

Competitive Molecular Adsorption at Liquid/Solid Interfaces: A Study by Sum-Frequency Vibrational Spectroscopy

Luning Zhang,* Weitao Liu, and Y. Ron Shen*

Department of Physics, University of California, Berkeley, California 94720

David G. Cahill

Center of Advanced Materials for the Purification of Water with Systems, Department of Materials Science and Engineering, University of Illinois, Urbana, Illinois 61801

Received: June 22, 2006; In Final Form: November 6, 2006

We used sum-frequency vibrational spectroscopy to study competitive adsorption of water–alcohol binary liquid mixtures at hydrophilic fused silica and hydrophobic alkyl silane-covered substrates. Monitoring the strength of the methyl stretching modes of alcohols in the mixtures allowed deduction of the surface coverage of alcohols and their adsorption isotherms. It was found that for both types of substrates, alcohol adsorbs preferentially than water at liquid/solid interfaces. The driving force behind preferential alcohol adsorption appears to be the strong hydrogen-bonding interaction among water molecules as they would like to maintain the three-dimensional hydrogen-bonding network and minimize loss of hydrogen bonds in the interfacial layer. The mechanism is believed to be generally true if interaction among molecules of one species is significantly stronger than other intermolecular interactions in a mixture and the interactions of different molecular species with the substrate are about the same.

1. Introduction

Binary mixtures containing water and aliphatic alcohol have been the focus of many experimental^{1–13} and theoretical^{9–20} studies because of their importance in surface chemistry and industrial applications. They are known to deviate from the ideal mixture in their physicochemical properties^{9,10,21} such as the mean molar volume,^{2,3} excess enthalpy of mixing,⁶ excess entropy,^{9–13} viscosity,²² surface potential,²³ and diffusion coefficients.²⁴ There are still controversies in understanding of the bulk anomalies.^{11–13} At the same time, much less is known about surfaces of these binary mixtures. Recent developments in neutron^{25,26} and X-ray grazing incidence reflection²⁵ and other techniques,²⁷ as well as theoretical simulations,^{16–20} have made the liquid/vapor interfaces more accessible. However, to probe interfacial structures at the molecular level, surface-specific sum-frequency vibrational spectroscopy (SFVS) is unique. It is applicable to all interfaces accessible by light. Wolfrum et al. first used SFVS to study vapor/methanol–water interfaces,²⁸ and later, Ma and Allen repeated the experiment.²⁹ They both found that the orientation of surface methanol molecules varied with their bulk concentration. More recently, however, Chen et al. reported a study on the same system but concluded that the surface methanol orientation did not change with bulk concentration.³⁰ Sung et al. reached the same conclusion in their study of vapor/ethanol–water interfaces.³¹

Compared with vapor/binary-liquid interfaces, little information is available on binary-liquid/solid interfaces although they are crucial in many important applications such as water purification, microarray devices, biochips, liquid chromatography, and electrochemistry.^{32–36} Competitive adsorption of

molecules at liquid/solid interfaces plays a central role in these applications. Preferential adsorption of a species depends not only on its binding energy with the solid substrate, but also interactions with surrounding molecules, interfacial structure, and other properties of the system.^{37,38} To understand the competitive adsorption process, molecular-level information on the interfacial structure is needed. Among the very few techniques available to probe liquid/solid interfaces, SFVS, which is capable of yielding vibrational spectra for the interfacial structure, has been most informative.^{39,40} Being a second-order nonlinear optical process, SFVS is forbidden in a centrosymmetric bulk, but necessarily allowed at an interface, making the process highly surface specific.⁴¹ It also has enough sensitivity to probe the vibrational resonances of the submonolayer of molecules, and is therefore suitable for monitoring molecular adsorption at an interface *in situ*. Currently, SFVS is the only technique that can yield interface-specific vibrational spectra for a buried interface.

In this paper, we report the use of SFVS to study competitive molecular adsorption of binary mixtures at liquid/solid interfaces. We focus on water mixtures with C1–C4 alcohols: methanol, ethanol, 1- and 2-propanol, and *tert*-butanol. The solid substrate used is hydrophilic fused silica. The system is interesting because C1–C4 alcohols are amphiphilic and fully miscible with water, making it subject to both polar and nonpolar interactions with neighboring molecules. Interactions of alcohols and water with silica are similar in strength, making their competitive adsorption process on silica rather intriguing. For reference and comparison, we have also studied interfaces of methanol–CCl₄, ethanol–CCl₄, and 2-propanol–methanol mixtures with fused silica, and methanol–water mixtures with an OTS (octyltrichlorosilane)-covered hydrophobic silica substrate. In all cases with alcohol–water mixtures, we found that alcohol molecules preferentially adsorbed at the interface. It is believed

* Address correspondence to this author. Fax: 1-86-510-643-8923. E-mail: zhangln@berkeley.edu (L.Z.), yrshen@calmail.berkeley.edu (Y.R.S.).

that maximization of hydrogen bonds must have dominated over maximization of entropy of mixing in establishing the interfacial hydrogen-bonding network that drives the alcohol molecules to the interface. Binding energies of alcohols and water with substrates would have played only a minor role.

We briefly describe the theoretical background and experimental arrangement of our work in sections 2 and 3, and then present the experimental results and analysis in section 4. Interpretation of the results and discussion appear in terms of thermodynamic properties and intermolecular hydrogen bonding in section 5. Finally, we summarize our understanding of competitive adsorption between alcohol and water at an interface in the concluding section 6.

2. Theoretical Background

2.1. Surface Sum-Frequency Vibrational Spectroscopy (SFVS). We consider here sum-frequency (SF) generation in reflection geometry from liquid at an interface. The theoretical background of SFG has been described in several reviews.^{41–45} The SF signal generated by overlapping a visible input with intensity I_1 and fixed frequency ω_1 and an IR input with intensity I_2 and tunable frequency ω_2 at the interface is given by

$$S(\omega=\omega_1+\omega_2) \propto |\vec{L}(\omega)\cdot\hat{e}| \cdot \chi_S^{(2)} : [\hat{e}_1 \cdot \vec{L}(\omega_1)] [\hat{e}_2 \cdot \vec{L}(\omega_2)]^2 I_1 I_2 \quad (1)$$

where \hat{e}_i and $\vec{L}(\omega_i)$ denote respectively the unit polarization vector and the tensorial Fresnel transmission coefficient of the surface at ω_i , and $\chi_S^{(2)}$ is the surface nonlinear susceptibility tensor that can be expressed as

$$\vec{\chi}_S^{(2)} = \chi_{NR}^{(2)} + \sum_q \frac{\vec{A}_q}{\omega_{IR} - \omega_q + i\Gamma_q} \quad (2)$$

with $\chi_{NR}^{(2)}$ describing the nonresonant contribution, and \vec{A}_q , ω_q , and Γ_q representing the amplitude, frequency, and damping constant of the q th surface vibrational mode, respectively. The amplitude $\vec{A}_{q,ijk}$ in the lab coordinates (x,y,z) is related to its counterpart $\alpha_{q,lmn}$ of the molecular hyperpolarizability in the molecular coordinates (ξ,η,ζ) through a coordinate transformation and an average over the molecular orientational distribution $f(\Omega)$:

$$A_{q,ijk} = N_S \int \sum_{l,m,n} \alpha_{q,lmn} (\hat{i}\cdot\hat{l})(\hat{j}\cdot\hat{m})(\hat{k}\cdot\hat{n}) f(\Omega) d\Omega \quad (3)$$

Fitting the SF vibrational spectra of different input/output polarization combinations with eqs 1 and 2 allows the deduction of surface density N_S since $A_{q,ijk}$, $\alpha_{q,lmn}$ are known. The ratios of various $A_{q,ijk}$ can provide information on the average orientation of the molecular moiety contributing to the q th vibrational mode through eq 3.

2.2. Adsorption Isotherm. Plotting the normalized surface density of alcohol, $\theta \equiv N_S/N_{S,sat}$, as a function of bulk concentration of alcohol, x , in a molar fraction at a given temperature T yields the adsorption isotherm of alcohol at the particular liquid/solid interface. Here $N_{S,sat}$ denotes maximum surface coverage by alcohol molecules. If the simple Langmuir kinetics for adsorption is assumed,³³ the adsorption isotherm has the expression

$$\theta = x/(x + e^{\Delta G/RT}) \cong xe^{-\Delta G/RT} \quad \text{for } x \ll 1 \quad (4)$$

The initial slope of this isotherm allows us to deduce the adsorption free energy ΔG . As we shall describe later, we

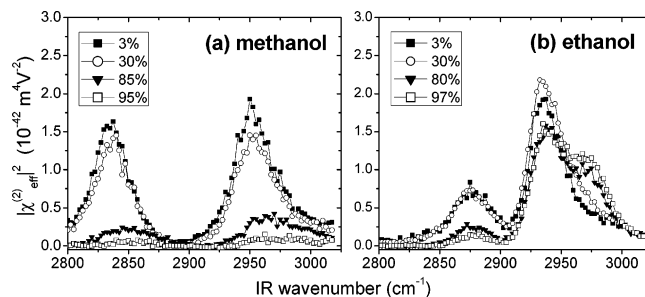


Figure 1. Surface sum-frequency spectra of an alcohol- CCl_4 mixture at a hydrophilic substrate (fused silica) for (a) methanol and (b) ethanol. Alcohol concentrations are in molar fraction.

obtained N_S , and hence coverage θ , by measuring the sum-frequency spectral intensity of a relevant vibrational mode of alcohol.

3. Experimental Arrangement

Hydrophilic fused silica surface was prepared by dip-cleaning in a mixture of sulfuric acid (98%) and nochromix reagent (GODAX Laboratories, Inc.), then rinsing in pure water with a resistance of $18.3 \text{ M}\Omega\cdot\text{cm}$, and finally drying with filtered nitrogen gas. This procedure is known to produce fully hydroxylated silica surface with a surface density of silanol of about $5/\text{nm}^2$.⁴⁶ To obtain the hydrophobic surface, an octyl-trichlorosilane (OTS) monolayer was self-assembled on the surface of fused silica following the method of Sagiv.⁴⁷ The quality of the OTS monolayer was monitored by SFVS. A well-ordered OTS monolayer comprised of nearly all-trans alkyl chains is characterized by a spectrum that exhibits clear CH_3 modes, but hardly detectable CH_2 modes, in the CH stretch region.^{48,49} Its interface with water displays a dangling OH stretch mode at about 3680 cm^{-1} nearly as strong as that of the vapor/water interface in SFVS. Alcohols of HPLC or reagent grade were purchased and used as received. For the water-alcohol mixtures, deuterated water was used to avoid influence on the spectrum of the CH stretching modes by OH stretching modes.

Our SFVS setup has been described elsewhere.^{50–52} A picosecond Nd:YAG laser with an optical parametric system generated a visible input pulse at 532 nm and an infrared input pulse tunable between 2.6 and $3.7 \mu\text{m}$, both having a pulse width of ~ 20 ps. The two pulses overlapped at the interface to be investigated with incident angles of 45° and 57° , respectively. The generated SF signal in the reflected direction was collected into a photodetector/gated integrator system. The signal was normalized by signal from a z-cut quartz plate.

4. Results and Data Analysis

We present here SFVS spectra and analyses of interfaces of alcohol-water mixtures with hydrophilic (fused quartz) and hydrophobic (OTS-covered fused silica) substrates. In the latter case, because overlapping of the CH stretch modes of alcohols (except methanol) and OTS complicates the analysis, we limited the investigated to only methanol-water mixtures. To help our understanding on how alcohol molecules adsorb at a hydrophilic surface, we shall first describe the SFVS spectra of interfaces of methanol- CCl_4 and ethanol- CCl_4 mixtures with fused silica. We shall also present the spectra of 2-propanol/methanol mixtures at fused silica to help us understand how different alcohols compete in adsorption.

4.1. Interfaces of Alcohol- CCl_4 Mixtures and Fused Silica. Parts a and b of Figure 1 display the SF vibrational

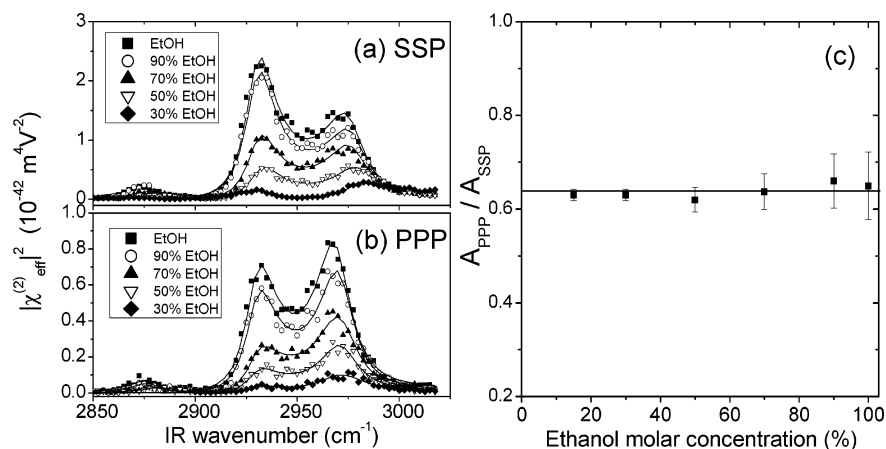


Figure 2. Sum-frequency vibrational spectra of the interfaces of ethanol–water mixtures with a hydrophilic substrate (fused silica) obtained with polarization combinations (a) SSP, (b) PPP, and (c) the ratio of the SSP and PPP amplitude of the methyl antisymmetric mode. The peaks at ~ 2975 and ~ 2930 cm^{-1} are from the methyl antisymmetric stretch and Fermi resonance modes of ethanol. The error bars in part c came from uncertainty in deducing $A_{q,ijk}$ from fitting the spectra.

spectra from interfaces of methanol– CCl_4 and ethanol– CCl_4 mixtures with silica in the CH range obtained with SSP polarization combination (S-, S-, and P-polarizations for SF output, visible input, and IR input, respectively). The peaks at 2830 and 2950 cm^{-1} in Figure 1a come from the symmetric (r^+) and Fermi resonance modes of methanol, and the three peaks at 2875, 2930, and 2975 cm^{-1} in Figure 1b are mainly from the symmetric (r^+), Fermi resonance, and antisymmetric (r^-) modes of ethanol, respectively. We found the r^- mode of methanol particularly hard to detect with either SSP or other polarization combinations. As seen in Figure 1, for an alcohol concentration between 3% and 30%, the spectra change only slightly. The spectral features are actually very similar to those of alcohol monolayers formed by gas-phase adsorption on fused silica.⁵³ This suggests that signal is more or less from an alcohol monolayer adsorbed at the liquid/solid interfaces in this concentration range. Furthermore, we know alcohol molecules readily establish hydrogen bonds with the silanol groups on silica while carbon tetrachloride does not, therefore, alcohol molecules adsorb to silica preferentially. The adsorption starts to saturate toward monolayer coverage even with only 3% of alcohol in bulk.

When alcohol concentration increases above 30%, the r^+ mode decreases in strength and the r^- mode (not observed in methanol¹) increases, as shown in Figure 1. At the higher concentrations, the spectra appear similar to those of pure alcohol/silica interface reported previously.⁵³ If the SF signal were still mainly from the adsorbed alcohol monolayer at the interface, the spectra would not have changed significantly. As discussed in ref 53 for the pure alcohol/silica interface, decrease of the r^+ mode and increase of the r^- mode are due to formation of an alcohol bilayer at the interface with a “head-to-head” molecular arrangement. The r^+ mode decreases because the “head-to-head” methyl groups vibrate out of phase with respect to each other and the SF signal from them experiences destructive interference. The r^- mode increases because the corresponding vibrations are partially in phase on average and the SF signal from them is enhanced through constructive interference. In the case of the pure alcohol/silica interface, the calculated changes of r^+ and r^- modes match well with measurements comparing the alcohol monolayer on silica to the alcohol/silica interface.⁵³

Thus we learn that in alcohol– CCl_4 mixtures, alcohol molecules first adsorb at the silica interface to form a monolayer with the methyl groups pointing into the liquid, and then as the

alcohol concentration increases above 30%, they adsorb at the interface via van der Waals interactions in a head-to-head arrangement with the first adsorbed monolayer to form a bilayer (the second monolayer being more disordered). We note that the Fermi resonance mode, which arises from mixing of r^+ with the overtone of the methyl bending mode, does not decrease as much as r^+ with increasing ethanol concentration presumably because formation of the bilayer affects the bending mode differently than the r^+ mode.

4.2. Hydrophilic Substrate (Fused Silica). Alcohol–Water Mixtures. The spectra of methanol–water (D_2O) and ethanol–water (D_2O) mixtures at fused silica resemble those of methanol– CCl_4 and ethanol– CCl_4 mixtures of high alcohol concentrations ($>30\%$) at fused silica presented in Figure 1. For methanol–water mixtures, they are hardly detectable at all concentrations. For ethanol–water mixtures, the r^- mode at 2975 cm^{-1} and the Fermi resonance at 2930 cm^{-1} dominate, as shown in Figure 2a for both SSP and PPP polarization combinations. In other words, the spectra are associated with the head-to-head bilayer arrangement of alcohol molecules adsorbed at fused silica discussed in the previous section. It is likely that being amphiphilic, ethanol and methanol molecules in water are forced by hydrophobic interaction with water to have their hydrophobic terminals ($-\text{CH}_3$ groups) face each other.¹¹ In comparison with alcohol– CCl_4 mixtures, the alcohol–water mixtures appear to have alcohol molecules adsorb at the interface in the form of head-to-head dimer units beginning at very low alcohol concentrations. As ethanol concentration increases, the overall spectral intensity increases and the r^+ and r^- modes appear to be red-shifted by about 5 to 8 cm^{-1} . The red shifts are presumably due to an increase of methyl interactions with neighboring hydrocarbon groups.

As seen from eq 3, the resonant SF signal from the q th vibrational mode is proportional to $|A_{q,ijk}|^2$ and hence depends on both the number density (N_S) and the orientation of adsorbed molecules. However, if $|A_{q,ijk}/A_{q,r'k}|$ is independent of N_S , then we can conclude that $A_{q,ijk}$ must be proportional to N_S .^{36,50,54} This is the case for alcohol–water mixtures. We show in Figure 2c the ratio of $|A_{r^-,PPP}/A_{r^-,SSP}|$ for the r^- mode as a function of ethanol concentration in an ethanol–water mixture, where $A_{r^-,PPP}$ and $A_{r^-,SSP}$ were obtained from fitting of the measured SSP and PPP SF spectra in Figure 2, parts a and b, respectively. The ratio of $|A_{r^-,PPP}/A_{r^-,SSP}|$ being approximately constant allows us to deduce the surface density N_S of ethanol from $A_{r^-,SSP}$ using pure alcohol as a reference. Thus we are able to find the

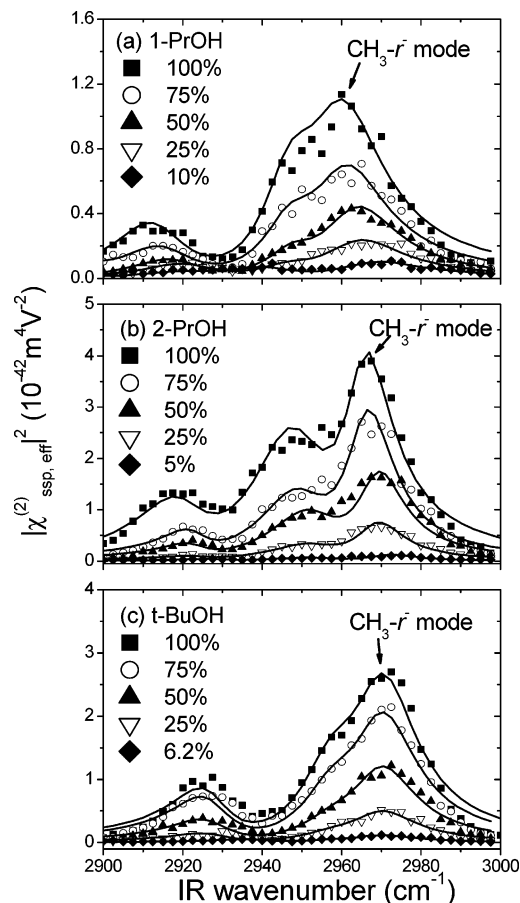


Figure 3. Sum-frequency vibrational spectra of alcohol–water mixtures at a hydrophilic substrate (fused silica): (a) 1-propanol, (b) 2-propanol, and (c) *tert*-butanol.

adsorption isotherm of ethanol adsorbed on silica from ethanol–water mixtures to be presented later.

The SF surface vibrational spectra for 1-propanol–D₂O, 2-propanol–D₂O, and *tert*-butanol–D₂O mixtures on fused silica have similar behavior as those of ethanol–water mixtures, featuring pair-like adsorption of alcohol molecules at the hydrophilic surface. The SSP spectra of different alcohol concentrations with fitting curves are displayed in Figure 3. The r^+ mode (not shown) is again weak in all cases, and the r^- mode is prominent and increases with alcohol concentration. Other than the r^- mode and the Fermi resonance around 2950 cm⁻¹ in the spectra, there is also a peak around 2910–2920 cm⁻¹ that can be assigned to the CH₂ antisymmetric mode (1-propanol and *tert*-butanol) and the CH stretching mode (2-propanol). Fitting of the spectra yielded the resonance frequencies and linewidths of the relevant modes summarized in Table 1.

The amplitude of the r^- mode from the fitting of the spectra for different alcohol concentrations then yields the adsorption isotherm of alcohol adsorbed on fused silica from the alcohol–D₂O liquid mixture. Figure 4 shows the deduced adsorption

isotherms for ethanol, 1-propanol, 2-propanol, and *tert*-butanol. As seen from the isotherms, all four alcohols show preferential adsorption than water at the liquid/silica interface. The adsorption free energy ΔG (free energy reduction in adsorption) was deduced from fitting to the initial slope using eq 4. The values are close to one another for all alcohols investigated and fall in the range of -3.2 to -3.7 kJ/mol.

2-Propanol–Methanol Mixtures. While all alcohols in alcohol–water mixtures are favored to adsorb on fused silica with nearly the same ΔG , one may wonder how different alcohols in alcohol mixtures may compete with each other in adsorption on silica. We also studied competitive adsorption of methanol and 2-propanol. The interfacial SSP spectra of 2-propanol–methanol mixtures at fused silica for different propanol concentrations are depicted in Figure 5a. The spectra have mainly contributions from 2-propanol because methanol hardly shows any spectral features. They are therefore similar to those of 2-propanol–water mixtures at silica presented in Figure 3b, with water replaced by methanol. We used the strength of the r^- mode of $-\text{CH}_3$ of 2-propanol at 2967 cm⁻¹ to derive the surface coverage, and obtained the adsorption isotherm for 2-propanol in Figure 5b. It shows that 2-propanol preferentially adsorbs at the interface with a ΔG of approximately -3.0 kJ/mol, which is lower in absolute value than $\Delta G \approx -3.5$ kJ/mol in the case of 2-propanol–water, indicating that preference is stronger in the latter case.

4.3. Hydrophobic Substrate (OTS-Covered Fused Silica). Methanol–Water Mixtures. Because the SF spectra of alcohols, except methanol, overlap with that of OTS in the CH stretch range, it is difficult to use SFVS to study alcohol adsorption on OTS-covered surface. Methanol is the only exception. Its $-\text{CH}_3$ group directly bonds to O, instead of C, causing the $-\text{CH}_3$ r^+ mode to red-shift to 2840 cm⁻¹, out of the range of OTS r^+ spectral peaks. This allows us to use the r^+ mode of methanol to probe methanol adsorption at the OTS-covered hydrophobic surface. We studied competitive adsorption of methanol and D₂O. We only sketch the results here with details appearing elsewhere.⁵⁵ Figure 6a shows the SF-SSP spectra of methanol–D₂O mixtures of various compositions at an OTS-covered silica surface in the C–H stretching range. Two peaks appear in the 2800–2900 cm⁻¹ range: the $-\text{CH}_3$ r^+ modes for methanol at 2835 cm⁻¹, and OTS at 2872 cm⁻¹. They resemble those observed at air/OTS^{48,49} and methanol/vapor^{56,57} interfaces. By measuring and analyzing spectra with different input/output polarization combinations, we found that the orientation of the C₃ axis of the methyl group of methanol tilts at about 35° from surface normal. The methanol methyl groups face the methyl groups of OTS and remain nearly the same for all methanol concentrations. We could then use the strength of the r^+ mode to deduce the methanol number density at the interface and obtain the adsorption isotherm for methanol shown in Figure 6b. Methanol adsorption at OTS is obviously more favored than water. The deduced adsorption free energy for methanol is about -7.0 kJ/mol. The finding that alcohol preferentially adsorbs at an OTS-coated substrate should be generally true for water mixtures with other alcohols.

TABLE 1: Peak Positions (ω_q : cm⁻¹) and Line Width (Γ : cm⁻¹) of C2–C4 Alcohol at the Liquid/Silica Interface

| | methyl symmetric mode (r^+) | | methyl antisymmetric mode (r^-) | | Fermi resonance | | other ($-\text{CH}$ or $-\text{CH}_2$) | | |
|----------------------|---------------------------------|----------|-------------------------------------|----------|-----------------|----------|--|----------|------|
| | ω_q | Γ | ω_q | Γ | ω_q | Γ | ω_q | Γ | |
| ethanol | 2878 | 8.6 | 2976 | 12.3 | 2930 | 9.0 | | | |
| 1-propanol | 2877 | 9.4 | 2961 | 14.0 | 2950 | 10.0 | 2913 (CH ₂ asym) | | 12.5 |
| 2-propanol | 2878 | 9.0 | 2967.5 | 13.0 | 2950 | 19.4 | 2916 (CH sym) | | 9.0 |
| <i>tert</i> -butanol | 2978 | 9.0 | 2970.0 | 14.5 | 2923 | 2956 | | | 10.5 |

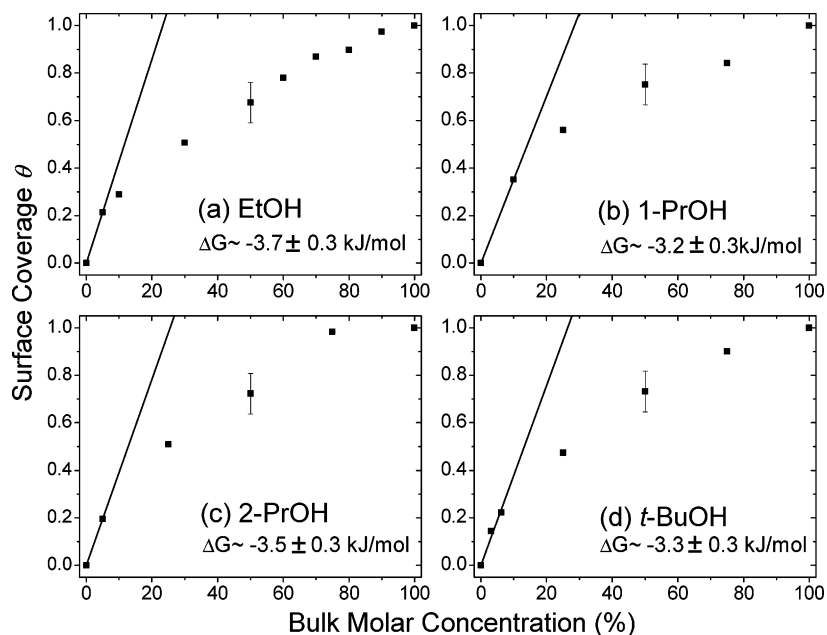


Figure 4. Adsorption isotherms of alcohols obtained from SF vibrational spectra in Figure 3 for alcohol–water mixtures at a hydrophilic substrate: (a) ethanol, (b) 1-propanol, (c) 2-propanol, and (d) *tert*-butanol.

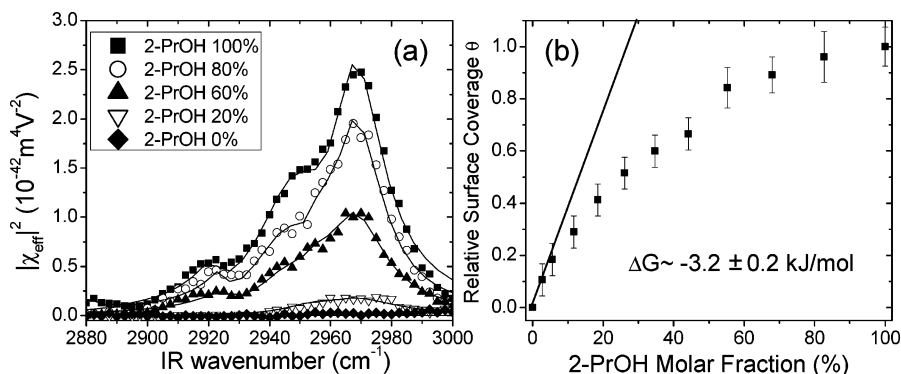


Figure 5. (a) SFG spectra and (b) propanol adsorption isotherm for 2-propanol–methanol mixtures at a hydrophilic substrate (fused silica).

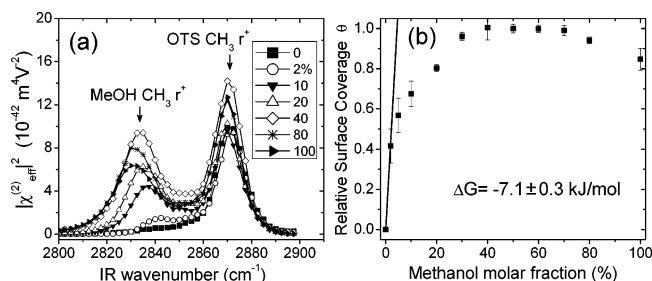


Figure 6. (a) SFG spectra and (b) methanol adsorption isotherm for methanol–D₂O mixtures at a hydrophobic substrate (OTS-covered silica).

2-Propanol–Methanol Mixtures. It is also interesting to know how different alcohols compete in adsorption on a hydrophobic surface. We studied competitive adsorption of methanol and 2-propanol on an OTS-covered surface where both alcohols have their methyl terminal facing OTS. Figure 7a gives the SSP sum-frequency spectra of interfaces of 2-propanol–methanol mixtures with OTS-covered fused silica. Because the r^+ mode of 2-propanol overlaps with that of OTS at 2870 cm^{-1} and the r^- mode of 2-propanol is weak, we had to use the r^+ mode of methanol at 2835 cm^{-1} to find the surface coverage of methanol, following the same analysis described earlier in Section 4.2. The deduced adsorption isotherm for 2-propanol (converted from methanol surface coverage) is shown in Figure 7b. We find that

2-propanol adsorbs preferentially with a free energy reduction of about -3.8 kJ/mol, which is less negative than the ΔG of -7.0 kJ/mol of methanol from the methanol–water mixture on OTS.

We want to point out that surface coverage of alcohols at hydrophilic and hydrophobic interfaces appears to have different meanings. At a hydrophilic interface, alcohol molecules adsorb from alcohol–water mixtures in dimer-like units, and the surface coverage corresponds to the surface density of the dimeric units. At a hydrophobic surface, this does not happen and the surface coverage corresponds to surface density of individual alcohol molecules.

5. Discussion

At both hydrophobic and hydrophilic substrates, alcohol molecules adsorb preferentially than water from alcohol–water mixtures, despite the stark differences in molecular interactions of the two interfaces. We discuss in this section our qualitative understanding of how molecular interactions can lead to the observed results.

First let us consider adsorbate–substrate interactions. At the fused silica surface, both water and alcohol molecules form hydrogen bonds with the surface silanol groups with about the same strength.^{58,59} The van der Waals interactions between adsorbates and silica are negligible comparing with H-bond.^{60,61}

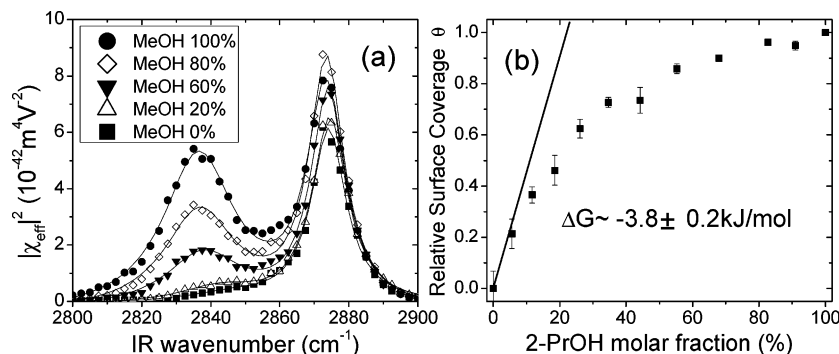


Figure 7. (a) SFG spectra and (b) propanol adsorption isotherm for a 2-propanol–methanol mixture at a hydrophobic substrate (OTS covered silica). The surface coverage of 2-propanol was converted from the measured methanol coverage.

Knowing that entropy is larger with more mixing of alcohol and water, minimization of free energy is not able to explain preferential adsorption of alcohols on silica. At the OTS-covered surface, both alcohol and water do not wet the surface. Unlike the case of alcohols on silica, no alcohol adsorption from vapor on OTS could be detected with SFVS. Although the van der Waals interaction between alcohol and OTS is larger than that between water and OTS, it is still several times weaker than hydrogen bonds (~ 1 kcal/mol versus ~ 4 kcal/mol). Thus the difference between interaction energies of alcohol and water with fused silica or with OTS-covered substrate cannot explain the observed preferential adsorption of alcohol at either surface. Obviously, the driving force behind competitive adsorption here is not just the adsorbate–substrate interaction, but, more importantly, the interactions between molecules at the interfacial region.

There are generally three factors in the free energy consideration that affect the interfacial structure: adsorbate–substrate interactions, intermolecular interactions in the interfacial liquid layer, and entropy.^{62,63} Sufficiently stronger interaction between molecules of the same species than other intermolecular interactions in a mixture tends to keep molecules of that species together and exclude the other species from the molecular network. Entropy of mixing, on the other hand, favors complete mixing of molecules of different species. For alcohol–water mixtures, the preferential adsorption of alcohol apparently must come from the first factor. We focus here on hydrogen bonding, which is the dominant attractive interaction between molecules.

We denote the overall binding energy between a certain molecule i with surround molecules j to be U_{ij} . Now the molecular interactions we consider are water–water, water–alcohol, and alcohol–alcohol molecular interactions: U_{ww} , U_{wa} , and U_{aa} , respectively. If the hydrogen bonds between different species are taken to be of roughly the same strength, then the difference in U_{ij} is proportional to the average number of hydrogen bonds formed by each species. In terms of the number of hydrogen bonds, Soper et al. found that U_{ww} is ~ 1.4 times U_{aw} and ~ 2 times U_{aa} .¹¹ In pure water, there are ~ 3.6 hydrogen bonds per molecule, while in pure methanol, there are only ~ 1.8 .^{11,64} This suggests that even for water–alcohol mixtures, water molecules like to retain their hydrogen-bonding structure in pure water, and at relatively low alcohol concentrations, alcohol molecules could be pushed to form clusters, as revealed in recent X-ray spectroscopy^{9,10} and neutron scattering studies.^{11–13,65,66} At an interface, to maximize the number of hydrogen bonds, alcohol molecules tend to be pushed to the interface for water to closely maintain most of their three-dimensional hydrogen-bonding structure. This leads to the preferential adsorption of alcohol. The equilibrium interfacial structure results of course from the balance of enthalpy

(preferential adsorption) and entropy (more complete mixing) contributions to the interfacial free energy. The dominance of intermolecular interactions in the free energy, however, makes alcohol preferentially adsorb than water irrespective of the surface, and entropy appears to play only a secondary role. Israelachvili described the interaction between solute (alcohol) and water as follows: “It is well to note that their interaction with water is actually attractive, due to the dispersion force, though the interaction of water with itself is much more attractive. Water simply loves itself too much to let some substances get in its way.”⁶⁷

There is some difference between the preferential alcohol adsorptions at hydrophilic and hydrophobic surfaces. The stronger interactions of water and alcohol with silica, compared to the interactions with OTS, reduce the effective driving force discriminating water from alcohol in the adsorption. This is seen in the difference of adsorption free energies of alcohols: -3.2 to -3.7 kJ/mol at fused silica as compared to -7.0 kJ/mol for methanol at OTS. For 2-propanol–methanol mixtures, the value of ΔG for liquid/silica (-3.0 kJ/mol) is smaller in absolute value than that for liquid/OTS (-3.8 kJ/mol), which agrees with alcohol–water studies.

We have ignored lateral interactions between hydrocarbon groups of adsorbed alcohol molecules in interfacial layers. Previous study on co-adsorption of long-chain alcohol and alkylamine molecules on silica showed that van der Waals interactions between long alkyl chains contribute significantly to the adsorption process.⁶⁸ In our case, however, the chain–chain interaction is weak because the alcohols we have studied have short chains, *tert*-butanol being the one with the longest chains. The fact that there is no significant difference in ΔG (see Figure 4) for ethanol, 1-propanol, 2-propanol, and *tert*-butanol indicates that the chain–chain interaction of alcohol molecules is indeed negligible.

The above picture suggests in general that the stronger interactions among molecules of one species tend to cause the weakly interacting species in a mixture to preferentially adsorb at an interface. This picture is further supported by our observations that 2-propanol preferentially adsorbs from 2-propanol–methanol mixtures to both the hydrophilic fused silica surface and the hydrophilic OTS-covered surface. The interaction strengths of 2-propanol and methanol with the surfaces are expected to be about the same. Again, the preferential adsorption originates from intermolecular interactions. It is generally accepted that methanol has more average hydrogen bonds per molecule than 2-propanol in liquid. The stronger hydrogen-bonding interaction among methanol molecules tends to push 2-propanol in a mixture to the interface, but because the interaction is not as strong as that between water, the adsorption free energy for propanol in methanol–propanol mixtures is not

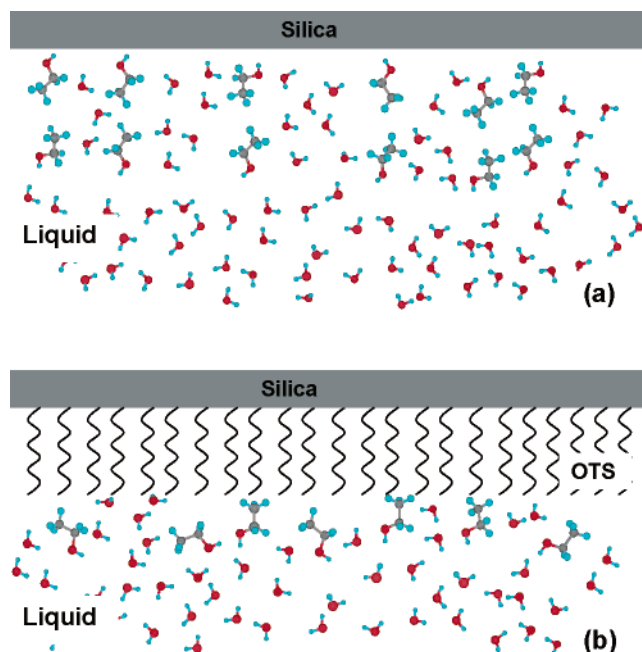


Figure 8. Schematics describing the interfacial structure of an ethanol–water mixture at (a) a hydrophilic surface and (b) a hydrophobic surface.

as negative as that in water–propanol mixtures. ($\Delta G \approx -3.0$ kJ/mol compared to -3.5 kJ/mol at fused silica). At the OTS-covered surface, since we do not have data on propanol–water mixtures, we compare ΔG of propanol–methanol mixtures with that of methanol–water mixtures, which is -3.8 kJ/mol compared to -7.0 kJ/mol. The propanol–water mixture is expected to have a ΔG close to -7.0 kJ/mol knowing that 2-propanol has only a slightly weaker hydrogen bond interaction than methanol.

In Figure 8, we present a sketch to illustrate the interfacial structures of an alcohol–water mixture at hydrophilic and hydrophobic interfaces. In the former case, pairs of head-to-head alcohol molecules (dimeric units) adsorb with the hydroxyl terminals hydrogen bonded to the hydrophilic surface. Wang et al. also proposed similar dimer structure from an atomic force microscopy study.⁶⁹ In the case of hydrophobic substrate, monomers of alcohol molecules adsorb to the OTS alkyl chains by van der Waals interaction with the methyl groups facing the surface.

6. Conclusions

Using SFVS, we have studied competitive adsorption of alcohol–water mixtures at hydrophilic fused silica and hydrophobic OTS-covered surfaces. Water-miscible short-chain alcohols—methanol, ethanol, 1-propanol, 2-propanol, and *tert*-butanol—have been investigated. From spectra obtained with different input/output polarization combinations, we found that the orientations of alcohol molecules at the mixture/substrate interfaces do not change appreciably with bulk alcohol concentration. This result allowed us to use the strength of methyl stretching modes in the spectra to deduce the surface densities of alcohol molecules and the adsorption isotherms of alcohols from alcohol–water mixtures. Assuming Langmuir adsorption kinetics at low alcohol concentrations, we extracted the adsorption free energies of different alcohols at the two substrates. We discovered that alcohols always preferentially adsorb at the interface, whether it is hydrophilic or hydrophobic. This cannot be explained by the difference in interaction strengths of water and alcohol with the surfaces because they do not differ

appreciably at both silica and OTS surfaces. It is the stronger hydrogen-bonding interactions among water molecules that tend to segregate alcohol molecules preferentially to the interfaces. The effect is more pronounced if the molecule–substrate interaction is weaker, as in the case of the hydrophobic OTS-covered surface. The same principle applies to competitive adsorption between different alcohol molecules. Our measurement showed that 2-propanol from 2-propanol–methanol mixtures preferentially adsorb at both fused silica and OTS-covered surfaces, although not as much as from 2-propanol–water mixtures. The result can be understood knowing that the hydrogen-bonding interactions among methanol molecules are stronger than methanol–propanol and propanol–propanol interactions, but not as strong as among water molecules.

In analyzing SF spectra of alcohols at fused silica interfaces, we recognized that the alcohol molecules must adsorb at the interface as dimer pairs with the methyl groups of the two molecules more or less facing each other and the hydroxyl group of one alcohol hydrogen bonded to silica. This configuration is obviously favored by the hydrogen-bonding interactions among molecules. At the OTS-covered surface, on the other hand, the hydrogen-bonding interactions favor adsorption of alcohol monomers.

Interfacial structures of hydrogen-bonding liquid mixtures are important in many practical applications. Here, we provide a qualitative molecular-level understanding of competitive adsorption of two completely miscible hydrogen-bonding liquids. The underlying principle could even be extended to non-hydrogen-bonded liquids. However, to confirm our picture, more serious theoretical investigations on the subject are needed.

Acknowledgment. This work was supported by the NSF Science and Technology Center of Advanced Materials for Purification of Water with Systems (Water CAMPWS; CTS-0120978). W.T.L. was supported by the Department of Energy under Contract No. DE-AC03-76SF00098.

References and Notes

- (1) Kiplin, J. J. *J. Colloid Sci.* **1963**, *18*, 502.
- (2) Katz, K. D.; Lochmuller, C. H.; Scott, R. P. W. *Anal. Chem.* **1989**, *61*, 349.
- (3) Scott, R. P. W. *Analyst* **2000**, *125*, 1543.
- (4) Soper, A. K.; Finney, J. L. *Phys. Rev. Lett.* **1993**, *71*, 4346.
- (5) D'Angelo, M.; Onori, G.; Santucci, A. *J. Chem. Phys.* **1994**, *100*, 3107.
- (6) Wakisaka, A.; Abdoul-Carime, H.; Yamamoto, Y.; Kiyozumi, Y. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 369.
- (7) Dixit, S.; Poon, W. C. K.; Crain, J. J. *Phys.: Condens. Matter* **2000**, *12*, L323.
- (8) Wilson, K. R.; Schaller, R. D.; Co, D. T.; Saykally, R. J.; Rude, B. S.; Catalano, T.; Bozek, J. D. *J. Chem. Phys.* **2002**, *117*, 7738.
- (9) Guo, J. H.; Luo, Y.; Augustsson, A.; Kashtanov, S.; Rubensson, J. E.; Shuh, D. K.; Agren, H.; Nordgren, J. *Phys. Rev. Lett.* **2003**, *91*, 157401.
- (10) Guo, J. H.; Luo, Y.; Augustsson, A.; Kashtanov, S.; Rubensson, J. E.; Shuh, D. K.; Zhuang, V.; Ross, P.; Agren, H.; Nordgren, J. *J. Electron Spectrosc.* **2004**, *137*, 425.
- (11) Dixit, S.; Crain, J.; Poon, W. C. K.; Finney, J. L.; Soper, A. K. *Nature* **2002**, *416*, 829.
- (12) Dougan, L.; Bates, S. P.; Hargreaves, R.; Fox, J. P.; Crain, J.; Finney, J. L.; Reat, V.; Soper, A. K. *J. Chem. Phys.* **2004**, *121*, 6456.
- (13) Finney, J. L.; Bowron, D. T.; Daniel, R. M.; Timmins, P. A.; Roberts, M. A. *Biophys. Chem.* **2003**, *105*, 391.
- (14) Okazaki, S.; Touhara, H.; Nakanishi, K. *J. Chem. Phys.* **1984**, *81*, 890.
- (15) Ferrario, M.; Haughney, M.; McDonald, I. R.; Klein, M. L. *J. Chem. Phys.* **1990**, *93*, 5156.
- (16) Allison, S. K.; Fox, J. P.; Hargreaves, R.; Bates, S. P. *Phys. Rev. B* **2005**, *71*, 024201.
- (17) Tarek, M.; Tobias, D. J.; Klein, M. L. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 559.
- (18) Chang, T. M.; Dang, L. X. *J. Phys. Chem. B* **2005**, *109*, 5759.

- (19) Matsumoto, M.; Takaoka, Y.; Kataoka, Y. *J. Chem. Phys.* **1993**, *98*, 1464.
- (20) Stewart, E.; Shields, R. L.; Taylor, R. S. *J. Phys. Chem. B* **2003**, *107*, 2333.
- (21) Wakisaka, A.; Ohki, T. *Faraday Discuss.* **2005**, *129*, 231.
- (22) Yilmaz, H. *Turk. J. Phys.* **2002**, *26*, 243.
- (23) Barraclough, C. G.; McTigue, P. T.; Ng, Y. L. *J. Electroanal. Chem.* **1992**, *329*, 9.
- (24) Wang, P.; Anderko, A. *Ind. Eng. Chem. Res.* **2003**, *42*, 3495.
- (25) Li, Z. X.; Lu, J. R.; Styrcas, D. A.; Thomas, R. K.; Rennie, A. R.; Penfold, J. *Mol. Phys.* **1993**, *80*, 925.
- (26) Li, Z. X.; Lu, J. R.; Thomas, R. K.; Rennie, A. R.; Penfold, J. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 565.
- (27) Raina, G.; Kulkarni, G. U.; Rao, C. N. R. *J. Phys. Chem. A* **2001**, *105*, 10204.
- (28) Wolfrum, K.; Graener, H.; Laubereau, A. *Chem. Phys. Lett.* **1993**, *213*, 41.
- (29) Ma, G.; Allen, H. C. *J. Phys. Chem. B* **2003**, *107*, 6343.
- (30) Chen, H.; Gan, W.; Lu, R.; Guo, Y.; Wang, H. F. *J. Phys. Chem. B* **2005**, *109*, 8064.
- (31) Sung, J.; Park, K.; Kim, D. *J. Korean Phys. Soc.* **2004**, *44*, 1394.
- (32) Kimura-Suda, H.; Petrovykh, D. Y.; Tarlov, M. J.; Whitman, L. J. *J. Am. Chem. Soc.* **2003**, *125*, 9014.
- (33) Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*, 6th ed.; Wiley and Sons: New York, 1997.
- (34) Guiochon, G.; Shirazi, S. G.; Katti, A. M. *Fundamentals of Preparative and Nonlinear Chromatography*; Academic Press: Boston, MA, 1994.
- (35) Quinones, I.; Guiochon, G. *J. Chromatogr. A* **1996**, *734*, 83.
- (36) Dong, Y.; Xu, Z. *Langmuir* **1999**, *15*, 4590.
- (37) Henry, M. C.; Yang, Y.; Pizzolatto, R. L.; Messmer, M. C. *Langmuir* **2003**, *19*, 2592.
- (38) Devlin, J. P.; Uras, N.; Sadlej, J.; Buch, V. *Nature* **2002**, *417*, 269.
- (39) Li, G.; Ye, S.; Morita, S.; Nishida, T.; Osawa, M. *J. Am. Chem. Soc.* **2004**, *126*, 12198.
- (40) Ostroverkhov, V.; Waychunas, G. A.; Shen, Y. R. *Phys. Rev. Lett.* **2005**, *94*, 046102.
- (41) Shen, Y. R. In *Frontiers in Laser Spectroscopy, Proceedings of the International School of Physics 'Enrico Fermi'*; Hansch, T. W., Inguscio, M., Eds.; Course CXX, North-Holland: Amsterdam, The Netherlands, 1994; pp 139–165.
- (42) Miranda, P. B.; Shen, Y. R. *J. Phys. Chem. B* **1999**, *103*, 3292.
- (43) Chen, Z.; Shen, Y. R.; Somorjai, G. A. *Annu. Rev. Phys. Chem.* **2002**, *53*, 437.
- (44) Richmond, G. L. *Chem. Rev.* **2002**, *102*, 2693.
- (45) Shultz, M. J.; Baldelli, S.; Schnitzer, C.; Simonelli, D. *J. Phys. Chem. B* **2002**, *106*, 5313.
- (46) Wolfrum, K.; Lobau, J.; Laubereau, A. *Appl. Phys. A: Solids Surf.* **1994**, *59*, 605.
- (47) Sagiv, J. *J. Am. Chem. Soc.* **1980**, *102*, 92.
- (48) Guyot-Sionnet, P.; Superfine, R.; Hunt, J. H.; Shen, Y. R. *Chem. Phys. Lett.* **1988**, *144*, 1.
- (49) Liu, Y.; Wolf, L. K.; Messmer, M. C. *Langmuir* **2001**, *17*, 4329.
- (50) Wei, X.; Miranda, P. B.; Zhang, C.; Shen, Y. R. *Phys. Rev. B* **2002**, *66*, 085401.
- (51) Zhang, J. Y.; Huang, J. Y.; Shen, Y. R.; Chen, C. J. *Opt. Soc. Am. B* **1993**, *19*, 1758.
- (52) Kim, D. Ph.D. Thesis, Department of Physics, University of California, Berkeley, 1997.
- (53) Liu, W.; Zhang, L.; Shen, Y. R. *Chem. Phys. Lett.* **2005**, *412*, 206.
- (54) Simonelli, D.; Shultz, M. J. *J. Chem. Phys.* **2000**, *112*, 6804.
- (55) Liu, W.; Zhang, L.; Shen, Y. R. *J. Chem. Phys.* **2006**, *125*, 144711.
- (56) Stanners, C. D.; Du, Q.; Chin, R. P.; Cremer, P.; Somorjai, G. A.; Shen, Y. R. *Chem. Phys. Lett.* **1995**, *232*, 407.
- (57) Lu, R.; Gan, W.; Wu, B. H.; Zhang, Z.; Guo, Y.; Wang, H. F. *J. Phys. Chem. B* **2005**, *109*, 14118.
- (58) Pelmenschikov, A. G.; Morosi, G.; Gamba, A. *J. Phys. Chem. A* **1997**, *101*, 1178.
- (59) Natal-Santiago, M. A.; Dumesic, J. A. *J. Catal.* **1998**, *175*, 252.
- (60) Fowkes, F. M. *Physico-Chemical Aspects of Polymer Surfaces*; Mittal, K. L., Ed.; Plenum: New York, 1983; Vol. 2, p 583.
- (61) van Oss, C. J.; Chaudhury, M. K.; Good, R. J. *Adv. Colloid Interface Sci.* **1987**, *28*, 35.
- (62) Fang, F.; Szleifer, I. *Langmuir* **2002**, *18*, 5497.
- (63) Fang, F.; Szleifer, I. *J. Chem. Phys.* **2003**, *19*, 1053.
- (64) Yamaguchi, T.; Hidaka, K.; Soper, A. K. *Mol. Phys.* **1999**, *96*, 1159.
- (65) Soper, A. K.; Finney, J. L. *Phys. Rev. Lett.* **1993**, *26*, 4346.
- (66) Dixit, S.; Soper, A. K.; Finney, J. L.; Crain, J. *Europhys. Lett.* **2002**, *59*, 377.
- (67) Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic Press: London, UK, 1985.
- (68) Vidyadhar, A.; Rao, K. H.; Chernyshova, I. V.; Pradip Forsberg, K. S. E. *J. Colloid Interface Sci.* **2002**, *256*, 59.
- (69) Wang, L.; Song, Y.; Zhang, B.; Wang, E. *Thin Solid Films* **2004**, *458*, 197.