

OFFICE OF NAVAL RESEARCH

Grant N00014-89-J-1261

R&T Code 4131038

ONR Technical Report #27

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Observed by Vibrational Sum Frequency Generation
by

D. E. Gragson, B. M. McCarty, and G. L. Richmond

J. Amer. Chem. Soc., 119 (6144) 1997

Department of Chemistry
1253 University of Oregon
Eugene, OR 97403

June 1998

19980623 044

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DTIC QUALITY INSPECTED 1

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE 30 May 1998		3. REPORT TYPE AND DATES COVERED Technical 6/1/97-5/31/98
4. TITLE AND SUBTITLE Ordering of Interfacial Water Molecules at the Charged Air/Water Interface Observed by Vibrational Sum Frequency Generation			5. FUNDING NUMBERS N00014-89-J-1261	
6. AUTHOR(S) D. E. Gragson, B. M. McCarty, and G. L. Richmond				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Dept. of Chemistry University of Oregon Eugene, OR 97403			8. PERFORMING ORGANIZATION REPORT NUMBER ONR Technical Report #27	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Dr. Peter Schmidt Office of Naval Research Physical Science and Technology, ONR 331 800 North Quincy Street Arlington, VA 22217-5000			10. SPONSORING/MONITORING AGENCY	
11. SUPPLEMENTARY NOTES J. Amer. Chem. Soc., 119 (6144) 1997				
12A. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release: distribution unlimited			12B. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Please see attached abstract				
14. SUBJECT TERMS Molecular Structure and Orientation of Interfacial Water Molecules at the Air/Water Interface			15. NUMBER OF PAGES 36	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT	

Ordering of Interfacial Water Molecules at the Charged Air/Water Interface Observed by Vibrational Sum Frequency Generation

D. E. Gragson, B. M. McCarty, and G. L. Richmond

Department of Chemistry, University of Oregon, Eugene, OR 97403

Abstract

The molecular structure and orientation of interfacial water molecules at the air/water interface in the presence of soluble cationic and anionic surfactants has been characterized. We have employed vibrational sum frequency generation (VSFG) to probe the orientation of interfacial water molecules as a function of both bulk surfactant concentration and solution ion strength. The observed ordering of interfacial water molecules is manifested by an enhancement of the OH stretching modes in the VSFG spectra. We attribute the observed enhancement to an alignment of the interfacial water molecules induced by the large electrostatic field present at these charged interfaces. The nature of this enhancement is further explored by studying mixed (cationic and anionic) surfactant systems as well as surfactant systems at different ionic strengths. From these studies we find that the interfacial water molecules attain their highest degree of alignment at surface surfactant concentrations well below maximum surface coverage.

Introduction

Surfactants have found widespread useage in many industrial applications. Commercially available surfactants can be found in a range of products including motor oils, lubricants, detergents and soaps. In addition they are used in the manufacture of many common materials such as plastics and textiles and are also used in the oil industry for enhanced and tertiary oil recovery. From a biological standpoint, the structure and order of surfactants along with their interactions with other surface molecules play a crucial role in many processes. However, even with their widespread application, the molecular structure of surfactants as they reside at oil/water,^{1,2} air/water,³⁻¹² and solid/water¹³⁻¹⁵ interfaces has only recently been determined. At present many questions concerning the physical behavior of surfactants at these interfaces remain unanswered. For example, at the water surface, where it is well known that the presence of a surfactant lowers the surface tension, experimental evidence for how the molecular structure of the highly coordinated surface water molecules changes with increasing surfactant concentration is nearly nonexistent.

The focus of the work in this paper is on understanding how the presence and molecular structure of surfactants alter the orientation of water molecules at the air/water interface. The molecular structure of *both water and* surfactant molecules at the surface are monitored with the surface sensitive technique of vibrational sum frequency generation (VSFG). In a previous letter³ we described our preliminary results regarding the ordering and orientation of interfacial water molecules at the air/water interface resulting from the presence of cationic and anionic surfactants at the surface. Water molecules at the surface were found to be highly oriented, with the alignment attributed to the large electrostatic field created in the interfacial region by the charged surfactant present at the water surface. X-ray scattering studies at the charged electrode/water interface have also shown the interfacial water molecules to be highly oriented.^{16,17} Previous second harmonic generation (SHG)

and VSFG studies at the charged quartz/water interface^{18,19} have shown that water molecules near a charged interface are highly oriented. Eisenthal and coworkers attributed an observed change in the sign of the SH response from the water surface in the presence of insoluble cationic and anionic surfactants to the differing alignment of water molecules for the oppositely charged surfactants.²⁰

For an aqueous solution of a soluble surfactant the concentration of surfactant molecules at the surface, or the surface density, is dependent on the bulk surfactant concentration up to the point where a monolayer has formed on the surface. Once monolayer coverage has been reached the surface density generally remains constant with increasing bulk concentration below the critical micelle concentration (cmc). Above the cmc increasing the bulk surfactant concentration leads to micelle formation while the surface concentration remains constant. These surfactant molecules are amphiphilic and thus have a hydrophilic end, or head group, pointing into the water and hydrophobic end, or tail, pointing away from the water. For some of the surfactants studied here, the head groups of the surfactant molecules are charged which results in the formation of an electrostatic field in the interfacial region. By probing the vibrational structure of both the water molecules and the surfactant molecules at the air/water interface we have shown that water molecules are indeed highly oriented in the presence of charged surfactants and that the direction of orientation depends upon the surface charge of the surfactant.³ We have attributed the ordering or alignment of the interfacial water molecules to the large electrostatic field in the interfacial region produced by the surface charge. Since the direction of the electrostatic field is dependent on the sign of the surface charge we have studied the order of interfacial water molecules with both cationic and anionic surfactants present at the surface. Our studies provide direct evidence that the direction of the electrostatic field at the interface causes water molecules to align in opposite directions for the surfactant charges of opposite sign. The opposing alignment is manifested by an interference between CH and OH stretching modes that is constructive for anionic

surfactants and destructive for cationic surfactants. It is this interference between these vibrational modes as well as other spectral features which allow us to obtain unique insight into water-surfactant interactions at the air/water interface.

Background

Vibrational sum frequency generation (VSFG) is a nonlinear optical technique that has been extensively used in the study of surfaces and interfaces.^{1,4,6,9} Since VSFG is a second order nonlinear process it is inherently surface sensitive. Further, for VSFG one combines a tunable infrared laser beam with a visible laser beam at a surface or interface. These two aspects of VSFG allow one to obtain a vibrational spectrum of molecules at an interface. The VSFG intensity is proportional to the square of the surface nonlinear susceptibility $\chi_s^{(2)}(\omega_{\text{sfg}}=\omega_{\text{vis}}+\omega_{\text{ir}})$ as

$$I_{\text{sfg}} \propto |\mathbf{P}_{\text{sfg}}|^2 \propto \left| \chi_{\text{NR}}^{(2)} + \sum_{\nu} |\chi_{\text{R}_{\nu}}^{(2)}| e^{i\gamma_{\nu}} \right|^2 I_{\text{vis}} I_{\text{ir}} \quad (1)$$

where \mathbf{P}_{sfg} is the nonlinear polarization at ω_{sfg} , χ_{NR} and $\chi_{\text{R}_{\nu}}$ are the non-resonant and resonant parts of $\chi_s^{(2)}$, γ_{ν} is the relative phase of the ν^{th} vibrational mode, and I_{vis} and I_{ir} are the visible and IR intensities. Since the susceptibility is in general complex the resonant terms in the summation are associated with a relative phase γ_{ν} which is used to account for any interference between two modes which overlap in energy. $\chi_{\text{R}_{\nu}}^{(2)}$ is also proportional to the number density of molecules, N , and the orientationally averaged molecular hyperpolarizability, β_{ν} , as follows

$$\chi_{\text{R}_{\nu}}^{(2)} = \frac{N}{\epsilon_0} \langle \beta_{\nu} \rangle. \quad (2)$$

Thus the square root of the measured SF intensity is proportional to the number density of molecules at the surface or interface. The molecular hyperpolarizability, β_v , is enhanced when the frequency of the IR field is resonant with a SF-active vibrational mode from a molecule at the surface or interface. This enhancement in β_v leads to an enhancement in the nonlinear susceptibility $\chi_{R_v}^{(2)}$ which can be expressed as

$$\chi_{R_v}^{(2)} \propto \frac{A_v}{\omega_v - \omega_{ir} - i\Gamma_v} \quad (3)$$

where A_v is the intensity of the v^{th} mode and is proportional to the product of the Raman and the IR transition moments, ω_v is the resonant frequency, and Γ_v is the line width of the transition. Since the intensity term, A_v , is proportional to both the IR and Raman transition moments, only vibrational modes which are both IR and Raman active will be SF-active. Thus molecules or vibrational modes which possess an inversion center will not be SF-active. The fact that some vibrational modes are SF-active and some are SF-inactive has a direct consequence on the study of monolayers of surfactants with alkyl chains. Specifically, surfactant molecules which are in the all-*trans* conformation possess a local inversion center along the C-C bond which renders the CH_2 symmetric stretching mode SF-inactive. However, this local inversion symmetry is lifted when there are *gauche* defects along the alkyl chain and the CH_2 modes become SF-active. Comparison of the intensities of CH_2 and CH_3 modes in the VSFG spectra has allowed researchers to monitor the relative order of various surfactants in terms of the amount of *gauche* defects present in the alkyl chains at the air/water^{4,7-9}, solid/water¹³⁻¹⁵ and oil/water^{1,2} interfaces.

In general the surface susceptibility $\chi_s^{(2)}$ is a 27 element tensor, however it can often be reduced to several nonvanishing elements by invoking symmetry constraints. Liquid surfaces as well as monolayers on liquid surfaces are isotropic in the plane of the surface.

The symmetry constraints for an in-plane isotropic surface reduces $\chi_s^{(2)}$ down to the following four independent non-zero elements

$$\chi_{zzz}^{(2)}; \chi_{xxz}^{(2)} = \chi_{yyz}^{(2)}; \chi_{xzx}^{(2)} = \chi_{zyy}^{(2)}; \chi_{zxx}^{(2)} = \chi_{zyy}^{(2)} \quad (4)$$

where \mathbf{z} is defined to be the direction normal to the surface. These four independent elements contribute to the VSFG under four different polarization conditions as follows

$$I_{ssp} \propto |F_i f_i f_z \chi_{iiz}^{(2)}|^2 \quad (5a)$$

$$I_{sps} \propto |F_i f_z f_i \chi_{izi}^{(2)}|^2 \quad (5b)$$

$$I_{pss} \propto |F_z f_i f_i \chi_{zii}^{(2)}|^2 \quad (5c)$$

$$I_{ppp} \propto |F_z f_i f_i \chi_{zii}^{(2)} + F_i f_z f_i \chi_{izi}^{(2)} + F_i f_i f_z \chi_{iiz}^{(2)} + F_z f_z f_z \chi_{zzz}^{(2)}|^2 \quad (5d)$$

where the polarizations are listed in the order of decreasing frequency (sf,vis,ir), the subscript i denotes x or y polarizations and F and f are the Fresnel coefficients for the reflected and incident waves respectively. Which vibrational modes are present under a certain polarization condition depends on the polarization of the IR field and the direction of the IR and Raman transition moments. The SSP polarization condition accesses vibrational modes with transition moments which have components perpendicular to the surface plane whereas the SPS and PSS polarization conditions accesses modes which have transition moments with components parallel to the surface plane. Since the intensity under PPP polarization conditions is dependent on all of the tensor elements, vibrational modes with components both perpendicular and parallel to the surface plane will be present in the VSFG spectra. Most of the vibrational modes of interfacial molecules essential to the description of the systems studied here possess transition moments with components out of the plane of the surface. Consequently we primarily use the SSP polarization condition. However, verification of the peak assignments has been made from spectra using all of the polarization combinations.

At the charged air/water interface a significant surface charge exists which produces a large electrostatic field E_0 . This electrostatic field can make an additional contribution to the non-linear polarization induced at the interface by the optical fields E_{vis} and E_{ir} through a third order polarization term $\chi^{(3)}$ as follows

$$P_{\text{sfg}} = \chi^{(2)} : E_{\text{vis}} E_{\text{ir}} + \chi^{(3)} : E_{\text{vis}} E_{\text{ir}} E_0. \quad (6)$$

The second term in equation (6) is the third order polarization term, $P_{\text{sfg}}^{(3)}$, and contains the electrostatic field dependence of the nonlinear polarization induced at the interface. Both $\chi^{(3)}$ and $\chi^{(2)}$ have resonant and non-resonant portions as described above and in fact the overall SF response can be represented by an effective surface susceptibility which is a combination of $\chi^{(3)}$ and $\chi^{(2)}$. The third order contribution to the nonlinear polarization results from several factors, namely the electronic nonlinear polarizability, $\alpha^{(3)}$, the alignment of the interfacial water molecules by the electrostatic field E_0 , and the magnitude of the electrostatic field E_0 . In the absence of a large electrostatic field one would expect the interfacial water molecules to be randomly oriented after a few water layers and thus not contribute to the nonlinear polarization. The presence of a large electrostatic field aligns the interfacial water molecules beyond the first few water layers and thus removes the centrosymmetry over this region allowing more water molecules to contribute to the nonlinear polarization.

Second harmonic studies at the air/water interface with an insoluble charged surfactant present have shown²⁰ that the SHG intensity is dependent on the interfacial potential which, in turn, is dependent on the surface charge density and the ionic strength of the surfactant solution. The relationship between $P_{\text{sfg}}^{(3)}$ and the interfacial potential can

be obtained²⁰ by integrating $\mathbf{P}_{\text{sfg}}^{(3)}$ over the region where the electrostatic field, \mathbf{E}_0 , is present

$$\mathbf{P}_{\text{sfg}}^{(3)} = \chi^{(3)} \mathbf{E}_{\text{vis}} \mathbf{E}_{\text{ir}} \int_0^\infty \mathbf{E}_0 dz. \quad (7)$$

Assuming $\chi^{(3)}$ is constant over the interfacial region and using the relationship between the electrostatic field $\mathbf{E}(\mathbf{z})$ and the interfacial potential $\Phi(\mathbf{z})$ equation (7) can be combined with equation(6) to give

$$\begin{aligned} P_{\text{sfg}} &= \chi^{(2)} \mathbf{E}_{\text{vis}} \mathbf{E}_{\text{ir}} + \chi^{(3)} \mathbf{E}_{\text{vis}} \mathbf{E}_{\text{ir}} \Phi(0) \\ &= [\chi^{(2)} + \chi^{(3)} \Phi(0)] \mathbf{E}_{\text{vis}} \mathbf{E}_{\text{ir}} \end{aligned} \quad (8)$$

Equation (8) demonstrates the linear dependence of the nonlinear polarization on the interfacial potential.

Eisenthal and coworkers have shown that for charged surfactants at the air/water interface the dependence of the interfacial potential on the ionic strength and the surface charge density can be explained with the Gouy-Chapman model²⁰

$$\Phi(0) = \frac{2kT}{ze} \sinh^{-1} \left(\sigma \sqrt{\frac{\pi}{2\epsilon k T I}} \right) \quad (9)$$

where σ is the surface charge density, z is the sign of the charged surfactant molecule, and I is the ionic strength of the bulk solution. Within the confines of the Gouy-Chapman model the depth of the interfacial region, called the double layer region or the Debye-Hückel screening length, over which the electrostatic field is present can be expressed as²¹

$$\frac{1}{\kappa} = \left(\sqrt{\frac{1000 D R T}{8 \pi N^2 \epsilon^2 I}} \right) \quad (10)$$

where D is the dielectric constant and I is the ionic strength of the bulk solution. In the experiments presented here we monitor the interfacial molecules, both surfactant and water, as the bulk surfactant concentration and solution ionic strength are varied. Changing the

bulk surfactant concentration affects the surface concentration which subsequently alters the surface charge density and thus the interfacial potential. Varying the ionic strength of the solution has a twofold effect on the interfacial potential created by the soluble charged surfactants used in this study. One effect is a change in the Debye-Hückel screening length, equation(10), brought about by the change in the number of ions present at the interface. For example, as the ionic strength increases the number of ions at the interface increases and the surface charge is screened in a smaller distance. The smaller Debye-Hückel screening length means that fewer interfacial water molecules interact with the electrostatic electric field which in turn produces a smaller third order nonlinear polarization. The other effect is a reduction in the interfacial potential, equation (9), with increasing ionic strength. Also pertinent to consider is that the surface concentration of soluble surfactants and the surface charge density are dependent on the ionic strength of the solution. For DAC and SDS the surfactant surface concentration increases by 10 to 15 percent over the range of ionic strengths studied here with most of the increase achieved before an ionic strength of 0.05 M.

Experimental

The laser system employed for the vibrational SFG studies has been described in detail elsewhere.^{22,23} Briefly it consists of a titanium:sapphire regenerative amplifier which pumps a two stage optical parametric amplifier seeded with a small portion of white light continuum. The system produces IR pulses tunable from 2.4 μm to 4.0 μm at a repetition rate of 1 kHz. The energy of the pulses over this range is approximately 10 μJ with a bandwidth of 18 cm^{-1} and a pulse duration of 1.9 ps. The IR pulses are combined at the interface with approximately 150 μJ of 800 nm light from the Ti:sapphire regenerative amplifier. All spectra presented were obtained under S_{sfg} , S_{vis} , P_{ir} polarization conditions with the 800 nm and IR beams directed onto the interface at an approximate angle of 56 and 68 degrees from the surface normal respectively. The generated sum frequency light is

collected in reflection with a PMT after filtering. The spectra were collected with gated electronics and a computer. Each scan was obtained with an increment of 1 cm^{-1} and an average of 200 laser shots per increment. The data was further averaged using the box averaging technique over a width of 9 cm^{-1} . This additional averaging produced no change in the spectral information since the laser bandwidth was 18 cm^{-1} . In addition, the spectra presented here show only one out of every ten data points for the sake of figure clarity.

Dodecylammonium chloride (DAC) was obtained from Eastman-Kodak and sodium dodecyl sulfate (SDS) was obtained from Sigma-Aldrich. Both surfactants were used as received without further purification and the solutions were made using HPLC grade water from Mallinckrodt. The surfactant solutions containing different ionic strengths were made by dissolving analytical reagent grade NaCl from Mallinckrodt in the HPLC water prior to dissolving the surfactant. A VSFG spectrum was obtained for each neat solvent at the air/solvent interface and the surface of the neat solvent at the air/solvent interface was determined to be free of organic contaminant by an absence of peaks in the CH stretching region in the VSFG spectra. Surface tension studies were conducted to monitor the surface concentration of as a function of bulk surfactant concentration. The surface tension measurements were obtained by the Wilhelmy balance method utilizing a platinum plate for SDS and a filter paper plate for DAC. The molecular area occupied by DAC and SDS at monolayer concentrations was found to be 35 \AA^2 and 45 \AA^2 respectively. Pentadecanoic acid (PDA), used as a reference VSFG spectra, from Sigma was spread at the air/water interface by placing approximately $50\text{ }\mu\text{L}$ of 0.1 mg/mL PDA in methanol on either a H_2O or D_2O surface with an area of 23.8 cm^2 which should place the monolayer in the liquid condensed (LC) phase. Further, at monolayer coverage in the LC region PDA has been shown to have a molecular area of approximately 25 \AA^2 per molecule.⁷ All experiments both surface tension and VSFG were conducted in a circular glass trough 55 mm in diameter.

Results and Discussion

A. Nonionic Surfactant

The relative order of alkyl surfactant molecules at an interface is typically gauged by the amount of *gauche* defects present in the alkyl chains. If the molecules at the interface are predominantly in the *trans* conformation they are assumed to have a high degree of order, whereas if many of the molecules have *gauche* defects the surfactant molecules are considered to have a lower degree of order. VSFG has previously been shown to be sensitive to the relative order of surfactant molecules at an interface.^{1,2,7,8} As was mentioned earlier this sensitivity arises from the fact that for surfactant molecules in the all-*trans* conformation the CH₂ vibrational modes are SF-inactive. Thus the absence of CH₂ stretching modes in the VSFG spectrum from surfactant molecules at an interface is an indication that the alkyl chains of the surfactant are predominantly in the all-*trans* conformation. The orientation of the interfacial water molecules can be monitored through the OH stretching modes. Previous studies have shown that the degree of alignment as well as the nature of the overall structure of the interfacial water molecules can be inferred from the OH stretching region of the VSFG spectrum.^{5,19} Table 1 shows the SF-active modes observed in VSFG studies under SSP polarization conditions along with the abbreviations used in this paper.

Pentadecanoic acid (PDA) on water has been studied previously by VSFG and has been shown to readily form a well ordered monolayer.^{7,8} We use PDA here as an example of a well ordered monolayer and use its VSFG spectrum for comparison with spectra obtained from soluble charged surfactants at the air/water interface. Figure 1 shows the VSFG spectra from a monolayer of PDA on water under S-sfg, S-vis, P-ir polarization conditions (SSP). The PDA on water spectrum is dominated by two peaks which have been assigned to the CH₃ symmetric stretch, CH₃-SS (2875 cm⁻¹), and the CH₃ Fermi

resonance, CH₃-FR (2935 cm⁻¹), of the symmetric stretch and overtones of the methyl bending modes.⁷ There is little or no intensity from the CH₂ symmetric stretch, CH₂-SS, which has been observed to occur at 2850 cm⁻¹. The resolution of our laser system limits our ability to separate the CH₂ asymmetric stretch, CH₂-AS, which has been observed to occur at 2937 cm⁻¹,¹⁴ from the CH₃-FR. However, previous studies on PDA have shown that the CH₃-FR dominates over the CH₂-AS at monolayer concentrations.^{7,8} As discussed above these characteristics are indicative of molecules with a high degree of order and few *gauche* defects.

Two other peaks appear in the PDA on water spectra which have not been observed in previous PDA studies. We assign these peaks to OH stretching modes from the interfacial water molecules. The first peak, designated OH-SS-S in Figure 1, is located at 3200 cm⁻¹ and has been attributed to the coupled OH symmetric stretch from tetrahedrally coordinated water molecules at the interface.¹⁹ This peak has been observed to have a strong intensity in the spectrum of ice and thus its strength is indicative of tetrahedral bond ordering in the molecular arrangement of water molecules or an “ice-like” structure.¹⁹ Further, we have performed polarization experiments which indicate that the transition moment of the OH-SS-S mode is predominantly perpendicular to the surface plane. The other peak, designated OH-SS-A, is located at 3450 cm⁻¹ and can be attributed to one of two possible modes: either the OH symmetric stretch of asymmetrically hydrogen bonded water molecules¹⁹ or water molecules with bifurcated hydrogen bonds.²⁴ The assignment of this mode is not crucial to the studies here since either assignment is indicative of bond disorder in the molecular arrangement or a “water-like” structure. Our polarization studies also indicate that the moment for the OH-SS-A mode is predominantly out of the plane of the surface. Through a comparison of the intensities of the OH-SS-S and OH-SS-A peaks one can infer the overall nature of the structure of the interfacial water molecules.¹⁹

B. Ionic Surfactants

Figures 2(a) and 2(b) show the VSFG spectra at the air/water interface of dodecylammonium chloride (DAC, cationic) and sodium dodecyl sulfate (SDS, anionic) for several different bulk concentrations under S-sfg, S-vis, P-ir polarization conditions. Spectra were obtained from the air/water interface of solutions with bulk concentrations of 0.05 mM, 0.10 mM, 0.50 mM, 1.0 mM, 7.0 mM, and 14 mM for DAC and 0.05 mM, 0.1 mM, 0.5 mM, 1.0 mM, 5.0 mM, 8.1 mM, and 10 mM for SDS. Figure 2 shows the VSFG spectra from only the 0.05 mM, 1.0 mM, and 14 mM solutions for DAC and the 0.05 mM, 1.0 mM, and 8.1 mM solutions for SDS. A large enhancement of the OH stretching peaks is observed when Figure 2 is compared to the spectrum of PDA on water. This enhancement increases for both OH peaks with increasing surfactant concentration for both DAC and SDS. We attribute this enhancement to the large electrostatic field present at the interface which is a result of the charged surfactants adsorbed to the surface. The electrostatic field aligns the interfacial water molecules thus removing the centrosymmetry of the double layer region and allowing more water molecules to contribute to the nonlinear polarization. The magnitude of the electrostatic field at moderate surface coverage, approximately 3 mM for DAC, can be as large as 10^7 V/m assuming a surface potential of 130 mV and a Debye length of 5.5 nm.²⁸ Previous SHG studies of a charged surfactant at the air/water interface have shown a similar enhancement in the nonlinear polarization.²⁰ The alignment of interfacial water molecules by a large electrostatic field has also been observed in SHG and SFG studies at the charged quartz/water interface^{18,19} as well as X-ray scattering studies¹⁷ at the charged electrode/water interface. From analysis of figure 2 we also find that the OH-SS-S peak dominates over the OH-SS-A peak at all concentrations for both surfactants which implies an "ice-like" structure in the arrangement of the interfacial water molecules. Finally, we see that even at a bulk concentration of 0.05 mM, which corresponds to a surface coverage of less than 10 percent of maximum coverage, the interfacial water molecules are highly aligned as compared to the air/water interface with a

nonionic surfactant present. In fact the small OH peaks observed in the VSFG spectrum of PDA on water could be indicative of a small amount of deprotonated PDA at the surface. This illustrates the high sensitivity of the VSFG technique to alignment of interfacial water molecules and the presence of a surface charge.

Coupled to the OH enhancement in the DAC spectra is the appearance of a destructive interference which occurs at approximately 2970 cm^{-1} between the OH-SS-S mode and the CH_3 -FR mode. In contrast, for SDS a constructive interference between the OH-SS-S mode and the CH_3 -FR mode is observed. We attribute the difference in the interference for cationic and anionic surfactants to differing orientation of the interfacial water molecules which results from opposite electrostatic fields created by surfactants of opposing charge. We have used this interference which is constructive for anionic surfactants and destructive for cationic surfactants along with chemical intuition to infer the orientation of interfacial water molecules at positively and negatively charged interfaces.³ For cationic surfactants one would expect the oxygen atom in the interfacial water molecules to be pointed towards the air and for anionic surfactants the oxygen atom to be pointed towards the bulk solution.

To understand what optical factors contribute to the enhanced OH response from water in the presence of the charged surfactants we return to the earlier discussion of the interaction between the electrostatic field, \mathbf{E}_0 , and the optical fields \mathbf{E}_ω (Eq. 6). This interaction occurs through a interfacial potential dependent third order coupling or a $\chi^{(3)}$ term which adds to the normal $\chi^{(2)}$ in the expression for the nonlinear polarization induced at the interface. The $\chi^{(3)}$ term originates from the field induced alignment of the water molecules in the double layer region where as the $\chi^{(2)}$ term is a more surface specific term and is independent of the interfacial potential. The $\chi^{(3)}$ term consists of a third order

polarizability term, $\alpha^{(3)}$, and an orientational term, both of which are dependent on the magnitude of the electrostatic field. Separation of these terms is difficult since both the alignment of the water molecules and the increased polarizability are very much dependent on the electrostatic field. Equation (8) shows that the nonlinear polarization is linearly dependent on the interfacial potential and equation (9) shows that the interfacial potential is proportional to the natural log of the surface charge density σ . If each surface surfactant molecule is assumed to be charged then σ can be calculated from the area per molecule, $\sigma=1/A$, determined from surface tension measurements. Therefore, a plot of the square root of the SF intensity, proportional to the SF polarization, versus the natural log of A should be linear. In addition, the slopes of the relationship between the SF polarization and $\ln(A)$ for the oppositely charged surfactants should have opposite signs as was the case for the SH studies mentioned earlier.²⁰

Figures 3(a) and 3(b) show the square root of the VSG intensity, proportional to the SF polarization (P_{sfg}), for the various CH and OH stretching modes for DAC and SDS respectively over the entire concentration range studied. We have performed surface tension measurements at the air/water interface of DAC and SDS solutions and find that the maximum surface coverage occurs at a bulk concentration of approximately 5-7 mM for DAC and 2-4 mM for SDS, both of which agree well with other data found in the literature.²⁵⁻²⁷ Surface concentrations were calculated from surface pressure data and the Gibbs equation²¹ and are included in Figures 3(a) and 3(b). It should also be noted that the critical micelle concentration occurs at a bulk concentration of 14 mM for DAC and 8.1 mM for SDS. In each case, DAC and SDS, we observe that the maximum in OH-SS-S intensity occurs well before maximum surface coverage. From this we infer that the interfacial water molecules have achieved their highest degree of alignment before the maximum interfacial potential is reached.

To test whether Equations (8) and (9) are an appropriate description of the SF response from water, the square root of the SF intensity for the OH-SS-S mode is plotted versus the natural log of the area per molecule A , the latter determined from surface pressure measurements, and inset in figures 3(a) and 3(b). If equations (8) and (9) hold, the nonlinear polarization should be linear with respect to the natural log of A . Inspection of these inset plots shows that the SF field decreases with increasing A for both cationic (DAC) and anionic (SDS) surfactants. At first this result might seem to be in contradiction with equations (8) and (9) which show that the dependence of the SF field on σ should be opposite for the oppositely charged surfactants. However, if the nonlinear polarization induced at the interface while on resonance with the OH-SS-S mode is dominated by $\chi^{(3)}\Phi(\mathbf{0})$, i.e. $\chi^{(2)}$ in equation (8) is negligible, then one would expect the SF field to decrease with increasing A regardless of surfactant charge. This leads us to conclude that while on resonance with the OH-SS-S mode the SF field is dominated by $\chi^{(3)}\Phi(\mathbf{0})$. This conclusion is not surprising since the interfacial water molecules are being probed specifically and it is their alignment by the electrostatic field that allows them to contribute to the nonlinear polarization through $\chi^{(3)}$. Thus the SF response in this IR spectral region is dominated by $\chi^{(3)}$ because of the large number of water molecules interacting with the optical fields. Further, in the absence of a surface charge, i.e. $\chi^{(2)}$ term only, we see little or no intensity in the OH stretching region again suggesting that $\chi^{(2)}$ is small in comparison to $\chi^{(3)}$.

Closer inspection of the inset plots of figures 3(a) and 3(b) shows that the SF field is not strictly linear with respect to $\ln(A)$. In fact, the SF field initially increases with decreasing A but then reaches maximum value beyond which it remains constant with further decreases in A . One might conjecture that this deviation from the linearity predicted

in Equation (8) is due to the increased ionic strength with increased bulk concentration, yet a plot of the SF field versus $\ln(A * \sqrt{I})$ also deviates from linearity. A more likely explanation which would be consistent with the SF field vs. $\ln(A)$ plot and the fact that VSFG is a resonant process is that the data reflects a significant contribution from dipole alignment of the interfacial water molecules. With alignment as the dominant contribution to the SF response one might expect the SF field to increase until maximum alignment of the interfacial water molecules has been achieved and then remain constant with further electrostatic field increases. Temperature experiments as well as experiments with insoluble surfactants are currently in progress to explore this observation further.

In studying the DAC and SDS alkyl chain structure, we find that the SF intensity in the CH stretching spectral region follows a trend similar to what is observed for the OH-SS-S peak from the water. However, we find that a tenfold increase in the surface concentration results in a much smaller increase in the square root of the VSFG intensity from the CH_3 modes for both surfactants. This seemingly small increase in VSFG intensity of the CH_3 modes for such a large concentration change is most likely caused by the interference between the CH and OH modes. Namely, the OH-SS-S mode couples with the CH_3 modes which results in a great enhancement at low concentrations while at higher concentrations, where the CH_3 mode intensities are increased due to alignment of surfactant molecules, the enhancement is proportionally smaller. This conclusion is evidenced by the fact that as the bulk surfactant concentration increases there is a corresponding increase in the OH-SS-S peak. The CH_3 peaks grow with bulk surfactant concentration because the surface concentration increases and the surfactant molecules align and have fewer *gauche* defects, both of which lead to an increasing VSFG signal. From the OH-SS-S peak intensities we find that the interfacial water molecules appear to achieve the highest degree of alignment before maximum surface coverage is attained. Correspondingly, we find that the CH stretching modes achieve a maximum intensity before maximum surface coverage is reached. This observation shows that the OH-SS-S

mode has a large effect on the CH modes which makes a detailed analysis of the alkyl chain structure difficult. We have performed experiments in D₂O to characterize the effect of the OH-SS-S interference on the CH modes since the OD stretches occur at frequencies further removed from the CH stretching region and have a much smaller effect on the CH modes. Under these conditions we find that the intensities of the CH modes are in much better agreement with the surface tension measurements.

An important distinction in the CH stretching region between SDS and DAC can be found by further inspection of the SF field versus bulk concentration data for SDS (Figure 3). The surface tension measurements show that the surface surfactant concentration increases with increasing bulk surfactant concentration up to a concentration of approximately 4 mM. In contrast to the behavior of the interfacial water molecules the intensity from the CH₃ peaks increases correspondingly with the surface tension measurements up to a bulk concentration of 2 to 3 mM. Beyond this point the SF data deviates from the surface tension data. In fact, each of the CH₃ peaks decreases in intensity beyond 1 mM with the CH₃-SS and CH₃-AS peaks having a comparable degree of decrease with increased concentration. The intensities from the CH₃-FR mode display a lesser degree of change with concentration. We attribute the slower rate of decrease of the CH₃-FR peak to the counteracting effect of the increasing OH-SS-S peak which constructively interferes with or enhances the CH₃-FR intensity. This anomalous behavior of the CH₃ stretches might be explained by an increased disorder, e.g. an increased number of *gauche* defects, occurring above 1 mM or monolayer concentrations. The increased chain disorder could be caused by micelle formation which could interfere with the surfactant structure at the surface and contribute to a decrease in the CH₃ stretching intensities by disrupting the chain-chain interactions which lead to increased order. There are two other possibilities which have been suggested as suspect contaminants affecting the formation of a surface layer of SDS.⁴ These possibilities are the incorporation of trace amounts of dodecanol formed by the hydrolysis of the sulfate head group into the surface layer or complexation

by Ca^{+2} ions present in the water. Either one of which could produce a higher degree of alignment in the CH_3 tails at low concentrations then giving away to the SDS contribution at high concentrations where the surface is dominated by SDS. It should be pointed out here that we have observed the same constructive interference between OH and CH modes for other anionic surfactants such as dodecylsulfonate, hexadecylsulfate, and benzyisulfate at the air/water interface.

C. Mixed Surfactants

We have attributed the enhancement in the OH spectral region observed in the spectra from both DAC and SDS to the electrostatic field at the interface due to the charged surfactant. Consequently, for an interface where the electrostatic field is zero, the enhancement should disappear. We have tested this prediction by examining an interface where there are approximately equal numbers of cationic and anionic surfactant molecules. Figure 4(a) shows the SSP VSFG spectra from the air/water interface of a solution of 0.02 mM DAC and 0.02 mM SDS. The OH peaks are not present in this spectrum which is consistent with what we observe at the neat air/water interface (again a small $\chi^{(2)}$ term). For comparison with the mixed surfactant case, Figures 4(b) and 4(c) show the SSP VSFG spectra from 0.05 mM SDS and DAC solutions respectively. In both the 0.05 mM SDS and DAC VSFG spectra the OH peaks are quite prominent. We attribute the disappearance of the OH peaks in the spectra from the mixed surfactant system to the cancellation of charge between the cationic and anionic surfactants and oppositely charged counter ions. The cancellation of surface charge leads to a much smaller field present at the interface and thus the interfacial water molecules are no longer aligned.

Accompanying the disappearance of the OH peaks in the mixed surfactant VSFG spectrum is an enhancement in the CH_3 -SS and CH_3 -FR peaks. This effect can be seen by comparing the CH_3 -SS and CH_3 -FR peaks from the mixed surfactant system, Figure 4(a), and the CH_3 -SS and CH_3 -FR peaks from the anionic, Figure 4(b), and cationic, Figure

4(c), surfactant systems. For both the anionic and cationic surfactants at bulk concentrations of 0.05 mM the CH_3 peaks are small and there is significant CH_2 -SS intensity which suggests a low degree of order or a high number of *gauche* defects relative to higher bulk concentrations. The spectra from the mixed surfactant system however, is dominated by the CH_3 -SS and CH_3 -FR peaks indicating a higher degree of order or fewer *gauche* defects in the surfactant molecules. The greater interfacial order of the mixed surfactant system can be explained by ion pairing at the interface. The Coulombic attraction of the oppositely charged surfactants allows them to pack more closely thus allowing a smaller volume for kinks in the tail groups.

D. Ionic Strength

Another factor affecting the interfacial potential $\Phi(0)$ is the ionic strength of the solution. The relationship between the interfacial potential and the ionic strength is given in equation (9). Increasing the ionic strength of the solution also decreases the Debye-Hückel screening length^{20,28} as shown by Equation (10). The decrease in the screening length is a result of the higher concentration of ions at the interface which screen the surface charge. The smaller Debye-Hückel screening length leads to fewer interfacial water molecules interacting with the electrostatic field which should have the effect of decreasing the third-order polarization attributed to the alignment of interfacial water molecules. Also of importance is the surface concentration of soluble surfactants which is mildly dependent on the ionic strength. We find that for DAC and SDS the surfactant surface concentration increases by 10 to 15 percent over the range of ionic strengths studied here with most of the increase achieved before an ionic strength of 0.05 M.

In changing the excess salt concentration from millimolar to molar concentrations the Debye-Hückel screening length can decrease by as much as 2 orders of magnitude or from approximately 40 nm at an ion concentration of 0.1 mM to 0.4 nm at an ion

concentration of 0.5 M. Assuming a nominal water diameter of 2 Å the number of water molecule layers that interact with the field as the ionic strength is increased ranges from approximately 200 at 0.1 mM to just 2 at 1.0 M. The effect of the ionic strength on the third-order polarization, $\chi^{(3)}$, has been observed in SHG studies of insoluble charged surfactants at the air/water interface.²⁰ The behavior of the SH intensity as a function of ionic strength has been attributed to the ordering of interfacial water molecules and is described within the confines of equation (9). However, as we saw in the case of the SF field dependence on σ , the ability to specifically probe the water molecules introduces different considerations in the analysis of the dependence on the ionic strength as described below.

Figures 5(a) and 5(b) show the SSP VSFG spectra from 1.0 mM DAC and SDS solutions respectively with varying ionic strength. Spectra were obtained from 1.0 mM surfactant solutions with 0.0 M, 0.05 M, 0.1 M, 0.5 M, and 1.0 M concentrations of excess NaCl. Inspection of the spectra shows that as the ionic strength is increased there is a clear reduction in the intensities of the OH stretching modes. This reduction illustrates the effect of increasing ionic strength on the number of interfacial water molecules interacting with the electrostatic field which is a result of a decreased Debye-Hückel screening length. Further, at NaCl concentrations above 0.5 M the OH peaks have diminished so much that the symmetric stretch from the NH_3^+ head group of DAC is visible around 3100 cm^{-1} . However, even at an ionic strength of 0.5 M, Debye length of approximately 4 Å or 2 water layers, we see enhancement in the OH stretching region which shows that the water molecules are aligned at shallow depths of the interface. We have performed similar ionic strength experiments using an insoluble charged surfactant, didodecyldimethyl ammonium chloride, and find the behavior of the enhanced OH modes in good agreement with results presented here for the soluble surfactants.

Figures 6(a) and 6(b) show the square root of the SF intensities for the CH₃-FR, CH₃-SS and OH-SS-S modes as a function of solution ionic strength for DAC and SDS respectively. Inset in each figure is a plot of the square root of the OH-SS-S versus ln(I) which should be linear according to equations (8) and (9). The plot shows that the SF field decreases with increasing ionic strength for both cationic and anionic surfactants demonstrating once again that $\chi^{(2)}$ is negligible relative to $\chi^{(3)}$. Again this conclusion is consistent with the fact that VSFG is a resonant process which allows us to specifically probe the interfacial water molecules through their OH stretching modes. The relationship between the SF field and ln(I) for each surfactant deviates from linearity, possibly due to the increased surface surfactant concentration with increased ionic strength which is not accounted for in the plot. This effect would be greatest for the low ionic strength solutions, i.e. 1 mM, and we find that it is this point that deviates from linearity. However, the surface concentration only increases by approximately 10 percent over the ionic strengths studied and correction by this factor does not seem to be large enough to improve the linearity of the relationship.

While the intensities of the OH stretches decrease with increasing ionic strength the intensities of the CH stretches remain relatively constant for DAC [Fig. 6(a)]. This observation is different than what is observed for the SDS spectra as a function of ionic strength [Fig. 6(b)]. As the ionic strength is increased the constructive interference between the OH and CH modes is greatly diminished for SDS whereas for DAC the change in the destructive interference is much smaller. We have performed experiments on dodecyltrimethylammonium chloride and find its behavior to be consistent with DAC thus allowing us to eliminate an explanation of this anomalous behavior based on an interference with the NH₃⁺ modes. We are currently in the process of studying a larger group of charged soluble and insoluble surfactants with different head groups in an attempt to better resolve this issue. The fact that the CH peaks remain relatively constant is, however, an indication that the surface concentration of the DAC remains relatively constant. This

observation has also been supported with surface tension measurements in this laboratory which show that the surface concentration reaches a maximum above a NaCl concentration of approximately 0.2 M.

The observation that the intensities of the CH modes of SDS decrease with increasing ionic strength while the surface tension data suggests the surface concentration is actually increasing slightly can be explained by the interference between the CH and the OH-SS-S peaks mentioned earlier. The interference is constructive for SDS and thus the CH₃-FR peak is enhanced by the presence of the OH-SS-S peak. This enhancement decreases when the OH-SS-S peak begins to diminish and continues up to NaCl concentration of 0.5 M which is the point at where most of the OH-SS-S intensity has disappeared. Thus the diminished enhancement, or the decrease in the CH₃-FR peak, results from the diminished OH-SS-S peak. The CH₃-SS peak initially goes down with increasing ionic strength and then goes back up after reaching a minimum at 0.1 M NaCl. The behavior of the CH₃-SS peak can also be explained in terms of the competing effects of increased surface concentration and diminished constructive interference from the OH-SS-S peak. For the CH₃-SS peak the enhancement is smaller so that the negating of the enhancement by diminishing the OH-SS-S peak occurs at a lower NaCl concentration. Once the constructive interference between the CH₃-SS and OH-SS-S peaks no longer contributes to the CH₃-SS peak intensity the CH₃-SS peak intensity increases due to the increased surface concentration.

Conclusions

We have employed VSFG to show that the presence of charged surfactants at the air/water interface induces an alignment of the interfacial water molecules. We find that the interfacial water molecules are highly aligned at surface coverages well below maximum surface coverage. The alignment of interfacial water molecules manifests itself in the VSFG spectra from the air/water interface by an enhancement in the OH stretching peaks

which results from an electrostatic field produced by the charged surfactant molecules at the interface. The electrostatic field couples to the optical fields through a $\chi^{(3)}$ term in the expression for the nonlinear polarization. We find that for the case of sum frequency generation while resonant with the OH-SS-S mode $\chi^{(2)}$ is negligible in comparison to $\chi^{(3)}$. This observation demonstrates that the sum frequency signal in the OH stretching region is dominated by the water molecules aligned by the electrostatic field in the double layer region rather than water molecules in the first layers or what normally is considered the surface. This conclusion is further confirmed by the lack of significant signal in the absence of charged surfactants.

By comparing the VSG spectra from a cationic (DAC) and an anionic (SDS) surfactant we have been able to infer the relative orientation of the interfacial water molecules. Specifically, the difference in the interference between the OH-SS-S and the CH modes for cationic and anionic surfactants is indicative of a flip in the orientation of the interfacial water molecules. X-ray scattering studies of the charged electrode/water interface have shown that the relative orientation of interfacial water molecules flips when going from a positively to negatively charged surface.¹⁷ We postulate that for cationic surfactants at the air/water interface the oxygen atom of the interfacial water molecules is directed towards the air, whereas for anionic surfactants the oxygen atom of the interfacial water molecules is directed towards the bulk solution. For the case of an aqueous solution where both cationic and anionic surfactants are present we find that the interfacial water molecules are not aligned in any particular direction and attribute this to a cancellation of surface charge and thus absence of the electrostatic field.

We conclude that the degree of alignment of the interfacial water molecules is dependent upon the bulk concentration of charged surfactant as well the ionic strength of the aqueous surfactant solution. The alignment of the interfacial water molecules is dependent on bulk surfactant concentration because the surface surfactant concentration is

dependent on the bulk surfactant concentration and the magnitude of the electrostatic field is dependent on the surface charge density. The effect of the ionic strength of the solution on the electrostatic field and thus the alignment of the interfacial water molecules can be understood in terms of a screening of the surface charge or a change in the Debye-Hückel screening length. We find that the enhanced OH-SS-S intensities of the interfacial water molecules decreases as the ionic strength of the solution increases. The decrease in the enhanced VSFG signal is attributed to a shortening of the Debye-Hückel screening length which limits the number of interfacial water molecules that can interact with the electrostatic field. For the extreme case of little or no electrostatic field present at the interface one does not expect the interfacial water molecules to be oriented and we have observed this lack of orientation as evidenced by the absence of OH stretching modes in the VSFG spectra from the mixed cationic and anionic surfactant system.

In general the relative order of the surfactant molecules at the air/water interface can be accessed by employing VSFG to monitor the CH stretching region of the surfactant molecules. However, for charged surfactants in water we find this procedure complicated due to the interference between OH and CH stretching modes in the VSFG spectra from the charged surfactants. We have had much more success in accessing the ordering of the charged surfactant molecules at the D_2O /air and D_2O/CCl_4 interfaces where this interference is not as strong. This observation is consistent with other researchers in the field trying to monitor the order of surfactant molecules at an interface.⁴ A more detailed analysis of the surfactant structure including accessing more molecular modes in the surfactant molecules is forthcoming with planned modifications of the laser system for bandwidth reduction and extended infrared tunability.

Acknowledgments: The authors gratefully acknowledge the Office of Naval Research for the support of this work.

Table and Figure Captions

Table 1

Frequencies and designations for SF-active modes observed under SSP polarization conditions in VSG spectra from various interfaces.

Figure 1

VSG spectra under SSP polarization conditions of the air/water interface of a monolayer of pentadecanoic acid (PDA) on water. Solid lines are a guide to the eye.

Figure 2

VSG spectra under SSP polarization conditions of the air/water interface of solutions of various bulk concentrations of DAC and SDS in water. 2(a) Bulk concentrations of 0.05 mM, 1.0 mM, and 14 mM DAC are shown. 2(b) Bulk concentrations of 0.05 mM, 1.0 mM, and 8.1 mM SDS are shown. Solid lines are a guide to the eye.

Figure 3

3(a) Square root of the CH₃-SS, CH₃-FR, and OH-SS-S peak intensities from Figure 2(a) with the surface coverage from surface tension measurements for DAC at different bulk surfactant concentrations. 3(b) Square root of the CH₃-SS, CH₃-FR, CH₃-AS and OH-SS-S peak intensities from Figure 2(b) with the surface coverage from surface tension measurements for SDS at different bulk surfactant concentrations. Inset in 3(a) and 3(b) is a plot of the square root of the OH-SS-S peak intensity versus ln(A) for the respective surfactant. Solid lines are a guide to the eye.

Figure 4

(a) VSG spectra under SSP polarization conditions of the air/water interface of an aqueous solution of (a) 0.02 mM DAC and 0.02 mM SDS, (b) 0.05 mM DAC, and (c) 0.05 mM SDS. Solid lines are a guide to the eye.

Figure 5

VSG spectra under SSP polarization conditions of the air/water interface of 1.0 mM solutions of DAC and SDS with 0.0 M, 0.05 M, 0.1 M, and 0.5 M excess NaCl. 5(a) DAC. 5(b) SDS. Solid lines are a guide to the eye.

Figure 6

Square root of the $\text{CH}_3\text{-SS}$, $\text{CH}_3\text{-FR}$, and OH-SS-S peak intensities from Figure 5 for DAC and SDS as a function of ionic strength. 6(a) DAC. 6(b) SDS. Inset in 6(a) and 6(b) is a plot of the square root of the OH-SS-S peak intensity versus $\ln(I)$ for the respective surfactant. Solid lines are a guide to the eye.

Designation	Mode	Frequency (cm ⁻¹)	Reference
CH ₂ -SS	Symmetric Stretch	2850	(2)
CH ₃ -SS	Symmetric Stretch	2875	(7)
CH ₂ -FR	Fermi Resonance	2900	(2)
CH ₂ -AS	Asymmetric Stretch	2925	(2)
CH ₃ -FR	Fermi Resonance	2935	(7)
NH ₃ ⁺ -Str.	N ⁺ -H Symmetric Stretch	3100	This Study
OH-SS-S	Sym. Stretch Sym. Coord. H ₂ O	3200	(17)
OH-SS-A	Sym. Stretch Asym. Coord. H ₂ O	3450	(17)

Figure 1

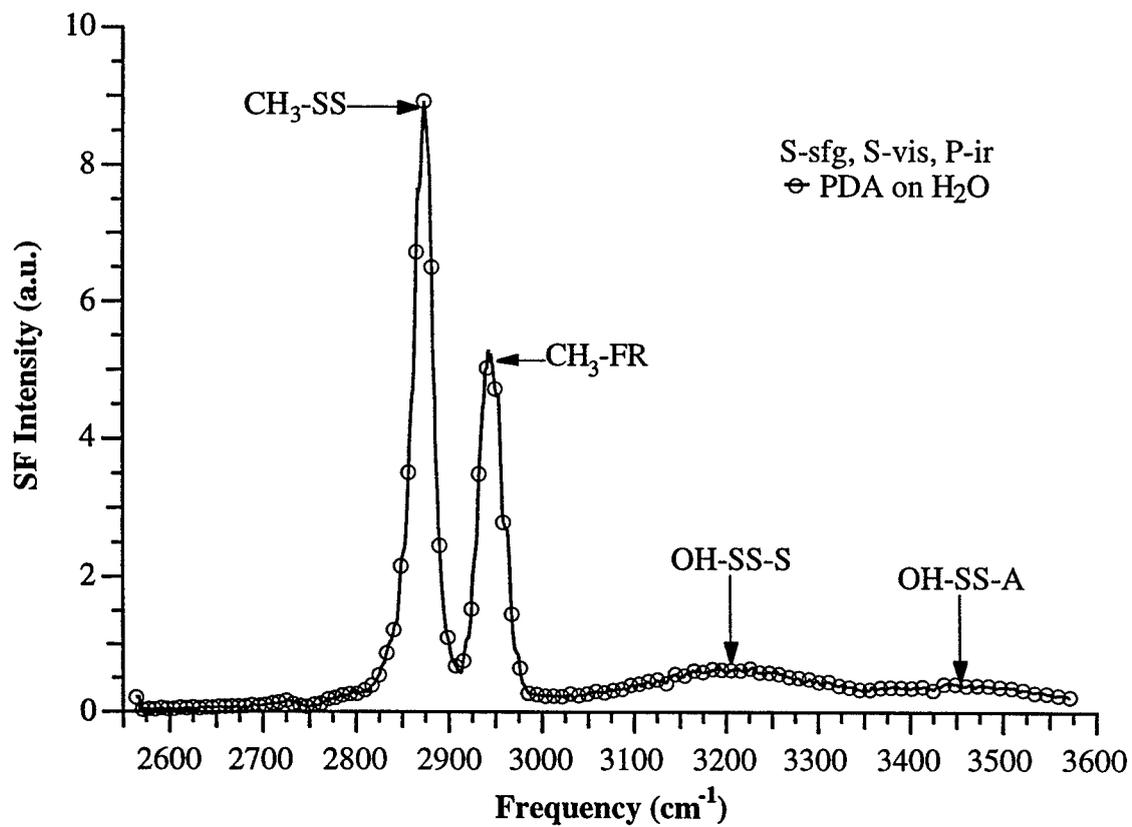


Figure 2

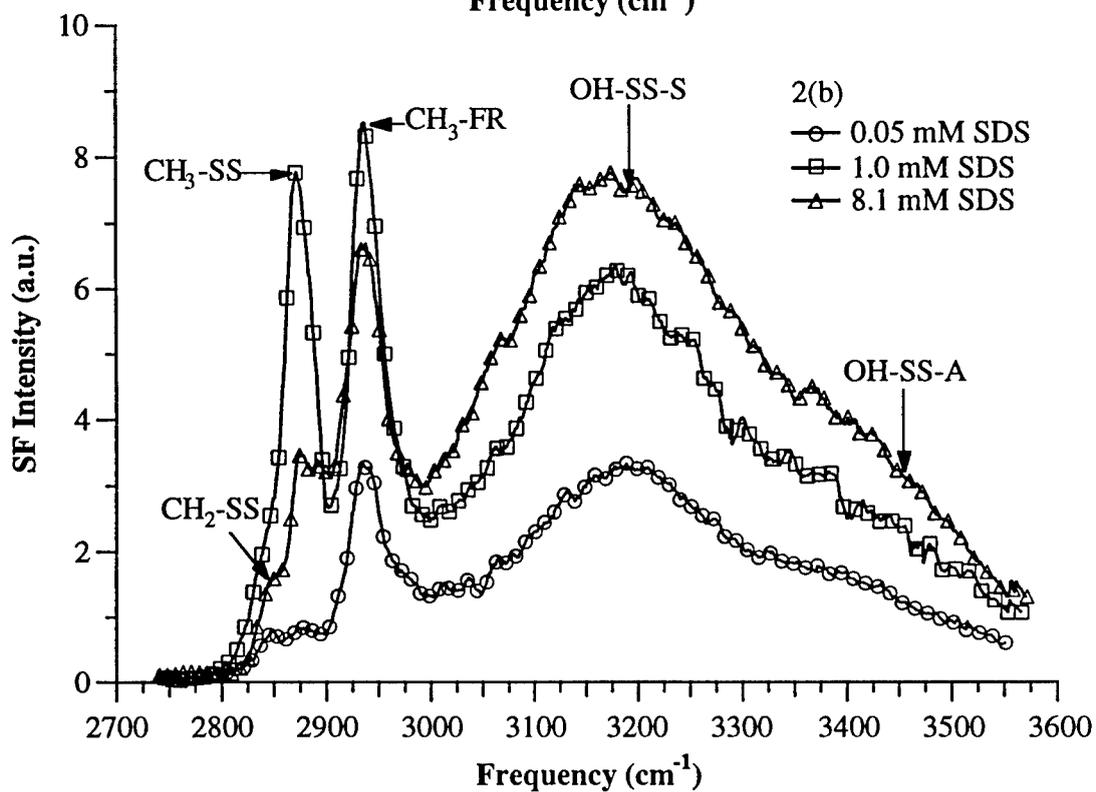
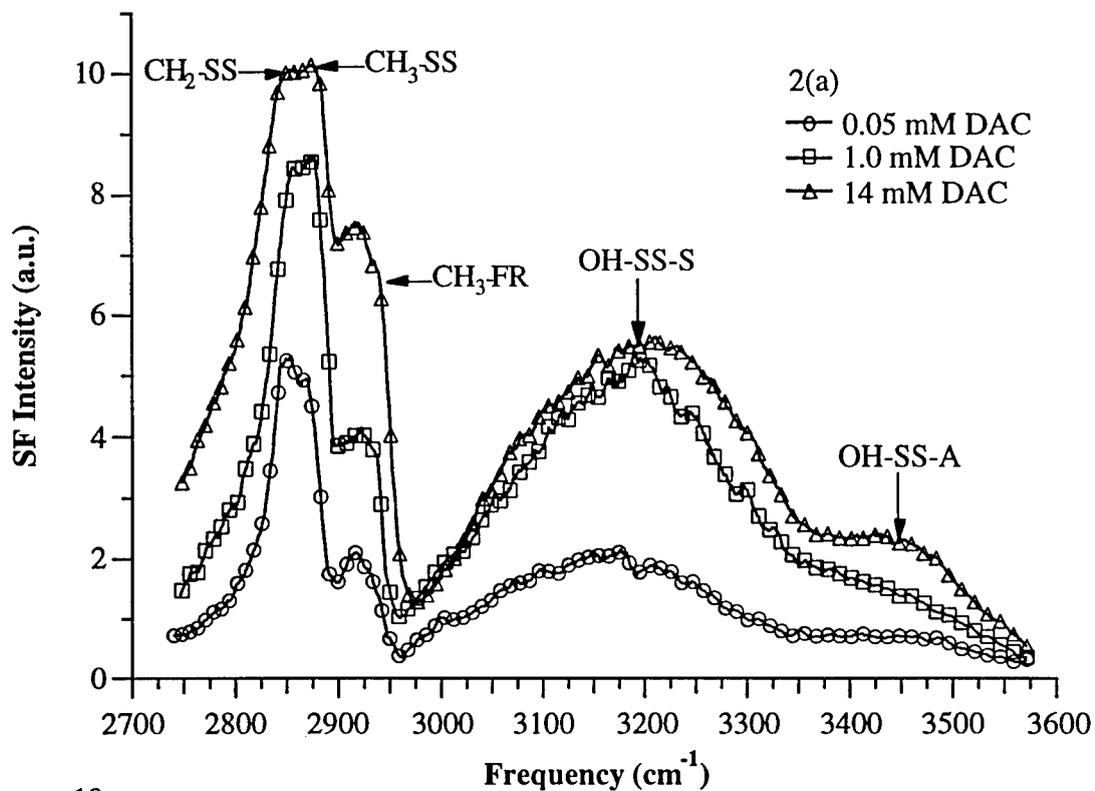


Figure 3

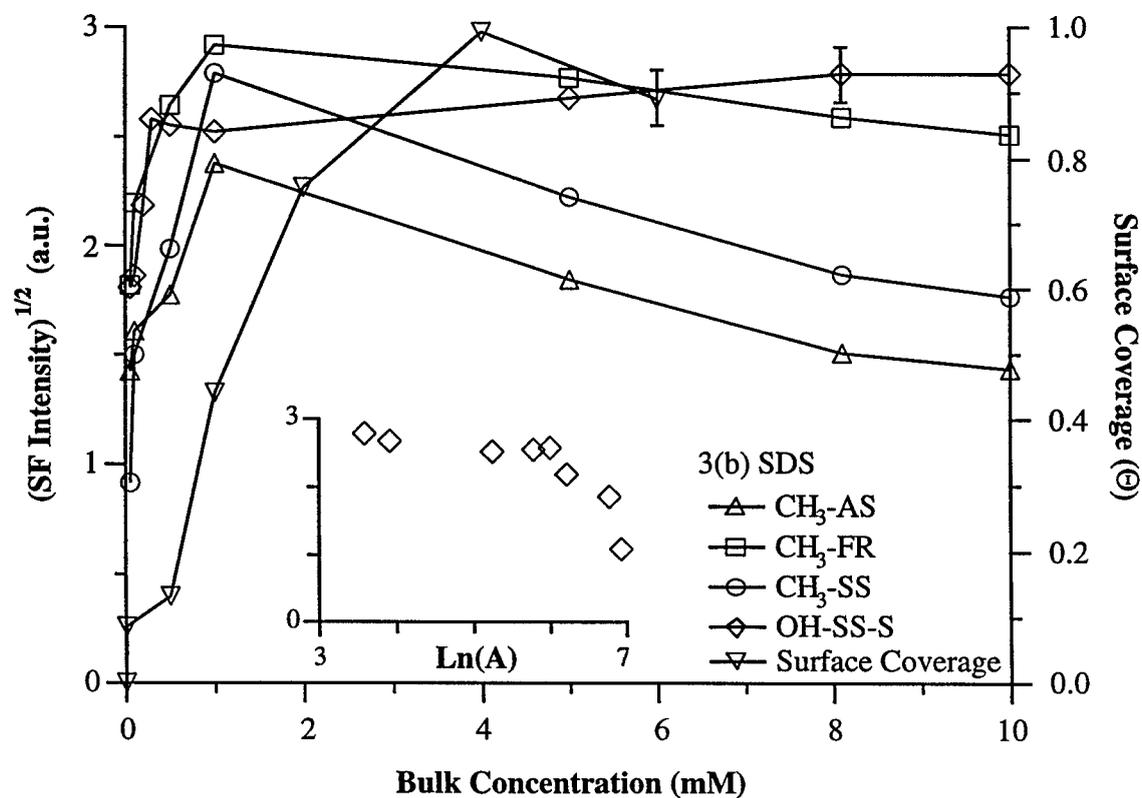
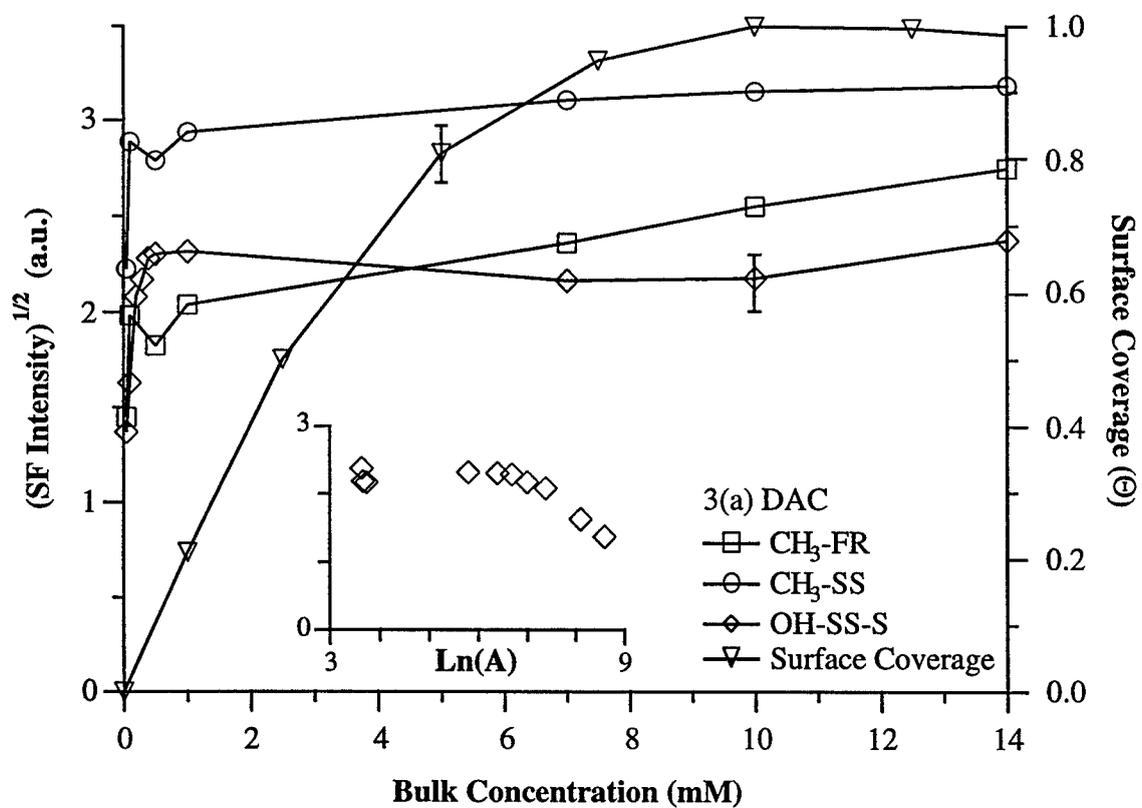


Figure 4

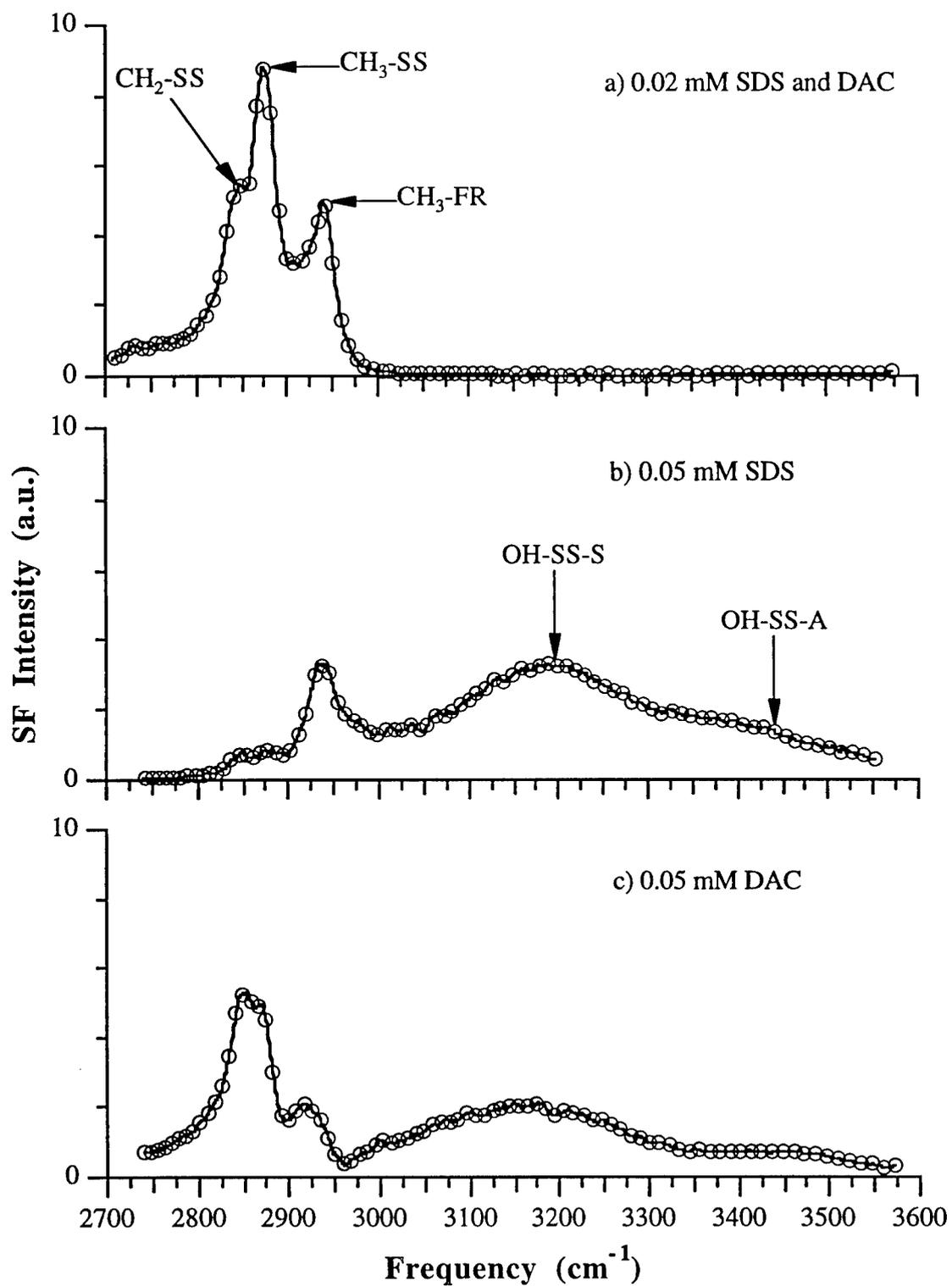


Figure 5

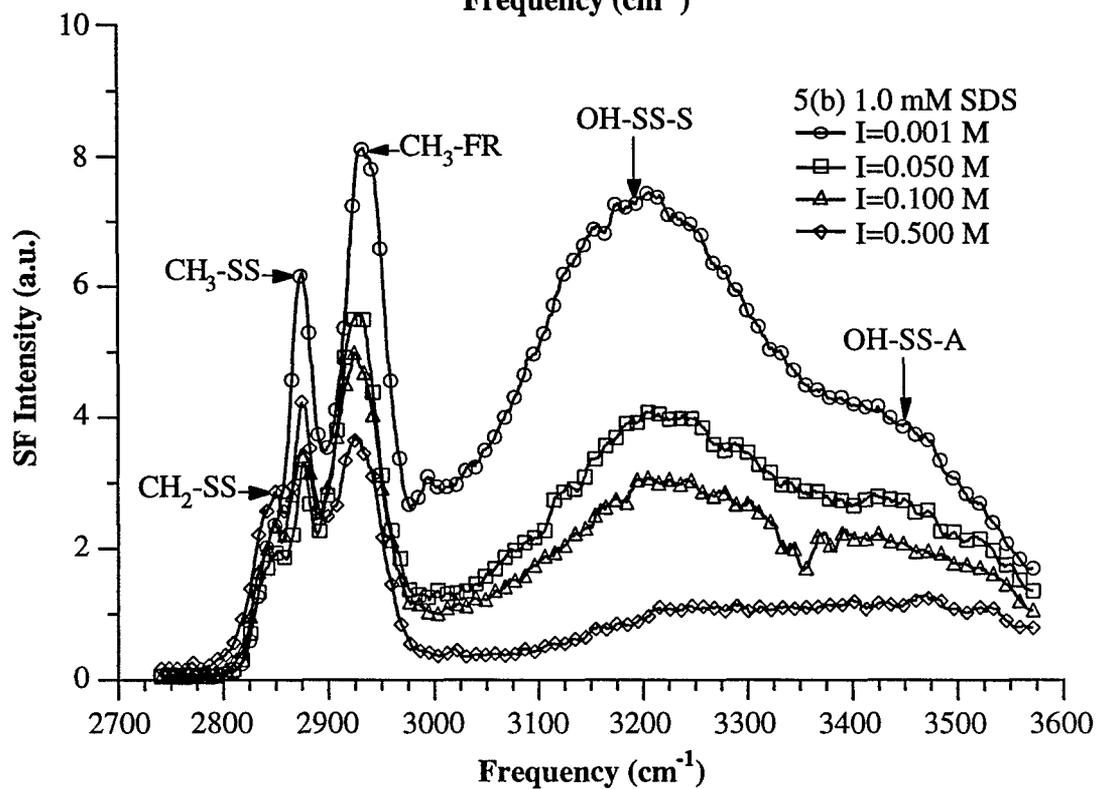
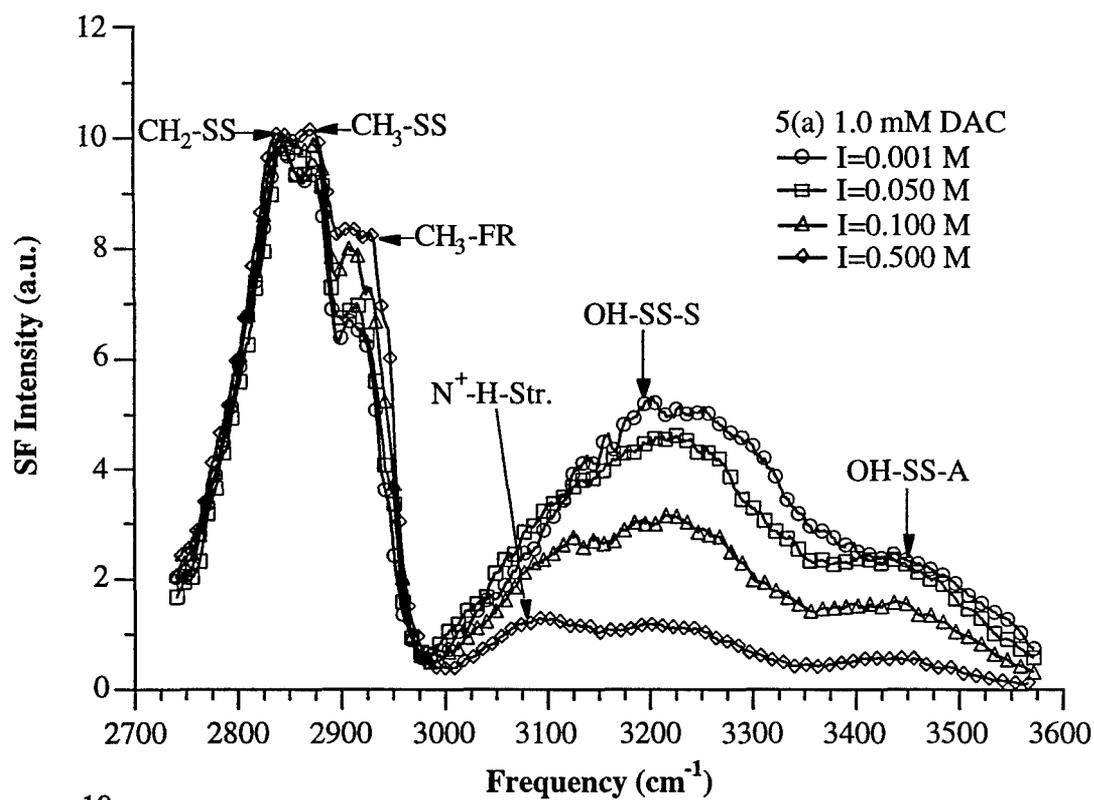
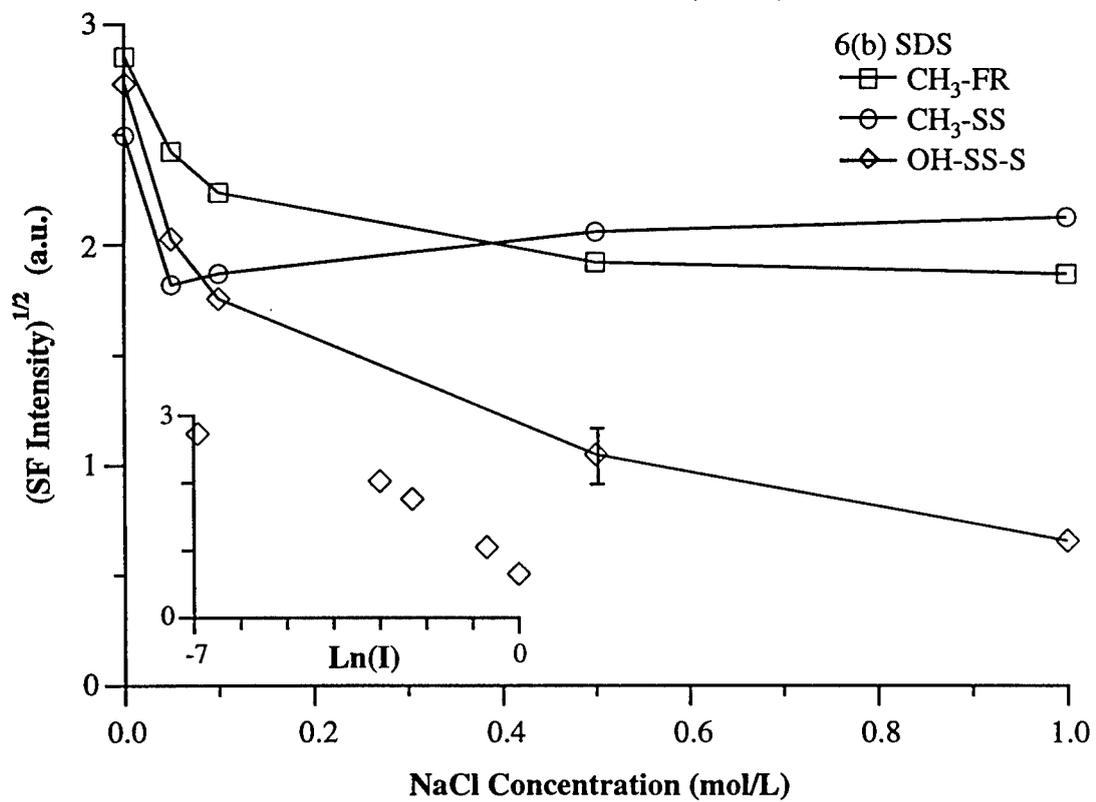
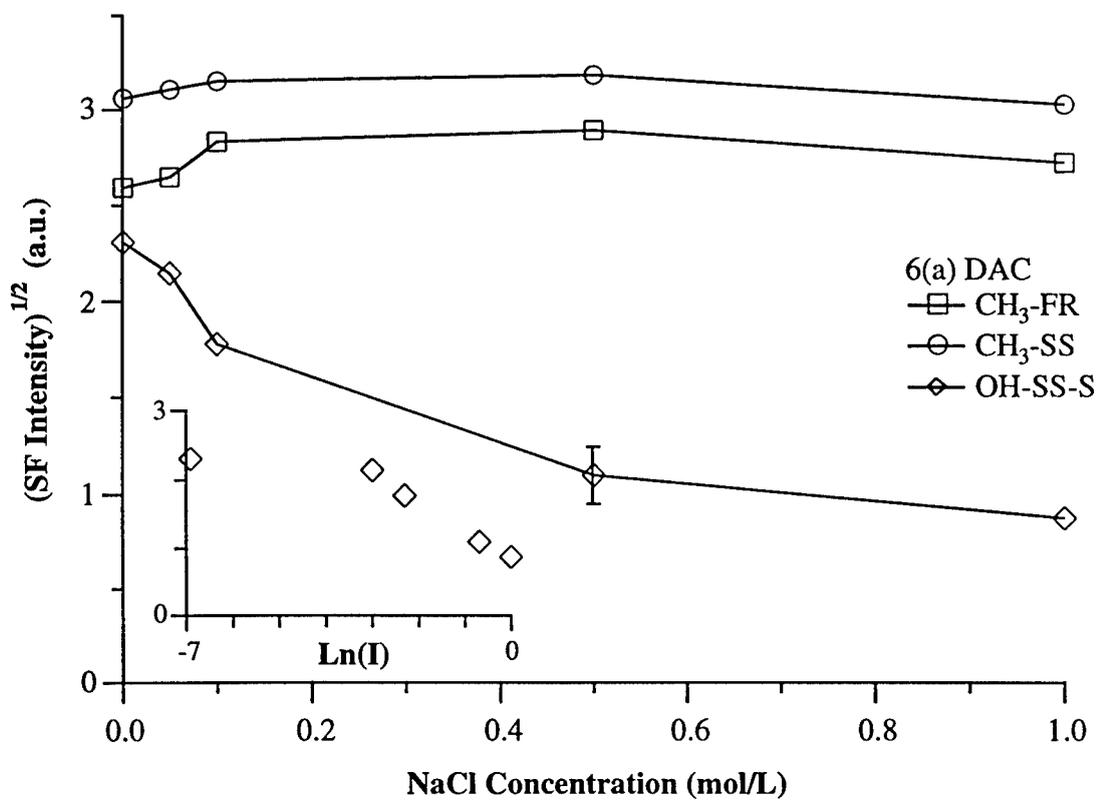


Figure 6



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