

Structure of the glycerol liquid/vapor interface studied by sum-frequency vibrational spectroscopy

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Surface-specific sum-frequency vibrational spectroscopy has been used to study the structures of the glycerol liquid/vapor interface. The results show that the molecules at the glycerol surface are highly polar ordered with the CH₂ and CH groups projecting into the vapor and the OH group remaining at the surface or pointing into the bulk. More quantitatively, we have also determined how the CH₂ groups of the molecules are oriented at the surface. © 2004 American Institute of Physics.

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Understanding the structures of liquid surfaces at a molecular level is directly relevant to the chemical reactivity of the system, such as solvation, atmospheric, and environmental chemistry, wetting, and biological properties.¹ In this work, we are interested in the liquid/vapor interface of glycerol. Glycerol droplets suspended in a nematic liquid crystal (LC) have recently been reported to form a crystal structure or an ordered pattern at the LC surface rather than in the bulk.^{2,3} The competition of the surface energy between glycerol/vapor and glycerol/LC plays an important role in these colloidal interactions. Since the surface energy is closely related to the molecular orientation at the surface, it is meaningful to study various interfaces with glycerol. As the first step toward this goal, we report on the average orientation of the glycerol molecules at the liquid/vapor interface. Glycerol has often been used as a model system to understand surface trapping, solvation, interfacial reaction, and migration into the bulk.^{4,5} Computer simulations have demonstrated that the density of the combined CH₂ and CH groups is larger than that of oxygen, although there are exposed OH groups at the surface.⁶

Infrared-visible sum-frequency vibrational spectroscopy (SFVS) is one of the most effective tools for probing molecular orientation and alignment at surfaces and interfaces.^{7,8} Applications of the techniques to the liquid/vapor interfaces of some liquids, such as alcohol,⁹ water,¹⁰ and acetone,¹¹ have shown that such molecules form an ordered structure at the liquid/vapor interface with its polar end toward the bulk. Previous SFVS on glycerol determined that the molecular axis is perpendicular to the interfacial plane and was found to partition to the surface of glycerol/water mixtures.¹² Here, the results are reported for SFVS and orientation analysis for a neat glycerol/air interface.

The experimental setup for SFVS is well known.^{13,14} In these experiments, the main laser source was an EKSPLA Nd:YAG laser with wavelength 1.06 μm, 30 mJ pulse energy, and 25 ps pulsewidth, operating at a repetition rate of 20 Hz. The laser pumped an optical parametric/difference-

frequency generation system to produce IR output tunable from 2.5 to 10 μm with ~200 μJ pulse energy, 25 ps pulsewidth, and, 6 cm⁻¹ bandwidth. The tunable IR beam was overlapped with a frequency-doubled output (532 nm) from the laser at the glycerol surface spatially and temporally with incidence angles of 57° and 45°, respectively. The sum-frequency signal was recorded by averaging 200 shots per point every 2.5 cm⁻¹. Special grade glycerol (>99%) (Wako Pure Chemical Industries, Ltd., Japan) was used as purchased without purification, and kept under a nitrogen atmosphere for measurements. The results from Ref. 12 indicate that small amounts of water do not influence the glycerol spectrum.

Figure 1(a) shows the SFVS spectra in the CH stretch region of a glycerol liquid/vapor interface taken with three input/output polarization combinations: SSP (denoting S-polarized SF output, S-polarized visible input, and P-polarized infrared input, respectively), PPP, and SPS. The two significant peaks appear at 2874 and 2939 cm⁻¹, which

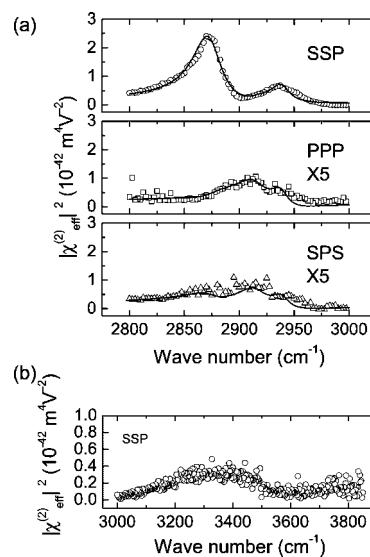


FIG. 1. (a) SFVS spectra in the range of CH stretch with SSP, PPP, and SPS polarization combinations, and (b) in the range of OH stretch with SSP polarization combination for the glycerol surface. The spectra are normalized by the SF signal from a z-cut quartz.

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TABLE I. Fitting parameters A_q , ω_q , and Γ_q of SFVS for the glycerol liquid/vapor interface, and geometrical parameters and Fresnel factors used for the calculation.

Mode	ω/cm^{-1}	Γ/cm^{-1}	$A_{q,ssp}$	$A_{q,ppp}$	$A_{q,sp}$
CH ₂ -s (d^+)	2874	16	2.34 ± 0.01	-0.076 ± 0.05	-0.20 ± 0.08
CH (m^+)	2917	16	0.48 ± 0.04	0.43 ± 0.05	-0.52 ± 0.08
CH ₂ -as (d^-)	2939	10	-1.00 ± 0.01	0.26 ± 0.04	-0.21 ± 0.05
			ω_{SF}	ω_{vis}	ω_{IR}
Wavelength $\lambda/\mu\text{m}$			0.461	0.532	3.47
Refractive index n (glycerol)			1.478	1.475	1.458
Beam angle β/deg			46.4	45.3	57.0
Fresnel factor L_{xx}			0.924	0.916	1.015
Fresnel factor L_{yy}			0.695	0.705	0.627
Fresnel factor L_{zz}			1.076	1.084	0.985

are assigned to the CH₂ symmetric (d^+) and asymmetric (d^-) vibrational modes, respectively.¹² The peak around 2917 cm^{-1} that can be assigned to CH stretch (m^+) mode is also included in the SSP spectrum, and it appears as low intensity in the PPP and SPS spectra. The peak amplitude is obtained by fitting the spectra to

$$\vec{\chi}^{(2)}(\omega_{\text{ir}}) = \vec{\chi}_{\text{NR}}^{(2)} + \sum_q \frac{\vec{A}_q}{(\omega_{\text{ir}} - \omega_q) + i\Gamma_q}, \quad (1)$$

with

$$\vec{A}_q = N_s \int \vec{a}_q(\Omega) f(\Omega) d\Omega,$$

where $\chi_{\text{NR}}^{(2)}$ denotes the nonresonant contribution, \vec{a}_q , ω_q , and Γ_q are the strength, resonant frequency, and damping constant of the q th resonant mode, respectively, Ω represents a set of orientational angles (θ, ϕ, ψ) for a functional group, N_s is the surface density of the functional group, and $f(\Omega)$ is an orientational distribution function. The fitting parameters are summarized in Table I. In the region of the OH stretch shown in Fig. 1(b), no resonances are observed at around 3700 cm^{-1} and a broad small bump can be seen from 3000 to 3500 cm^{-1} , indicating that there are no free OH and some hydrogen bonded OH groups were detected. However, since their signal is extremely weak compared to the CH₂ group, the surface must be dominated by the CH₂ and CH groups and most of the OH group must remain in the surface plane or point into the bulk with highly ordered hydrogen bonds as suggested in Ref. 12.

The fact that the d^+ mode appears in the SSP polarization combination indicates that the CH₂ axis ζ would protrude out of the surface. Here, we take the symmetry axis as ζ , and ξ is such that the two CH bonds are in the $\xi\zeta$ plane as shown in Fig. 2. The d^- mode is clearly discernible in SSP, suggesting that the axis ζ is not completely along the surface normal and ξ is not on the surface plane, i.e., the axis ζ has a certain tilt and twist angle with respect to the surface normal. These qualitative pictures can be more understandable if the spectra are compared to those of a poly(vinyl alcohol) film¹⁴ in which the CH₂ axis is nearly along the surface normal.

More quantitative information is deduced about the orientation distribution of the CH₂ group using the same analysis described in Refs. 13 and 14. This analysis is limited to only the CH₂ group since the CH peak is such a low intensity that quantitative analysis would not give a significant guide

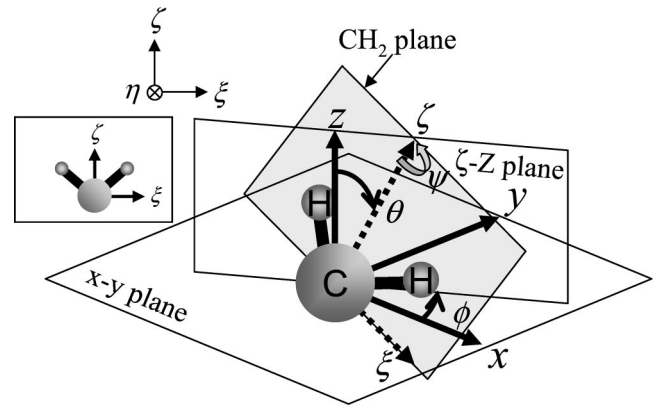


FIG. 2. Geometric relations between the molecular coordinates and the lab coordinates.

to the orientation. The three independent nonvanishing elements A_q for an azimuthally isotropic interface, namely, $(A_q)_{xxz} = (A_q)_{yyz}$, $(A_q)_{xzx} = (A_q)_{yzy} = (A_q)_{zxx} = (A_q)_{zyy}$, $(A_q)_{zzz}$,¹⁵ can be determined simultaneously with the other parameters from the fitting of the SFVS spectra obtained with different input/output polarization combinations.

For the CH₂ group with C_{2v} symmetry, there are three nonvanishing elements in the hyperpolarizability tensor, $\alpha_{\xi\xi\xi}^{(2)} = r_a \alpha_{\zeta\xi\xi}^{(2)} = r_b \alpha_{\eta\eta\xi}^{(2)}$ for the d^+ mode, where $r_a = 2 + R/1 + 2R$ and $r_b = 2 + R/3R$. The parameter R describes how anisotropic the polarizability derivative of a single CH bond is and can be taken from theoretical calculations ($R = 0.14$).¹⁶ Since each $(A_q)_{ijk}$ element is related to the molecular hyperpolarizability $\alpha^{(2)}$, we can find for an azimuthally isotropic surface the ratio of the effective (A_q) values for different polarization combinations. Since the d^- mode is overlapped with the m^+ mode in the SSP spectrum, we use the d^+ mode for the analysis. Although the d^+ mode did not provide intensity in the PPP spectrum, this information does give us a limit of the possible orientation. The amplitude ratio of the d^+ mode between the PPP and SSP spectra is given by

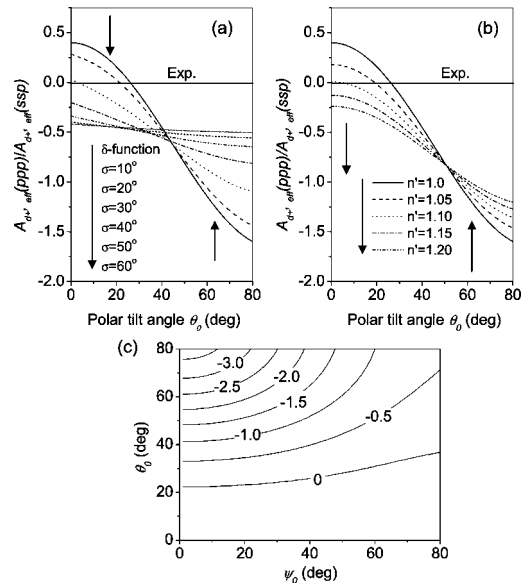


FIG. 3. (a) $A_{d^+, \text{eff}}^{(2)}(\text{PPP})/A_{d^+, \text{eff}}^{(2)}(\text{SSP})$ vs θ_0 of the CH₂ group with a δ -function and a Gaussian function. (b) $A_{d^+, \text{eff}}^{(2)}(\text{PPP})/A_{d^+, \text{eff}}^{(2)}(\text{SSP})$ vs θ_0 as a function of n' with a δ -function. (c) Contour lines for $A_{d^+, \text{eff}}^{(2)}(\text{PPP})/A_{d^+, \text{eff}}^{(2)}(\text{SSP})$ as functions of θ_0 and ψ_0 of the CH₂ group with a δ -function.

$$\frac{A_{d^+, \text{eff}}^{(2)}(ppp)}{A_{d^+, \text{eff}}^{(2)}(ssp)} = 0.0219 \frac{(\langle \cos \theta \rangle - \langle \cos^3 \theta \rangle)(2 - r_a - r_a/r_b)}{(\cos \theta)(2 + r_a + r_a/r_b) - \langle \cos^3 \theta \rangle(2 - r_a - r_a/r_b)} + \left(\frac{1.231}{n'^4} \right) \frac{2(\langle \cos \theta \rangle(r_a/r_b - r_a) + \langle \cos^3 \theta \rangle(2 + r_a - r_a/r_b))}{(\cos \theta)(2 + r_a + r_a/r_b) - \langle \cos^3 \theta \rangle(2 - r_a - r_a/r_b)} - 0.833, \quad (2)$$

where n' is the interfacial refractive index. Shown in Fig. 3(a) is the relationship of $A_{d^+, \text{eff}}^{(2)}(ppp)/A_{d^+, \text{eff}}^{(2)}(ssp)$ to the possible polar tilt angle θ_0 , assuming $n' = 1$. Some parameters needed for the calculation are also summarized in Table I.¹⁷ From the experimentally obtained value of $A_{d^+, \text{eff}}^{(2)}(ppp)/A_{d^+, \text{eff}}^{(2)}(ssp) \approx 0$, we can deduce for the azimuthally isotropic glycerol surface the possible polar tilt angle of the CH₂ group, $\theta_0 \approx 27^\circ$ with a δ -function to $\theta_0 \approx 23^\circ$ with $\sigma = 10^\circ$, $\theta_0 \approx 6^\circ$ with $\sigma = 20^\circ$. We also plotted, as in Fig. 3(b), the relationship of $A_{d^+, \text{eff}}^{(2)}(ppp)/A_{d^+, \text{eff}}^{(2)}(ssp)$ to θ_0 as a function of n' with a δ -function. To have $A_{d^+, \text{eff}}^{(2)}(ppp)/A_{d^+, \text{eff}}^{(2)}(ssp) \approx 0$, n' should be in the range from 1.0 to 1.1. We proceed to the discussion below only for the case of $n' = 1$ to simplify the analysis.

In the analysis above, the azimuthal ϕ and twist ψ angles were averaged over all orientation since the surface is isotropic and there is free rotation around the C—C bond. As seen in Fig. 1(b), however, no resonances were detected in the free OH stretch region. This suggests that if the tilt angle θ from the surface normal is large enough, the twist angle ψ cannot be averaged over due to the fact if you twist the CH₂ group far enough then the OH group will not be directed down into the bulk liquid. Since the free OH is not observed, then there seems to be a constraint on the range of ψ . To analyze this problem, we recalculate the ratio of $A_{d^+, \text{eff}}^{(2)}(ppp)/A_{d^+, \text{eff}}^{(2)}(ssp)$ without averaging over ψ . Here we simply assume δ -functions for both θ and ψ . The ratio of $A_{d^+, \text{eff}}^{(2)}(ppp)/A_{d^+, \text{eff}}^{(2)}(ssp)$ is then given by

$$\frac{A_{d^+, \text{eff}}^{(2)}(ppp)}{A_{d^+, \text{eff}}^{(2)}(ssp)} = 0.0219 \frac{(\cos \theta - \cos^3 \theta)(1 - r_a \cos^2 \psi - r_a \sin^2 \psi/r_b)}{\cos \theta(1 + r_a \sin^2 \psi + r_a \cos^2 \psi/r_b) - \cos^3 \theta(1 - r_a \cos^2 \psi - r_a \sin^2 \psi/r_b)} + 1.231 \frac{2(\cos \theta(r_a \sin^2 \psi/r_b - r_a \cos^2 \psi) + \cos^3 \theta(1 + r_a \cos^2 \psi - r_a \sin^2 \psi/r_b))}{\cos \theta(1 + r_a \sin^2 \psi + r_a \cos^2 \psi/r_b) - \cos^3 \theta(1 - r_a \cos^2 \psi - r_a \sin^2 \psi/r_b)} - 0.833, \quad (3)$$

Figure 3(c) shows contour plots for the calculated $A_{d^+, \text{eff}}^{(2)}(ppp)/A_{d^+, \text{eff}}^{(2)}(ssp)$ as functions of θ_0 and ψ_0 . Since the experimentally obtained value of $A_{d^+, \text{eff}}^{(2)}(ppp)/A_{d^+, \text{eff}}^{(2)}(ssp) \approx 0$, this indicates that the CH₂ group tilts by 22° – 32° from the surface normal with ψ_0 being $\psi_0 \approx 0^\circ$ – 90° . From these considerations, it would be required to take into account the range of ψ if θ is large. For the case of glycerol, however, the results allow us to average over ψ because θ is small, and also support the above analysis in which the twist ψ angles were averaged over all orientation.

In conclusion, we have shown that the glycerol molecules at the surface are polar ordered with the CH₂ and CH groups protruding out of the surface with the small amount of the hydrogen bonded OH group. The tilt angle of the CH₂ group has quantitatively been analyzed with the confirmation that the twist angle ψ can be averaged over all orientation around the C—C bond because the tilt angle is small.

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