Orientations of nonlocal vibrational modes from combined experimental and theoretical sum frequency spectroscopy

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Article info
Article history:
Received 7 December 2016
In final form 7 January 2017
Available online 9 January 2017

Keywords:
Sum frequency generation
Orientation analysis
Interfaces
DFT calculations

ABSTRACT
Inferring molecular orientations from vibrational sum frequency generation (SFG) spectra is challenging in polarization combinations that result in low signal intensities, or when the local point group symmetry approximation fails. While combining experiments with density functional theory (DFT) could overcome this problem, the scope of the combined method has yet to be established. Here, we assess its feasibility for determining the distributions of molecular orientations for one monobasic ester, two epoxides, and three alcohols at the vapor/fused silica interface. We find that molecular orientations of nonlocal vibrational modes cannot be determined by polarization-resolved SFG measurements alone.

1. Introduction
The determination of molecular orientations of small-oxygenated molecules at solid surfaces is beneficial for understanding processes relevant to heterogeneous catalysis and the environment [1–4]. Vibrational sum frequency generation (SFG) spectroscopy holds the promise of providing exquisite surface-sensitivity to study such systems [5–15]. With SFG spectroscopy, molecular orientation analyses are generally carried out by polarization control of the infrared, visible, and output sum frequency beams [16–23]. Specifically, polarization null angle (PNA) [16,17,24–27] or polarization intensity ratio (PIR) [28,29] methods [22,23] are often used, both methods commonly employ peak fitting of experimental spectra and assumptions of local point group symmetry of the vibrational mode of interest. However, in our previous work we have shown that these point group symmetry assumptions may not necessarily apply for strained systems like epoxides and bicyclic systems that have delocalized, or nonlocal, vibrational modes [30–32]. Furthermore, the PIR method often requires collecting spectra in two polarization combinations, ssp and ppp-polarized spectra; however, SFG signal intensities in the ppp polarization combination are often much lower in intensity compared to ssp making peak assignments difficult. To overcome this challenge, here we pair SFG spectroscopy with density functional theory (DFT) calculations of SFG spectra and show how molecular orientation distributions of small-oxygenated compounds having non-local normal modes can be determined at vapor/solid interfaces. We follow a recently published hybrid experimental/DFT method that uses DFT to calculate vibrational frequencies, dipole and polarizability derivatives, which are then used in a custom Python script to calculate molecular hyperpolarizabilities, and subsequent SFG spectra, at any molecular orientation. This method is useful for interpreting SFG spectra collected from experiment and also for reliably predicting SFG spectra and molecular orientations of compounds that have not yet been synthesized, or that are difficult to measure [31]. To expand the scope of our approach from the epoxydiol we have studied so far, we report standard (10–15 cm−1) [11,33,34] and high-resolution (0.6 cm−1) [35–40] SFG spectra in the C–H stretching region for one monobasic ester, two epoxides, and three alcohols (Fig. 1A) at the vapor/fused silica interface collected from experiment and computed using DFT. We find that theoretical distributions of orientation of molecules displaying normal modes with \( \text{C}_2v \) and \( \text{C}_3v \)
(compounds 1–4 in Fig. 1A, indicated in red) symmetries are in good agreement with those determined from experimental polarization-resolved SFG spectra, whereas molecules characterized by non-local normal modes (compounds 5 and 6 in Fig. 1A) require an orientation analysis that is based on finding the best match, or the lowest sum of squared difference as described in the Methods section, between experimental and calculated SFG spectra.

2. Methods

2.1. Samples studied

(R)-methyl lactate (Santa Cruz), (R)-epoxybutane (Santa Cruz), (R)-propylene oxide (Santa Cruz), 1-hexanol (Sigma Aldrich), and 1-propanol (Sigma Aldrich) were purchased and used as received. 2-Methyl-1,4-butanediol was synthesized by oxidizing methyl succinic acid through a procedure described in the Section 8 of the Supplementary Materials.

2.2. Standard and high-resolution SFG spectroscopy

The standard (Northwestern University, 10–15 cm\(^{-1}\)) [11,33,34] and high (Pacific Northwestern National Lab, 0.6 cm\(^{-1}\)) [35–38] resolution SFG laser systems have been detailed in previous work. All of the spectra reported were measured at the vapor/fused silica interface with ssp and ppp polarization combinations. For the standard resolution SFG laser system, we utilized a home-built Teflon vapor cell, wherein one drop of liquid compound was injected into the cell, which was then placed on a sample stage sealed by a fused silica optical window and a Viton o-ring. The vapor was allowed to equilibrate for ~10 min before spectral data acquisition. For the viscous 2-methyl-1,4-butanediol compound, one drop was placed at the bottom of the fused silica window and pressed against a home built Teflon sample cell. The visible and IR beams were aligned directly above the sample droplet to probe the vapor/solid interface. The spectra reported here are an average of 4–7 individual spectra each taken for ~2–5 min each. For the high-resolution SFG system, 1–2 drops of liquid sample were placed at the edge of shallow Teflon beaker that was then capped with a fused silica optical window. The vapor was allowed to equilibrate for ~10 min before spectral data acquisition. The spectra reported are an average of 2–3 individual acquisitions each recorded for ~5–10 min. The datapoints in the high-resolution SFG spectra reported were boxcar averaged by 5 points, or by 1.73 cm\(^{-1}\), in Igor Pro Version 6.11 (WaveMetrics, Lake Oswego, OR, USA).

2.3. Orientation analyses from polarization intensity ratios

Orientation analyses from experimentally obtained polarization intensity ratios were performed on all compounds in this work. To do so, we measured SFG spectra in ppp and ssp polarization combinations and compared the signal intensities (I\(_{ppp}\) and I\(_{ssp}\), respectively) for the particular peak that corresponded to a localized vibrational mode as determined by DFT discussed next (Section D). We use custom written Igor Pro macros to calculate tilt angle, \(\theta\), values of moieties having \(C_{2v}\) or \(C_{3v}\) point group symmetries (CH\(_2\) or CH\(_3\) group) and either symmetric and asymmetric stretches, that are based on work described elsewhere [22]. Using a number of input parameters (Table S7), including incident angles and refractive indices, we then plot computed I\(_{ppp}/I_{ssp}\) values for \(C_{2v}\) or \(C_{3v}\) tilt angles between 0° and 90°, assuming a monomodal Gaussian distribution of angles. We find where the experimentally determined

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1 For interpretation of color in Fig. 1, the reader is referred to the web version of this article.
The methods used to calculate SFG spectra have been detailed in our previous work [7,14,15,31,32]. Briefly, DFT calculations (B3LYP [41–44]/6-311G(d,p), [45,46] Gaussian 09 Rev. D.01 software suite) [47] were shown to be appropriate for carrying out SFG calculations of a small epoxide at the vapor/silica interface [31], after optimizing the geometry of each conformer and performing a harmonic frequency analysis. The dipole and polarizability derivatives (’freq + raman iop(7/33 = 1)’ keyword in the Gaussian input file) were used to compute the effective nonlinear susceptibility for each normal mode at a particular molecular orientation with our custom-written Python script utilizing the parameters of Table S7. Frequency scaling factors were applied to the calculated spectra (Table S1 in the Supplementary Materials), and a Lorentzian broadening function was applied to each SFG intensity. While our approach is practical and applicable to large systems, state-of-the-art techniques based on the vibrational self-consistent field (VSCF) method at the second-order vibrational quasi-degenerate level [48], could be used to predict vibrational frequencies within 20 cm$^{-1}$ [49]. We did not include Fermi resonances in the calculated SFG spectra, as by neglecting Fermi resonances we generally obtain better matches to the experimental SFG spectra at the level theory used (shown in Section 6 of the Supplementary Materials). Lorentzian linewidths of 5 cm$^{-1}$ and 12 cm$^{-1}$ were applied to the calculated spectra, at high and standard resolution, respectively. The SFG amplitudes were averaged over the azimuthal direction in 5$^\circ$ increments. All calculated spectra correspond to the ssp polarization combination.

For each molecule, we computed an SFG spectrum at all combinations of the tilt and twist angles in 10$^\circ$ increments. These spectra were then visualized in a custom Mathematica notebook, where we compute the sum of squared differences between each computed spectrum and the experimentally determined spectrum. We determine the most likely average orientations to those with the smallest sum of squared difference values with a range of $\sim 5^\circ$. Furthermore, we found that for compounds having a number of possible conformers, only one conformer produced spectra that matched the experiment (see Section 2 in the Supplementary Materials) reasonably well.

3. Results and discussion

3.1. Group symmetry validation of localized vibrational oscillators by DFT for carrying out orientational analyses by polarization-resolved SFG

To begin, the point group symmetries for the various C–H stretches were determined by visualizing the atomic displacement animations in GaussView 5.0 [50]. Graphical representations of the atomic displacements for the vibrational modes of interest are provided in Fig. 1B. For example, hexanol (1) has a distinct localized CH$_3$ symmetric stretch at a scaled frequency of 2880 cm$^{-1}$ (Fig. 1B). This mode is found to have C$_{3v}$ symmetry. In addition to (1), for compounds (2–4), we identified peaks in the ssp- and ppp-polarized SFG spectra that correspond to frequencies associated with localized vibrational modes as determined by DFT. Compounds (5) and (6), however, are characterized by non-local normal modes, which we define as one vibrational mode of a particular frequency that has atomic displacement contributions from more than one hydrocarbon group in a molecule with a geometry that has a minimum potential energy, for example, one mode with atomic displacements occurring at both a CH$_2$ and CH$_3$ group in a molecule. Below, our results for compounds (1–4) will be presented first, followed by a discussion of our findings for compounds (5) and (6).

3.2. Molecular orientations obtained from DFT calculations agree with orientations obtained from SFG PIR orientation analysis method of localized oscillators

Using the well-established PIR method [22], we determined the tilt angles of the terminal CH$_3$ groups of hexanol (1) and propanol (2), one of the CH$_3$ groups of methyl lactate (3), and the 6CH$_2$ group of epoxybutane (4). The orientations of the terminal methyl groups of (1) and (2) were triangulated based on the symmetric stretches at 2880 cm$^{-1}$ and 2947 cm$^{-1}$, respectively, that have sufficient signal intensities in the ssp and ppp polarization combinations (Fig. 2C and G, respectively). By assuming full C$_{3v}$ symmetry of the methyl groups as shown in the DFT calculations, the tilt angles of the CH$_3$ groups of (1) and (2) were determined to be 65(±7)$^\circ$ and 64(±4)$^\circ$ from the surface normal, respectively. These experimentally derived tilt angles agree well with the calculated tilt angles that are associated with the best matches to both the standard (Fig. 2A and E) and high-resolution (Fig. 2B and F) SFG spectra.

The symmetric stretch of the highlighted CH$_3$ group of methyl lactate (3) was determined to be near 2878 cm$^{-1}$ (shown in Fig. 2G), with an experimentally derived tilt angle of 64(±6)$^\circ$ from the surface normal. Our DFT calculations show reasonable agreement with both standard and high-resolution SFG spectra (Fig. 2I and J). We obtain the best matches when that methyl group is oriented parallel to the surface (Fig. 2L), with a tilt angle from this calculation that agrees well with the tilt angle derived from experiments.

Lastly, we were able to obtain some signal intensity from the 6CH$_2$ group on the epoxide ring of epoxybutane (4) near 3018 cm$^{-1}$, specifically the asymmetric CH$_2$ stretch (Fig. 1B), to triangulate the group tilt angle. We determined an experimental tilt angle of 31(±5)$^\circ$ from the surface normal by analyzing the ppp and ssp-polarization intensity ratio (Fig. 3C). However, there is likely some error in this estimate, given the weak signal intensity in ppp-polarized spectrum. From our calculations, we determine a tilt angle near 40$^\circ$ from the surface normal (Fig. 4D), with reasonable spectral agreement to the experimental standard (Fig. 4A) and high-resolution (Fig. 4B) SFG spectra.

3.3. Molecular orientations for molecules with nonlocal vibrational modes as revealed by DFT underdetermined by polarization-resolved SFG measurements alone

For the remaining compounds (5) and (6), we were unable to identify any prominent peaks in the SFG spectra that were associated with localized vibrational modes. For example, for 2-methyl-1,4-butanediol (5), the 2965 cm$^{-1}$ peak in the ssp-polarized spectrum (Fig. 3E) is associated with a mode consisting of the methylene and methyl vibrations within the molecule (Fig. 1B). Therefore, it was difficult to approximate the appropriate point group symmetry of that mode. However, we carried out orientation analyses assuming both C$_{3v}$ and C$_{2v}$ symmetries for the mode, and found that the ppp/ssp-polarization intensity ratio of the 2945 cm$^{-1}$ peak did not fall in the range of any theoretical value. Therefore, we could not determine a tilt angle or compare it to the calculated tilt angle.

We carried out a similar analysis for propylene oxide (6), which has three distinguished peaks (Fig. 4A). However, the peak with the largest signal intensity at 2945 cm$^{-1}$ is dominated by a single non-local, or delocalized, vibrational mode that has contributions from all C–H groups in the molecule as shown by DFT (CH$_2$, CH, and CH$_3$).
Although we were unable to identify the particular point group symmetry of that mode, we went on to assume that the mode was dominated by contributions of the CH₃ asymmetric stretching motion, and carried out the orientation analysis. When assuming the 2945 cm⁻¹ mode had C₃ᵥ symmetry and was asymmetric, the tilt angle was predicted to be 45(±7)°. However, the calculation shows that the tilt angle of the methyl group is near 90° (Fig. 4D). This discrepancy stresses the importance of identifying the proper group symmetry of a particular vibrational mode, and point group symmetry assumptions of delocalized vibrational modes may not be valid.

Despite the obvious disagreement between orientations derived from our DFT calculations and those derived from experiment, the fact that our calculated spectra align with our experimental spectra emphasizes the advantage of using this calculation method for systems that are not simple or contain delocalized vibrational modes. For example, propylene oxide is an important intermediate for producing fine chemicals, for which our approach could be essential.
for determining the molecular orientations on newly developed heterogeneous catalysts. While we have shown our approach works well for vapor/silica and, in principle, liquid/silica interfaces, providing excellent agreement between calculated and experimentally determined molecular orientations, it can most importantly be used for systems where an experimental orientation analysis may not be possible for the reasons given above.

4. Conclusion

We have shown that DFT is suitable for calculating SFG spectra for standard and high-resolution SFG spectra for a series of oxygenated organic compounds in contact with fused silica surfaces. The molecular orientations of local normal modes obtained from computed spectra that matched experimental spectra were found to be in reasonable agreement with orientations derived from polarization-resolved experimental spectra. While these conclusions hold for four of the compounds surveyed, we also have shown that orientation analyses are not appropriate for vibrational modes that are not localized to one group having particular point group symmetry. For such modes, we find that it is necessary to determine molecular orientations by methods other than polarization-resolved SFG measurements alone, preferably by pairing them with computational methods.

Acknowledgements

H.M.C. gratefully acknowledges support from a National Science Foundation (NSF) Graduate Research Fellowship under Grant No. DGE-1324585 and from the Institute for Sustainability and Energy at Northwestern (ISEN). This work made use of the FTIR spectrometer in the Integrated Molecular Structure Education and Research Center (IMSERC, Northwestern University). M.A.U. gratefully acknowledges support from a National Aeronautics and Space Administration Earth and Space (NASA ESS) Fellowship and from an NSF Graduate Research Fellowship. B.R. gratefully acknowledges support from an NSF Graduate Research Fellowship under Grant No. DGE-1122492. Part of this work was conducted at the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL) at the PNNL and sponsored by the Department of Energy’s Office of Biological and Environmental Research (BER). S.L.C. and Z. C. are Alternate Sponsored Fellow (ASF) at PNNL, and L.F. was the William Wiley postdoctoral fellow at EMSL during this work. V.S. B. acknowledges supercomputer time from NERSC and the Yale High Performance Computing Center and support from NSF Grant CHE-1465108. F.M.G. and R.J.T. acknowledge support from NSF Grant CHE-1607640.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cplett.2017.01.015.

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