 9–15.

(15) Wang, H.-F.; Gan, W.; Lu, R.; Rao, Y.; Wu, B.-H. Quantitative Spectral and Orientational Analysis in Surface Sum Frequency Generation Vibrational Spectroscopy (SFG-VS). *Int. Rev. Phys. Chem.* **2005**, *24*, 191–256.

(16) Yan, E. C. Y.; Fu, L.; Wang, Z.; Liu, W. Biological Macromolecules at Interfaces Probed by Chiral Vibrational Sum Frequency Generation Spectroscopy. *Chem. Rev.* **2014**, *114*, 8471–8498.

(17) Roy, S.; Covert, P. A.; FitzGerald, W. R.; Hore, D. K. Biomolecular Structure at Solid–Liquid Interfaces Revealed by Nonlinear Optical Spectroscopy. *Chem. Rev.* **2014**, *114*, 8388–8415.

(18) Mifflin, A. L.; Velarde, L.; Ho, J.; Psciuk, B. T.; Negre, C. F. A.; Ebben, C. J.; Upshur, M. A.; Lu, Z.; Strick, B. F.; Thomson, R. J.; et al. Accurate Line Shapes from Sub-1 cm⁻¹ Resolution Sum Frequency Generation Vibrational Spectroscopy of α -Pinene at Room Temperature. J. Phys. Chem. A **2015**, 119, 1292–1302.

(19) Velarde, L.; Zhang, X.-y.; Lu, Z.; Joly, A. G.; Wang, Z.; Wang, H.-f. Communication: Spectroscopic Phase and Lineshapes in High-Resolution Broadband Sum Frequency Vibrational Spectroscopy: Resolving Interfacial Inhomogeneities of "Identical" Molecular Groups. J. Chem. Phys. 2011, 135, 241102.

(20) Gan, W.; Zhang, Z.; Feng, R.-r.; Wang, H.-F. Identification of Overlapping Features in the Sum Frequency Generation Vibrational Spectra of Air/Ethanol Interface. *Chem. Phys. Lett.* **2006**, *423*, 261–265.

(21) Perchard, J. P.; Josien, M. L. Vibrational Spectra of 12 Isotopic Species of Auto-Associated Ethanols. *J. Chim. Phys.* **1968**, *65*, 1856–1875.

(22) Ishiyama, T.; Imamura, T.; Morita, A. Theoretical Studies of Structures and Vibrational Sum Frequency Generation Spectra at Aqueous Interfaces. *Chem. Rev.* **2014**, *114*, 8447–8470.

(23) Ishiyama, T.; Morita, A. Molecular Dynamics Simulation of Sum Frequency Generation Spectra of Aqueous Sulfuric Acid Solution. *J. Phys. Chem. C* **2011**, *115*, 13704–13716.

(24) Ishiyama, T.; Takahashi, H.; Morita, A. Vibrational Spectrum at a Water Surface: A Hybrid Quantum Mechanics/Molecular Mechanics Molecular Dynamics Approach. *J. Phys.: Condens. Matter* **2012**, *24*, 124107.

(25) Morita, A. Improved Computation of Sum Frequency Generation Spectrum of the Surface of Water. J. Phys. Chem. B **2006**, 110, 3158–3163.

(26) Morita, A.; Hynes, J. T. A Theoretical Analysis of the Sum Frequency Generation Spectrum of the Water Surface. *Chem. Phys.* **2000**, 258, 371–390.

(27) Shiratori, K.; Yamaguchi, S.; Tahara, T.; Morita, A. Computational Analysis of the Quadrupole Contribution in the Second-Harmonic Generation Spectroscopy for the Water/Vapor Interface. *J. Chem. Phys.* **2013**, *138*, 064704.

(28) Stiopkin, I. V.; Weeraman, C.; Pieniazek, P. A.; Shalhout, F. Y.; Skinner, J. L.; Benderskii, A. V. Hydrogen Bonding at the Water Surface Revealed by Isotopic Dilution Spectroscopy. *Nature* **2011**, 474, 192–195.

(29) Valley, N. A.; Blower, P. G.; Wood, S. R.; Plath, K. L.; McWilliams, L. E.; Richmond, G. L. Doubling Down: Delving into the Details of Diacid Adsorption at Aqueous Surfaces. *J. Phys. Chem. A* **2014**, *118*, 4778–4789.

(30) Walker, D. S.; Richmond, G. L. Interfacial Depth Profiling of the Orientation and Bonding of Water Molecules across Liquid–Liquid Interfaces. J. Phys. Chem. C 2008, 112, 201–209.

(31) Messmer, M. C.; Conboy, J. C.; Richmond, G. L. Observation of Molecular Ordering at the Liquid–Liquid Interface by Resonant Sum Frequency Generation. J. Am. Chem. Soc. **1995**, *117*, 8039–8040.

(32) Gragson, D. E.; McCarty, B. M.; Richmond, G. L. Surfactant/ Water Interactions at the Air/Water Interface Probed by Vibrational Sum Frequency Generation. J. Phys. Chem. **1996**, 100, 14272–14275.

(33) Holte, L. K.; Kuran, B. A.; Richmond, G. L.; Johnson, K. E. Computational Modeling of Lauric Acid at the Organic–Water Interface. *J. Phys. Chem. C* 2014, *118*, 10024–10032.

(34) Kawaguchi, T.; Shiratori, K.; Henmi, Y.; Ishiyama, T.; Morita, A. Mechanisms of Sum Frequency Generation from Liquid Benzene: Symmetry Breaking at Interface and Bulk Contribution. *J. Phys. Chem.* C **2012**, *116*, 13169–13182.

(35) Auer, B. M.; Skinner, J. L. Vibrational Sum-Frequency Spectroscopy of the Water Liquid/Vapor Interface. *J. Phys. Chem. B* **2009**, *113*, 4125–4130.

(36) Hall, S. A.; Jena, K. C.; Covert, P. A.; Roy, S.; Trudeau, T. G.; Hore, D. K. Molecular Level Surface Structure from Nonlinear Vibrational Spectroscopy Combined with Simulations. *J. Phys. Chem. B* **2014**, *118*, 5617.

(37) Sulpizi, M.; Salanne, M.; Sprik, M.; Gaigeot, M.-P. Vibrational Sum Frequency Generation Spectroscopy of the Water Liquid–Vapor Interface from Density Functional Theory Based Molecular Dynamics Simulations. J. Phys. Chem. Lett. **2013**, *4*, 83.

(38) Morita, A.; Hynes, J. T. A Theoretical Analysis of the Sum Frequency Generation Spectrum of the Water Surface. *Chem. Phys.* **2000**, 258, 371.

(39) Morita, A.; Hynes, J. T. A Theoretical Analysis of the Sum Frequency Generation Spectrum of the Water Surface. II. Time-Dependent Approach. J. Phys. Chem. B **2002**, 106, 673–685.

(40) Guthmuller, J.; Cecchet, F.; Lis, D.; Cuadano, Y.; Mani, A. A.; Thiry, P. A.; Peremans, A.; Champagne, B. Theoretical Simulation of Vibrational Sum-Frequency Generation Spectra from Density Functional Theory: Application of p-Nitrothiophenol and 2,4-Dinitroanaline. *ChemPhysChem* **2009**, *10*, 2132–2142.

(41) Carr, J. K.; Wang, L.; Roy, S.; Skinner, J. L. Theoretical Sum Frequency Generation Spectroscopy of Peptides. *J. Phys. Chem. B* **2014**, DOI: 10.1021/jp507861t.

(42) Xiao, D.; Fu, L.; Liu, J.; Batista, V. S.; Yan, E. C. Y. Amphiphilic Adsorption of Human Islet Amyloid Polypeptide Aggregrates to Lipid/Aqueous Interfaces. *J. Mol. Biol.* **2012**, *421*, 537–547.

(43) Fu, L.; Wang, Z.; Yan, E. C. Y. Chiral Vibrational Structures of Proteins at Interfaces Probed by Sum Frequency Generation Spectroscopy. *Int. J. Mol. Sci.* **2011**, *12*, 9404–9425.

(44) Fu, L.; Liu, J.; Yan, E. C. Y. Chiral Sum Frequency Generation Spectroscopy for Characterizing Protein Secondary Structures at Interfaces. J. Am. Chem. Soc. **2011**, 133, 8094–8097.

(45) Liang, C.; Louhivuori, M.; Marrink, S. J.; Jansen, T. L. C.; Knoester, J. Vibrational Spectra of a Mechanosensitive Channel. *J. Phys. Chem. Lett.* **2013**, *4*, 448–452.

(46) Roeters, S. J.; van Dijk, C. N.; Torres-Knoop, A.; Backus, E. H. G.; Campen, R. K.; Bonn, M.; Woutersen, S. Determining in Situ Protein Conformation and Orienation from the Amide-I Sum-Frequency Generation Spectrum: Theory and Experiment. *J. Phys. Chem. A* **2013**, *117*, 6311–6322.

(47) Valley, N. A.; Robertson, E. J.; Richmond, G. L. Twist and Turn: Effect of Stereoconfiguration on the Interfacial Assembly of Polyelectrolytes. *Langmuir* **2014**, *30*, 14226–14233.

(48) Lee, C. M.; Mohamed, N. M. A.; Watts, H. D.; Kubicki, J. D.; Kim, S. H. Sum-Frequency-Generation Vibration Spectroscopy and Density Functional Theory Calculations with Dispersion Corrections (DFT-D2) for Cellulose 1a and 1b. *J. Phys. Chem. B* **2013**, *117*, 6681– 6692.

(49) Bates, K. H.; Crounse, J. D.; St. Clair, J. M.; Bennett, N. B.; Nguyen, T. B.; Seinfeld, J. H.; Stoltz, B. M.; Wennberg, P. O. Gas Article

2014, 118, 1237–1246. (50) Chan, M. N.; Surratt, J. D.; Claeys, M.; Edgerton, E. S.; Tanner, R. L.; Shaw, S. L.; Zheng, M.; Knipping, E. M.; Eddingsaas, N. C.; Wennberg, P. O.; et al. Characterization and Quantification of Isoprene-Derived Epoxydiols in Ambient Aerosol in the Southeastern United States. *Environ. Sci. Technol.* 2010, 44, 4590–4596.

(51) Lin, Y.-H.; Zhang, Z.; Docherty, K. S.; Zhang, H.; Budisulistiorini, S. H.; Rubitschun, C. L.; Shaw, S. L.; Knipping, E. M.; Edgerton, E. S.; Kleindienst, T. E.; et al. Isoprene Epoxydiols as Precursors to Secondary Organic Aerosol Formation: Acid-Catalyzed Reactive Uptake Studies with Authentic Compounds. *Environ. Sci. Technol.* 2012, 46, 250–258.

(52) Liu, Y.; Kuwata, M.; Strick, B. F.; Thomson, R. J.; Geiger, F. M.; McKinney, K. A.; Martin, S. T. Uptake of Epoxydiol Isomers Accounts for Half of the Particle-Phase Material Produced from Isoprene Photooxidation Via the HO₂ Pathway. *Environ. Sci. Technol.* **2015**, *49*, 250–258.

(53) Upshur, M. A.; Strick, B. F.; McNeill, V. F.; Thomson, R. J.; Geiger, F. M. Climate-Relevant Physical Properties of Molecular Constituents for Isoprene-Derived Secondary Organic Aerosol Material. *Atmos. Chem. Phys.* **2014**, *14*, 10731–10740.

(54) Boyd, R. W. *Nonlinear Optics;* Academic Press: New York, 2003. (55) Shen, Y. R.; Ostroverkhov, V. Sum-Frequency Vibrational Spectroscopy on Water Interfaces: Polar Orientation of Water Molecules at Interfaces. *Chem. Rev.* **2006**, *106*, 1140–1154.

(56) Geiger, F. M. Second Harmonic Generation, Sum Frequency Generation, and $X^{(3)}$: Dissecting Environmental Interfaces with a Nonlinear Optical Swiss Army Knife. *Annu. Rev. Phys. Chem.* **2009**, *60*, 61–83.

(57) Richmond, G. L. Molecular Bonding and Interactions at Aqueous Surfaces as Probed by Vibration Sum Frequency Spectroscopy. *Chem. Rev.* **2002**, *102*, 2693–2724.

(58) Esenturk, O.; Walker, R. A. Surface Structure at Hexadecane and Halo-Hexadecane Liquid/Vapor Interfaces. *J. Phys. Chem. B* **2004**, *108*, 10631–10635.

(59) Gopalakrishnan, S.; L, D.; Allen, H. C.; Kuo, M.; Shultz, M. J. Vibrational Spectroscopic Studies of Aqueous Interfaces: Salts, Acids, Bases, and Nanodrops. *Chem. Rev.* **2006**, *106*, 1155–1175.

(60) Zhuang, X.; Miranda, P. B.; Kim, D.; Shen, Y. R. Mapping Molecular Orientation and Conformation at Interfaces by Surface Nonlinear Optics. *Phys. Rev. B* **1999**, *59*, 12632–12640.

(61) Hayes, P. L.; Keeley, A. R.; Geiger, F. M. Structure of Cetyltrimethylammonium Surfactant at Fused Silica/Aqueous Interfaces Studied by Vibrational Sum Frequency Generation. *J. Phys. Chem.* B **2010**, *114*, 4495–4502.

(62) Zhang, Z.; Lin, Y. H.; Zhang, H.; Surratt, J. D.; Ball, L. M.; Gold, A. Technical Note: Synthesis of Isoprene Atmospheric Oxidation Products: Isomeric Epoxydiols and the Rearrangement Products cisand trans-3-Methyl-3,4-Dihydroxytetrahydrofuran. *Atmos. Chem. Phys.* **2012**, *12*, 8529–8535.

(63) Corey, E. J.; Gilman, N. W.; Ganem, B. E. New Methods for the Oxidation of Aldehydes to Carboxylic Acids and Esters. *J. Am. Chem. Soc.* **1968**, *90*, 5616–5617.

(64) Skucas, E.; Kong, J. R.; Krische, M. J. Enantioselective Reductive Coupling of Acetylene to *N*-Arylsulfonyl Imines Via Rhodium Catalyzed C–C Bond-Forming Hydrogenation: (*Z*)-Dienyl Allylic Amines. J. Am. Chem. Soc. **2007**, 129, 7242–7243.

(65) Voges, A. B.; Stokes, G. Y.; Gibbs-Davis, J. M.; Lettan, R. B.; Bertin, P. A.; Pike, R. C.; Nguyen, S. T.; Sheidt, K. A.; Geiger, F. M. Insights into Heterogeneous Atmospheric Oxidation Chemistry: Development of a Tailor-Made Synthetic Model for Studying Tropospheric Surface Chemistry. *J. Phys. Chem. C* **2007**, *111*, 1567– 1578.

(66) Shrestha, M.; Zhang, Y.; Ebben, C. J.; Martin, S. T.; Geiger, F. M. Vibrational Sum Frequency Generation Spectroscopy of Secondary Organic Material Produced by Condensational Growth from α -Pinene Ozonolysis. J. Phys. Chem. A **2013**, 117, 8427–8436.

(67) Becke, A. D. Density-Function Thermochemistry. III. The Role of Exact Exchange. J. Chem. Phys. **1993**, 98, 5648–5652.

(68) Lee, C.; Yang, W. S.; Parr, R. G. Development of the Colle–Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785–789.

(69) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* **1994**, *98*, 11623–11627.

(70) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; et al. *Gaussian 09*, revision D.02; Gaussian, Inc.: Wallingford, CT; 2009.

(71) Halls, M. D.; Velkovski, J.; Schlegel, H. B. Harmonic Frequency Scaling Factors for Hartree-Fock, S-VWN, B-LYP, B3-LYP, B3-PW91, and MP2 with the Sadlej pVTZ Electric Property Basis Set. *Theor. Chem. Acc.* **2001**, *105*, 413–421.

(72) Scott, A. P.; Radom, L. Harmonic Vibrational Frequencies: An Evalutation of Hartree-Fock, Møller-Plesset, Quadratic Configuration Interaction, Density Functional Theory, and Semiempirical Scale Factors. *J. Phys. Chem.* **1996**, *100*, 16502.