Vibrational Polarization Spectroscopy of CH Stretching Modes of the Methylene Group at the Vapor/Liquid Interfaces with Sum Frequency Generation

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In this paper we report detailed examples of the surface sum frequency generation vibrational spectroscopy (SFG-VS) as a polarization spectroscopic technique for vibrational spectral band assignment and orientational analysis for molecular groups at the interfaces. Surface sum frequency generation vibrational spectroscopy (SFG-VS) has been widely used as an important spectroscopy probe for chemical bonding, structural conformation and molecular interactions of both fundamentally and technologically important interfaces. However, the potential for SFG-VS as a polarization spectroscopic technique is yet to be fully explored. In IR and Raman studies, polarized spectroscopy (PS) can provide information on molecular symmetries, which is necessary for accurate vibrational band assignment in complex chemical environments. We shall show that SFG-vibrational polarization spectroscopy (VPS) is the polarization spectroscopic tool on this purpose for the interface, along with its advantage of submonolayer sensitivity. This ability of SFG-VPS comes from the fact that vibrational bands from different symmetry types do not have strongest peak intensities in the same polarization configuration of the SFG-VPS spectra, because molecular groups are aligned or partially aligned at the interface. We chose to study the SFG-VPS of three diols, namely, ethylene glycol, 1,3-propanediol, and 1,5-pentanediol, at the vapor/liquid interfaces as model systems for the methylene-only molecules. The polarization analysis of the SFG spectra resulted in few explicit polarization selection rules or guidelines for the assignment of the CH stretching modes of the methylene groups. These results could be used to provide clarifications for some of the disagreements and controversies still exist in the literatures. These results can also shed light on the IR and Raman studies on methylene group in the bulk condensed phases.

1. Introduction

Interface is ubiquitous in heterogeneous chemical and biological processes in natural and artificial worlds.[1] The structures and properties of interfaces, are determined by the uneven molecular forces across the interfacial layer, which is usually not more than 1 nm thick. These uneven forces directly result in alignments and chemical conformational changes of the molecules, and consequently bequeath unique molecular chemical activities to the interfacial chemical species. These molecular chemical activities dictate the equilibrium properties and chemical reactivities of the interface. Therefore, spectroscopic identification of chemical species at interfaces, their bond structure and conformation, interactions and dynamics under specific chemical environment, has been one of the central subjects in modern chemistry and has served as the basis for understanding and controlling the functions and properties of biological membranes and material surfaces.[2,3]

Surface sum frequency generation vibrational spectroscopy (SFG-VS) has been widely used as an effective spectroscopic probe for chemical bonding, structure, and molecular interaction of both fundamentally and technologically important interfaces.[2,4–9] SFG-VS is a second-order nonlinear process, in which a visible (vis) and an infrared (IR) laser pulse overlap simultaneously at the optically accessible interface, and subse-

quently a frequency at the sum of these two laser pulses is generated. By tuning the IR wavelength, the resonance enhanced intensity of the sum frequency signal gives the vibrational spectrum of the interfacial chemical species. The advantage of SFG-VS over other surface probing spectroscopic techniques is that it is nondestructive and is with unique surface specificity and submonolayer sensitivity.[5,10,11] As well as surface second harmonic generation (SHG), SFG is symmetrically forbidden in media having a center of inversion. This centrosymmetry is naturally broken at the interface layer, and consequently makes SFG and SHG surface specific.[12] Besides studies on the fundamentally important liquid and colloidal interfaces,[13–17] SFG-VS has been applied to study biological membrane and polymeric interfaces, the so-called "soft" interfaces.[18–23] In SFG-VS studies, clear assignment and accurate mode association of the vibrational modes plus accurate spectral fitting have been employed to reveal surprisingly new structural information of the liquid interfaces.[24] However, it seems that the potential for SFG-VS as a polarization spectroscopic technique has not been fully explored. It has been pointed out that the detailed polarization analyses are the exception rather than the rule,[25,26] because of the known difficulties in determining values for molecular polarization tensors[27] and the interfacial dielectric constant.[28]

Many of the common chemical functional groups, such as $-CH_3$, $-OH$, $-CN$, $C=O$, $-CH$ in the aromatic ring, $-NH$ and even $-SiH$, have been studied with SFG-VS and reviewed in the literature.[7] The CH stretching region between 2800 and

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3000 cm^{-1} has been the most extensively studied in SFG-VS. The symmetric stretching (ss), the asymmetric stretching (as), and the Fermi resonance (FR) modes of methyl group have been relatively well-characterized and assigned in most of the spectra according to their IR and Raman data in the bulk media. Sometimes, the quantitative information on methyl group orientational angle or ordering could be deduced from the SF data at different polarization configurations.[28-30] However, very good quantitative analysis is not always attainable, because the contribution of the methylene group, which is less clearly understood as we shall demonstrate in the present report, usually superimposes or partially overlaps with that of the methyl group in the SFG-VS spectra. Nevertheless, the assignments of the CH stretching modes of methylene group were also in disagreement with each other in the SFG-VS literatures. Such problems could also impact other fields of studies.

The common practice for spectral assignment in SFG-VS studies has been to compare the spectra with the IR and Raman results in the bulk media,[31-33] and sometimes assisted with ab initio calculations of the IR or Raman band positions of free molecules in the gas phase.[25] This is the natural approach because the selection rule of SFG dictates that any sum frequency active molecular vibrational mode has to be both IR and Raman active.[34] Even though above practice has been common, it has been generally believed that "... there is no simple relationship between observed peak positions and intensities and the properties of the underline modes, and the parameters can be extracted by curve fitting."[33]

In Raman and IR studies, the general consensus for methylene CH stretching modes is that the band near 2850 cm^{-1} is the fundamental symmetric CH$_2$ stretching (ss or d$^+$) mode, the band near 2890 cm^{-1} is the antisymmetric CH$_2$ stretch (as or d$^-$), and band near 2940 cm^{-1} is the Fermi resonance (FR) of the overtone state of the CH$_2$ bending mode with the fundamental of ss mode.[35-39] In different chemical environments, the above frequencies shift a few cm^{-1}, and sometimes some of the FR peaks would vanish because of loss of the accidental degeneration.[40] In general, these assignments are consistent with the surface-enhanced Raman scattering results for different molecules at metal surfaces.[41,42] However, in some IR and Raman literature, the CH$_2$ antisymmetric and the CH$_2$ Fermi peaks exchanged positions.[43-45] A few of these papers have been widely used in SFG-VS studies.[32,33] Consequently, there are the following assignments for the methylene group in the SFG-VS studies: (1) 2850-2880 cm^{-1} the ss, 2910-2940 cm^{-1} the as, and no FR peak whatsoever;[46,47] (2) 2850 cm^{-1} the ss, 2900 cm^{-1} the FR, and 2920 cm^{-1} the as;[48] (3) 2850 cm^{-1} the ss, 2890-2930 cm^{-1} the broad band of FR, and a hidden 2925 cm^{-1} the as;[49] (4) 2860 cm^{-1} the ss, 2920 cm^{-1} the as, and 2940 cm^{-1} the FR band.[20] (More examples are listed in the Supporting Information.) Therefore, the dominant influence of the IR and Raman spectroscopy on the SFG-VS spectra assignment is an important issue that needs to be carefully addressed.

IR and Raman spectroscopy have been used for molecular identification extensively in organic and material chemistry.[50,51] However, it is not so easy for many applications in IR and Raman studies where the information on structural and conformational change is limited because this requires comparisons of the intensity changes of different vibrational peaks attributed to particular functional groups or modes. In the condensed phase, the vibrational spectra are usually congested with overlapping peaks of symmetric and antisymmetric vibrational modes, their

Fermi resonances, and sometimes overtones and combinational modes, especially in the CH modes in the 2800-3000 cm^{-1} region.[39] Therefore, accurate assignment and decomposition of the spectral peaks of all possible vibrational modes are necessary to obtain useful and explicit information. In IR and Raman spectroscopy, the knowledge of the symmetry property, i.e., polarization property, of each vibrational peak is crucial for determination of its symmetry category, leading to explicit assignment of the spectra.[52] Polarized Raman and IR spectroscopy have been used to measure the depolarization ratio (ρ) of the vibrational modes.[53-55] The Raman polarization ratio data obtained from isotropic bulk samples are also used for determination of the molecular hyperpolarizability ratio (r or R in different literatures) required in quantitative orientational calculations in SFG-VS.[14,28] However, the linear polarized Raman experiment on isotropic samples, which provides most of the measured depolarization data in the literatures,[54,56] usually requires concentrated samples and long path lengths. This sometimes causes significant uncertainties of the measured ρ values. Accurate measurement of ρ can be achieved by using nonlinear optical methods, such as polarization resolved coherent anti-Stokes Raman scattering (CARS) spectroscopy[57] but only a handful of molecular vibrational modes have been thus accurately measured.

There have been a few recent works demonstrated the use of SFG-VS intensities[28,58] and orientation analysis[26] for deducing the orientational angle or hyperpolarizability ratio of certain functional groups. But it is rare to use the spectral intensity relationship between different polarization configurations to help spectral assignments.[30] In fact, it has never been systematically considered. Actually, in SFG-VS studies, the spectrum has always been taken at specific polarization configuration. There have been four explicit polarization configurations, namely ssp, sps, pss, and ppp, commonly described in the SFG-VS literature.[28] (Polarization state s and p are defined in section 2.1.) These polarization configurations have been used for quantitative derivation of useful molecular information, such as orientational order, hyperpolarizability ratio (r),[14,28] and sometimes the interfacial refractive index.[30] Therefore, because polarized IR and Raman are capable of symmetry analysis and spectral assignment, we expect that SFG, as a natural-born polarization spectroscopic (PS) technique, could be used to address the disagreements or ambiguity for spectral assignments, spectral fittings, and the subsequent chemical interpretations.

In this work, we are going to study the CH stretching vibrational modes of the methylene group at the interface with SFG-vibrational polarized spectroscopy (VPS). To avoid complications from the methyl group in the SFG-VPS spectral, we shall study the SFG-VPS spectrum at the vapor/liquid interfaces of three diol molecules, namely, ethylene glycol (HOCH$_2$CH$_2$-OH), 1,3-propanediol (HOCH$_2$CH$_2$CH$_2$OH), and 1,5-pentanediol (HOCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$OH), as model methylene-only molecular systems. The 1,4-butanediol is not presented because we could not obtain a sample as pure as the other three diols. Nevertheless, the SFG spectra of the less pure 1,4-butanediol showed no disagreement with the main conclusions in this report. With these studies, we shall demonstrate that SFG-VPS is capable of detailed spectral assignment for the CH stretching vibrational modes of the methylene groups. The pertinence of this work is not only that these results can help clarify the disagreements in existing SFG-VS studies on the methylene groups but also that this approach could be easily applied to vibrational spectroscopy of other molecular groups in SFG-VS

at interfaces. Furthermore, these results can also help elucidate IR and Raman spectra in molecular films and condensed phases as shown in the following sections.

2. Interfacial SFG Polarization Analysis of the Methylene Group

2.1. Interfacial SFG of CH Stretching Vibrational Modes of Methylene Group. To perform polarization analysis of the methylene group, we need to derive the explicit polarization dependent expressions for the SFG-VPS intensities in terms of the molecular sum frequency polarizabilities of the methylene group. As we have known, these molecular polarizability tensors can be directly determined from its C_{2v} symmetry.[59] Even though there was discussion on whether this local mode treatment of the methylene group with C_{2v} symmetry is completely valid,[60] here we avoid such complication because it has been generally accepted in molecular spectroscopy textbook that "... in the case of C−H stretches, the high frequency of the local vibration of the C−H bond tends to uncouple that motion from that of the rest of the molecule".[61] Therefore, slight deviation from the exact C_{2v} symmetry of the methylene group in actual molecules can be treated with small perturbations, and we have found that the treatment with C_{2v} symmetry is adequate not to affect the validity of the selection rules or guidelines thus derived in the following sections.

The SFG intensity is proportional to the incident laser intensities and the square of the absolute value of the effective sum frequency susceptibility $\chi_{\text{eff}}^{(2)}$, which contains all the measurable information of the response of the molecular system to the incident optical fields at the sum frequency ω.[28]

$$I(\omega) = \frac{8\pi^3\omega^2 \sec \beta^2}{c_0^3 n_1(\omega) n_1(\omega_1) n_1(\omega_2)}|\chi_{\text{eff}}^{(2)}|^2 I(\omega_1) I(\omega_2) \quad (1)$$

where $n_i(\omega_i)$ is the refractive index of medium i at frequency ω_i, β_i is the incident or reflection angle of light beam of the corresponding optical frequency, $I(\omega_i)$ is the intensity of the input field at ω_i, and obviously c_0 is the speed of light in the vacuum.

$\chi_{\text{eff}}^{(2)}$ depends on the experimental geometry. Among the infinite number of experimental combinations, there are four most commonly used experimental polarization combinations of the input and output beams as follows.

$$\chi_{\text{eff}}^{(2),\text{ssp}} = L_{yy}(\omega) L_{yy}(\omega_1) L_{zz}(\omega_2) \sin \beta_2 \chi_{yyz}$$

$$\chi_{\text{eff}}^{(2),\text{sps}} = L_{yy}(\omega) L_{zz}(\omega_1) L_{yy}(\omega_2) \sin \beta_1 \chi_{yzy}$$

$$\chi_{\text{eff}}^{(2),\text{pss}} = L_{zz}(\omega) L_{yy}(\omega_1) L_{yy}(\omega_2) \sin \beta \chi_{zyy}$$

$$\begin{aligned}
\chi_{\text{eff}}^{(2),\text{ppp}} = &-L_{xx}(\omega) L_{xx}(\omega_1) L_{zz}(\omega_2) \cos \beta \cos \beta_1 \sin \beta_2 \chi_{xxz} \\
&- L_{xx}(\omega) L_{zz}(\omega_1) L_{xx}(\omega_2) \cos \beta \sin \beta_1 \cos \beta_2 \chi_{xzx} \\
&+ L_{zz}(\omega) L_{xx}(\omega_1) L_{xx}(\omega_2) \sin \beta \cos \beta_1 \cos \beta_2 \chi_{zxx} \\
&+ L_{zz}(\omega) L_{zz}(\omega_1) L_{zz}(\omega_2) \sin \beta \sin \beta_1 \sin \beta_2 \chi_{zzz} \quad (2)
\end{aligned}$$

Here χ_{yyz}, χ_{yzy}, χ_{zyy}, χ_{xxz}, χ_{xzx}, χ_{zxx}, and χ_{zzz} are the 7 nonzero elements out of the 27 symmetry-allowed macroscopic sum frequency susceptibility tensor elements for the interface system rotationally isotropic in the surface plane (xy plane in the laboratory coordinates system $\lambda(x,y,z)$); p denotes the polarization of the optical field in the xz plane, with z as the surface

normal, whereas s is the polarization perpendicular to the xz plane. L_{ii} ($i = x, y, z$) is the Fresnel coefficient determined by the refractive index of the two bulk phases and the interface layer, and the incident and reflected angles.[28] The macroscopic sum frequency susceptibility tensors $\chi_{ijk}^{(2)}$ are related to the microscopic hyperpolarizability tensor elements $\beta_{i'j'k'}^{(2)}$ in the molecular coordinates system $\lambda'(a,b,c)$ through the ensemble average over all possible molecular orientations.[28]

$$\chi_{ijk}^{(2)} = N_s \sum_{i'j'k'} \langle R_{ii'} R_{jj'} R_{kk'} \rangle \beta_{i'j'k'}^{(2)} \quad (3)$$

where N_s is the number density of the interface moiety under investigation and $R_{\lambda\lambda'}$ is the element of the Euler rotation transformation matrix from the molecular coordination $\lambda'(a,b,c)$ to the laboratory coordination $\lambda(x,y,z)$.[62] All the mathematical expressions connecting the 27 $\chi_{ijk}^{(2)}$ and 27 $\beta_{i'j'k'}^{(2)}$ have been meticulously worked out by Hirose et al. through transformation of all three Euler angles (θ, ϕ, ψ).[62] In any application, one only needs to make appropriate symmetry considerations and angular average to obtain the expressions of the nonvanishing $\chi_{ijk}^{(2)}$ elements as the linear combination of the nonvanishing $\beta_{i'j'k'}^{(2)}$ elements.

In SFG-VS, the IR frequency is near resonance to the molecular vibrational transition, and the second-order molecular polarizability is

$$\beta^{(2)} = \beta_{\text{NR}}^{(2)} + \sum_q \frac{A_q}{\omega_{\text{IR}} - \omega_q + i\Gamma_q} \quad (4)$$

where the first term $\beta_{\text{NR}}^{(2)}$ represents nonresonant contributions, which are usually very small, and A_q, ω_q, and Γ_q are the sum frequency strength factor tensor, resonant frequency, and damping constant of the qth vibrational mode, respectively. In the theory of SFG-VS, the tensor elements of A_q are related to the IR and Raman properties of the vibrational mode,[58,63]

$$A_q^{i'j'k'} = -\frac{1}{2\epsilon_0\omega_q} \frac{\partial\alpha_{i'j'}^{(1)}}{\partial Q_q} \frac{\partial\mu_{k'}}{\partial Q_q} \quad (5)$$

in which $\partial\alpha_{i'j'}^{(1)}/\partial Q_q$ and $\partial\mu_{k'}/\partial Q_q$ are partial derivatives of the Raman polarizability tensor and IR dipole of the qth vibrational mode, and Q_q is the normal coordinate of the same mode.[58] This is why any nonzero sum frequency vibrational mode has to be both IR and Raman active.

The molecular symmetry determines the nonzero elements of the molecular polarizability tensor $\beta_{i'j'k'}^{(2)}$, or the sum frequency strength factor tensor $A_q^{i'j'k'}$. For the methylene group, which has a C_{2v} symmetry, the nonvanishing SFG tensor elements are, for the symmetric stretching mode in the a₁ symmetry category, $\beta_{aac}^{(2)}$, $\beta_{bbc}^{(2)}$, and $\beta_{ccc}^{(2)}$ and, for the asymmetric stretching mode in the b₁ symmetry category, $\beta_{aca}^{(2)} = \beta_{caa}^{(2)}$.[58,59] In the molecular-fixed coordinates for methylene, the c axis is along the direction of the bisector line of the two CH bonds away from the H-atom side, the a axis is along in the H−C−H plane, and b is out of the plane.[59] With this information on nonvanishing elements of the methylene group, and eq 3, the average over the Euler angles can be performed for the rotationally isotropic (no azimuthal angle ψ dependence) system in the interface plane, because it is reasonable to assume that the liquid interface has no twist angle (ϕ) dependence. Thus,

we have the following nonvanishing tensor elements for methylene symmetric-stretching mode (ss),

$$\chi_{xxz}^{(2),ss} = \chi_{yyz}^{(2),ss} = \frac{1}{4}N_s(\beta_{aac}^{(2)} + \beta_{bbc}^{(2)} + 2\beta_{ccc}^{(2)})\langle\cos\theta\rangle +$$
$$\frac{1}{4}N_s(\beta_{aac}^{(2)} + \beta_{bbc}^{(2)} - 2\beta_{ccc}^{(2)})\langle\cos^3\theta\rangle$$

$$\chi_{xzx}^{(2),ss} = \chi_{zxx}^{(2),ss} = \chi_{yzy}^{(2),ss} = \chi_{zyy}^{(2),ss}$$
$$= -\frac{1}{4}N_s(\beta_{aac}^{(2)} + \beta_{bbc}^{(2)} - 2\beta_{ccc}^{(2)})(\langle\cos\theta\rangle - \langle\cos^3\theta\rangle)$$

$$\chi_{zzz}^{(2),ss} = \frac{1}{2}N_s(\beta_{aac}^{(2)} + \beta_{bbc}^{(2)})\langle\cos\theta\rangle - \frac{1}{2}N_s(\beta_{aac}^{(2)} + \beta_{bbc}^{(2)} - 2\beta_{ccc}^{(2)})\langle\cos^3\theta\rangle \quad (6)$$

and the nonvanishing tensor elements for methylene asymmetric-stretching mode (as),

$$\chi_{xxz}^{(2),as} = \chi_{yyz}^{(2),as} = -\frac{1}{2}N_s\beta_{aca}^{(2)}(\langle\cos\theta\rangle - \langle\cos^3\theta\rangle)$$

$$\chi_{xzx}^{(2),as} = \chi_{zxx}^{(2),as} = \chi_{yzy}^{(2),as} = \chi_{zyy}^{(2),as} = \frac{1}{2}N_s\beta_{aca}^{(2)}\langle\cos^3\theta\rangle$$

$$\chi_{zzz}^{(2),as} = N_s\beta_{aca}^{(2)}(\langle\cos\theta\rangle - \langle\cos^3\theta\rangle) \quad (7)$$

This methylene asymmetric mode tensors bear the same expressions as those of methyl group with C_{3v} symmetry.[30] Equations 6 and eq 7 can be greatly simplified by known relationships between the nonvanishing $\beta_{i'j'k'}^{(2)}$ tensor elements of the methylene group.[58,59,64] They are $\beta_{aac}^{(2)} + \beta_{bbc}^{(2)} = 2\beta_{ccc}^{(2)} \approx 0.98a_0$ and $\beta_{aca}^{(2)} \approx 0.66a_0$, where a_0 is the polarizability constant defined for a single C−H bond.[58] One of the most significant consequences of this simplification is that all the terms with $\beta_{aac}^{(2)} + \beta_{bbc}^{(2)} - 2\beta_{ccc}^{(2)}$ vanish, and all the ss elements contain only $\langle\cos\theta\rangle$ term ($\chi_{xxz}^{(2),ss}$, $\chi_{yyz}^{(2),ss}$, and $\chi_{zzz}^{(2),ss}$) or vanish ($\chi_{xzx}^{(2),ss}$, $\chi_{zxx}^{(2),ss}$, $\chi_{yzy}^{(2),ss}$, and $\chi_{zyy}^{(2),ss}$). An important fact from eq 6 and 7 is that the $\chi_{xxz}^{(2),ss}$ and $\chi_{xxz}^{(2),as}$ terms always have opposite signs. This immediately suggests that the overlapping ss and as modes of the methylene group would always negatively interfere with each other in any ssp spectra. This is also a very important rule for SFG band assignment.

It has to be noted that the values of the three nonvanishing $\beta_{i'j'k'}^{(2)}$ tensor elements depend on the choice of the ratio of the perpendicular and parallel components of the bond polarizability derivative under the bond additivity approximation.[29,59] The ratio used in the calculation was 0.14.[58,65] Using a different value of this ratio from 0 to 1.0 does not change the fact that the term $\beta_{aac}^{(2)} + \beta_{bbc}^{(2)} - 2\beta_{ccc}^{(2)}$ vanishes for methylene at the standard bond angle 109.5°. Even though the bond angle is set several degrees away from 109.5°, the value of $\beta_{aac}^{(2)} + \beta_{bbc}^{(2)} - 2\beta_{ccc}^{(2)}$ remains a very small number compares to the rest of the terms in both eqs 6 and 7. In addition, even though the relative values of the three nonvanishing $\beta_{i'j'k'}^{(2)}$ tensor elements would change to some extent when varying these parameters, our analysis has shown that the polarization selection rules or guidelines in the following section are not affected within a broad range of physically allowed values.

Inserting into eqs 1 and 2 the above expressions for ss and as modes for methylene, one can obtain the expressions for the SFG-VS experimental intensity of all four polarization configurations of both modes.

As we have shown in a previous report,[66] to have convenient orientational analysis for SHG and SFG, the $\chi_{\text{eff}}^{(2)}$ in eq 1 could be simplified as

$$\chi_{\text{eff}}^{(2)} = N_s d(\langle\cos\theta\rangle - c\langle\cos^3\theta\rangle) = N_s dr(\theta) \quad (8)$$

$r(\theta)$ is the *orientational field functional*, which contains all orientational information at a given SFG experimental configuration, whereas the dimensionless parameter c is called the *general orientational parameter*, which determines the orientational response $r(\theta)$ to the molecular orientation angle θ; d is the susceptibility strength factor, which is a constant in a certain experimental configuration with a given molecular system. The d and c values are both functions of the related Fresnel coefficients including the refractive index of the interface and the bulk phases, and the experimental geometry. They could be derived for methylene accordingly.[66]

To compare with SFG-VPS experiment, we have the SFG intensity of any SFG experimental configuration as[66]

$$I(\omega) = Ad^2R(\theta)N_s^2I(\omega_1)\,I(\omega_2) \quad (9)$$

$$R(\theta) = |r(\theta)|^2 = |\langle\cos\theta\rangle - c\langle\cos^3\theta\rangle|^2 \quad (10)$$

in which A is the experimental constant, including the prefactors in eq 1 times the instrumental response constant, whereas $R(\theta)$ is called the *orientational functional*. It is easy to see that the d and c values of the ss and as vibrational modes are solely responsible for their SF intensity in the four experimental polarization configurations at a given orientation of the methylene group at the interface. This is the basis for quantitative polarization analysis of the methylene group SFG-VPS study.

2.2. Polarization Selection Rules for the Methylene Group in SFG-VPS. To calculate the d and c values for SFG polarization analysis, we need to know the values of the dielectric constant or optical refractive indices of all three optical fields in the air, in the liquid phase and in the interface layer.

There are nine refractive indices in total that need to be accounted for, namely, $n_1(\omega_1)$, $n_1(\omega_2)$, $n_1(\omega)$ in air, $n_2(\omega_1)$, $n_2(\omega_2)$, $n_2(\omega)$ in the liquid phase, and $n'(\omega_1)$, $n'(\omega_2)$, $n'(\omega)$ in the interface layer. It is trivial that the refractive indices of the three optical fields in the air phase can all take the refractive indices of the vacuum, i.e., $n_1(\omega_i) = 1.0$. In principle, the refractive indices of the three fields in the liquid bulk phase could either be found in the handbook of in the literature or be experimentally determined through known procedures. But for practical reasons they might not be easily obtained. Plus, the ultimate trouble always lies in how to obtain the three refractive indices in the interface layer, or in other words, the microscopic local field factor in the interface layer.[28,67]

Because the frequencies of the visible and the SF fields are usually not in resonance with the molecular system, and their wavelengths are not very far from each other, their refractive indices in the bulk phase and in the interface layer are with negligible differences, i.e., $n_2(\omega_1) = n_2(\omega)$ and $n'(\omega_1) = n'(\omega)$. This essentially reduces the four corresponding indices into two, with only the refractive index of the interface unknown. It is known that this interfacial refractive index is somewhere between the vacuum value and the bulk phase value for the air/liquid interface. Its value has been discussed extensively in the literature, and reasonable formulation has been generally considered and widely accepted.[28]

Because the IR field in SFG is usually in resonance with the molecular vibration frequency, the refractive indices in both the

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bulk phase and the interface layer should become complex values. The dispersion of the refractive index of the infrared field is strong and will vary significantly across the C−H wavelength region. Fortunately, the value of the refractive indices of the infrared field is not as critical for the polarization analysis, especially with the copropagating geometry in our experiment. In eq 2, the second and third terms for $\chi_{eff}^{(2),ppp}$ always have opposite signs. In the copropagating geometry, such as in our experiment, $\beta_1 = 60°$ and $\beta = 59°$; therefore, these two terms essentially cancel each other and have very insignificant contribution to the $\chi_{eff}^{(2),ppp}$. Consequently, the ratio between $\chi_{eff}^{(2),ssp}$ and $\chi_{eff}^{(2),ppp}$, which is the important parameter in SFG polarization analysis, should show essentially very weak dependence on the value of either of the two infrared refractive indices. This is the very reason we underline the following statement in one of the most educational papers in this field: "... we will use the same n' for all moieties and show that our results give a self-consistent picture of the molecular geometry at the interface" with also a copropagating experimental geometry.[28] Thus, we also make the same approximation in this work and give all the interfacial n' with the same value. We tested the sensitivity of n' for the infrared by changing it up to 0.3 unit and observed essentially no effect on the polarization analysis with all the SFG spectra presented in the following.

In contrast, the ratio between $\chi_{eff}^{(2),ssp}$ and $\chi_{eff}^{(2),ppp}$ has a much greater dependence on the value of the $n'(\omega_2)$ for the infrared under the counterpropagating experimental geometry, because there should always be a significant difference between β_1 and β. This would certainly make the counterpropagating geometry less desirable for SFG polarization analysis, even though the counterpropagating geometry could have some other advantages.[7,33] One such advantage is that in the counterpropagating geometry the ppp spectra would contain peaks of most of the SFG active modes. However, the disadvantage is that the polarization selection rules or guidelines would become less clear-cut in contrast to these under the copropagating geometry.

On the basis of above considerations, here we use a model liquid with a refractive index of 1.44 for the methylene group polarization analysis, because the three diols in this study have their refractive index at room temperature as 1.43, 1.44, and 1.45, respectively. Under the copropagating experimental geometry, this difference of refractive index is minor and will not affect the effectiveness of the following analysis. Then the refractive index of the interface for this model liquid is $n' = 1.19$.[28]

Accordingly, with the copropagate experimental geometry in our experiment, which is widely used in the SFG literature, the d and c values for the ss mode are as follows: (ssp) $d = 0.106a_0$, $c = 0$; (sps) $d = 0$, $c = 1$; (pss) $d = 0$, $c = 1$; (ppp) $d = 0.016a_0$, $c = 0$. For the as mode: (ssp) $d = -0.071a_0$, $c = 1$; (sps) $dc = 0.077a_0$, $c = \infty$; (pss) $dc = 0.076a_0$, $c = \infty$; (ppp) $d = 0.182a_0$, $c = 1.004$. Because for sps and pss of the as mode only has $\langle \cos^3 \theta \rangle$ terms, to keep the consistent form for $R(\theta)$, we let $c = \infty$, and let dc a finite value. This will not affect the $d^2R(\theta)$ values, which is directly proportional to the SFG intensity.

Figure 1 shows the $d^2R(\theta)$ values against the orientational angle θ, assuming a narrow δ function distribution, of the methylene group at the vapor/liquid interface. It is clear to see that for the ss mode, the $d^2R(\theta)$ values for sps and pss are zero for all possible θ, whereas that of ssp is always about 44 times that of ppp for all θ. Therefore, the two primary rules or guidelines for identifying the ss mode of methylene group in
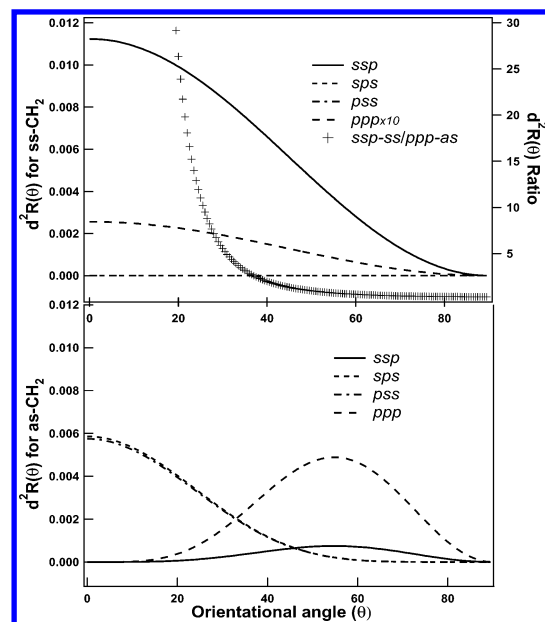

Figure 1. Orientational parameter $d^2R(\theta)$ vs orientational angle θ with a δ distribution function at four polarization configurations. (Above) symmetry stretching vibration, the + curve is the ratio between ssp-ss and ppp-as, which will be used in section 4.2. (Below) antisymmetric stretching vibration. Note that the ppp-ss curve is amplified by a factor of 10.

SFG-VPS are *(a) no ss peak would appear in sps and pss spectra* and *(b) ssp intensity is always many times of that of ppp*.

Because the Fermi resonance of the ss mode bears the same symmetry with the ss mode, therefore, its selection rules are the same as these of the corresponding ss mode.[50]

For the as mode, when θ is small, the intensity for sps and pss should be much bigger than that of the ppp and ssp, whereas, when θ is larger than 35°, ppp starts overtaking the SFG intensity. It is also important to see that with the as mode the intensity for ppp is always 6.5 times that for ssp. Therefore, the two primary rules or guidelines for identifying the as mode of the methylene group in SFG-VPS are *(c) any peak in the sps and pss spectra should come from the as mode with a relatively small tilt angle θ* and *(d) ppp intensity is always several times of that of ssp. That is to say, if there is any peak which is stronger in the ssp than ppp spectra, it can not be from the as mode*.

There is also an important selection rule or guideline concerning the ss and as peaks in any ssp spectra, as we discussed earlier: *(e) in the ssp spectra, the ss and as modes of the methylene groups with similar orientation negatively interfere with each other*.

As we have shown, the above five major polarization selection rules or guidelines are based on rigorous polarization analysis according to molecular symmetry. There could be additional rules if more analysis is considered. These rules or guidelines differ from some of the current common perceptions. One such perception claims that the ssp polarization probes surface vibrational modes with a projection dipole moment perpendicular to the interface, whereas the sps and pss access modes have transition dipole components parallel to the interface.[26,68−71] We find that this claim is correct for uniaxial molecular groups that have one ss mode, but certainly not correct for C_{2v} and C_{3v} molecular groups. The safe way to get polarization selection rules or guidelines is to perform rigorous polarization analysis for the particular molecular group and experimental configuration, as we demonstrated in this report.

In the internal reflection geometry,[72] the big difference of the Fresnel factors would sometimes make the intensity for the ss mode in the ppp spectra stronger. Our calculation shows that for as, ppp is still significantly stronger than ssp. However, for the ss mode, the relationship between the intensity of ppp and ssp is not so simple. Sometimes ppp could become a few tens of percent stronger than ssp for cases when both incoming beams approach to the total internal reflection incident angles. Consistent with above calculations, the ss intensity of ppp was indeed slightly larger than that of the ssp for phospholipid molecule DLPC at the CCl$_4$/water interface studied in an internal reflection geometry.[73] All these issues could make the analysis for the internal reflection geometry complicated, especially when different modes overlap with each other. The case for internal reflection geometry certainly needs further detailed investigation in our future studies.

The polarization selection rules were obtained with the assumption of a δ angular distribution function of the orientational angle θ. The calculation with the non-δ angular distribution function showed that the polarization selection rules were essentially conserved. This should ensure these rules are applicable to a broad range of interfacial systems.

The above analysis can also be extended to other molecular groups at the interface. We have noticed from our calculation that the methyl group, which has a C_{3v} symmetry, would have very different polarization selection rules for its ss mode in the counterpropagating experimental geometry, whereas the selection rule for its as mode remains the same as that for methylene group. Nevertheless, with complicated orientational distribution, the selection rules for the ss mode of the C_{3v} groups could be not so simple and need to be further examined. For the transmission SFG-VPS experiment,[74] the d and c values are quite different due to different Fresnel coefficients, and the above rules may or may not hold, which is worth future investigation.

We also have to point out a common misconception about the molecular orientation and SFG intensity at the interface. In quite a few previous literatures both with SHG and SFG studies,[23,75,76] people often assumed that the more upright (smaller θ) the molecular dipole, the bigger the SHG or SFG intensity. It is clear for the ppp and ssp of the as mode in Figure 1, it is quite the opposite. We have pointed out this fact for the SHG studies elsewhere.[66] In SHG, the most popularly used s_{in}/p_{out} configuration would have $c \equiv 1$, just like the case for ppp and ssp of the as in SFG.[76] In SHG and SFG studies, effective polarization analysis has to be accompanied with effective orientational analysis, and vice versa.

Besides the above polarization selection rules, other quantitative information could also be obtained from the polarization and orientation analysis. We go into details in the Results and Discussion.

3. Experimental Section

Our picosecond sum frequency generation (SFG) spectrometer laser system was built by EKSPLA, using a copropagating configuration. The details of the similar SFG system from EKSPLA has been described by other research groups.[30,47] Briefly, the visible signal at 532 nm and IR pulses around 2750–3000 cm^{-1} are about 23 ps at 10 Hz. The full range of the IR tunability is 1000–4300 cm^{-1}. The incident angle of the visible beam is 60° (β_1), and it is 55° (β_2) for the IR beam. The SFG signal is collected within a small range (about 0.3°), depending on the corresponding IR wavelength (from 2750 to 3000 cm^{-1} in our experiment), around 59° (β) at the reflection geometry. In all experiments, each scan was obtained with an increment
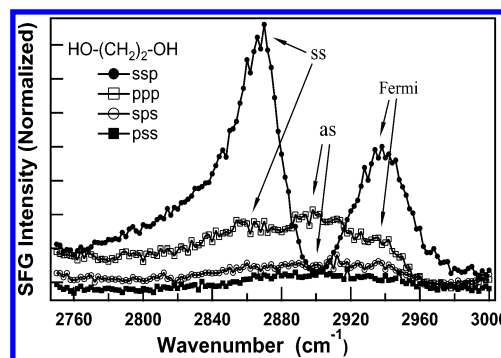

Figure 2. Polarized SFG spectra of ethylene glycol at vapor/liquid interfaces. The solid line is connected between points to guide the eyes.
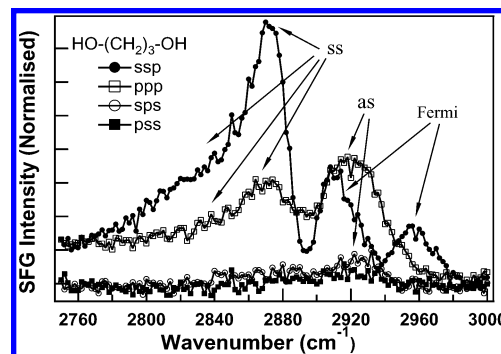

Figure 3. Polarized SFG spectra of 1,3-propanediol at vapor/liquid interfaces.

of 2 cm^{-1} and an average over 100 laser shots per point. The energy of the visible beam is typically about 300 μJ and that of the IR beam about 200 μJ. Such energy cannot damage the liquid sample and also cannot cause any heat effect or other photochemical reactions. In this work, we did all four polarization combinations, ssp, ppp, sps, and pss, in which s and p denote the out-of-incident-plane and the in-plane polarizations, respectively. The three letters by order represent the polarizations of the sum frequency (SF) beam, the incident visible beam, and the IR beam, respectively. All the spectrum intensity is normalized by the intensities of the corresponding visible and IR laser pulses.

All measurements were carried out at controlled room temperature (22.0 ± 0.5 °C). The liquid samples, ethylene glycol (Fluka, >99.0%), 1,3-propanediol (Fluka, >99.0%), and 1,5-pentanediol (Fluka, >99.0%), were placed in a round Teflon beaker. The air flow is blocked to prevent evaporation by enclosing the whole experimental setup on the optical table in a plastic housing.

4. Results and Discussion

4.1. Methylene Spectral Assignment with SFG-VPS. With the above polarization selection rules for SFG-VPS of the methylene group, we can make explicit vibrational mode assignments for the three diols at their vapor/liquid interface. As shown in Figures 2–4, the SFG-VPS spectra for the three diols, ethylene glycol, 1,3-propanediol, and 1,5-pentanediol, respectively, in all four SFG polarization configurations all give distinctive band features in spectra with different polarization. All the SFG spectra have not been reported before, except a brief report for ethylene glycol adsorbed on fused quartz.[4,77]

4.1.1. Ethylene Glycol. For ethylene glycol, there are two strong peaks at 2870 and 2938 cm^{-1} in the ssp spectra. Both peaks are much weaker (more than 1 order of magnitude weaker) in the ppp spectra, and almost invisible on sps and pss. By fitting the ssp spectra, we have to use an additional dip positioned at
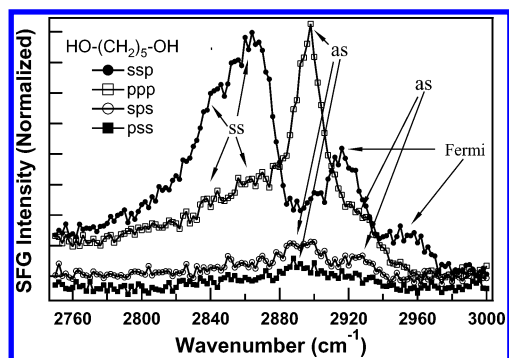
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Figure 4. Polarized SFG spectra of 1,5-pentanediol at vapor/liquid interfaces.

2900 cm^{-1}, which has the phase of the strength factor A_q opposite those of the two strong peaks. This is consistent with the calculation earlier that the d value is negative for the as mode on ssp polarization. This 2900 cm^{-1} peak appears in the ppp spectra, with the same phase and slightly bigger intensity as the other two peaks at 2870 and 2938 cm^{-1} on the ppp spectra.

Because ethylene glycol only has two CH_2 groups each attached to a OH group, according to the SFG-VPS selection rules in section II, the 2870 and 2938 cm^{-1} peaks apparently belong to the ss mode of the methylene group, and the 2900 cm^{-1} peak belongs to the as mode of the methylene group. The peak at 2870 cm^{-1} is assigned to the ss mode, and the 2938 cm^{-1} peak should be the Fermi resonance of the ss mode. Two kinds of methylene group frequencies have been reported in Raman studies. For Raman spectra of $CD_3CH_2CD_3$, 2876 cm^{-1} was assigned to the ss, and 2940 cm^{-1} was the Fermi resonance,[35] whereas for $CD_3CD_2CH_2CD_2CD_3$, 2851 cm^{-1} was assigned to the ss, and 2919 cm^{-1} was the Fermi resonance.[37] Therefore, our assignment means that the two CH_2 groups in ethylene glycol have indistinguishable vibrational spectra in the CH stretch region.

The SFG spectra of glycerol ($HOCH_2CHOHCH_2OH$) at the vapor/liquid interface in all four polarizations have been reported before.[46] The 2880 cm^{-1} peak was assigned to the ss of the methylene group, whereas the 2940 cm^{-1} peak, which has the same polarization properties, was assigned to its as mode. The single CH group, which is supposed to be at about 2900 cm^{-1}, was not observed. According to the evidence we have now, this assignment for the 2940 cm^{-1}, which is strong on the ssp spectrum and essentially vanishes on the ppp spectrum, has to be assigned to the Fermi resonance. In the same paper, the constant ratio of these two peaks at the glycerol/water mixture interface at different mole fractions was used to demonstrate the constant orientation of the glycerol molecule at the interface. We have to say that the constant ratio of these two peaks over different mixing ratios does not give information on the molecular orientation at the interfaces. It rather indicates that the Fermi coupling strength does not change at these interfaces.[50] We have also found that it is not unusual in the existing SFG studies to mistake the Fermi resonance peak as the as mode of the methylene group.[32,46,78]

4.1.2. 1,3-Propanediol. On SFG-VPS spectra of the 1,3-propanediol, which has three CH_2 groups, there are three apparent peaks at 2870, 2920, and 2954 cm^{-1} on the ssp spectra, all are assigned to belong to the ss mode. In the spectral fitting, there is one imbedded peak at about 2850 cm^{-1}, and a dip around 2900 cm^{-1} also with the opposite phase of its SFG strength factor. According to their polarization properties and frequencies, these peaks for the ss modes are assigned as

follows, 2850 and 2870 cm^{-1} belong to the ss modes of two kinds of methylene groups in 1,3-propanediol ($HOCH_2CH_2CH_2$-OH) and the 2920 and 2954 cm^{-1} modes are the corresponding Fermi resonance peaks. According to the SFG spectra of ethylene glycol discussed above, it is reasonable to assign the 2870 cm^{-1} peak to the two methylene groups directly attached to the OH group, whereas the 2850 cm^{-1} peak is assigned to the methylene groups that is not attached to the OH group.

On the ppp spectrum of 1,3-propanediol, which is dominated by the as modes according to the polarization selection rules, there are two apparent peaks, one at about 2870 cm^{-1}, and another broader peak at about 2920 cm^{-1}. The peak at 2870 cm^{-1} on ppp is weaker than the same peak position on the ssp spectrum belonging to the ss mode. However, according to the polarization selection rules, the broad peak around 2920 cm^{-1} cannot be assigned to the ss Fermi resonance mode, even though it appears at the same frequency on the ssp spectra. Otherwise, it should have had much smaller peak intensity. Spectral fitting shows that this broad peak contains two overlapping as modes, one at about 2900 cm^{-1}, which is much weaker, and another at about 2928 cm^{-1}, stronger. This is because on the sps and pss, there is a small but discernible peak at about 2928 cm^{-1}. This means these two as modes are from different CH_2 groups in the 1,3-propanediol molecule. Apparently, like ethylene glycol, the 2900 cm^{-1} mode belongs to the two end methylene groups attached to the OH, whereas the 2928 cm^{-1} mode belongs to the middle methylene group. Both positions have been reported for the CH as modes of the methylene groups in IR and Raman studies.[37] There is a 2920 cm^{-1} peak for the ss Fermi resonance on the ssp spectra, and a 2928 cm^{-1} peak for the as mode on the ppp and sps spectra. These two modes are so close that it could not be easily separated in Raman and IR spectra, even though it has been mentioned in the literature that the 2920 cm^{-1} as band contains some features "associated with the effects of Fermi resonance interaction".[43] Here we have provided clear evidences for this claim through polarization analysis with SFG-VPS. It is also clear that without these polarization selection rules, it is impossible to accurately and unambiguously assign these as and ss Fermi bands.

From Figure 1, we could also derive the relative orientational angle of the bisectional axis of these two kinds of CH_2 groups in 1,3-propanediol at the vapor/liquid interface. Because the intensities of the 2900 and 2928 cm^{-1} peaks on ppp spectra are apparently 1 order of magnitude stronger than these on the sps and pss spectra, both CH_2 groups must have an orientational angle larger than 40°. Between these two peaks, because the 2928 cm^{-1} peak is stronger than the 2900 cm^{-1} peak on both the sps and ppp spectra, we surmise from Figure 1 that the orientational angle of the center CH_2 (2928 cm^{-1}) is close to 55°, whereas the end CH_2 group (2900 cm^{-1}) has an orientational angle larger than 55°. However, the end CH_2 cannot orient too close to 90°, i.e., flat on the surface plane, where its SFG signal would vanish in all polarizations.

4.1.3. 1,5-Petanediol. The SFG-VPS spectra for 1,5-petanediol in Figure 4 show a remarkably strong peak at 2900 cm^{-1} on the ppp spectra. This can be explicitly assigned to one of the as modes of the methylene group according to the polarization selection rules. This peak also appears on the sps and pss spectra with larger intensity than the apparent as mode at 2926 cm^{-1} on both polarization spectra. The intensity of this 2900 cm^{-1} mode on the ppp spectra is slightly larger than the intensity of the 2865 and 2845 cm^{-1} peak on the ssp spectra, apparently the ss mode of the methylene group. From Figure 1, we are able to conclude that the methylene group that produces this

TABLE 1: Methylene Group Stretching Vibrational Frequency (cm^{-1}) for the Three Diols^a

diols	polarization	ss	ss	as	as	FR	FR
ethyleneglycol	ssp	—	2870	2900(−)	—	2938	—
	sps	—	—	—	—	—	—
	pss	—	—	—	—	—	—
	ppp	—	2870	2900	—	2938	—
1,3−propanediol	ssp	2850	2870	2900(−)	—	2920	2954
	sps	—	—	—	2928	—	—
	pss	—	—	—	2928	—	—
	ppp	—	2870	—	2920(b)	—	—
1,5−pentanediol	ssp	2845	2865	2900(−)	—	2916	2954
	sps	—	—	2900	2926	—	—
	pss	—	—	2900	2926	—	—
	ppp	2845	2865	2900	2926	—	—

^{a} − denotes no signal; (−) denotes opposite phase; (b denotes broad peak.

2900 cm^{-1} peak has an orientational angle close to 55°, where the $d^2R(\theta)$ is maximum for the as mode on the ppp polarization. The two as peaks at 2900 and 2926 cm^{-1} are apparent on the sps spectra. On the ppp spectra, there is a shoulder at about 2926 cm^{-1}, whose position is clearly distinguishable from that of the 2916 cm^{-1} ss peak on the ssp spectra. This ability of discerning overlapping positions in the unpolarized spectra proves again the potential and effectiveness of SFG-VPS for vibrational spectra assignment.

Like 1,3-propanediol, the ssp spectra of 1,5-petanediol has four apparent peaks at 2845 (imbedded), 2870, 2916, and 2954 cm^{-1}. When the spectra are fit, there is also a dip at 2900 cm^{-1} as in the other two diols. The assignment of these four major peaks should also be the same as 1,3-propanediol, which clearly indicates two kinds of CH$_2$ groups in this molecule. However, there are three kinds of methylene groups in 1,5-petanediol (HOCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$OH). In the Raman studies on CD$_3$-CD$_2$CH$_2$CD$_2$CD$_3$,[37] the as mode of the center methylene group appears at 2901 cm^{-1}. If this is also the case for the center methylene group in 1,5-petanediol, it should have a similar vibrational spectrum as that of the CH$_2$ at the end, rather than that of the CH$_2$ at the β position. This interesting alternation has been confirmed with simple ab initio calculations with Gaussian 98.

4.1.4. Summary of SFG-VPS Spectral Assignments. Table 1 lists the above assignment of their peak positions and the polarizations on the SFG-VPS spectra. We can immediately see that the four types of assignments we reviewed in the Introduction section are all partially correct. The major differences and new discoveries are as follows.

(i) The 2938 cm^{-1} peak for ethylene glycol is clearly assigned to the ss Fermi resonance of the methylene group. We have noticed that this ss Fermi resonance peak appears only in ethylene glycol, but not the other two diols. This means that the methylene group directly attached to one OH group experiences a certain influence from the other OH that is separated by one methylene group. This fact is important when we try to investigate similar methylene groups in polymers and biomolecules.

(ii) We clearly identified two as peaks, one around 2900 cm^{-1} and another around 2926 or 2928 cm^{-1}, belonging to different methylene groups. The 2926 or 2928 cm^{-1} peak is close to one of the ss Fermi resonance peaks around 2920 cm^{-1}. They would certainly overlap in an unpolarized spectra, but they appear separately on SFG spectra with different polarizations. Because the as peak should appear on the ppp spectra much stronger than in the ssp spectra, it is erroneous to assign the peaks around 2920 cm^{-1} on the ssp spectra to the as mode without observing

a much stronger peak on the ppp spectra at the same position, as much previous SFG literature had. (See Supporting Information.)

(iii) There are two ss Fermi resonance peaks on the ssp SFG spectra, when there is more than one kind of methylene groups. We have presented clear polarization identification of these two types of vibrational modes. We have not seen any report on the assignment of the peak around 2954 cm^{-1}, even though it presented in the spectra before.[20]

The peak positions of the methylene group could be shifted in different chemical environments. Therefore, we are not here to tie any certain peak position to a certain vibrational mode. The most important lesson from the above analysis is that quantitative polarization analysis of the SFG spectra is an effective way for detailed SFG vibrational spectra assignment. Because molecules or molecular groups are naturally aligned or partially aligned at the interfaces, this makes the interface an ideal environment for polarization spectroscopic studies.[53] The coherent nature of the SFG process plus the alignment of molecular groups apparently makes the inhomogeneous broadening of the vibrational spectra to be less than that in the bulk liquid with IR and Raman. When we are trying to compare IR and Raman spectra of molecules in liquid or solid with SFG spectra, we usually find narrower peaks and more features in the SFG-VPS. (See Supporting Information.) This is also why simply using IR or Raman assignment for SFG is not sufficient to identify all the spectral features, as clearly demonstrated with the three diol molecules studied in the present work. Therefore, SFG-VPS can conversely clarify some spectra assignments in the existing IR and Raman spectroscopy.

4.2. Ethylene Glycol Orientation and Conformation at Its Vapor/Liquid Interface. Diols can form a hydrogen bond network in bulk liquid, similar to a water molecule. Ethylene glycol is the simplest among them and has been considered as a water analogue. Because of its unique physicochemical properties, ethylene glycol has been widely used as solvent, especially for cryogenic purposes. This makes ethylene glycol one of the most extensively studied diol molecules.[79] It has been pointed out that in liquid, ethylene glycol can exist in either gauche or trans form, or in a mixture of both.[79] To our knowledge, the structure and conformation of ethylene glycol at liquid interface has not been reported.

One important conclusion about the ethylene glycol vapor/liquid interface is that the gauche conformer is clearly present, because strong methylene CH stretching modes are detected in the SFG spectra (Figure 2). It has been generally believed that the SFG spectra of the trans conformer methylene group would not be detectable, because of the internal centrosymmetry of the two methylene groups in the trans conformation. Additionally, we were not able to detect any free OH peak on its SFG spectra between 3600 and 3800 cm^{-1} at the interface, whereas the hydrogen bonded OH band between 3200 and 3500 cm^{-1} was clearly detected. This evidence explicitly indicates that the trans conformer scarcely exists at the vapor/liquid interface. This makes the air/ethylene glycol interface pronouncedly different from the air/water interface, where about 20% of the surface is covered by the free OH bond projected out of the interface.[13] This means that on one hand ethylene glycol behaves like a water molecule to form a hydrogen network, but on the other hand it behaves like methanol or ethanol, for which the hydrophobic alkyl groups totally dominate the interface layer.[80]

Polarization analysis of the d ratio dependence on the interfacial refractive index n' in Figure 5 indicates very different sensitivities for different modes in different spectral polariza-
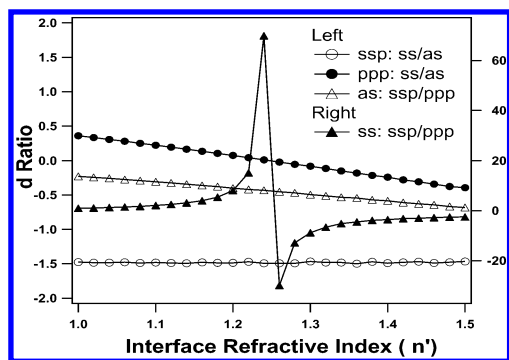
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Figure 5. Dependence of *d* ratios over interfacial refractive index.

tions. For the ss mode, the *d* ratio between the ssp and ppp changes dramatically around $n' = 1.24$. From the ethylene glycol SFG-VPS spectra in Figure 2, the intensity ratio for its ss mode is somewhere between 10 and 20, which means the *d* ratio is between 3 and 5. Because we have known from the spectral fitting this ratio has to be positive, it gives $n' = 1.16 \pm 0.02$ from Figure 5. This value is in good agreement with the value we used to calculate the model liquid.[28] It is possible to derive the interfacial refractive index n' from the ss mode ratio, just because the ssp and ppp has the same $c = 0$ value, i.e., the same orientational function $r(\theta)$. This also indicates that we cannot use the intensity ratio between the ss modes in different polarization to calculate tilt angle θ of the methylene bisectional axis. However, with known n', from the $d^2R(\theta)$ ratio between ssp−ss and ppp−as (Figure 1 above), we estimated that the tilt angle θ is about 26−36°, with the estimated intensity ratio (between 3 and 10) of these two modes from Figure 2. Another estimation comes from the intensity ratio ($\sim$3−5) of the 2900 cm^{-1} peak on the ppp and sps spectra, which gives the tilt angle about 41−45°. Such an approach has been used by Shultz et al. and others before.[26] These two estimation are close but not quite the same. Here we implicitly assumed that the two methylene groups in ethylene glycol are identical, which is rather arbitrary. This discrepancy also could come from the neglect of the orientational angular distribution width. Further quantitative analysis with the known information might be able to give a more accurate answer. However, it is reasonable for us to rest on a tilt angle value around $37 \pm 8°$ with a not very broad distribution width.

The above analysis indicates that if certain components in the SFG-VPS spectra are used, fairly accurate determination of the interfacial refractive index and molecular group tilt angle could be achieved. We are pretty afraid of the way to "accurately" fit the SFG spectra to obtain these quantities, because from our experiences, multiple parameter fitting of overlapping peaks in the SFG spectra can generate quite unreasonable numbers. However, as we demonstrated above, interfacial refractive index and molecular tilt angle can both be quite accurately determined if proper experimental quantities are chosen, even though these quantities are not so accurately measured or fitted.

The orientation and conformation analysis of ethylene glycol vapor/liquid interface is based on the polarization analysis and correct assignment of the methylene vibrational modes. Without such information, the orientation and conformation analysis would be certainly erroneous. As shown in the literature, the SFG spectral peaks intensity ratio of the methylene and methyl group was usually considered an indicator for the alkyl chain orientation order and conformation of the backbone.[73] This makes the correct assignment of the methylene modes impera-

tive for the understanding of polymeric and biomaterial interfaces.

Even though the SFG-VPS data for the other two diols would allow us to obtain more information about their orientation and conformation at the vapor/liquid interfaces, the multiple number of methylene groups presented in each molecule would make the analysis quite complicated. We will leave these for future report.

5. Conclusion

In conclusion, we have demonstrated the potential for SFG-VPS as a polarized spectroscopic technique, which enables accurate and detailed vibrational spectral assignment of the methylene CH modes in model diol molecules, independent of IR and Raman spectral assignments. We derived the polarization selection rules for such spectral assignment and discovered that the 2920 cm^{-1} region contains both ss Fermi and as modes in separate SFG polarization spectra. We also identified the 2954 cm^{-1} ss Fermi band and the mostly neglected 2900 cm^{-1} as band. This as band could be surprisingly strong for 1,5-pentanediol. These results should qualify SFG-VPS as an independent and sometimes more advantageous technique for spectral identification in SFG studies than IR and Raman spectra studies. With accurate spectra assignment, polarization and orientational analysis of the SFG-VPS data would allow more accurate and detailed determination of the interfacial refractive index and tilted angle of the methylene group of ethylene glycol at its vapor/liquid interface. The results and methodology here provide direct clarification for some of the confusions and consequent misinterpretations in the existing SFG-VS literatures, as well as spectral ambiguities in IR and Raman studies on methylene group in the condensed phases.

It is also a natural step to extend this SFG-VPS approach directly to other molecular groups at various interfaces with broad applications. In a future report, we are going to report our progresses on molecules with more congested spectra with modes from different molecular groups. We will report the development on the polarization selection rules for the methyl group, and on the detailed band assignment for the SFG spectra of a series of air/liquid alcohol interface with different chain lengths, in which both methylene and methyl groups are present.

Supporting Information Available: Table of spectral data and IR and raman spectra for ethylene glycol, 1,3-propanediol, and 1,5-pentanediol. This material is available free of charge via the Internet at http://pubs.acs.org.

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