Beyond Local Group Modes in Vibrational Sum Frequency Generation

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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=C 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,41,42 proteins,43−46 and polymers47,48 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
idealyl desirable, is often not available, thus making it challenging to use this approach in a predictive fashion.

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).54–56 This compound contains multiple polar 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 resulting in a narrow range of preferred orientations that we quantify using experiment and computation. 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.5,6 One way to express the intensity of the sum frequency signal is given that has a frequency that oscillates at the sum of the two input frequencies. Typically, this signal is quantified using experiment and computation. Furthermore, this signal is dominated by its resonant contribution as the nonresonant component has been shown to be negligible at oxide surfaces.7,8,15,54 This compound contains multiple polar groups that facilitate hydrogen bonding to the silica surface, resulting in a narrow range of preferred orientations that we quantify using experiment and computation. 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.

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Here, $N_{ab}$ 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

$$\beta_{\nu,q} \propto \frac{\partial \alpha_\nu}{\partial Q_\nu} \frac{\partial \mu_\nu}{\partial Q_\nu}$$

(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 $\chi^{(2)}_{ijk}$ using a $z-y-z$ Euler transformation matrix according to

$$\chi^{(2)}_{ijk} = N \sum_{i,j,k} \langle R_{i}\mu_{j}R_{k}\mu_{k} \rangle \beta_{\nu,q}$$

(4)

The molecular orientation is defined by a “tilt” angle, $\theta$, and a “twist” angle, $\psi$. The in-plane rotation is defined as $\phi$, and for a rotationally isotropic noninteracting surface, $\phi$ is averaged by integrating from 0 to $2\pi$. 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

$$\chi^{(2)}_{ssp} = L_{yy} \langle \alpha_{SSG} \rangle L_{zz} \langle \alpha_{IR} \rangle \sin \alpha_{RI} \chi_{yy}$$

(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 p-polarized IR beams. As a note, “s” designates a light field polarization that is parallel to the plane of incidence, and “p” 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.6,6 The synthesis of trans-β-IEPOX-δ2 (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 MnO2 and NaCN produced methyl ester 4 in 53% yield.6,4 Reduction to the primary alcohol with LiAlD4 followed by epoxidation with MCPBA afforded deuterium-labeled epoxyde 5 in 73% yield over the two steps. Finally, removal of the silyl-protecting group with TBAF gave desired trans-β-IEPOX-δ2.
(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, 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. All DFT calculations are performed with the hybrid B3LYP functional and 6-311G(d,p) basis set with the Gaussian 09 package. 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 $\beta_{\text{mon}}$ 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 ($\chi^{(2)}_{ij}(\phi,\psi,\theta)$) for a particular set of orientation angles. By averaging $\chi^{(2)}_{ij}$ over phi ($\phi$) angles for every $\psi$ from 0 to 360°, we invoke full azimuthal rotational symmetry. This step results in a molecular orientation defined by a tilt ($\theta$) and a twist ($\psi$) 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. 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-β-IEPOX obtained from both experiment and theory. The latter was obtained for a tilt angle of $70^\circ$ and a twist angle of $90^\circ$ ($70^\circ$, $90^\circ$) of the $C_{3v}$ 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 $\theta$ and $\psi$ 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-β-IEPOX possesses multiple hydrogen-bonding sites that can interact with the Si–OH groups on the silica substrate, resulting in a net preferred orientation within $5^\circ$–$20^\circ$ for $\theta$ and $\psi$. 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-β-IEPOX at the vapor/silica interface 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
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-$\beta$-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 in destructive interference and an overall low-intensity signal at around 2865 cm$^{-1}$, as shown in Table 2. Deuterating one of the CH$_2$ groups removes the destructive interference, and an overall increase in the CH$_3$ 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-$\beta$-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. In that work, which was based on a Lorentzian peak fitting of the experimental ssp spectrum, we assumed...
uncoupled localized group vibrations. Moreover, we assumed that the SFG band at 2880 cm\(^{-1}\) was entirely due to the CH\(_3\) symmetric stretching mode. This local group mode approach resulted in a reported tilt angle of \(\sim 40^\circ\) 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 CH\(_3\) tilt angle of approximately 70–80\(^\circ\) 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\(^\circ\), 90\(^\circ\)) 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 assignments for trans-\(\beta\)-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-\(\beta\)-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 \(\sim 2943\) 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 \(\sim 2865\) 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 deutering 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-\(\beta\)-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.

![Figure 5. Predicted ssp-polarized SFG spectra of IEPOX isotopologues that have not been synthesized. The left-hand column includes trans-\(\beta\)-IEPOX, \(d_\text{H}\)-trans-\(\beta\)-IEPOX, and other isotopologues surveyed that contain CH\(_3\) groups. The right-hand column includes all isotopologues surveyed that contain CD\(_3\) groups.](image-url)
Experimental synthesis, $^1$H- and $^{13}$C-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.

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**REFERENCES**

Simulations. The Journal of Physical Chemistry A

tational Theory: Application of p-Nitrothiophenol and 2,4-Dinitroana-
Vibrational Sum-Frequency Generation Spectra from Density Func-
Orientation and Bonding of Water Molecules across Liquid–Water Interfaces.
J. Phys. Chem. C
Symmetry Breaking at Interface and Bulk Contribution.
2014
C
Vibrational Spectroscopy Combined with Simulations.
2009
C