

Surfaces of Alcohol–Water Mixtures Studied by Sum-Frequency Generation Vibrational Spectroscopy

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Sum-frequency generation vibrational spectroscopy was used to investigate the surface molecular structure of binary mixtures of water and alcohol (methanol, ethanol, and propanol) at the air/liquid interface. In this study, it is shown that the sum-frequency signal from the alcohol molecules in the CH-stretch vibration region is always larger for mixtures than that from pure alcohol. For example, the sum-frequency signal from a propanol mixture surface at a 0.1 bulk mole fraction was ~ 3 times larger than that from a pure propanol surface. However, the ratio between the sum-frequency signals taken at different polarization combinations was found to be constant within experimental errors as the bulk alcohol concentration was changed. This suggested that the orientation of surface alcohol molecules does not vary appreciably with the change of concentration and that the origin of the signal enhancement is mainly due to the increase in the surface number density of alcohol molecules contributing to the sum-frequency signal for the alcohol/water mixture as compared to the pure alcohol surface.

Introduction

The interfacial properties of liquids have drawn much interest for a long time, not only for their importance in basic science but also because of their relevance in environmental problems, biological phenomena, and industrial applications.^{1–5} Because of their intrinsic asymmetry at the interface, molecules at the air/liquid interfaces have different physical properties from those of the bulk. A recent calculation predicted that even the chemical properties such as energy levels and reactivity could be altered for molecules at the liquid surface.⁶ As the liquid surface is more sensitive to the presence of surface-adsorbed species as compared to the solid surface, the molecular level study is crucial for the understanding of various chemical processes at the liquid interface.^{7,8} However, despite these key issues, our understanding of air/liquid interfaces is still limited mainly because of the lack of proper experimental tools.

The most well-known and important tool to study liquid surfaces has been the surface tension measurement of the liquid, from which the thermodynamic properties of the surface could be obtained.^{9–11} Liquid surfaces and Langmuir molecular monolayers at the water surface were studied by surface tension measurement, X-ray and neutron scattering, ellipsometry, and Brewster angle microscopy.^{12–16} Popular spectroscopic tools of surface sciences such as X-ray photoemission spectroscopy and electron energy-loss spectroscopy were unsuitable to probe the liquid surfaces because of the high vapor pressure unless a special experimental setup was used to overcome this difficulty.^{17–19} As an alternative surface-sensitive spectroscopic technique, sum-frequency generation (SFG) vibrational spectroscopy has been established as a powerful tool to study liquid surfaces and molecular monolayers on water.^{20–25} Since SFG is a second-order nonlinear optical process, it is forbidden in a centrosymmetric bulk medium and is only allowed at the

surface, where the inversion symmetry is broken. Unlike electron spectroscopy, this technique can probe any surface or interface accessible by light. Therefore, it is an ideal probe for studying liquid surfaces and the only technique for getting spectroscopic information of the liquid surface.²¹ For example, SFG studies on air/liquid interfaces, Langmuir monolayers, and the buried interfaces between immiscible liquids found many interesting properties unobtainable by other methods.^{26–29}

Compared to the surface of pure liquids, the surfaces of mixed liquids are far less understood. For example, even for miscible solutes such as ethanol or methanol in water, the surface concentration of the alcohol is known to be higher than the bulk concentration. The thermodynamic equation that relates this surface concentration to surface tension is the equation of Gibbs surface excess.³⁰ However, this famous problem has not been studied quantitatively by experiments because of the lack of surface-specific probes. Previous SFG studies on water–acetonitrile and water–acetone mixtures reported that the SFG signals from the mixtures were larger than those from pure liquids.^{31–33} Several studies on water–methanol mixtures also observed that the SFG signal from the methanol–water mixture surface was larger than that from a pure methanol surface.^{34–37} For the case of methanol mixtures, earlier reports tried to explain this finding by proposing that the surface methanol molecules are more upright (and generate a stronger sum-frequency signal per molecule) upon dilution, such that the surface orientational distribution of methanol molecules would become narrower and more δ -function-like at low concentrations.^{34–36} However, this proposition is opposed to the results obtained from neutron scattering and molecular dynamics simulations, which suggested that surface ethanol and methanol molecules of low-concentration water–alcohol mixtures have a broad orientational distribution.^{38–44} Recently, Chen et al. proposed that the origin of the SFG signal enhancement is not the orientational change of surface alcohol molecules but an antiparallel double-layer structure, which becomes more pronounced and contributes less

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to the SFG as a result of cancellation at higher concentrations.³⁷ The orientational distribution of surface methanol molecules deduced from the analysis was also very narrow around the surface normal, and the double layer model and Langmuir isotherm were used to explain the data.^{33,37}

In this report, we investigated the surface of water–alcohol (methanol, ethanol, and propanol) mixtures of varying concentrations by using SFG surface vibrational spectroscopy. It was also found that the sum-frequency signal was maximized at some low bulk concentrations of alcohol. As the chain of alcohol gets longer, the maximum becomes more pronounced and shifts to lower concentrations. Analysis of the data indicated that the origin of this enhancement is mainly the increase in the surface number density of alcohol molecules contributing to the sum-frequency signal at lower concentrations.

Experimental Section

Alcohols purchased from Aldrich had a purity exceeding 99.5% and were used without further purification. Alcohols with a molecular weight heavier than propanol were not miscible throughout the whole concentration range and were not studied in this report. The water (HPLC grade) used for the preparation of the mixtures was purchased from J. T. Baker, and the use of doubly distilled water (Mill-Q, resistivity 18 MΩ cm) yielded the same result. D₂O (purity better than 99.9%) was purchased from Aldrich. Binary solutions of water and alcohol were prepared with concentrations between 0.01 and 1.0 mole fraction. Para-, ortho-, and meta-xylene (purity exceeding 98%) were purchased from Junsei Chemicals. The hexadecanol (Aldrich, purity better than 99%) monolayer was prepared by spreading a small flake of a hexadecanol crystal on water. The surface tension was measured using a DuNuoy Tensiometer (Surface Tensionmat., Fisher) with a platinum ring having a mean circumference of 6 cm and a ring/wire radius ratio of 53.8. The sample temperature was room temperature (21 °C) for all the experiments.

The SFG experiment employed a home-built optical parametric generator/amplifier (OPG/OPA) system pumped with a picosecond Nd:YAG laser (Continuum PY61–10, 10-Hz repetition rate). An OPG/OPA based on a LiNbO₃ crystal generated a tunable IR pulse from 2.5 to 4 μm, and the second harmonic of the Nd:YAG fundamental beam was used as the visible input beam. Typical input energies were 1 mJ/pulse and ~200 μJ/pulse, and incident angles were β_{vis} = 49° and β_{IR} = 60° for the visible and the tunable infrared beams, respectively. The two beams were focused and overlapped at the air/liquid interface, and the sum-frequency output in the reflection direction was spatially and spectrally filtered and detected by a photomultiplier tube. Typically, the data for the spectra were taken at every 5 cm⁻¹, and at least 300 laser shots were averaged for each data point. The spectrum was normalized to the sum-frequency spectrum from a z-cut quartz sample. The frequency of the infrared beam was calibrated by measuring the absorption spectrum from a polystyrene film.

Theory

The surface tension of the mixture can be used to yield the surface chemical composition (number density) of the binary mixture system using Gibbs' adsorption equation.³⁰

$$\Gamma = -\frac{1}{RT} \frac{d\gamma}{d \ln a} \quad (1)$$

where Γ, *a*, γ, *R*, and *T* are the surface excess, activity of the

solute–solvent system, surface tension of the mixture, ideal gas constant, and temperature, respectively. To calculate the surface excess from the above equation, the solute concentration of the bulk mixture needs to be converted into activity *a*. However, in many cases, the activity of the specific solute–solvent system is not well-known, and the quantitative determination of the surface excess (and surface concentration of the solute molecule) is not an easy task.^{45,46}

The basic theory of SFG for surface studies has already been described elsewhere.^{47,48} In this section, we give only a brief description for the convenience of later discussions. The SFG output intensity in the reflection direction with visible and infrared input beams of intensities *I*(ω_{vis}) and *I*(ω_{IR}) is given by

$$I(\omega_{\text{SF}}) \propto |\chi_{\text{eff}}^{(2)}|^2 I(\omega_{\text{vis}}) I(\omega_{\text{IR}}) \quad (2)$$

with

$$\chi_{\text{eff}}^{(2)} = [\hat{e}(\omega_{\text{SF}}) \cdot \vec{L}(\omega_{\text{SF}})] [\hat{e}(\omega_{\text{vis}}) \cdot \vec{L}(\omega_{\text{vis}})] [\hat{e}(\omega_{\text{IR}}) \cdot \vec{L}(\omega_{\text{IR}})] \chi^{(2)} \quad (3)$$

where $\hat{e}(\Omega)$ is the unit polarization vector of the light field at frequency Ω and $\vec{L}(\Omega)$ is the Fresnel factor at frequency Ω. The nonlinear susceptibility χ⁽²⁾ is related to the molecular hyperpolarizability by

$$\chi_{ijk}^{(2)} = N_s \sum < (\hat{i} \cdot \hat{\xi})(\hat{j} \cdot \hat{\eta})(\hat{k} \cdot \hat{\zeta}) > \alpha_{\xi\eta\zeta}^{(2)} \quad (4)$$

where *N_s* is the surface density of the molecules, (*i*, *j*, *k*) refer to the lab coordinates (*x*, *y*, *z*), (ξ, η, ζ) refer to the coordinates attached to each molecule, and the angle bracket denotes an average over a molecular orientational distribution. Near the resonance, the molecular hyperpolarizability can be written as

$$\tilde{\alpha} = \tilde{\alpha}_{\text{NR}} + \sum_q \frac{\tilde{\alpha}_q}{(\omega_{\text{IR}} - \omega_q) + i\Gamma_q} \quad (5)$$

where $\tilde{\alpha}_{\text{NR}}$ is the nonresonant contribution to the hyperpolarizability and $\tilde{\alpha}_q$, ω_{*q*}, and Γ_{*q*} denote the strength, resonant frequency, and damping factor of *q*th vibrational mode, respectively. Here, $\tilde{\alpha}_q$ can be written in terms of the product of the infrared dipole derivative and the Raman polarizability tensor of the *q*th vibrational mode, ∂μ/∂*Q_q* and ∂α⁽¹⁾/∂*Q_q*, respectively

$$\alpha_{q,\xi\eta\zeta}^{(2)} = -\sum_{\xi\eta\zeta} \frac{1}{2\epsilon_0\omega} \frac{\partial\mu_{\xi\eta}}{\partial Q_q} \frac{\partial\alpha_{\zeta}^{(1)}}{\partial Q_q} \quad (6)$$

where ε₀ is the permittivity of air and *Q_q* denotes the normal mode coordinates. From the above discussion, we have

$$I(\omega_{\text{SF}}) \propto |\chi_{\text{NR}}^{(2)} e^{i\phi} + \sum_q \frac{A_q}{(\omega_{\text{IR}} - \omega_q) + i\Gamma_q}|^2 \quad (7)$$

where φ is the phase difference between the resonant and the nonresonant SFG signals.

Results and Discussion

Figure 1 shows the surface tension of alcohol–water mixtures with varying bulk alcohol concentration. The surface tension decreases monotonically from the value of pure water (72 mN/m) to values corresponding to pure alcohols (~23 mN/m), and this decrease happens more abruptly at lower concentrations

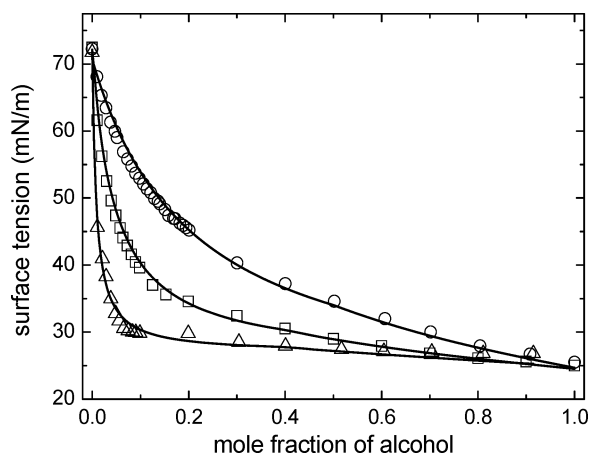


Figure 1. Surface tension of alcohol–water mixtures vs the bulk mole fraction of alcohol. Circle: methanol–water mixtures. Square: ethanol–water mixtures. Triangle: propanol–water mixtures. The lines are guides for the eye.

for the alcohols of longer chain lengths, in good agreement with previous reports.^{10,46,49} From the Gibbs adsorption equation in eq 1, the change in surface tension is related to the surface excess, and from the initial big drop, it is expected that the surface excess is larger for mixtures of alcohols with longer chain lengths.

Shown in Figure 2 are the SFG vibrational spectra of alcohol–water mixtures with different concentrations taken in the range from 2800 to 3050 cm^{-1} . Parts a and b of Figure 2 show SFG spectra of methanol–water mixtures with (a) SSP polarization combinations (S: sum frequency polarization, S: visible polarization, P: IR polarization), and (b) PPP. The other graphs in Figure 2 show the SFG spectra for ethanol–water mixtures (Figure 2c: SSP, Figure 2d: PPP) and propanol–water mixtures (Figure 2e: SSP, Figure 2f: PPP). Peak assignments for all the alcohol–water mixtures followed the previous reports and are shown in Table 1.^{50–54} A change in the frequency of the peak position of the CH_3 symmetric stretch mode was also seen in our experiments for the case of methanol such that $r+$ mode in Table 1 is blueshifted by about 5 cm^{-1} for the lowest concentration (the value listed in the table is for pure methanol).^{36,37} As shown in Figure 2, sum frequency signals with SSP polarization combinations for all the alcohol–water mixtures at low intermediate bulk mole fractions are larger than those of pure alcohols. Especially for propanol, the SFG signal for the mixture of 0.1 bulk mole fraction is about three times larger than that from a pure propanol surface. For methanol and ethanol, the signal enhancements at the maxima are about a factor of 1.5 and 2 larger, respectively.

For a more quantitative analysis, the sum-frequency peak strengths (A_q) were obtained by fitting the experimental spectra using eq 7, and the result is shown in Figure 3 for the CH_3

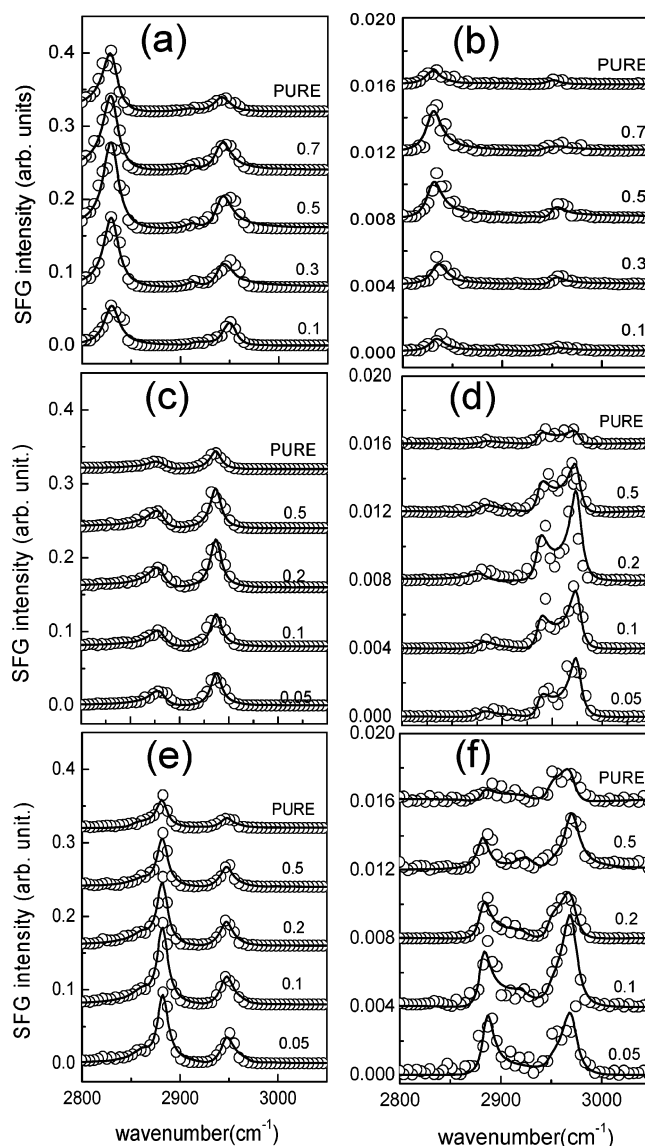


Figure 2. SFG spectra of alcohol–water mixtures with varying bulk alcohol concentrations with different polarization combinations for (a) methanol–water, SSP; (b) methanol–water, PPP; (c) ethanol–water, SSP; (d) ethanol–water, PPP; (e) propanol–water, SSP; (f) propanol–water, PPP. The lines are fits to the experimental data using eq 7. Each spectrum is shifted vertically for clarity.

symmetric stretch modes of all three alcohols. For the alcohol–water mixtures we investigated, the peak strengths were larger at intermediate concentrations as compared to those of the pure alcohols. The enhancement defined as $A_q(\text{SSP, mixture})/A_q(\text{SSP, pure alcohol})$ was as much as 1.7 for the propanol–water mixtures and ~ 1.5 for the ethanol–water mixtures. For the

TABLE 1: Fitting Parameters for SFG Spectra of the Alcohol–Water Mixture Interface

	peak assignment	peak position(cm^{-1})	peak width(cm^{-1})
methanol ^{50,51}	CH_3 symmetric stretch ($r+$)	2830	9.4
	CH_3 fermi resonance ($\text{CH}_{3,\text{fr}}$)	2912	9
	CH_3 fermi resonance	2942	10
	CH_2 symmetric stretch ($d+$)	2880	9.8
ethanol ^{52,53}	$r+$	2937	6.8
	CH_2 or CH_3 asymmetric stretch ($d-/r-$)	2975	7
	$d+$	2864	11
	$r+$	2882	6.8
propanol ⁵⁴	$d-$	2925	10
	$\text{CH}_{3,\text{fr}}$	2947	7.8
	$r-$	2970	9

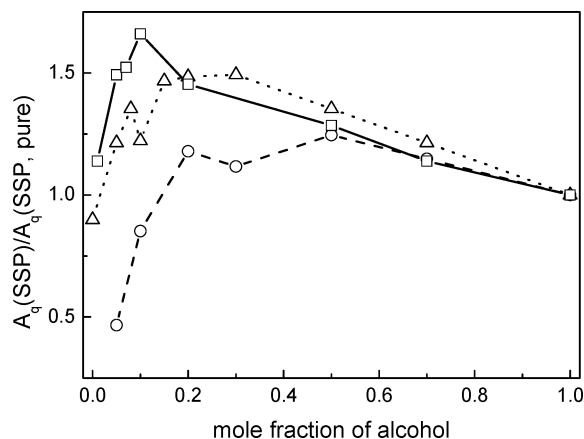


Figure 3. (a) Peak strength enhancements of the CH₃ symmetry stretch mode vs bulk concentration for the SSP polarization. Circle: methanol–water mixtures. Triangle: ethanol–water mixtures. Square: propanol–water mixtures.

methanol mixtures, the overall trend including a rather small enhancement was similar to the previous reports.^{34–37} Concentrations corresponding to maximum enhancements were 0.1 for propanol, 0.2 for ethanol, and 0.5 bulk mole fraction for methanol. As D₂O is known to have a slightly higher molecular dipole moment than that of H₂O, the experiment was repeated by mixing with D₂O instead of H₂O, yielding essentially the same result.⁵⁵ Changing pH values of the mixtures by adding NaOH or HCl did not change the result either.

From eq 4, the sum-frequency peak strength A_q could be factored into the surface number density N_s and the molecular orientation factor (the sum-frequency hyperpolarizability was not taken into account by assuming its magnitude does not change with concentration). As one or both of the above factors is responsible for the observed SFG signal enhancement, we should find out the exact origin of this enhancement. In principle, the surface number density of the alcohol mixture could be obtained from surface tension measurements using Gibbs' equation.^{45,46} However, this is not easy as the bulk mole fraction of the mixture needs to be converted into the activity of the specific alcohol–water system. As an alternative route, we compared the ratio of the CH₃ symmetric stretch modes in the SSP and the PPP spectra for each concentration to find out the possible change in molecular orientation and conformation. By taking the ratio of the SFG peak strengths, the surface concentration factor (as well as the molecular hyperpolarizability) would cancel out from the numerator and the denominator, and the resulting value would depend purely upon the orientations of the surface molecules. Figure 4 represents the experimental values of $A_q(\text{PPP})/A_q(\text{SSP})$ of the CH₃ symmetric stretch mode versus concentration. The ratio values for each alcohol are nearly the same regardless of the alcohol bulk mole fraction, suggesting a possibility that the orientation of alcohol molecules on the surface of alcohol–water mixtures does not change too much with the change of the bulk alcohol concentration.

For a more quantitative analysis, $A_q(\text{SSP})$ and $A_q(\text{PPP})$ for the CH₃ symmetric stretch mode can be expressed from eq 3 and 4 as follows:

$$A(\text{SSP}) = L_{yy}(\omega_{\text{sfg}})L_{yy}(\omega_{\text{vis}})L_{zz}(\omega_{\text{ir}}) \sin \beta_{\text{ir}} \times \left\{ \frac{1}{2} N_s \alpha [\langle \cos \theta \rangle (1 + r) - \langle \cos^3 \theta \rangle (1 - r)] \right\} \quad (8)$$

$$A(\text{PPP}) =$$

$$\begin{aligned} & -L_{xx}(\omega_{\text{sfg}})L_{xx}(\omega_{\text{vis}})L_{zz}(\omega_{\text{ir}}) \cos \beta_{\text{sfg}} \cos \beta_{\text{vis}} \sin \beta_{\text{ir}} \times \\ & \left\{ \frac{1}{2} N_s \alpha [\langle \cos \theta \rangle (1 + r) - \langle \cos^3 \theta \rangle (1 - r)] \right\} - \\ & L_{xx}(\omega_{\text{sfg}})L_{zz}(\omega_{\text{vis}})L_{xx}(\omega_{\text{ir}}) \cos \beta_{\text{sfg}} \sin \beta_{\text{vis}} \cos \beta_{\text{ir}} \times \\ & \left\{ \frac{1}{2} N_s \alpha [\langle \cos \theta \rangle - \langle \cos^3 \theta \rangle] (1 - r) \right\} + \\ & L_{zz}(\omega_{\text{sfg}})L_{xx}(\omega_{\text{vis}})L_{xx}(\omega_{\text{ir}}) \sin \beta_{\text{sfg}} \cos \beta_{\text{vis}} \cos \beta_{\text{ir}} \times \\ & \left\{ \frac{1}{2} N_s \alpha [\langle \cos \theta \rangle - \langle \cos^3 \theta \rangle] (1 - r) \right\} + \\ & L_{zz}(\omega_{\text{sfg}})L_{zz}(\omega_{\text{vis}})L_{zz}(\omega_{\text{ir}}) \sin \beta_{\text{sfg}} \sin \beta_{\text{vis}} \sin \beta_{\text{ir}} \times \\ & \{ N_s \alpha [r \langle \cos \theta \rangle - \langle \cos^3 \theta \rangle (1 - r)] \} \quad (9) \end{aligned}$$

where $\alpha = \alpha_{\xi\xi\xi}^{(2)}$ and $r = \alpha_{\xi\xi\xi}^{(2)}/\alpha_{\xi\xi\xi}^{(2)}$ is the ratio of molecular hyperpolarizabilities of the CH₃ symmetric stretch mode (ξ is along the symmetry axis of CH₃, and ξ is the unit vector normal to ζ). In the calculation of the Fresnel factors, we used the known refractive index values for water and the alcohols,^{56–58}

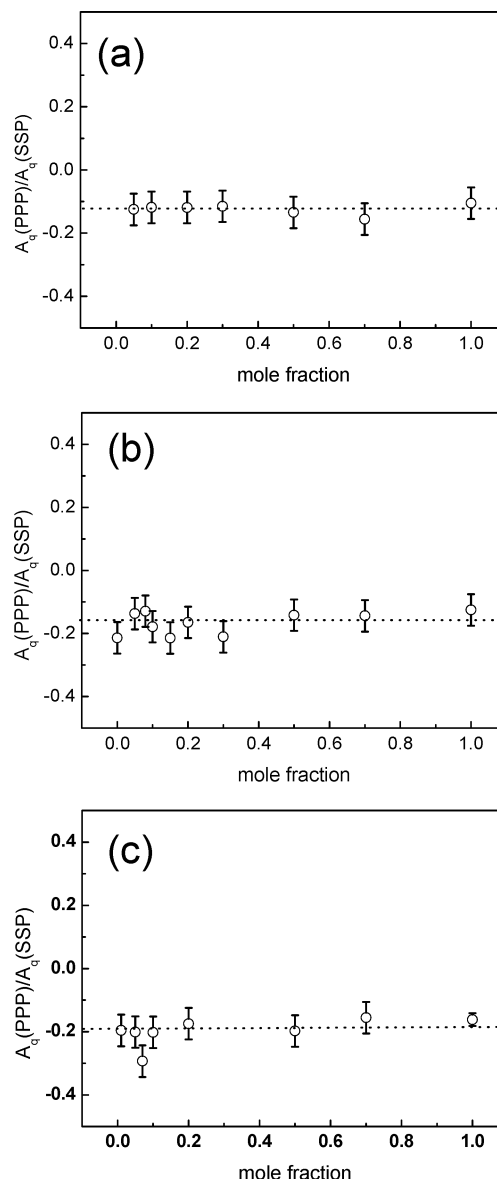


Figure 4. $A_q(\text{PPP})/A_q(\text{SSP})$ of the CH₃ symmetry stretch mode vs bulk alcohol concentration. (a) Methanol–water mixture, (b) ethanol–water mixture, and (c) propanol–water mixture. The horizontal dotted lines are guides for the eye.

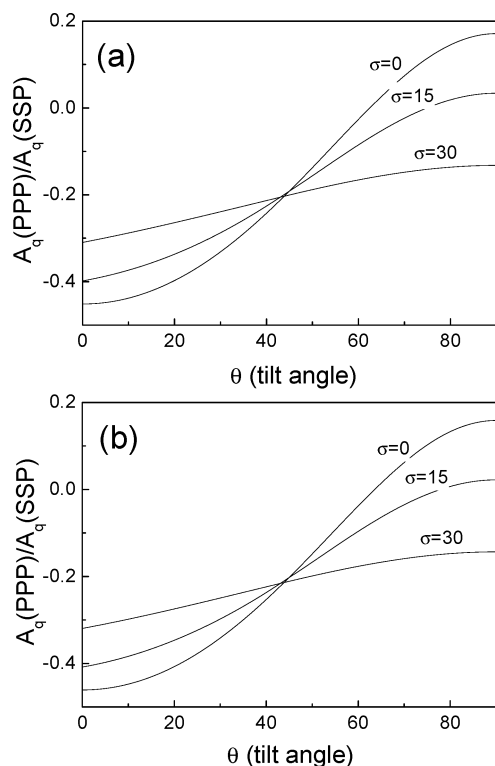


Figure 5. Calculated $A(\text{PPP})/A(\text{SSP})$ of the CH_3 symmetry stretch mode vs polar tilt angle of the surface methyl groups using eqs 8 and 9. (a) For water subphase [$n_2(\text{vis}) = n_2(\text{SFG}) = 1.33$, $n_2(\text{IR}) = 1.39$]. (b) For bulk propanol [$n_2(\text{vis}) = n_2(\text{SFG}) = 1.38$, $n_2(\text{IR}) = 1.39$]. θ_0 and σ are defined in eq 10.

and the linearly interpolated values for the mixtures. As the refractive indices do not differ too much for these liquids, the monolayer refractive index n' is not expected to vary too much for samples of different concentrations.⁵⁹ We calculated the theoretical values of $A_q(\text{PPP})/A_q(\text{SSP})$ from eqs 8 and 9 by allowing n' to vary from 1.14 to 1.17 depending on the alcohol concentration and by assuming the following Gaussian function for the polar orientational distribution function of the surface molecules

$$f(\theta) \propto \exp[-(\theta - \theta_0)^2/(2\sigma^2)] \quad (10)$$

from which the tilt angle and the width of the distribution of the terminal methyl group could be inferred. The lines in Figure 5a show the calculated results for the set of refractive indices corresponding to a water subphase (for very diluted mixtures), and those in Figure 5b are for the cases of pure propanol. As seen in Figures 5, the change in the alcohol concentration and the corresponding change in the bulk and the monolayer refractive indices are expected to have little influence on the expected orientation of methyl groups. The polar tilt angle $\theta_0 \sim 40^\circ$ from the surface normal for the terminal methyl group of alcohol molecules with a Gaussian distribution width $\sigma = 15\sim 30^\circ$ is one of the possible distributions that can explain the experimental result [$A_q(\text{PPP})/A_q(\text{SSP}) \sim -0.2$] throughout the entire concentration range of the water–propanol mixture investigated by SFG, although the possibility of the tilt angle and distribution width varying with concentration within experimental uncertainties while keeping the ratio $A_q(\text{PPP})/A_q(\text{SSP})$ constant cannot be ruled out. As the parameters such as n' and the depolarization ratio r are not known exactly, the quantitative determination of the surface structure would be difficult, especially for methanol and ethanol, where the

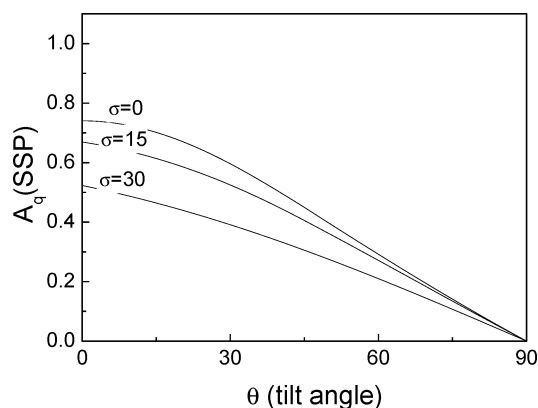


Figure 6. Calculated $A(\text{SSP})$ of the CH_3 symmetry stretch mode vs polar tilt angle of the surface methyl groups for different angular distribution widths.

depolarization ratio can be different from the above value. As a specific example, by accepting that the interfacial refractive n' is model-dependent and allowing it to vary from 1.14 to 1.18, the expected polar tilt angle θ_0 changes by 4° . However, the near-constant values of $A_q(\text{PPP})/A_q(\text{SSP})$ throughout the whole concentration range suggested that the molecular orientation would not change too much as the concentration of alcohol in the mixture is varied.

The above conclusion differs from the previous proposals for the water–methanol mixture, in which it was concluded that the main origin of sum-frequency signal enhancement is the change of surface molecular orientation.^{34–36} It was estimated that the methyl group of the surface molecule for pure methanol was pointing toward the air side with an average tilt angle less than 40° and a full-width at half-maximum of $\sim 70^\circ$ (corresponding to $\sigma \sim 30^\circ$ in eq 10). And at low concentrations, the methyl groups were oriented nearly vertically with a very narrow angular distribution of $\sim 16^\circ$. However, such an orientation is almost the same as a neat hexadecanol Langmuir monolayer, where the PPP SFG signal at the peak of the CH_3 symmetric stretch was larger than $1/10$ of the SSP SFG signal.⁵⁹ In our case, a much smaller relative PPP signal ($\sim 1/60$ of the SSP signal, from Figure 2a and b) was measured, indicating that the molecules are not likely to have such an upright configuration, even when we account for the possible difference in depolarization ratios between methyl groups in methanol and in hexadecanol.

Moreover, as the surface number density of pure alcohol should not differ too much from that of a hexadecanol monolayer, the SFG signals from the alcohol mixture and the hexadecanol monolayer should be comparable if they have a similar angular conformation. However, the measured sum-frequency signal (SSP, at the CH_3 symmetric peak) from the surface of a propanol mixture at the concentration corresponding to maximum SFG is still only $1/3$ of that from a hexadecanol monolayer.⁶⁰ For a more quantitative analysis, $A_q(\text{SSP})$ for different tilt angles and distribution widths of terminal methyl groups is plotted in Figure 6 using eq 8. Indeed, the calculation shows that $A_q(\text{SSP})$ decreases as the terminal methyl group is tilted from the upright position, and the experimental ratio of $A_q(\text{SSP}, 0.1 \text{ mole propanol mixture})/A_q(\text{SSP}, \text{C}_{16}\text{H}_{33}\text{OH}) \sim 1/\sqrt{3}$ could be explained for the tilt angle $\theta_0 \sim 40^\circ$ with a distribution width $\sigma \sim 30^\circ$ (θ_0 and σ defined in eq 10) of the methyl groups in the surface of a propanol mixture. Molecular dynamics simulations and neutron scattering results for water–alcohol binary mixture also showed that the tilt angle of alcohol molecules at low concentrations is nearly 40° with a broad

angular distribution.^{39–41} Thus, the small alcohol molecules at the surface (at low concentrations corresponding to the maximum SFG signal) would not have an upright orientation with a narrow distribution but are expected to have a broad orientational distribution as in the pure alcohol surface. Finally, it needs to be remembered that the SPS signal from the CH₃ symmetric stretch mode of an alcohol solution is very small and strongly affected by motional averaging,⁶¹ so the orientation of the molecules deduced from the ratio $A(\text{SPS})/A(\text{SSP})$ would have a large uncertainty.

Thus, the previous explanation of the change in the molecular orientation could be disregarded as the main cause of the SFG enhancement. If we rule out the possibility of the tilt angle and distribution width varying together with concentration while keeping the ratio $A_q(\text{PPP})/A_q(\text{SSP})$ constant within experimental uncertainties, we can choose the simpler explanation that $A_q(\text{PPP})/A_q(\text{SSP})$ is constant because the angular conformation of surface molecules does not change too much with concentration. Surprisingly, with our result, the surface concentration of alcohol molecules contributing to the SFG signal in low-mole fraction mixtures should be larger than that of pure alcohols. As it seems unreasonable to have more surface alcohol molecules at a low concentration than in the pure case, this proposition needs to be investigated more carefully. Recently, Chen et al. also proposed that the SFG signal enhancement from a methanol mixture originates not from a change in the orientation but from the increase in the number of methanol molecules contributing to the SFG signal.³⁷ It was proposed that the methanol molecules at the interface form dimers where two molecules having hydrogen bonding are directed in opposite directions.⁶² It was suggested that fewer surface methanol molecules at low concentrations form dimers compared to the case of higher concentrations or pure methanol. By assuming that the SFGs from paired dimer molecules cancel each other out, they were able to explain the data quantitatively using a double-layer adsorption model.

Then, the question is how much the molecules underneath the top layer contribute to the SFG signal. For surface SFG, depth resolution from bulk samples such as liquids or polymers is not well-known and may well differ depending on the nature of the surface. The interfacial region for the alcohol solution is expected to be a few molecular layers,^{39–41} and we want to know whether the sum-frequency signal would originate from the top monolayer in the interfacial region or from more than a monolayer. Shown in Figure 7 are the SFG spectra from the surfaces of pure para-, ortho-, and meta-xylene. As the methyl groups of these molecules are attached differently, the sum-frequency signal strengths from the surfaces of these samples are expected to be different. However, the observed SFG signals at 2860 and 2920 cm⁻¹ (due to the CH₃ fermi resonance and the CH₃ symmetric stretch modes, respectively) were almost the same for the three xylene samples, including the signal strength.^{63–65} Our sum-frequency spectrum of meta-xylene also agrees with the published result.⁶⁵ As it is expected that the air side of the interface should look similar for all these samples, with one of the methyl groups of the molecules protruding out, this spectral similarity indicates that the sum-frequency signal mainly comes from the molecules and functional groups above the air–liquid interface. The lower side of the interface would look more different for these samples, but the SFG signal contributing from the lower side should be very small, presumably because of the isotropic nature of the environment or the pairing of the submerged methyl group with the methyl groups of the bulk molecules in opposite directions. Having more

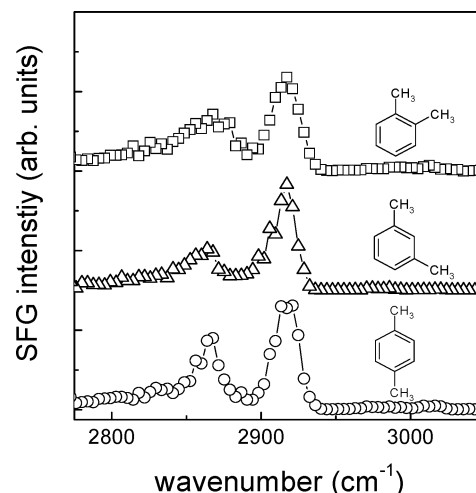


Figure 7. SFG spectra (SSP) from pure xylene surfaces. Circle: para-xylene. Triangle: meta-xylene. Square: ortho-xylene. Each spectrum is shifted vertically for clarity.

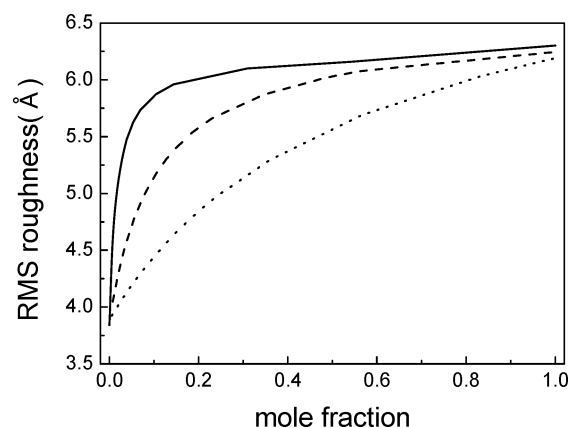


Figure 8. Surface thermal roughness vs alcohol bulk concentration calculated using the surface tension data in Figure 1 and eq 11. Dotted line: methanol–water. Dashed line: ethanol–water. Solid line: propanol–water.

associative intermolecular interaction as compared to the xylenes, the interfacial layer for the alcohol–water mixture is expected to be even thinner (or at least comparable), and it can be concluded that the SFG signal from the alcohol–water mixture should mainly come from the topmost layer. Thus, the proposition by Chen et al. of SFG cancellation within dimer pairs is put to question, at least in a quantitative way.^{33,37}

As an alternative model to explain the data, the change in the interfacial layer thickness with concentration can be examined. The interfacial layer thickness is known to be mainly affected by thermal fluctuation, called the thermal capillary wave,^{66,67} and this thermal fluctuation has the following mean square thickness:

$$\xi^2 = \frac{k_B T}{4\pi\gamma} \ln(K_m^2 a^2 + 1) \quad (11)$$

where γ is the interface surface tension, $a^2 = \gamma/\rho g$ is the capillary length, and K_m is an upper cut-off wave vector for the capillary wave. By using the above equation and the surface tension data in Figure 1, we plotted, in Figure 8, the surface thermal roughness with varying bulk concentrations for methanol–water, ethanol–water, and propanol–water mixtures. In this calculation, mass density values for different alcohol concentrations were obtained from the CRC handbook.⁵⁸ As

shown in Figure 8, the thermal roughness increases with the increasing alcohol bulk mole fraction and is maximized for pure alcohol surfaces. It can be imagined that the molecules are more densely populated at the top when the interfacial layer is thin and the surface is less rough, thus, contributing more to the SFG at low concentrations. Although such a model is plausible, a quantitative prediction is not possible unless a more detailed picture at the surface is obtained by other methods. It should also be considered that the roughness of the liquid surface could make the apparent tilt angle converge to the same value irrespective of the possible variation in the local orientation of the surface molecules, as first discovered in the case of surface SHG by Simpson and Rowlen.^{68,69} That our estimated tilt angle ($\sim 40^\circ$) is closed to the “SHG magic angle” makes it more convincing that the roughness of the liquid surface should be taken into account in the analysis of the SFG.

There have been several attempts to determine the surface excess of alcohol–water mixtures by obtaining the activity of the alcohol from the partial vapor pressure.^{45,46} It is quite remarkable that these surface excess values deduced in a more reliable way (activity values deduced from the partial vapor pressures) have maxima at ~ 0.3 , ~ 0.15 , and ~ 0.05 mole fractions,⁴⁶ in concentrations similar to the SFG enhancement concentrations of methanol, ethanol, and propanol (Figure 3). Thus, it can be imagined that SFG mainly detects the surface excess molecules defined by the Gibbs equation, while other bulk molecules could be centrosymmetrically oriented and would not contribute much to SFG. It should be remembered that neutron scattering and molecular dynamic simulation studies showed the well-separated maximum position of surface alcohol, which is well into the air side from the Gibbs dividing surface of the water.^{39–41} If we identify the molecules around this maximum region that is separated from the density profile of the water as the surface excess molecules, it is possible that the structures of these molecules, including the orientational distribution, differ from the underlying alcohol molecules, and these molecules contribute mainly to the SFG. It is hoped that the above ideas proposed to explain the intriguing SFG signal enhancement could be tested by using other auxiliary methods such as X-ray scattering, neutron scattering, and molecular dynamic simulations.

Conclusion

The surface of alcohol–water mixtures of varying bulk alcohol concentrations were investigated using the SFG vibrational spectroscopic technique. The sum-frequency signal in the CH-stretch vibration region was larger at low intermediate concentrations than that from pure alcohol, and the propanol–water mixture showed the largest signal enhancement at the lowest concentration among methanol, ethanol, and propanol mixtures. An analysis of the SFG peak strengths showed that this enhancement is mainly due to the surface number density of alcohol molecules contributing to SFG, while the molecular orientation of alcohol molecules remains the same throughout the concentration range investigated. Various models were proposed to explain the sum-frequency signal enhancement at low intermediate concentrations.

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