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SURFACE-ENHANCED RAMAN STUDIES OF THE LIQUID/SOLID INTERFACE

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Abstract Since surfaced-enhanced Raman scattering (SERS) can detect adsorbed monolayers without interference from molecules in adjacent bulk phases, it is an ideal spectroscopic tool for studying adsorbate structure at the liquid/solid interface and for relating adsorbate structure to macroscopic properties at the interface.

We have used SERS to examine the molecular conformation of a surfactant - a long chain alkyl thiol-on a silver-island film. For surfactant coated substrates in contact with air or a nonwetting fluid, the entire alkyl chain of the surfactant takes on an all trans conformation, similar to the conformation of the thiol in the neat solid. However, when a wetting fluid contacts the surfactant coated substrate, the carbons near the surface maintain their trans conformation while carbons farther from the surface alter their conformation and exhibit more gauche bonding. Such conformational changes suggest that wetting fluids penetrate adsorbed surfactant layers as opposed to nonwetting fluids which are hydrophobically excluded.

The wettability of a solid is just one example of a macroscopic property that can be greatly affected by molecular adsorbates. Amphiphilic molecules, possessing a polar head group attached to a long, nonpolar tail, are probably the most common surface-active agents used to alter wettability and surface tensions at the liquid/solid interface. To what extent is adsorbate structure and conformation affected by this fluid contact and how might such microscopic information provide insight into the large-scale processes occurring at the liquid/solid interface? We explore such question in the present surface-enhanced Raman scattering (SERS) study.

The amphiphile used here was 1-hexadecane thiol (C\textsubscript{16}H\textsubscript{33}SH, hereafter HXDSH), which was found to strongly chemisorb to silver surfaces. SERS spectra were obtained from
HXDSH adsorbed on silver-island films whose production, morphology and optical properties have been thoroughly characterized. HXDSH was deposited onto the films from dilute solutions (10^{-2} to 10^{-5} M) of the thiol in chloroform or other volatile solvents. The HXDSH-containing solution remained in contact with the island film for ~15s after which time the excess solution was removed by spinning the substrate for 30s at 2000 RPM, leaving behind a thin, even coating of adsorbed HXDSH. The exciting 488.0 nm light was line-focused onto a spinning sample and an optical multi-channel analyzer was used for fast acquisition of the SERS spectra.

A SERS spectrum of the C-S stretching region is shown in Figure 1 and compared to the neat liquid and solid thiol. The HXDSH is almost certainly bound to the silver surface via its sulfur atom, as has been observed for many other organo-sulfur compounds. The absence of the distinctive S-H stretch and the appearance of a weak signal at ~260 cm^{-1} suggestive of the Ag-S stretch in bulk alkyl thiols lend support to this claim.

![Figure 1](image1.png)

Figure 1. Carbon-sulfur stretching region in HXDSH (a) liquid, (b) solid, (c) adsorbed. (G) and (T) are gauche and trans conformations.

![Figure 2](image2.png)

Figure 2. (a) Frequency of C-S vibration as a function of coverage. Errors bars represent variation in frequency found in different samples. (b) Contact angle (measured in air) for water on HXDSH coated films as a function of coverage.
The C-S stretching region of the adsorbed HXDSH is dominated by a single intense band near 700 cm\(^{-1}\), and comparison of the SERS spectrum to the Raman spectra of the neat thiol reveals a close kinship between adsorbed and solid HXDSH where the 700 cm\(^{-1}\) band dominates over the other C-S feature near 650 cm\(^{-1}\). Stretching frequencies of the C-S bond are acutely sensitive to molecular conformation near the sulfur head group: the 650 cm\(^{-1}\) stretch originates from gauche rotamers and the 700 cm\(^{-1}\) stretch from trans rotamers. Hence, the preponderant 700 cm\(^{-1}\) band in the SERS spectrum offers evidence that the conformation of that part of the HXDSH molecule nearest the sulfur atom, and therefore nearest the surface, is largely trans, reminiscent of HXDSH in the solid phase. While the SERS spectrum always shows a single intense band in the C-S stretching region, the position of this band shifts to lower frequency as coverage is decreased (Figure 2a). The 30 cm\(^{-1}\) frequency decrease observed when going from HXDSH solution concentrations of \(10^{-2}\) M to \(10^{-5}\) M is due to a decreasing interaction between adjacent adsorbed HXDSH molecules, and is similar to vibrational shifts observed for CO on nickel surfaces in ultra vacuum conditions. The macroscopic wetting behavior of the HXDSH coated island film also changes with adsorbate coverage. As shown in Figure 2b, as the solution concentration decreases, the adsorbate coverage decreases and therefore the surface changes from the very hydrophobic state at high coverages toward the water wet state of the uncoated island film.

In contrast to the C-S stretching region which conveys structural information from that portion of the HXDSH molecule very near the silver surface, the C-C stretching region (shown in Figure 3) conveys conformational details from the more distant...
carbon skeleton. The SERS spectrum with its intense 1130 cm\(^{-1}\) band and weaker 1090 cm\(^{-1}\) neighbor - indicative of a large number of trans bonds with gauche bonds appearing at the ends of long trans segments - suggests that the adsorbed HXDSH layer has a "solid-like" structure, extending beyond the region near the surface-bound sulfur and into the hydrocarbon tail.

To explore how adsorbed molecules were affected by contact with overlying bulk fluids, we recorded the SERS spectrum of HXDSH-coated island films in contact with various neat liquids. The effects of some overlying neat liquids as reflected in the C-C stretching region of the SERS spectrum are displayed in Figure 4. Contact with bulk water caused no change in the trans (1130 cm\(^{-1}\))/gauche (1090 cm\(^{-1}\)) ratio of adsorbed HXDSH. The "solid-like" structure of the adsorbed layer inferred from spectroscopic analysis of the C-S and C-C stretching regions implies sizeable adsorbate-adsorbate interaction and therefore close physical proximity of adsorbed HXDSH molecules. We believe the unaltered trans/gauche ratio upon contact with water can be ascribed to the formation of a well-packed layer of adsorbed HXDSH and the hydrophobic exclusion of water by the alkyl chain.

In contrast to the polar water overlayer, nonpolar chloroform in contact with adsorbed HXDSH clearly reduces the number of trans segments as inferred from the decrease in the intensity of the "trans marker" at 1130 cm\(^{-1}\) relative to the band at 1090 cm\(^{-1}\) sensitive to gauche conformations. The effect of the chloroform overlayer was found to be reversible; and when the overlayer was removed, the SERS spectrum of the HXDSH reverted to its original, in-air appearance. Interestingly, while the appearance of the SERS spectrum in the C-C region was dramatically altered, the C-S region remained unchanged, still dominated by a single intense trans stretch near 700 cm\(^{-1}\). Given the adsorbate configuration discussed earlier, this implies that the effect of the liquid chloroform overlayer is confined to that region of the HXDSH molecule relatively distant from the metal surface. Thus, while the long, carbon tail of HXDSH becomes more "liquid-like" when in contact with chloroform, the carbons nearer the surface-bound sulfur retain their "solid-like" character.

A similar decrease in the number of trans conformers is observed in Raman spectra of dipalmitoyl phosphatidycholine dispersions in water as the dispersed amphiphile undergoes phase transitions between lamellar phases with decreasing order in the hydrocarbon tails. We conclude, therefore, that the effect of the chloroform overlayer is to facilitate disordering of the long alkyl chain, perhaps through impregnation by the nonpolar solvent molecules.

Visual observation of small drops of chloroform and water on HXDSH-coated island films makes clear that chloroform more fully wets the surface than does water. It is tempting therefore, to associate the ability of a liquid to wet a surfactant film with conformation changes induced in the amphiphile by the wetting liquid. Indeed, a canvassing of different overlying liquids (hexane, cyclohexane and carbon tetrachloride) is consistent with this idea; each of these liquids wetted HXDSH-coated island films and also caused a decrease in the SERS intensity of the "trans marker". In the mating of novel microscopic probes (like SERS) with traditional probes of large-scale surfactant properties (like contact angle measurements), we hope to gain insight into fundamental processes at the liquid/solid interface.

References