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



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1. Introduction

The determination of molecular orientations of smalloxygenated 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 surfacesensitivity to study such systems [5–15]. With SFG spectroscopy, molecular orientation analyses are generally carried out through 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, sspand ppp-polarized spectra; however, SFG signal intensities in the

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 of 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 using polarization-resolved SFG measurements alone.

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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 $C_{2\nu}$ and $C_{3\nu}$

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Fig. 1. Compound structures and numbering scheme used in this work (A). (B) Shows the graphical representation of vibrational modes used to carry out orientation analyses. The arrows represent the atomic displacements at that particular vibrational mode.

(compounds **1–4** in Fig. 1A, indicated in red¹) 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, $10-15 \text{ cm}^{-1}$) [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 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, θ , values of moieties having C_{2v} or C_{3v} point group symmetries (CH₂ or CH₃ 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

 $^{^{1}\,}$ For interpretation of color in Fig. 1, the reader is referred to the web version of this article.

 I_{ppp}/I_{ssp} ratio intersects the computed ratios in order to determine the tilt angle and range of tilt angles.

2.4. DFT SFG calculations

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° 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° 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 ~5°. 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 CH₃ 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 CH₃ groups of hexanol (1) and propanol (2), one of the CH₃ groups of methyl lactate (3), and the ^RCH₂ 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 CH₃ groups of (1) and (2) were determined to be $65(\pm7)^{\circ}$ and $64(\pm4)^{\circ}$ 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. 2), with an experimentally derived tilt angle of $84(\pm 6)^{\circ}$ 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 ^RCH₂ group on the epoxide ring of epoxybutane (**4**) near 3018 cm⁻¹, specifically the asymmetric CH₂ stretch (Fig. 1B), to triangulate the group tilt angle. We determined an experimental tilt angle of $\sim 31(\pm 5)^{\circ}$ 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 $\sim 40^{\circ}$ 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 nonlocal, or delocalized, vibrational mode that has contributions from all C–H groups in the molecule as shown by DFT (CH₂, CH, and CH₃)



Fig. 2. The hexanol (1) *ssp*-polarized vapor/silica standard (A) and high (B) resolution spectra as well as the corresponding best-matching calculated spectra (black traces). The orientation was determined by comparing experimental *ssp*- and *ppp*-polarized spectra (C) that agrees well with the orientation determined through calculations. The range of tilt angles determined by experiment are shown in the shaded red area (D). The propanol (**2**) *ssp*-polarized vapor/silica standard (E) and high (F) resolution spectra as well as the corresponding best-matching calculated spectra (black traces). The orientation was determined by comparing experimental *ssp*- and *ppp*-polarized was determined by comparing experimental *ssp*- and *ppp*-polarized spectra (G) and agrees well with the orientation determined through calculated spectra (black traces). The orientation was determined by experiment are shown in the shaded red area (G) and agrees well with the orientation determined through calculations. The range of tilt angles determined by experiment are shown in the shaded red area (H). The methyl lactate (**3**) *ssp*-polarized vapor/silica standard (I) and high (J) resolution spectra and the corresponding best-matching calculated spectra (black traces). The *ssp* and *ppp*-polarized spectra (K), and the orientation determined by comparing *pp* and *ssp* intensity ratios agree with that determined through calculations (L).



Fig. 3. The epoxybutane (**4**) *ssp*-polarized vapor/silica standard (E) and high (F) resolution spectra and the corresponding best-matching calculated spectra (black traces). The *ssp*- and *ppp*-polarized spectra (G), and the orientation determined by comparing *ppp* and *ssp* intensity ratios agree with that determined through calculations (H). The vibrational modes of 2-methyl-1,4-butanediol (**5**) in the experimental *ssp* and *ppp*-polarized SFG data were highly delocalized, therefore the orientation analysis yielded an orientation that did not align with the calculated molecular orientation. However, the calculations of the standard (E) and high (F) resolution spectra (black traces) result in an orientation shown in (H).

(Fig. 1B). 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 C_{3v} 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



Fig. 4. Standard resolution SFG spectra of propylene oxide (**6**) (A, purple trace) overlaid with the best-matching *ssp*-polarized calculated spectrum (black trace). The standard (purple trace) and high-resolution (green trace) spectra agree very well (B). The majority of the peak contribution in both *ssp* and *ppp*-polarized SFG spectra (C) is dominated by delocalized vibrational modes, therefore we did not get good agreement between the experimental orientation analysis and calculated molecular orientations as described in the text. The molecular orientation associated with the best matching spectrum is determined (D) with a CH₃ tilt angle close to 90° from the surface normal. The orientation analysis predicts a CH₃ near 45° from the surface normal.

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.

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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.

References

- C. Keresszegi, D. Ferri, T. Mallat, A. Baiker, Unraveling the surface reactions during liquid-phase oxidation of benzyl alcohol on Pd/Al₂O₃: an in Situ ATR-IR study, J. Phys. Chem. B 109 (2005) 958.
- [2] G.A. Somorjai, C. Aliaga, Molecular studies of model surfaces of metals from single crystals to nanoparticles under catalytic reaction conditions. Evolution from prenatal and postmortem studies of catalysts, Langmuir 26 (2010) 16190.

- [3] J.E. Rekoske, M.A. Barteau, Kinetics, selectivity, and deactivation in the aldol condensation of acetaldehyde on anatase titanium dioxide, Ind. Eng. Chem. Res. 50 (2011) 41.
- [4] J. van den Brand, O. Blajiev, P.C.J. Beentjes, H. Terryn, J.H.W. de Wit, Interaction of anhydride and carboxylic acid compounds with aluminum oxide surfaces studied using infrared reflection absorption spectroscopy, Langmuir 20 (2004) 6308.
- [5] H. Vanselous, P.B. Petersen, Extending the capabilities of heterodyne-detected sum-frequency generation spectroscopy: probing any interface in any polarization combination, J. Phys. Chem. C 120 (2016) 8175.
- [6] C. Calabrese, H. Vanselous, P.B. Petersen, Deconstructing the heterogeneity of surface-bound catalysts: rutile surface structure affects molecular properties, J. Phys. Chem. C 120 (2016) 1515.
- [7] M.L. Clark, B. Rudshteyn, A. Ge, S.A. Chabolla, C.W. Machan, B.T. Psciuk, J. Song, G. Canzi, T. Lian, V.S. Batista, C.P. Kubiak, Orientation of cyano-substituted bipyridine Re(I) *fac*-tricarbonyl electrocatalysts bound to conducting Au surfaces, J. Phys. Chem. C 120 (2016) 1657.
- [8] J. Wang, M.L. Clark, Y. Li, C.L. Kaslan, C.P. Kubiak, W. Xiong, Short-range catalyst-surface interactions revealed by heterodyne two-dimensional sum frequency generation spectroscopy, Phys. Chem. Lett. 6 (2015) 4204.
- [9] J.M. Krier, W.D. Michalak, X. Cai, L. Carl, K. Komvopoulos, G.A. Somorjai, Sum frequency generation vibrational spectroscopy of 1,3-butadiene hydrogenation on 4 nm Pt@SiO₂, Pd@SiO₂, and Rh@SiO₂ core-shell catalysts, Nano Lett. 15 (2015) 39.
- [10] Z. Li, C.N. Weeraman, J.M. Gibbs-Davis, Following the azide-alkyne cycloaddition at the silica/solvent interface with sum frequency generation, ChemPhysChem 15 (2014) 2247.
- [11] A.M. Buchbinder, N.A. Ray, J. Lu, R.P. Van Duyne, P.C. Stair, E. Weitz, F.M. Geiger, Displacement of hexanol by the hexanoic acid overoxidation product in alcohol oxidation on a model supported palladium nanoparticle catalyst, J. Am. Chem. Soc. 133 (2011) 17816.
- [12] G.Y. Stokes, A.M. Buchbinder, J.M. Gibbs-Davis, K.A. Scheidt, F.M. Geiger, Chemically diverse environmental interfaces and their reactions with ozone studied by sum frequency generation, Vib. Spectrosc. 50 (2009) 86.
- [13] G. Kennedy, L.R. Baker, G.A. Somorjai, Selective amplification of C=O bond hydrogenation on Pt/TiO₂: catalytic reaction and sum-frequency generation vibrational spectroscopy studies of crotonaldehyde hydrogenation, Angew. Chem. Int. Ed. 53 (2014) 3405.
- [14] C.L. Anfuso, D. Xiao, A.M. Ricks, C.F. Negre, V.S. Batista, T. Lian, Orientation of a series of CO₂ reduction catalysts on single crystal TiO₂ probed by phasesensitive vibrational sum frequency generation spectroscopy (PS-VSFG), J. Phys. Chem. C 116 (2012) 24107.
- [15] A. Ge, B. Rudshteyn, B.T. Psciuk, D. Xiao, J. Song, C.L. Anfuso, A.M. Ricks, V.S. Batista, T. Lian, Surface-induced anisotropic binding of a rhenium CO₂-reduction catalyst on rutile TiO2 (110) surfaces, J. Phys. Chem. C 120 (2016) 20970.
- [16] J.L. Achtyl, A.M. Buchbinder, F.M. Geiger, Hydrocarbon on carbon: coherent vibrational spectroscopy of toluene on graphite, Phys. Chem. Lett. 3 (2012) 280.
- [17] L. Velarde, H.-F. Wang, Unique determination of the –CN group tilt angle in langmuir monolayers using sum-frequency polarization null angle and phase, Chem. Phys. Lett. 585 (2013) 42.
- [18] F. Cecchet, D. Lis, J. Guthmuller, B. Champagne, G. Fonder, Z. Mekhalif, Y. Caudano, A.A. Mani, P.A. Thiry, A. Peremans, Theoretical calculations and experimental measurements of the vibrational response of *p*-NTP SAMs: an orientational analysis, J. Phys. Chem. C 114 (2010) 4106.
- [19] C.M. Johnson, E. Tyrode, A. Kumpulainen, C. Leygraf, Vibrational sum frequency spectroscopy study of the liquid/vapor interface of formic acid/ water solutions, J. Phys. Chem. C 113 (2009) 13209.
- [20] W. Gan, Z. Zhang, R.-R. Feng, H.-F. Wang, Spectral interference and molecular conformation at liquid interface with sum frequency generation vibrational spectroscopy (SFG-VS), J. Phys. Chem. C 111 (2007) 8726.
- [21] Y. Rao, M. Comstock, K.B. Eisenthal, Absolute orientation of molecules at interfaces, J. Phys. Chem. B 110 (2006) 1727.
 [22] H.-F. Wang, W. Gan, R. Lu, Y. Rao, B.H. Wu, Quantitative spectral and
- [22] H.-F. Wang, W. Gan, R. Lu, Y. Rao, B.H. Wu, Quantitative spectral and orientational analysis in surface sum frequency generation vibrational spectroscopy (SFG-VS), Int. Rev. Phys. Chem. 24 (2005) 191.
- [23] H.-F. Wang, L. Velarde, W. Gan, L. Fu, Quantitative sum-frequency generation vibrational spectroscopy of molecular surfaces and interfaces: lineshape, polarization, and orientation, Annu. Rev. Phys. Chem. 66 (2015) 189.
- [24] H. Groenzin, I. Li, M.J. Shultz, Sum-frequency generation: polarization surface spectroscopy analysis of the vibrational surface modes on the basal face of ice *I_h*, J. Chem. Phys. 128 (2008) 214510.
- [25] H. Chen, W. Gan, B.-H. Wu, D. Wu, Z. Zhang, H.-F. Wang, Determination of the two methyl group orientations at vapor/acetone interface with polarization null angle method in SFG vibrational spectroscopy, Chem. Phys. Lett. 408 (2005) 284.
- [26] W. Gan, B.-H. Wu, H. Chen, Y. Guo, H.-F. Wang, Accuracy and sensitivity of determining molecular orientation at interfaces using sum frequency generation vibrational spectroscopy, Chem. Phys. Lett. 406 (2005) 467.
- [27] W. Gan, H.-F. Wang, R. Lu, Novel method for accurate determination of the orientational angle of interfacial chemical groups, Chin. Sci. Bull. 48 (2003) 2183.
- [28] F. Wei, W. Xiong, W. Li, W. Lu, H.C. Allen, W. Zheng, Assembly and relaxation behaviours of phosphatidylethanolamine monolayers investigated by

polarization and frequency resolved SFG-VS, Phys. Chem. Chem. Phys. 17 (2015) 25114.

- [29] F. Cecchet, D. Lis, J. Guthmuller, B. Champagne, Y. Caudano, C. Silien, A. Addin Mani, P.A. Thiry, A. Peremans, Orientational analysis of dodecanethiol and pnitrothiophenol SAMs on metals with polarisation-dependent SFG spectroscopy, ChemPhysChem 11 (2010) 607.
- [30] H.M. Chase, B.T. Psciuk, B.F. Strick, R.J. Thomson, V.S. Batista, F.M. Geiger, Beyond local group modes in sum frequency generation spectroscopy, J. Phys. Chem. A 119 (2015) 3407.
- [31] H.M. Chase, B. Rudshteyn, B.T. Psciuk, M.A. Upshur, B.F. Strick, R.J. Thomson, V. S. Batista, F.M. Geiger, Assessment of DFT for computing sum frequency generation spectra of an epoxydiol and a deuterated isotopologue at fused silica/vapor interfaces, J. Phys. Chem. B 120 (2016) 1919.
- [32] J. Ho, B.T. Psciuk, H.M. Chase, B. Rudshteyn, M.A. Upshur, L. Fu, R.J. Thomson, H.-F. Wang, F.M. Geiger, V.S. Batista, Sum frequency generation spectroscopy and molecular dynamics simulations reveal a rotationally fluid adsorption state of α-pinene on silica, J. Phys. Chem. C 120 (2016) 12578.
- [33] C.J. Ebben, I.S. Martinez, M. Shrestha, A.M. Buchbinder, A.L. Corrigan, A. Guenther, T. Karl, T. Petäjä, W.W. Song, S.R. Zorn, P. Artaxo, M. Kulmala, S.T. Martin, L.M. Russell, J. Williams, F.M. Geiger, Contrasting organic aerosol particles from boreal and tropical forests during HUMPPA-COPEC-2010 and AMAZE-08 using coherent vibrational spectroscopy, Atmos. Chem. Phys. 11 (2011) 10317.
- [34] O. Esenturk, R.A. Walker, Surface structure at hexadecane and halohexadecane liquid/vapor interfaces, J. Phys. Chem. B 108 (2004) 10631.
- [35] L. Velarde, X.-Y. Zhang, Z. Lu, A.G. Joly, Z. Wang, H.-F. Wang, Communication: spectroscopic phase and lineshapes in high-resolution broadband sum frequency vibrational spectroscopy: resolving interfacial inhomogeneities of "Identical" molecular groups, J. Chem. Phys. 135 (2011).
- [36] A.L. Mifflin, L. Velarde, J. Ho, B.T. Psciuk, C.F. Negre, C.J. Ebben, M.A. Upshur, Z. Lu, B.F. Strick, R.J. Thomson, V.S. Batista, H.-F. Wang, F.M. Geiger, Accurate lineshapes from Sub⁻¹ cm⁻¹ resolution sum frequency generation vibrational spectroscopy of α-pinene at room temperature, J. Phys. Chem. A 119 (2015) 1292.
- [37] M.A. Upshur, H.M. Chase, B.F. Strick, C.J. Ebben, L. Fu, H. Wang, R.J. Thomson, F. M. Geiger, Vibrational mode assignment of α-pinene by isotope editing: one down, seventy-one to go, J. Phys. Chem. A 120 (2016) 2684.
- [38] L. Fu, S.-L. Chen, H.-F. Wang, Validation of spectra and phase in Sub⁻¹ cm⁻¹ resolution sum-frequency generation vibrational spectroscopy through internal heterodyne phase-resolved measurement, J. Phys. Chem. B 120 (2016) 1579.
- [39] L. Velarde, H.-F. Wang, Unified treatment and measurement of the spectral resolution and temporal effects in frequency-resolved sum-frequency generation vibrational spectroscopy (SFG-VS), Phys. Chem. Chem. Phys. 15 (2013) 19970.
- [40] H.-F. Wang, Sum frequency generation vibrational spectroscopy (SFG-VS) for complex molecular surfaces and interfaces: spectral lineshape measurement and analysis plus some controversial issues, Prog. Surf. Sci. 91 (2016) 155.
- [41] C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, Phys. Rev. B 37 (1988) 785.
- [42] S.H. Vosko, L. Wilk, M. Nusair, Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis, Can. J. Phys. 58 (1980) 1200.
- [43] A.D. Becke, Density-functional thermochemistry. III. The role of exact exchange, J. Chem. Phys. 98 (1993) 5648.
- [44] P. Stephens, F. Devlin, C. Chabalowski, M.J. Frisch, Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields, J. Phys. Chem. 98 (1994) 11623.
- [45] T.H. Dunning Jr, Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen, J. Chem. Phys. 90 (1989) 1007.
- [46] R.A. Kendall, T.H. Dunning Jr, R.J. Harrison, Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions, J. Chem. Phys. 96 (1992) 6796.
- [47] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Gaussian Inc., Wallingford, CT, 2010.
- [48] K. Yagi, S. Hirata, K. Hirao, Vibrational quasi-degenerate perturbation theory: applications to fermi resonance in CO₂, Phys. Chem. Chem. Phys. 10 (2008) 1781.
- [49] T. Ohto, E.H.G. Backus, W. Mizukami, J. Hunger, M. Bonn, Y. Nagata, Unveiling the amphiphilic nature of TMAO by vibrational sum frequency generation spectroscopy, J. Phys. Chem. C 120 (2016) 17435.
- [50] V. GaussView, Dennington, R.; Keith, T.; Millam, J. Semichem Inc., Shawnee Mission KS, 2009.