

C–H Stretching Vibrations of Methyl, Methylene and Methine Groups at the Vapor/Alcohol ($n = 1-8$) Interfaces

Rong Lu,^{†,‡,§} Wei Gan,^{†,§} Bao-hua Wu,[†] Zhen Zhang,[†] Yuan Guo, and Hong-fei Wang*

State Key Laboratory of Molecular Reaction Dynamics, Institute of Chemistry, the Chinese Academy of Sciences, Beijing, P.R. China, 100080

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In IR and Raman spectral studies, the congestion of the vibrational modes in the C–H stretching region between 2800 and 3000 cm^{-1} has complicated spectral assignment, conformational analysis, and structural and dynamics studies, even with quite a few of the simplest molecules. To resolve these issues, polarized spectra measurement on a well aligned sample is generally required. Because the liquid interface is generally ordered and molecularly thin, and sum frequency generation vibrational spectroscopy (SFG-VS) is an intrinsically coherent polarization spectroscopy, SFG-VS can be used for discerning details in vibrational spectra of the interfacial molecules. Here we show that, from systematic molecular symmetry and SFG-VS polarization analysis, a set of polarization selection rules could be developed for explicit assignment of the SFG vibrational spectra of the C–H stretching modes. These polarization selection rules helped assignment of the SFG-VS spectra of vapor/alcohol ($n = 1-8$) interfaces with unprecedented details. Previous approach on assignment of these spectra relied on IR and Raman spectral assignment, and they were not able to give such detailed assignment of the SFG vibrational spectra. Sometimes inappropriate assignment was made, and consequently misleading conclusions on interfacial structure, conformation and even dynamics were reached. With these polarization rules in addition to knowledge from IR and Raman studies, new structural information and understanding of the molecular interactions at these interfaces were obtained, and some new spectral features for the C–H stretching modes were also identified. Generally speaking, these new features can be applied to IR and Raman spectroscopic studies in the condensed phase. Therefore, the advancement on vibrational spectra assignment may find broad applications in the related fields using IR and Raman as vibrational spectroscopic tools.

1. Introduction

Molecular level understanding of interfaces, especially liquid interfaces, is key to important problems in chemistry, environmental, and biological sciences, such as surface catalysis, material surface processing, structure and function of biological membrane, protein folding, etc.^{1–6} In the past 2 decades, sum frequency generation vibrational spectroscopy (SFG-VS) has been proven to be a uniquely important and effective technique for probing chemical bonding, structure, and molecular interaction at fundamentally and technologically important interfaces.^{6–10} The advantages of SFG-VS over other interface probing techniques are that it is nondestructive and it has unique surface specificity and submonolayer sensitivity.^{6,11,12} 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 subsequently a radiation with the frequency at the sum of these two laser pulses is generated. It has been well established that for many interfacial systems, especially the air/liquid interfaces as well as many liquid/liquid interfaces, the interface contribution to the SFG-VS signal does dominate.^{13–16} By tuning the IR wavelength, the resonance

enhanced intensity of the sum frequency signal gives the vibrational spectra of the interfacial chemical species. Moreover, controlling the polarizations of the IR, visible and sum frequency fields in SFG-VS experiment enables determination of the orientational information on molecular groups at the interface under investigation.^{9,17–19} Recent development with the so-called broadband SFG-VS technique also enables much more rapid spectra acquisition as compared with painstaking IR tuning, and this opens the way for broad applications in chemical and biological interface studies.^{20–22}

Despite all the advantages of SFG-VS for interface studies, the application of SFG-VS for quantitative measurement of the interfacial phenomena at the molecular level is still limited to a few model systems in the research laboratory,^{9,23–27} instead of becoming a common analytical instrument for general practice. Besides difficulties in instrument implementations, the ability of SFG-VS for accurate vibrational spectral assignment and polarization analysis, the key methodologies for quantitative conformation and orientational analysis,^{9,17,18} are yet to be fully developed. Recently, the null angle (NA) measurement approach with SFG-VS has been demonstrated for accurate determination of methyl group orientation at the air/methanol interface.¹⁷ The effectiveness and variations of this NA approach have also been examined in detail, and this research will be reported elsewhere.²⁸ A detailed polarization dependent analysis of the SFG spectra of a series of vapor/diol liquid interfaces has produced a set of polarization selection rules for spectral assignment of the C–H modes of the interfacial methylene groups.¹⁸ Using

* Author to whom correspondence should be addressed. E-mail: hongfei@mrdlab.icas.ac.cn. Tel. 86-10-62555347, Fax 86-10-62563167.

[†] Also graduate students of the Graduate School of the Chinese Academy of Sciences.

[‡] Present address: Reaction and Excitation Dynamics Group, Materials Engineering Laboratory, National Institute for Material Science, Sengen, Tsukuba, Japan.

[§] These two authors contributed to this work equally.

the polarization selection rules, some inconsistency and ambiguity in previous spectral assignments for the methylene groups in SFG-VS, as well as in the condensed phase IR and Raman vibrational spectroscopy, has been examined. Nevertheless, there are more to be done in terms of experimental and analytical methodology if more quantitative information is expected from the applications of the SFG-VS technique.

It has been realized in our previous studies¹⁸ that sum-frequency generation vibrational polarization spectroscopy (SFG-VPS) can be used to elucidate the details of vibrational spectra of molecules in the condensed phase. Here we call SFG-VS as SFG-VPS not because people have not known that SFG-VS itself has always been measured in different polarization combinations, but because systematic polarization analysis has not been fully employed in spectral assignment in SFG-VS.^{9,18} For example, many previous SFG-VS studies measured spectra in mostly one or two polarization combinations, and relied heavily on the spectra band fittings from IR and Raman spectral assignment for gaseous and condensed phase samples. Spectra polarization analysis for band intensities in different polarization combinations can produce unambiguous polarization selection rules for identifying the symmetry properties of SFG vibrational spectra peaks, which showed a few surprising disagreements with previous IR and Raman assignments.¹⁸ One example is that the 2940 cm^{-1} peak for the ethylene glycol (EG) molecule, which has long been considered the asymmetric C–H stretching mode in the literature,^{7,29,30} was unambiguously identified as the Fermi resonance peak of the EG methylene symmetric stretching mode through polarization analysis. Therefore, as we have mentioned in our previous report,¹⁸ it is natural to extend this SFG-VPS approach to molecular groups other than methylene, such as methyl, methine, etc.

The C–H stretching region between 2800 and 3000 cm^{-1} has been the most extensively studied in SFG-VS on various interfaces.^{18,31} Moreover, many important structure and dynamics studies using advanced Raman techniques rely on the assignments of the C–H stretching modes.^{32–35} Specific features of the C–H stretching region of Raman and coherent anti-Stokes Raman spectroscopy (CARS) are also widely used to investigate conformational order and for imaging in polymer and biomembrane studies.^{36–42} However, it is well-known that in IR and Raman studies the C–H stretching spectra in this region are notoriously complex due to the congestion of the symmetric, asymmetric, and Fermi resonance modes, which are quite sensitive to the specific couplings of conformational and environmental influences.^{41,43–46} Therefore, the spectra mode assignment in this region has been tedious and difficult. As a consequence, the general conception in SFG-VS studies remains that "...there is no simple relationship between observed peak positions and intensities and the properties of the underline modes, and the parameter can be extracted by curve fitting (from "known" IR and Raman peaks)."⁴⁷

If one looks into this matter closely, however, it is not hard to find the logical flaw in the spectra fitting approach in SFG-VS, because almost all SFG-VS spectra show narrower peaks and have more separated peaks than the same molecule measured with IR and Raman spectroscopy in the condensed phase.¹⁸ This is due to the relatively ordered interfacial structure and the less dynamic nature of the interactions of the molecules at the interface than that in the condensed phase under the same ambient conditions.^{48,49} Consequently, there is always more identifiable features in the SFG-VS spectra than the commonly obtained IR and Raman spectra in the condensed phase. As we have shown for the methylene group SFG-VPS studies, it is

feasible to use polarization analysis and selection rules in SFG-VPS to discern complex vibrational mode and structures for the methylene only molecular interfaces, and new features for the methylene Fermi resonance modes were explicitly identified.¹⁸ Reciprocally, this development can certainly add new insights in IR and Raman spectroscopic and dynamic studies. With the methylene problem generally solved, it is now imperative to study the spectral assignment problems of methyl and methine groups, for they ubiquitously exist in chemical and biological surfaces, membranes and materials.

In this work, we shall develop the polarization selection rules for the methyl and methine groups in SFG-VPS spectra analysis, using the same methodology as we did for the methylene group.¹⁸ The analysis is based on the recent simplified formulation for using the nonlinear optical techniques to study ordered molecular systems.^{18,50,51} We choose to analyze SFG-VPS spectra of simple normal alcohols ($n = 1-8$) as the model system of methyl studies. Normal alkanes were naturally chosen in IR and Raman studies for understanding the C–H stretching modes of methyl and methylene groups.^{41,43–46} However, some normal alkanes tend to lying flat at the interface,^{52,53} and quite a few short alkanes are not in liquid state at room temperature. Dissimilarly from the alkanes, the O–H group in the 1-alcohol would certainly help anchor one end of the simple alcohol molecule and make the other end tilt away from the interface.⁵⁴ Furthermore, using 1-alcohol molecules also makes the spectra analysis easier, for each of the simple alcohols has only one methyl group plus increasing numbers of methylene groups. So the vibrational spectra of these alcohols usually have only one Fermi resonance associated with the methyl group. As Snyder et al. have shown for polymethylene,^{43,45} the complexity of the C–H stretching region of the SFG-VS spectra of the vapor/alcohol interfaces are filled with many Fermi resonance modes associated with the methylene groups as the chain growing longer. SFG-VS spectra of vapor/1-alcohol ($n = 1-8$) interfaces in one polarization (*ssp* polarization) were reported previously, where the alcohols were found polar oriented at the vapor/alcohol interfaces.⁵⁴ To do polarization analysis, SFG-VS in all four independent polarizations are presented in this work. For methine group, we studied the vapor/2-propanol interfaces.

We shall show in this report that with the polarization selection rules for methyl, methylene and methine groups, detailed features in the SFG-VPS spectra of the vapor/alcohol interface could be explicitly assigned. The following important conclusions could therefore be drawn. (a) Polarization selection rules in SFG-VPS can be used to perform explicit spectral assignment in addition to the knowledge from IR and Raman studies. (b) Some ambiguities and mistakes in the IR and Raman spectral assignment could be examined with SFG-VPS studies. (c) It is desirable for future SFG-VS studies that SFG spectra in different polarizations be carefully obtained and compared for accurate spectral assignment as the basis for conformational and orientational analysis of the interfacial molecular groups. The polarization selection rules developed and the spectral features identified here should find broad applications in chemical and biological spectroscopic and dynamics studies.

2. Derivation of the Polarization Selection Rules

2.1. Theory of SFG, Molecular Symmetry, and the Susceptibility Tensors. The SFG intensity from a interface region is a square function of the effective sum frequency susceptibility $\chi_{\text{eff}}^{(2)}$.^{9,18}

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

ω , ω_1 , and ω_2 are the frequencies of the SF signal, visible laser beam, and IR laser beam, respectively. $n_i(\omega_i)$ is the refractive index of bulk medium i at frequency ω_i , and $n'(\omega_i)$ is the effective refractive index of the interface layer at ω_i . β_i is the incident or reflection angle from interface normal of the i th light beams; $I(\omega_i)$ is the intensity of the SFG signal or the input laser beams, respectively. The notations and the experiment geometry were described in detail previously.^{9,18}

It has been shown that for SFG and SHG (second harmonic generation) from a rotationally isotropic achiral interface ($C_{\infty v}$) the $\chi_{\text{eff}}^{(2)}$ could be simplified into⁵⁰

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

Then

$$I(\omega) = A d^2 R(\theta) N_s^2 I(\omega_1) I(\omega_2) \quad (3)$$

$$R(\theta) = |r(\theta)|^2 = |\langle \cos \theta \rangle - c \langle \cos^3 \theta \rangle|^2 \quad (4)$$

N_s is the molecular number density at the interface. $r(\theta)$ is called the *orientational field functional*, which contains all molecular orientational information at a given SFG experimental configuration, while 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 polarization 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. Both d and c could be derived from the expressions of the $\chi_{\text{eff}}^{(2)}$ in relationship to the macroscopic susceptibility and microscopic (molecular) hyperpolarizability tensors for a particular molecular vibrational modes, as we have shown for the methylene group analysis previously.^{18,50} With the known d and c values of the four independent polarization configurations in SFG-VS experiment, namely *ssp*, *ppp*, *sps*, and *pss*, the polarization selection rules for each molecular vibrational modes could be derived by plotting the function $d^2 R(\theta)$ against the tilting angle θ , and could be used for assigning the SFG-VPS spectra.¹⁸ It has also been shown¹⁸ and shall be clear from below that these polarization selection rules are firmly rooted in the intrinsic molecular symmetry requirements.

$\chi_{\text{eff}}^{(2)}$ for the above four polarization configurations are related to the 7 nonzero macroscopic susceptibility tensors of a rotationally isotropic interface ($C_{\infty v}$) in the following general forms.^{9,18}

$$\begin{aligned} \chi_{\text{eff}}^{(2),ssp} &= L_{yy}(\omega) L_{yy}(\omega_1) L_{zz}(\omega_2) \sin \beta_2 \chi_{yyz} \\ \chi_{\text{eff}}^{(2),sps} &= L_{yy}(\omega) L_{zz}(\omega_1) L_{yy}(\omega_2) \sin \beta_1 \chi_{zyy} \\ \chi_{\text{eff}}^{(2),pss} &= L_{zz}(\omega) L_{yy}(\omega_1) L_{yy}(\omega_2) \sin \beta_2 \chi_{zyy} \\ \chi_{\text{eff}}^{(2),ppp} &= -L_{xx}(\omega) L_{xx}(\omega_1) L_{zz}(\omega_2) \cos \beta_2 \cos \beta_1 \sin \beta_2 \chi_{xxz} - \\ &\quad L_{xx}(\omega) L_{zz}(\omega_1) L_{xx}(\omega_2) \cos \beta_1 \sin \beta_1 \cos \beta_2 \chi_{xzx} + \\ &\quad L_{zz}(\omega) L_{xx}(\omega_1) L_{xx}(\omega_2) \sin \beta_1 \cos \beta_1 \cos \beta_2 \chi_{zxx} + \\ &\quad L_{zz}(\omega) L_{zz}(\omega_1) L_{zz}(\omega_2) \sin \beta_1 \sin \beta_1 \sin \beta_2 \chi_{zzz} \end{aligned} \quad (5)$$

It is so defined that the xy plane in the laboratory coordinates

system $\lambda(x, y, z)$ is the plane of interface; all the light beams propagate in the xz plane; p denotes the polarization of the optical field in the xz plane, with z as the surface normal, while s denotes the polarization perpendicular to the xz plane. The consecutive superscript, such as *ssp*, represents the following polarization combinations: SF signal s polarized, visible beam s polarized, IR beam p polarized, and so forth. L_{ii} ($i = x, y, z$) is the Fresnel coefficient determined by the refractive index of the two bulk phase and the interface layer, and the incident and reflected angles.^{9,18} $\chi_{ijk}^{(2)}$ tensors are related to the molecular $\beta_{ijk}^{(2)}$ in the molecular coordinates system $\lambda'(a, b, c)$ through the ensemble average over all possible molecular orientations.^{9,18}

$$\chi_{ijk}^{(2)} = N_s \sum_{i'j'k'} \langle R_{ii'} R_{jj'} R_{kk'} \rangle \beta_{i'j'k'}^{(2)} \quad (6)$$

where N_s is the number density of the interface moiety under investigation; $R_{\lambda\lambda'}$ is the element of the Euler rotational transformation matrix from the molecular coordination $\lambda'(a, b, c)$ to the laboratory coordination $\lambda(x, y, z)$.^{51,55}

In general, the methyl group can be treated as with C_{3v} symmetry, since the perturbations to the C–H high-frequency stretching vibrations by other parts of the molecule is often insignificant.^{18,56,57} Thus, there are 11 nonzero microscopic hyperpolarizability elements for methyl.^{58,59} Those bearing the symmetric stretching (*ss*) modes are $\beta_{aac}^{(2)} = \beta_{bbc}^{(2)}$ and $\beta_{ccc}^{(2)}$; the asymmetric stretching (*as*) modes are $\beta_{aca}^{(2)} = \beta_{bcb}^{(2)}$, $\beta_{caa}^{(2)} = \beta_{cbb}^{(2)}$, and $\beta_{aaa}^{(2)} = -\beta_{bba}^{(2)} = -\beta_{abb}^{(2)} = -\beta_{bab}^{(2)}$. In the molecular coordinates system, c is along the symmetry axis of the methyl group, a and b axes forms the plane perpendicular to c with the a axis along projection of one C–H bond in the ab plane. Then we have^{35,60}

$$\begin{aligned} \chi_{xxz}^{(2),ss} &= \chi_{yyz}^{(2),ss} = \frac{1}{2} N_s \beta_{ccc}^{(2)} [(1 + R) \langle \cos \theta \rangle - (1 - R) \langle \cos^3 \theta \rangle] \\ \chi_{xzx}^{(2),ss} &= \chi_{zxx}^{(2),ss} = \chi_{zyy}^{(2),ss} = \chi_{zyy}^{(2),ss} \\ &= \frac{1}{2} N_s \beta_{ccc}^{(2)} (1 - R) [\langle \cos \theta \rangle - \langle \cos^3 \theta \rangle] \\ \chi_{zzz}^{(2),ss} &= N_s \beta_{ccc}^{(2)} [R \langle \cos \theta \rangle + (1 - R) \langle \cos^3 \theta \rangle] \end{aligned} \quad (7)$$

and with $\beta_{aca}^{(2)} = \beta_{bcb}^{(2)} = \beta_{caa}^{(2)} = \beta_{cbb}^{(2)}$ for SFG measurement with both the SF and visible frequencies off resonance, we have

$$\begin{aligned} \chi_{xxz}^{(2),as} &= \chi_{yyz}^{(2),as} = -N_s \beta_{aca}^{(2)} (\langle \cos \theta \rangle - \langle \cos^3 \theta \rangle) \\ \chi_{xzx}^{(2),as} &= \chi_{zxx}^{(2),as} = \chi_{zyy}^{(2),as} = \chi_{zyy}^{(2),as} = N_s \beta_{aca}^{(2)} \langle \cos^3 \theta \rangle \\ \chi_{zzz}^{(2),as} &= 2N_s \beta_{aca}^{(2)} (\langle \cos \theta \rangle - \langle \cos^3 \theta \rangle) \end{aligned} \quad (8)$$

Here the hyperpolarizability ratio $R = \beta_{aac}^{(2)} / \beta_{ccc}^{(2)} = \beta_{bbc}^{(2)} / \beta_{ccc}^{(2)}$ is different for the methyl group in different molecules, which can be explicitly determined from the independently measured Raman depolarization ratio.^{9,61} It is known that R has to be in the range of about 1.66 to 4.0 for methyl group,^{9,57,59,62,63} with $R = 1.7$ for methanol, $R = 3.4$ for ethanol and longer chain 1-alcohols, $R = 1.9$ for acetone, $R = 2.3$ for acetonitrile, and $R = 2.3$ for DMSO.^{25,61–64} θ is the tilt angle of the methyl C_3 axis from the surface normal, and the operator $\langle \rangle$ denotes the orientational ensemble average over different molecular orientations. It is noted that the last 4 of the 11 nonzero hyperpolarizability elements for methyl group vanish in eqs 7 and 8 due to the orientational ensemble average. It is also noted that the

asymmetric susceptibility tensor terms for the methyl group are different from the corresponding terms for the asymmetric terms of the methylene group by a factor of 2,^{18,35,60} instead of bearing the exact same forms,⁶⁵ unless the 2-fold degeneracy of the CH_3 -*as* mode is lifted.

Similar to the single O–H bond, the methine group is with $C_{\infty v}$ symmetry, with its molecular coordinate *c* axis along the C–H bond. The nonzero hyperpolarizability terms for methine and single O–H group are all symmetric;⁶⁶ i.e., $\beta_{aac}^{(2)} = \beta_{bbc}^{(2)} = R\beta_{ccc}^{(2)}$, with the *R* value falling into 0 to 0.28 for C–H, equal to its bond polarizability ratio *r*.^{9,59,63} It is easy to show that the nonzero elements for the methine and O–H susceptibility tensors terms follow the same expressions as those for the *ss* mode of the methyl group in eq 7. However, as we shall show later, the different *R* values for the methyl and methine groups should lead to quite different polarization selection rules for the two groups. The *r* value for the single O–H group is about 0.32 or less,^{66,67} the treatment for the methine group here should be readily applied to the analysis to stretching mode of the O–H group, the C=O group, and other molecular groups with the $C_{\infty v}$ symmetry.

2.2. Polarization Selection Rules for Methyl and Methine Groups. Using the bond polarizability approximation,^{57,59} the general orientational parameter *c* and the strength factor *d* values for the interfacial methyl group in alcohol could be calculated using the following parameters for vapor/ethanol interface. In our copropagating experimental configuration, $\beta_1 = 60^\circ$, $\beta_2 = 55^\circ$, and $\beta = 59^\circ$. As discussed in our previous report and following the treatment by Zhuang et al.,^{9,18} the refractive index used are following: $n_1(\omega_1) = n_1(\omega_2) = n_1(\omega_3) = 1.0$; $n_2(\omega_1) = n_2(\omega_2) = n_2(\omega_3) = 1.36$, the bulk refractive index of ethanol at room temperature; $n'(\omega_1) = n'(\omega_2) = n'(\omega_3) = 1.16$. As we have discussed previously, the refractive index for the IR wavelength would not be sensitive to the calculated ratio between $d^2R(\theta)$ for *ssp* and *ppp* for the copropagating configuration. This fact would make copropagating configuration advantageous for polarization analysis because the polarization selection rule would not be affected in a very broad range of IR refractive indexes.¹⁸ For the methyl group of ethanol, the hyperpolarizability ratio $R = 3.4$, corresponding to the bond polarizability ratio $r = 0.025$.^{57,59,63} Using above parameters, the *d* and *c* values are following.

For *ss* modes: *ssp*, $d = 0.558\beta_{ccc}$, $c = -0.545$; *sps*, $d = -0.327\beta_{ccc}$, $c = 1$; *pss*, $d = -0.324\beta_{ccc}$, $c = 1$; *ppp*, $d = 0.369\beta_{ccc}$, $c = 1.99$. For *as* mode: *ssp*, $d = -0.127\beta_{aca}$, $c = 1$; *sps*, $dc = -0.136\beta_{aca}$, $c = \infty$; *pss*, $dc = -0.135\beta_{aca}$, $c = \infty$; *ppp*, $d = 0.305\beta_{aca}$, $c = 1.00$. According to the treatment by Hirose et al., $\beta_{aca}/\beta_{ccc} \approx 3.4$,^{57,59} which can be used to compare the SFG intensity between the *ss* and *as* modes. Figure 1 plots the value of $d^2R(\theta)$ against the tilt angle θ of the methyl group from the surface normal, using a δ distribution function of θ . Thus, the following polarization selection rules (or guidelines) could be reached.

(a) For *ss* mode, *ssp* intensity is always many times of that for *ppp*, as well as for *sps* and *pss*.

(b) For *as* mode, *ppp* intensity is always many times of that for *ssp*, and both of them would be largest when $\theta = 54.7^\circ$.

(c) For small θ , *sps* and *pss* intensity is the largest for the *as* mode, and the smallest for the *ss* mode.

(d) In *ssp* spectra, the *as* mode would negatively interfere with the *ss* mode when their frequency are overlapped.

These rules are similar to those for the methylene groups except for some minor differences.¹⁸ From $n = 3$ –8 alcohols, all the parameter used to calculate *d* and *c* for their methyl

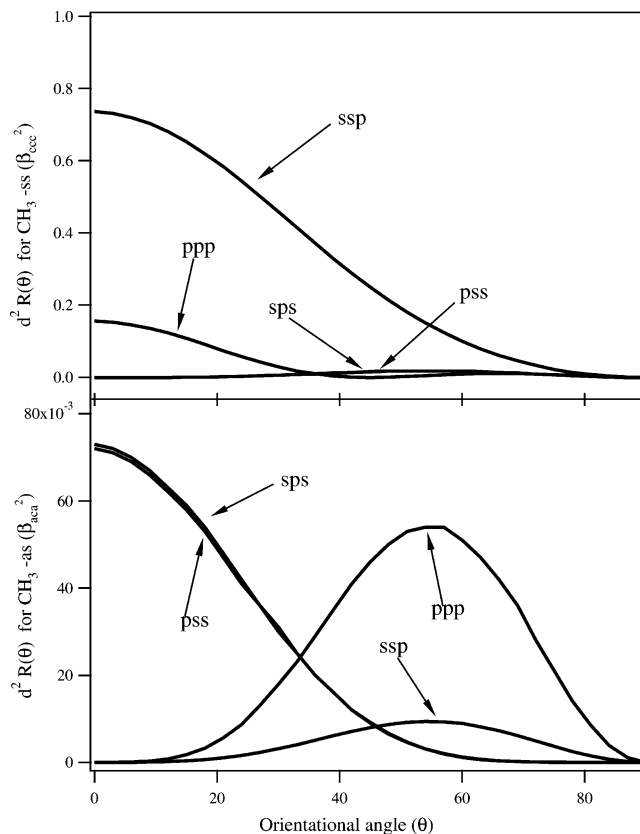


Figure 1. $d^2R(\theta)$ vs orientational angle θ with a δ distribution function at four polarization configurations for methyl group. Top: Symmetric stretching vibration; Bottom: Antisymmetric stretching vibration. $\beta_{aca}/\beta_{ccc} \approx 3.4$ for methyl groups of $n = 2$ –8 alcohols. The methyl group for methanol has different but similar curves.

groups are essentially the same as those for ethanol. It is important to note that for methanol, $R = 1.7$ with $r = 0.27$, $n_2(\omega_i) = 1.33$ and $n'(\omega_i) = 1.15$. Calculation shows that as long as $R > 1$, the differences of these parameters would lead to different *d* and *c* values, but shall not alter the polarization selection rules listed above. The validity of the polarization selection rules with different experimental configurations, different parameters, and non δ orientational distribution functions have been discussed in detail in our previous reports for methylene group studies.¹⁸ The conclusion with similar treatment is that the polarization selection rules do hold for the methyl group in varying experimental configurations and the parameters within physically allowed ranges. We also noticed that a big difference for methanol from the other 1-alcohols is that $\beta_{aca}/\beta_{ccc} \approx 1.0$.^{57,59,61,63} Along with the different *d* and *c* values, this much smaller ratio furthermore explains well of the puzzle that there was no *as* mode peaks ever observed in all the vapor/methanol interface SFG-VS measurement.^{14,27,62}

The dielectric constants and local field factors of metal or electrochemical interfaces are very different from those for dielectric interfaces discussed in this report. Therefore, the polarization dependence of SFG and SHG for adsorbates at metal or electrochemical interfaces would be dominated with *ppp* signals.^{68–70} Certainly the polarization selection rules derived for dielectric interfaces here would not be applicable to these interfaces.

Figure 2 plots the value of $d^2R(\theta)$ against the tilt angle θ for the methine group, using a δ distribution function of θ . Here we use $R = r = 0.27$ along with the rest of the parameters the same as those used for ethanol listed above. We use the value $R = r = 0.27$ because the methine group discussed in this work

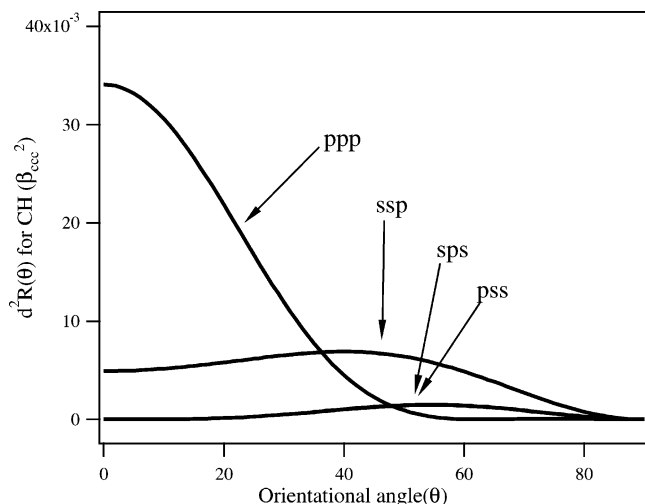


Figure 2. $d^2R(\theta)$ vs orientational angle θ with a δ distribution function at four polarization configurations for methine group with $R = 0.27$.

was directly connected to O–H group. This would make the bond polarizability ratio r of these C–H bonds bigger than that of C–H bonds in saturated hydrocarbon.^{57,59,63} This is inline with the fact that the bond polarizability of C–H for methyl group in methanol ($r = 0.27$) is also much bigger than that of ethanol ($r = 0.025$) molecule. Then we have the following d and c values: *ssp*, $d = 0.164\beta_{ccc}$, $c = 0.575$; *sps*, $d = 0.101\beta_{ccc}$, $c = 1$; *pss*, $d = 0.100\beta_{ccc}$, $c = 1$; *ppp*, $d = -0.050\beta_{ccc}$, $c = 4.69$. Therefore, the following polarization selection rules can be reached. These selection rules are also valid for stretching vibrational modes of O–H, C=O, and C≡N groups, since their R values are all much smaller than 1.

- ppp* intensity is the strongest when θ is at smaller angles.
- ssp* intensity is the strongest when θ is at large angles.
- sps* (*pss*) intensities are comparable to the *ssp* intensity when the R value is small enough.

Since each long chain molecules may have many methylene groups, the SFG-VS spectra will have many spectral features from the methylene modes. For *ss* modes of methylene group: *ssp*, $d = 0.22\beta_{ccc}$, $c = 0$; *sps*, $d = 0\beta_{ccc}$, $c = 1$; *pss*, $d = 0\beta_{ccc}$, $c = 1$; *ppp*, $d = 0.033\beta_{ccc}$, $c = 0$. For the *as* mode: *ssp*, $d = -0.11\beta_{aca}$, $c = 1$; *sps*, $d = -0.12\beta_{aca}$, $c = \infty$; *pss*, $d = -0.12\beta_{aca}$, $c = \infty$; *ppp*, $d = 0.28\beta_{aca}$, $c = 1.00$.⁷¹ Here the units of d are different from those in our previous report. This definition makes the d value independent from the r values of the CH bond,⁷¹ even though the relative intensity between the *ss* and *as* modes for methylene group still depend on the r value of the single bond. Nevertheless, the polarization selection rules from Figure 3 are the same for the methylene C–H stretching modes as in our previous report.¹⁸

- No *ss* peak would appear in *sps* and *pss* spectra.
- ssp* intensity of the *ss* mode is always many times of that of *ppp*.
- Any peak in the *sps* and *pss* spectra should come from the *as* mode with a relatively small tilt angle θ .
- ppp* intensity of the *as* mode is always several times of the of *ssp*. That is to say, if there is any peak which is stronger in the *ssp* than *ppp* spectra, it cannot be from the *as* mode.
- In the *ssp* spectra, the *ss* and *as* modes of the methylene groups with similar orientation negatively interfere with each other.

Unlike the methyl and methine groups which has a freedom of rotation around their symmetrical axis, the methylene group rotation around its C_2 symmetrical axis is hindered if the

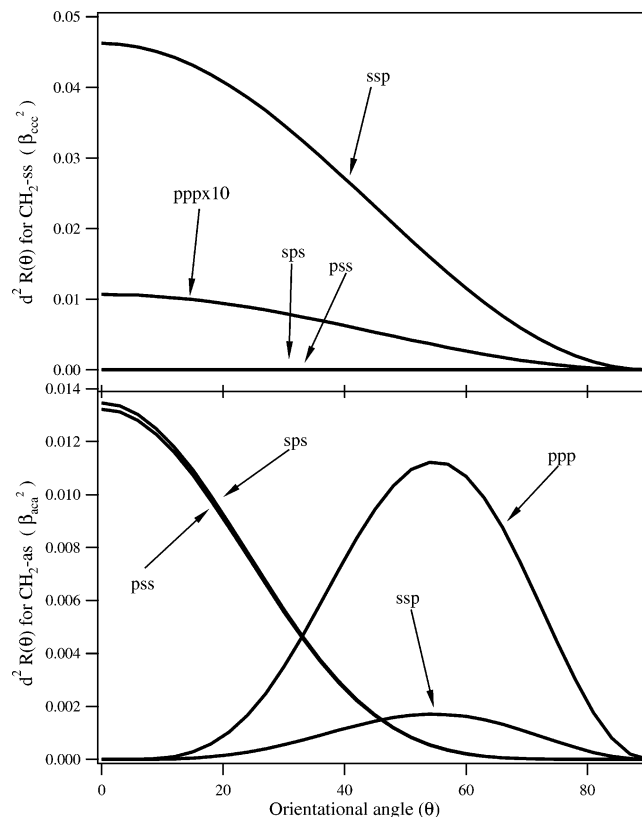


Figure 3. $d^2R(\theta)$ vs orientational angle θ with a δ distribution function at four polarization configurations for methylene group.

molecule assumes a particular orientation. Consequently, the rotational average over the ψ angle with the Euler transformation in eq 6 cannot be treated as ψ rotational isotropic. This shall certainly modify the selection rules above for the methylene group. For example, *ss* mode might appear on the *sps* and *pss* spectra with small intensities. Therefore, even though the effect is very weak, and the *sps* and *pss* spectra are usually very small, the selection rules a and c need to be reconsidered. Nevertheless, the selection rules frequently used in the determination of the *ss* mode and *as* mode in *ssp* and *ppp* polarization, i.e., rules b and d, remain unaffected. The detailed analysis will be presented elsewhere.⁷¹

3. Experimental Section

The details of SFG-VS experiment are the same as in our previous reports.^{17,18} Briefly, the 10 Hz and 23 ps SFG spectrometer laser system was purchased from EKSPLA, using a copropagating configuration. Some of the SFG polarization optics were rearranged from the original design by EKSPLA to improve the polarization control in the SFG experiment.¹⁷ The visible wavelength is fixed at 532.1 nm and the full range of the IR tunability is 1000–4300 cm^{-1} . The specified spectral resolution of this SFG spectrometer is $<6 \text{ cm}^{-1}$ in the whole IR range, and about 2 cm^{-1} around 3000 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 around 59° (β) at the reflection geometry, within a small range (about 0.3°) which depends on the corresponding IR wavelength tuning range (from 2800 to 3000 cm^{-1} in the experiment). Each scan was with an 2 cm^{-1} increment and was averaged over 100 laser pulses per point. The energy of visible beam is typically less than 300 microjoules and that of IR beam less than 200 mJ. So the intensity in our experiment condition cannot damage or cause

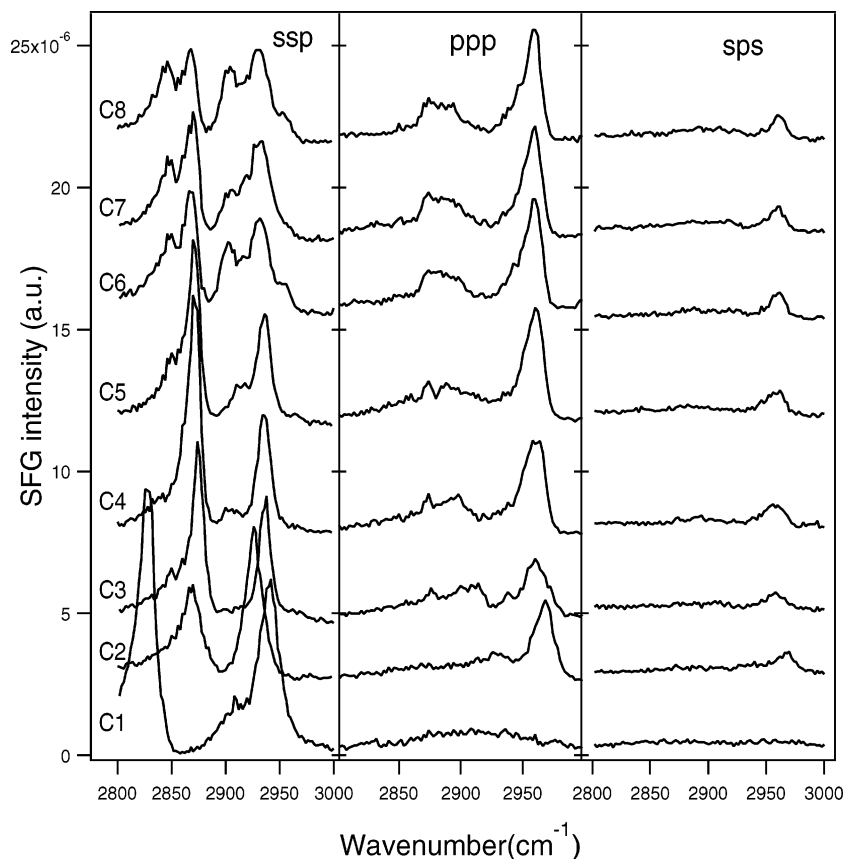


Figure 4. SFG-VS spectra of *ssp*, *ppp*, and *sps* for vapor/1-alcohol interfaces ($n = 1-8$). The *pss* spectra are not listed because they are almost the same as the *sps* spectra. The solid line is the line connecting experimental points. Detailed spectra for each curve are in the supporting material.

any heat effect or other photochemical reactions to the liquid samples. The spectrum intensity is normalized to 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 were all GC grade, and were obtained from Fluka: methanol (> 99.8%), ethanol (> 99.8%), 1-propanol (> 99.8%), 1-butanol (> 99.5%), 1-pentanol (> 99.0%), 1-hexanol (> 99.0%), 1-heptanol (> 99.0%), 1-octanol (> 99.5%), and 2-propanol (> 99.5%). All the liquid samples were filled in a round Teflon beaker (diameter ~ 5 cm.) for SFG measurement. The whole experimental setup on the optical table was covered in a plastic housing to reduce the air flow and the evaporation.

4. Results and Discussion

4.1. CH₃ and CH₂ Spectral Assignment for Vapor/1-Alcohol Interfaces. The *ssp*, *ppp*, and *sps* SFG-VPS spectra for the eight vapor/1-alcohols interfaces ($n = 1-8$) are presented in Figure 4. The *pss* spectra are not shown because they just overlap with those of *sps*. The *ssp* spectra (~ 5 cm⁻¹ per step with IR bandwidth of 12 cm⁻¹) of the vapor/1-alcohols interfaces were reported by Shen et al. previously,⁵⁴ which are fully consistent with the *ssp* spectra reported in this work. Moreover, the *ssp* spectra in this work are with better spectral resolution (2 cm⁻¹ per step with IR bandwidth of ~ 2 cm⁻¹), and they exhibit finer features than the previous results. The *ppp* and *sps* and *pss* are all reported for the first time except for vapor/methanol and vapor/ethanol interfaces.

We found that many features in these SFG-VS spectra are extremely difficult to be explicitly assigned according to previous IR and Raman studies. The SFG-VS spectra of vapor/alcohol interfaces are complex and congested with close peak

positions because there are many Fermi resonance modes of methyl and methylene *ss* modes.⁴⁶ Some of the simple vapor/liquid interfaces, such as acetone, acetonitrile, and DMSO would have simpler SFG-VS spectra because they are without methylene group, and their methyl groups are without Fermi resonance modes.^{25,61,64} Assignment of SFG-VS for these simple liquid interfaces would be simple and straightforward from the IR and Raman spectral assignments. Nevertheless, the polarization selection rules of methyl group derived above are as effective and are in full agreement with these assignments.

As we have noticed in our previous report on the vapor/diol interfaces,¹⁸ the standard IR and Raman spectra for these molecules in condensed phases taken at 4 cm⁻¹ (for example, the spectra in the NIST Chemistry Webbook Database) show much broader peaks than the SFG-VS spectra with similar spectral resolution. This inarguably tells the intrinsic difference between the broadening mechanisms of molecule at the liquid interface and in the liquid or solid phase. It is clear that at the liquid interface, the spectra broadening is much less than that in the bulk liquid. Usually the fwhm of vibrational mode at the vapor/liquid interface from SFG-VS spectra is around 10 cm⁻¹ or less. Therefore, to capture spectral details, the SFG-VS experiments should be carried out with a resolution few times smaller than this width. Our picosecond SFG laser system is ideal for such purpose.

It is clear that all the spectra features in Figure 4 in the 2800–3000 cm⁻¹ range belong to the interfacial methyl and methylene groups. With increasing chain length, the SFG-VS spectra become increasingly complex. From the polarization selection rules for methyl and methylene groups we have derived here and previously,¹⁸ we can see as a rule of thumb that the features in the *ssp* spectra generally belong to the *ss* modes and their

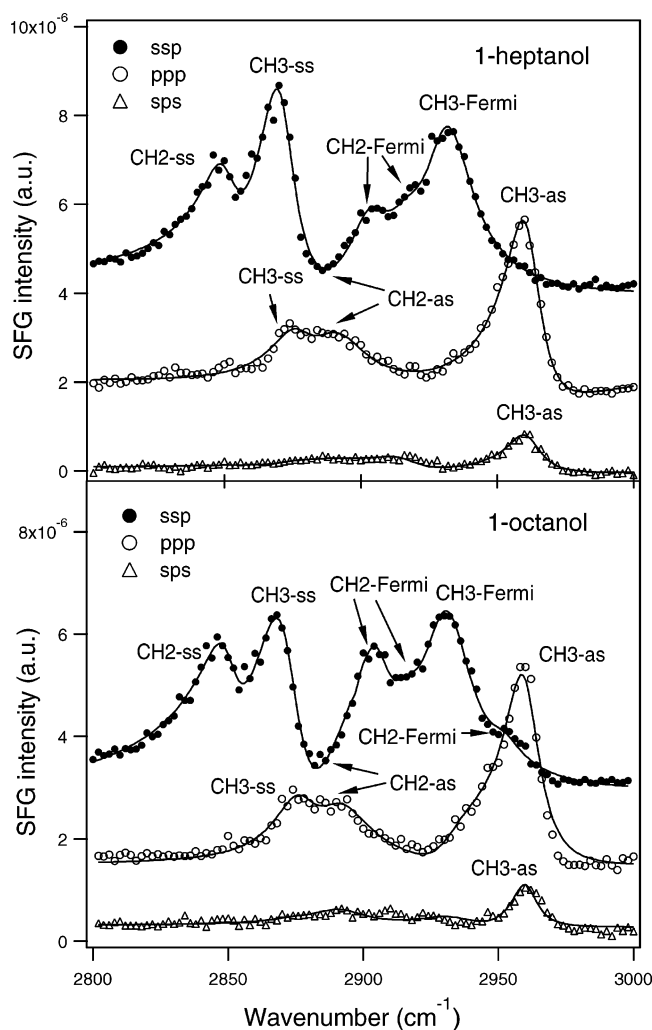


Figure 5. SFG-VS spectra and assignments of the vapor/1-heptanol (top) and vapor/1-octanol interface (bottom). All the spectra features are assigned according to the polarization selection rules for methyl and methylene groups. The solid lines are fitting curves with Lorentzian line shape function.

Fermi resonance modes; while the major features in the *ppp* and *sps* belong to the *as* modes. Using the full polarization selection relationships, we have made explicit assignments of all these spectra features. Later we shall also show that we can further obtain detail new knowledge on both spectral assignment and the structural information on these liquid interfaces.

Figure 5 presents the detailed assignment with the polarization selection rules for the two most complex spectra, namely, vapor/1-heptanol and vapor/1-octanol, in this series of vapor/alcohol interfaces. (See the detailed spectral assignments for all the

molecules studied in the Supporting Information section.) It is clear that such detailed assignment for these congested spectra would not have been possible with only the *ssp* spectra, as practiced in many previous SFG-VS studies.^{72,73}

The positions of all the assigned major peaks for all SFG spectra of vapor/1-alcohol interfaces are listed in Table 1. Here we listed the position of the apparent peaks because it is more clear for apply the polarization selection rules. The fitted peak positions are different by 1 to 4 cm^{-1} . Such difference are well within the spectral peak fwhm. One of the advantages of employing the polarization selection rules in spectral assignment is that spectrum can be correctly assigned with relative peak intensities in the spectra of different polarizations before detailed spectral fitting is conducted. One does not need to worry about very small hidden peaks, because it is generally clear in spectrum of one of the four different polarizations, and the relative intensities of the peak in different polarization can be qualitatively assessed for effective application of the selection rules.

To make easier comparison with past literature, the C–H stretching mode notations used by Snyder et al. for methyl and methylene groups are also labeled in Table 1.^{45,46} It should be noted that all the *ss* modes and their Fermi resonances (bear the same symmetry as the *ss* mode^{18,74}) for methyl and methylene groups have their strongest features in the *ssp* spectra. These modes may have very small features on the *ppp* spectra sometimes, but would have even smaller or no features on the *sps* and *pss* spectra. On the other hand, except for vapor/methanol interface whose *as* modes were completely not observed, the *as* modes for other vapor/1-alcohol interfaces have their strongest features on the *ppp* spectra, slight smaller or comparable features on the *sps* and *pss* spectra, and most of time much smaller on the *ssp* spectra. Since it is very easy to distinguish these modes according to the polarization selection rules, the assignments of all the spectra are explicit and straightforward.

4.2. New Spectral Features for CH₃ and CH₂ Groups. It is clear that the CH₂-*ss* mode around 2850 cm^{-1} , CH₃-*ss* mode around 2870 cm^{-1} , CH₃-FR mode around 2935 cm^{-1} , and CH₃-*as* mode around 2960 cm^{-1} agree well with assignments in previous SFG-VS, IR, and Raman studies in the literature, except those for ethanol (which shall be discussed later).^{9,45,75} Despite the good agreements, there are disagreements for the CH₂-*as* and CH₂-FR, and CH₃-*as* modes. As we have reported in the previous vapor/diol interfaces SFG-VPS studies,¹⁸ there are multiple CH₂-FR modes, when there are multiple CH₂ groups present,⁴³ around 2916, 2938, and 2954 cm^{-1} , and there are also CH₂-*as* around 2900 and 2925 cm^{-1} . We also pointed out that one of the common mistake in the literature was to take the 2900 cm^{-1} on the *ppp* SFG-VS spectra as the CH₂-FR mode and the peak around 2920 cm^{-1} on the *ssp* spectra as the CH₂-*as* mode.¹⁸ Both would violate the polarization selection rules

TABLE 1: Assignment to the SFG-VS Spectral Data (cm^{-1}) of Vapor/1-Alcohol ($n = 1-8$) Interfaces^a

assignment (notation ^{45,46}) polarization spectral data	CH ₂ - <i>ss</i> (d^+) ssp	CH ₃ - <i>ss</i> (r^+) ssp	CH ₂ - <i>as</i> (d^-) ppp & sps	CH ₂ -FR (d^+ -FR) ssp	CH ₂ -FR (d^+ -FR) ssp	CH ₃ -FR (r^+ -FR) ssp	CH ₃ - <i>as</i> (r^-) ppp & sps
methanol		2828				2910, 2940	
ethanol		2868				2926	2970
1-propanol	2850	2874	2908 (br)			2938	2960
1-butanol	2850	2872	2898 (br)	2904		2938	2960
1-pentanol	2850	2870	2890 (br)		2918	2934	2960
1-hexanol	2848	2868	2884 (br)	2904	2918, 2954	2932	2960
1-heptanol	2848	2870	2884 (br)	2906	2918	2932	2960
1-octanol	2846	2868	2884 (br)	2904	2918, 2954	2930	2960

^a br = broad peak

for methylene group. In this report, we identified for the vapor/1-alcohol interfaces that there is one relatively broad CH_2 -*as* band on the *ppp* spectra, whose position progressed from 2908 to 2884 cm^{-1} from 1-propanol to 1-octanol. According to the relationships in Figure 1, the left and right side of this broad band on *ppp* may have contributions from the CH_3 -*ss* mode around 2870 cm^{-1} and CH_2 -FR mode around 2904 cm^{-1} , both of which are much stronger on the *ssp* spectra, respectively. However, the center part of this broad band is unambiguously from the CH_2 -*as* mode. We believe that it is possible to resolve these peaks, if proper polarization or experimental configuration is employed.^{18,50} We also identified that the CH_2 -FR modes are around 2904 cm^{-1} , 2918 and 2954 cm^{-1} from 1-propanol to 1-octanol. Moreover, we noticed that there is no clearly resolved 2954 cm^{-1} feature on the *ppp*, *sps*, and *pss* spectra. This means that the 2954 cm^{-1} feature observed on the *ssp* spectra does not belong to the CH_3 -*as* mode. Therefore, at vapor/1-alcohol interfaces, the degeneracy of two degenerate CH_3 -*as* modes is not lifted, and the CH_3 with C_3 symmetry is free from attachment to other molecules.^{45,46}

We also found out that unlike the vapor/diol interfaces, there is no identifiable feature for CH_2 -*as* mode around 2920 cm^{-1} position because its peak does not appear on the *ppp* and *sps* spectra. Our SFG-VS data on 1-hexadecane, 1-nonane, and 1-decane vapor interfaces also show negative results for 2920 cm^{-1} to be CH_2 -*as* mode.⁷⁶ These simple facts are surprising for us, because from previous *n*-alkanes and polyethylene IR and Raman studies, there was a so-called IR active CH_2 -*as* mode showing a strong peak around 2920 or 2930 cm^{-1} , which does not appear on the Raman spectra; and there was also a so-called Raman active mode around 2890 and 2900 cm^{-1} , which does not appear on the IR spectra.^{42,45,46,77–79} These modes were also reported in previous SFG-VS studies.^{15,80} However, these SFG-VS studies did not present enough data for full polarization analysis on these bands. Therefore, it is not possible to know whether these interpretations are correct or not. On the other hand, because the fundamental principle for SFG-VS requires a mode to be both IR and Raman active,^{8,81} it is rather odd to be able to observe in SFG-VS spectra any of the so-called IR active (around 2920 cm^{-1}) or Raman active (around 2890 or 2900 cm^{-1}) CH_2 -*as* modes.^{45,46} The CH_2 -*as* band from 2908 to 2884 cm^{-1} identified with polarization selection rules show clear *as* properties, and it is in good accord with the so-called Raman active CH_2 -*as* mode in the literature. This indicates that the so-called Raman active *as* mode should also be IR active, even though it is very weak on the IR spectra. It should be noted that there is no symmetry requirement for the CH_2 modes be strictly Raman or IR mutual exclusive. Thus, what could be the reason that the IR active CH_2 -*as* mode does not appear in the SFG-VS spectra of these alcohols, according to the polarization selection rules? This let us wonder the nature of the so-called IR active CH_2 -*as* mode around 2920 or 2930 cm^{-1} in the literature. Even though in textbooks and literature it is generally accepted that there is a CH_2 -*as* mode around 2920 or 2903 cm^{-1} from alkane and polyethylene IR and Raman studies,^{78,82–84} much to our surprise, we have not found decisive direct experimental evidence based on symmetry properties measurement on assigning it. We now propose the possibility that this band could have been misinterpreted from a CH_2 -*ss* Fermi resonance mode. We believe that this problem warrants further investigation in the future.

One of the interesting phenomena for the longer chain 1-alcohols is that the intensities of the 2904, 2918, and 2954 cm^{-1} CH_2 -FR modes show odd/even alternating patterns. To

our knowledge, this kind of phenomenon in the C–H stretching region has not been reported before, even though the band structure of many Fermi resonance in the polymethylene chain was well studied earlier by Snyder et al.⁴³ These patterns should be attributed to the coupling between the different CH_2 groups in the same carbon chain. However, it is yet to be answered whether this is an bulk phenomenon, an interface one, or a property of the molecule itself. Nevertheless, these interesting features clearly have demonstrated the capability of SFG-VPS for investigating spectroscopic details of molecular structure and interactions. In previous IR or Raman studies, such spectra details can only emerge well below the liquid hydrogen temperature with crystalline samples where the spectra line broadening is greatly suppressed.^{43,45,46,85}

It is clear from above that SFG-VPS with the polarization selection rules is able to discern details of the congested C–H stretching vibrational spectra. These assignments also suggest that conclusions on molecular structure, conformation, and dynamics according to C–H vibrational spectral assignments have to be carefully checked in the light of such complexity of the C–H stretching vibration modes.

Recently, SFG-VS on the C–H modes have found many applications on polymer interface studies.^{86–88} The polarization selection rules on methyl, methylene, and methine groups are readily applicable to this field of studies. One common group in many important polymers, such as PMMA, PVC, and PMA, etc. is the ester methyl group, whose SFG-VS spectra showed features at higher frequencies than the methyl group analyzed in this work.^{65,88–90} They should also obey the same polarization selection relationships as analyzed in this work. One recent effort on polarization comparison of the SFG-VS spectra for PMMA and PMA was attempted to help assignment of the ester methyl group C–H modes.⁶⁵ However, systematic polarization analysis for spectra assignment is rare.¹⁸ We believe that systematic polarization analysis as demonstrated in this report should help on ascertaining the assignments of the complex spectra for ester methyl groups,⁹¹ which is yet to be carefully investigated. We shall report elsewhere our progresses on the polarization analysis of ester methyl, and the methine groups on benzene rings, which is also at higher stretching vibrational frequencies.

4.3. Spectral Assignment for the Methanol and Ethanol Interfaces. For all the 1-alcohol studied here, methanol and ethanol are inarguably the most important ones, and they show different spectra features from other 1-alcohols. This should be expected from the fact that the O–H group are more strongly coupled to the CH_3 as well as the CH_2 groups. Even though methanol and ethanol have been under intensive studies, it is still too hasty to concluded that their vibrational spectra have been well understood.

The vapor/methanol interface is the first liquid interface studies with SFG-VS,¹⁴ and it has been extensively studied in the literature.^{14,17,27,62} It is accepted that the 2828, 2910, and 2940 cm^{-1} belong to CH_3 symmetric stretching and Fermi resonance modes. One of the puzzles is that unlike other alcohols, no asymmetric mode is observed for methanol on the *ppp* and *sps* spectra. Here we think this could be explained by the fact that for methanol $\beta_{\text{acc}}/\beta_{\text{ccc}} \approx 1.0$, while for other alcohols, $\beta_{\text{acc}}/\beta_{\text{ccc}} \approx 3.4$,^{57,59,61,63} its asymmetric peak should be more than 11.5 times smaller from this factor along. Since these SFG-VS spectral positions for vapor/methanol interface are at the same positions as the IR and Raman spectra of liquid methanol, the assignment for the liquid methanol IR and Raman spectra should be attributed to the same modes as at the vapor/methanol interface. However, in the literature and standard

databases, the 2940 cm^{-1} peak was assigned to the asymmetric stretching mode of CH_3 .⁹² This incorrect assignment has led to self-contradictory interpretations for ultrafast dynamics studies on liquid methanol recently.^{33,93}

The vapor/ethanol interface has also been studied with SFG-VS previously.^{54,94} Following the deuterated IR and Raman studies,^{95,96} the 2868 , 2926 , and 2970 cm^{-1} peaks were assigned to the $\text{CH}_2\text{-ss}$, $\text{CH}_3\text{-ss}$, and $\text{CH}_3\text{-as}$ mode, respectively.^{54,94} These assignments excluded the existence of the Fermi resonance modes for the $\text{CH}_2\text{-ss}$ and $\text{CH}_3\text{-ss}$ modes in the ethanol spectra. Such assignment would also make ethanol the only molecule in the $n = 1\text{--}8$ 1-alcohols without Fermi mode. This is a highly unlikely case and could be clarified with simple analysis below.⁹⁷

Since the CH_3 spectra for the vapor/ethanol interface exhibit following simple relationships: $I_{\text{ppp},\text{CH}_3\text{-as}} > I_{\text{sps},\text{CH}_3\text{-as}} > I_{\text{ssp},\text{CH}_3\text{-as}}$, simple orientational analysis using Figure 1 would give a tilt angle around $40 \pm 5^\circ$ for the CH_3 group. Thus, the tilt angle of the CH_2 group of ethanol would be $85 \pm 5^\circ$, i.e., close to parallel to the interface plane. Such a CH_2 orientation would allow only tiny SFG intensity on any experimental configuration, which is in direct contradiction to assignment of strong $\text{CH}_2\text{-ss}$ to the 2868 cm^{-1} band on *ssp* spectra. Therefore, our conclusion is that the 2868 cm^{-1} peak should be assigned to $\text{CH}_3\text{-ss}$ and 2926 cm^{-1} to its Fermi resonance. The CH_2 SFG spectra should be very weak because it lies close to flat on the interface. Such assignments have been directly confirmed by our recent deuterated ethanol ($\text{CH}_3\text{CD}_2\text{OH}$ and $\text{CD}_3\text{CH}_2\text{OH}$) SFG-VS experiments, to be reported somewhere else. These advancements warrant close examinations of the ethanol IR and Raman spectra, and they also cast doubt on the validity of works using the incorrect assignments for the ethanol spectra.³²

4.4. Methine Group at Vapor/2-Propanol Interface. Methine group is present in all 20 natural amino acids, except for glycine. The methine stretching mode is generally hard to be identified in IR and Raman spectroscopy.^{84,98} Extremely low temperature⁴⁵ and gaseous⁴¹ Raman experiments with hydrocarbons contain $-\text{CHD}-$ and $-\text{CHD}_2$ groups have shown that the methine stretching is around 2900 cm^{-1} . To our knowledge, there is only one recent SFG-VS study on L-leucine at the air/water interface presented a slight feature at 2902 cm^{-1} on the *ssp* spectra for the methine group.^{31,99} To use SFG-VS to identify the methine group in amino acids could be a possible way for probing structure and dynamics for membrane proteins.

Figure 6 presents the SFG-VS for vapor/1-propanol and vapor/2-propanol interfaces. It is evident that the CH_2 features on the 1-propanol spectra are missing on the 2-propanol spectra, as the latter does not have CH_2 group. In the previous report on the *ssp* spectra for vapor/1-alcohol interfaces ($n = 1\text{--}8$),⁵⁴ no CH_2 was observed for 1-propanol. However, in our *ppp* spectra, there is a clear broad feature for $\text{CH}_2\text{-as}$ mode around 2908 cm^{-1} , as well as a recognizable $\text{CH}_2\text{-ss}$ feature on the *ssp* spectra around 2850 cm^{-1} .

There is a new feature on the 2-propanol spectra at 2914 cm^{-1} with comparable intensities on both *ssp* and *ppp* spectra. This feature should belong to the methine group in 2-propanol, for it satisfies the polarization selection rules for methine group with a tilted angle larger than 45° . Since the 2914 cm^{-1} peak intensity on *ssp* is about one time larger than that on *ppp*, these cannot be explained with the methyl and methylene (possible impurity since 2-propanol does not have methylene group) polarization selection rules. However, the position of this methine peak is shifted away from 2900 to 2914 cm^{-1} . We think it could be explained by the fact that the methine group is

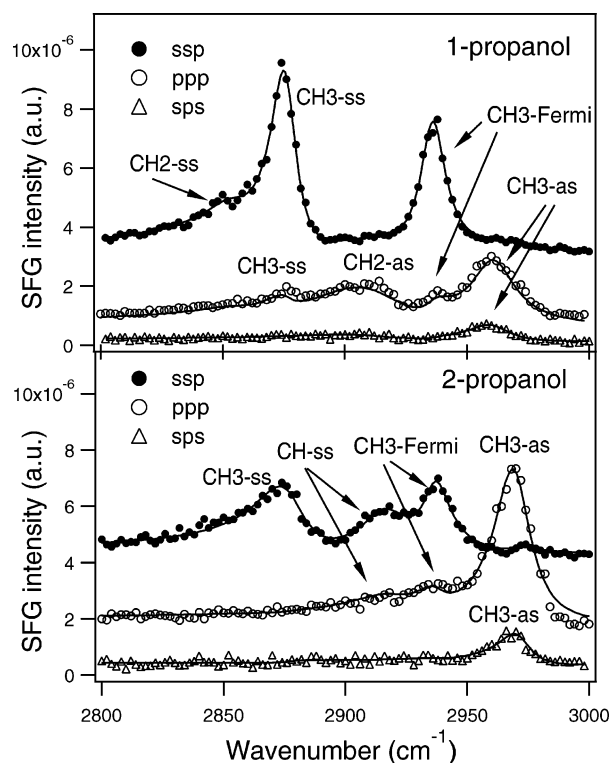


Figure 6. SFG-VS spectra and assignments for vapor/1-propanol (top) and vapor/2-propanol (bottom) interfaces. The solid lines are fitting curves with Lorentzian line shape function.

directly connected to the O–H group in 2-propanol.⁸³ We have seen similar effect that the $\text{CH}_2\text{-ss}$ SFG-VS spectra shifted to 2870 cm^{-1} instead of the normal $\text{CH}_2\text{-ss}$ position at 2850 cm^{-1} at the vapor/ethylene glycol (EG) interface, since the two CH_2 groups of EG are both connected to O–H groups.¹⁸ It is very encouraging for future applications of the SFG-VS studies on biological interfaces that the polarization selection rules for methine group, along with methyl and methylene groups, could be used to identify this methine spectra feature in the SFG-VS spectra, even though the spectra position is shifted away from the normally accepted position for methine in the Raman spectra.

The spectra details could also help us compare the orientational changes of the methyl group for 1-propanol and 2-propanol at their vapor/liquid interfaces. It is apparent from the relative intensities of the $\text{CH}_3\text{-ss}$ mode on *ssp* spectra and the $\text{CH}_3\text{-as}$ mode on *ppp* spectra that the methyl group for 1-propanol orients more close to the interface normal than those for both of the methyl groups in 2-propanol. Should the methine group orient more close to the surface normal, much pronounced spectra feature on the *ppp* spectra for methine group would be observed. Such orientational analysis can produce rich information on interfacial structure and conformation. It will be discussed in a future report.

5. Conclusion

In this report the polarization selection rules for interfacial methyl, methylene, and methine groups are developed for assignment of SFG-VS spectra in different polarization configurations. Using these polarization selection rules, detailed spectra features in the SFG-VS spectra of a series of vapor/alcohol interfaces were explicitly assigned.

SFG-VS has been used only as an interface probing technique, relying on the spectral assignment rules from IR and Raman

studies. We have demonstrate here that with the polarization selection rules, which are based on quantitative molecular symmetry and orientational analysis,^{18,50} unusual details in the SFG-VS spectra, which are not necessarily showing in the IR and Raman spectra, could be readily identified and properly assigned. As we have shown, it is an essential step to sum up the polarization dependence relationships into sets of polarization selection rules. This approach has provided clear physical pictures and conceptual tools for understanding and assignment for the SFG-VS spectra. Using the concepts of polarization selection rules and the calculated quantitative relationships, SFG-VS can become a powerful tool for discerning vibrational spectral details, not only for interfacial applications but also for general vibrational spectroscopic applications.

The ability to perform polarization measurement on oriented molecular samples is the key for success in spectral assignment. Because such measurement of spectra can directly lead to molecular symmetry properties. It is generally difficult to prepare a well-ordered molecular sample for such spectroscopic measurement. However, SFG-VPS is a natural polarization spectroscopic technique, and the molecules at the liquid interface are naturally ordered due to the anisotropic forces across the interfacial region. Furthermore, because the interfacial region is molecularly thin, the depolarization effect normally associated with oriented thin films or molecular crystals do not become a source of systematic error on polarization measurement. Such advantages for SFG, as well as SHG, as a molecular spectral assignment tool have not been explicitly realized before. The work in this report on methyl, methylene, and methine C–H stretching vibration spectral assignment is just an explicit example for such practices. Since SFG-VS and SHG have submonolayer sensitivity, their application is generally applicable to all kinds of molecular interfaces. There are certainly more important applications ahead.

The treatment on the molecular hyperpolarizability tensors using the empirical bond polarizability model proposed by Hirose et al. is reasonably successful for the quantitative polarization and orientational analysis of the SFG-VS spectra in this and our previous works.^{17,18} In all of our analysis, we considered contributions to the SFG-VS spectra only from the interfacial dipolar terms. This is valid at least for SFG-VS studies on the vapor/liquid interfaces in a reflection geometry.^{13–16} The effectiveness of our quantitative SFG-VPS analysis points to a few areas for future studies: (a) accumulate of experimental and theoretical calculation data on Raman depolarization ratio and bond polarizability tensor relations; (b) extend and test the analysis to other experimental arrangements, such as visible-IR double resonance SFG-VS; (c) examine and test the analysis for other interfaces, such as liquid/solid and liquid/liquid interfaces; (d) find applications.

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Appendix

The expressions for parameter d and c for the methyl group at the four polarization configurations can be expressed as follows.

For ssp,ss mode:

$$d_{ssp,ss} = \frac{1}{2}(1 + R)\beta_{ccc}^{(2)}L_{yy}(\omega)L_{yy}(\omega_1)L_{zz}(\omega_2)\sin\beta_2$$

$$c_{ssp,ss} = \frac{1 - R}{1 + R} \quad (9)$$

For sps,ss mode:

$$d_{sps,ss} = \frac{1}{2}(1 - R)\beta_{ccc}^{(2)}L_{yy}(\omega)L_{zz}(\omega_1)L_{yy}(\omega_2)\sin\beta_1$$

$$c_{sps,ss} = 1 \quad (10)$$

For pss,ss mode:

$$d_{pss,ss} = \frac{1}{2}(1 - R)\beta_{ccc}^{(2)}L_{zz}(\omega)L_{yy}(\omega_1)L_{yy}(\omega_2)\sin\beta$$

$$c_{pss,ss} = 1 \quad (11)$$

For ppp,ss mode:

$$d_{ppp,ss} =$$

$$-\frac{1}{2}(1 + R)\beta_{ccc}^{(2)}L_{xx}(\omega)L_{xx}(\omega_1)L_{zz}(\omega_2)\cos\beta\cos\beta_1\sin\beta_2 -$$

$$\frac{1}{2}(1 - R)\beta_{ccc}^{(2)}L_{xx}(\omega)L_{zz}(\omega_1)L_{xx}(\omega_2)\cos\beta\sin\beta_1\cos\beta_2 +$$

$$\frac{1}{2}(1 - R)\beta_{ccc}^{(2)}L_{zz}(\omega)L_{xx}(\omega_1)L_{xx}(\omega_2)\sin\beta\cos\beta_1\cos\beta_2 +$$

$$R\beta_{ccc}^{(2)}L_{zz}(\omega)L_{zz}(\omega_1)L_{zz}(\omega_2)\sin\beta\sin\beta_1\sin\beta_2$$

$$b_{ppp,ss} =$$

$$-\frac{1}{2}(1 - R)\beta_{ccc}^{(2)}L_{xx}(\omega)L_{xx}(\omega_1)L_{zz}(\omega_2)\cos\beta\cos\beta_1\sin\beta_2 -$$

$$\frac{1}{2}(1 - R)\beta_{ccc}^{(2)}L_{xx}(\omega)L_{zz}(\omega_1)L_{xx}(\omega_2)\cos\beta\sin\beta_1\cos\beta_2 +$$

$$\frac{1}{2}(1 - R)\beta_{ccc}^{(2)}L_{zz}(\omega)L_{xx}(\omega_1)L_{xx}(\omega_2)\sin\beta\cos\beta_1\cos\beta_2 -$$

$$(1 - R)\beta_{ccc}^{(2)}L_{zz}(\omega)L_{zz}(\omega_1)L_{zz}(\omega_2)\sin\beta\sin\beta_1\sin\beta_2$$

$$c_{ppp,ss} = \frac{b_{ppp,ss}}{d_{ppp,ss}} \quad (12)$$

with $b_{ppp,ss}$ as an intermediate parameter for convenience in the deduction.

It is easy to see that plotting $d^2R(\theta)$ or $dr(\theta)$ against θ is mathematically equivalent to the approach of plotting the $|\chi_{eff,ijk}^{(2)}|^2$ or $\chi_{eff,ijk}^{(2)}$ against θ in previous SFG-VS studies.^{19,100} However, as we have shown,^{18,50} the formulation with the parameters d and c are not only with clear physical meanings, but also very useful tools when analyzing the orientational and intensity contributions to the SFG and SHG intensities in particular polarization configurations. Plotting $d^2R(\theta)$ against θ can be used to have explicit polarization analysis on intensity dependence.¹⁸ While plotting $R(\theta)$ against θ can be used to have explicit orientational analysis,⁵⁰ accurate measurement of molecular orientation,^{17,50} orientational order parameter calculation,⁵⁰ and microscopic local field factor calculations. Separating d and c factors are also extremely useful when detailed interference effects in SHG and SFG-VS spectra studies need to be discerned.¹⁰¹

The detailed derivation of these parameters and the deduction of the parameter c and d for an optional polarization combination

other than the four standard geometries are listed in the Supporting Information.

Supporting Information Available: Figures showing SFG-VPS spectra and assignments for vapor/1-alcohol ($n = 1-8$) interfaces and vapor/2-propanol interface and text giving detailed deduction of parameter c and d for the methyl group, in methanol as an example. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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