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"Sum Frequency Study of Langmuir-Blodgett Films on Single Gold Crystals: A Comparison of Chemisorbed and Physisorbed Systems"

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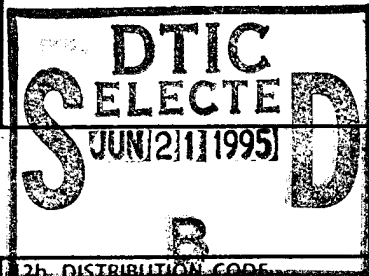
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# Sum Frequency Study of Langmuir-Blodgett Films on Single Gold Crystals: A Comparison of Chemisorbed and Physisorbed Systems

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## Abstract

The sum frequency rotational anisotropy signal from a single crystal gold with multiple Langmuir-Blodgett layers of chemisorbed and physisorbed molecules is examined. Using polarization selection and rotational anisotropy of the sum frequency signal, various portions of the non-linear response have been examined. These measurements show that it is possible to separate the resonant, non-resonant, and interaction components of the nonlinear response of these systems. It is shown that the dominant contribution to the nonlinear response by a chemisorbed species on gold is due to the bonding interaction with the surface. The dominant contribution to the nonlinear response by a physisorbed species on gold is from the resonant component from molecular resonances. This technique is shown to be useful as a probe of the type of the surface interaction of adsorbed layers on crystalline gold.

## I. Introduction

The study of interfacial systems has been an active field in the physical sciences in recent years because of the predominance of heterogeneous systems in chemistry and materials science. In particular, the solid/air and solid/liquid interfaces have been investigated extensively to understand structure, dynamics, and order in these regions, as well as to explore the many uses for these systems. Solid/air interface studies have investigated the arrangement of molecules at the interface in self-assembled monolayers (SAM)<sup>1</sup> and Langmuir-Blodgett (LB) films<sup>2</sup>. These systems have a present and potentially extensive use in many fields of science and engineering including electronics, optical signal processing, protective coatings, and chemical sensors<sup>3</sup>. The importance of understanding these systems is two-fold: microscopic details of the interfacial regions can be significant in leading to an understanding of the interactions important in these applications, and it is of great practical importance to optimize and control the characteristics of such systems. Many studies have been done to understand multilayer structure, reactivity, order and stability of organized molecular assemblies on solid surfaces by techniques such as grazing angle FTIR, X-Ray diffraction, XPS, and secondary ion mass spectrometry<sup>4</sup>. The focus of most of this work has been on the structure of the adsorbate molecules themselves. But to completely understand these systems and fully exploit their uses, the effect that these well-ordered layers have on the surfaces themselves must be fully realized. It is essential to understand the properties of the metal surface, the adsorbate layers, and the interaction between them. Properties such as symmetry and nonlinear polarizabilities will be affected by the addition of these materials to the surface and can be excellent probes of the surface-adsorbate interaction.

In this paper, the study of these systems is approached from a different angle. In contrast to direct studies of the multilayers, the effect that the adsorbates have on fundamental properties of the substrate and the interaction between the substrate and the adsorbate is examined. In particular, the effect of these layers on the nonlinear

polarizabilities of the metal as manifested in the nonlinear polarizability tensor,  $\chi^{(2)}$ , is examined. This has been achieved through studies of the rotational anisotropy in the sum frequency response from gold single crystals with deposited Langmuir-Blodgett multilayers. The results show the effect of molecular resonances in the adsorbate layers on the susceptibility tensor for sum frequency generation as well as the effect of metal-layer bond formation. Comparisons of these tensor elements for the bare metal and the metal/multilayer interface quantitatively and qualitatively show the effect of the addition of resonant layers, and the distinction between different types of surface bonding on the metal surface polarizability.

Sum frequency generation (SFG) is a novel technique employed to study the spectral and symmetry characteristics of surfaces and interfaces<sup>5-7</sup>. When one of the two incident light sources is tunable, SFG is capable of probing spectral features of surfaces. This makes SFG a more powerful tool than second harmonic generation because it allows the study of the effect of molecular resonance on the nonlinear susceptibility tensor. When crystalline materials are employed rather than amorphous media, separation of the symmetric and non-symmetric components of the measured nonlinear response can be achieved. Specifically, portions of the surface response possessing angular dependence (in the plane of the surface) can be readily separated from those possessing no angular dependence (out of plane of the surface).

The systems studied are Langmuir-Blodgett multilayers of stearic acid (SA) which forms physisorbed layers, and octadecane thiol (ODT) which forms chemisorbed layers on the gold (111) surface. By comparing the SFG response for these two types of layered systems, which bind very differently to the gold surface, one can determine the effect of the bond formation and the resonant component on the surface nonlinear response. Polarization studies of the nonlinear response yield qualitative information about the elements of the nonlinear susceptibility tensor,  $\chi^{(2)}$  and the angular dependence. Since the elements comprising the susceptibility tensor are complex, the phase angle

between them and magnitude ratios can be determined. Phase angle measurements are commonly used to characterize metal and semiconductor surfaces<sup>8</sup> and have proven to be a good probe of surface electronic structure. In addition, the magnitude ratios of several elements can be determined from the rotational anisotropy measurements and shed light on the type of interaction that the adsorbate has with the metal surface.

Nonlinear techniques such as second harmonic and sum frequency generation have been used to investigate many types of interfacial systems<sup>5, 9, 10</sup>. These techniques take advantage of the fact that the interface between two centro-symmetric materials is not be symmetric and therefore a nonlinear polarization can be induced. At sufficient input light intensities, the result of this induced polarization is the production of second harmonic or sum frequency light. These techniques are unique in that they are surface sensitive and selectively probe the interface where the broken symmetry occurs. In resonant sum frequency generation, the input fields come from one fixed frequency source and one tunable source. Tunability of this second input field allows one to exploit the resonances on the surface and to observe spectral characteristics of the surface. Sum frequency generation of surface adsorbates is especially useful as a probe of molecular structure due to the added constraint of a change in the polarizability ellipsoid (Raman allowed) of the transition as well as the necessity of an asymmetric induced polarization caused by the incident electromagnetic field. For example, for adsorbates consisting of long alkyl chains, only the methyl group will cause any resonant enhancement in the sum frequency signal and resulting spectra are uncongested by methylene C-H vibrational modes.

The sum frequency signal is related to the intensities of the visible and IR input light fields and the second order susceptibility of the medium by the following expression:

$$I_{SF}(\omega_{SF}) \propto \left| \chi_{SF,vis,IR}^{(2)} \right|^2 I_{vis} I_{IR} \quad (1)$$

where  $I_{SF}$  is the sum frequency intensity,  $\chi_{SF,vis,IR}$  is the susceptibility tensor for visible and IR input and sum frequency output and  $I_{vis}$  and  $I_{IR}$  are the respective input intensities. When one beam is at the frequency of a molecular resonance, the molecular hyperpolarizability is increased. The molecular hyperpolarizability as a function of frequency  $\omega$ , can be written in terms of the infrared and Raman transition dipoles of the molecules<sup>11</sup>:

$$\beta_{\alpha\beta\gamma}^{(2)}(\omega) = \frac{A_n M_{nm} \Delta p}{(\omega - \omega_{res} - i\Gamma_\omega)} \quad (2)$$

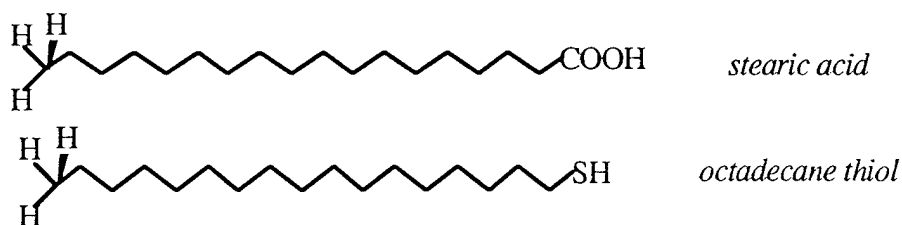
where  $\omega_{res}$  is the frequency of molecular resonance,  $\Gamma_\omega$  is the bandwidth of the resonance,  $A_n$  is the IR transition dipole,  $M_{nm}$  is the Raman transition dipole, and  $\Delta p$  is the difference in population between the vibrational excited state and the ground state.. The macroscopic polarizability tensor element for polarizations of  $\alpha, \beta, \gamma$ , for  $\omega_3$  (SF),  $\omega_1$  (vis),  $\omega_2$  (IR), respectively, is given by the number of molecules on the surface,  $N$ , and the orientational average of the molecular hyperpolarizability  $\beta$ :

$$\chi_{\alpha\beta\gamma}^{(2)}(\omega) = N \cdot \langle \beta_{\alpha\beta\gamma}^{(2)}(\omega) \rangle \quad (3)$$

As can be seen from the above equations, the second order susceptibility increases as the resonance condition is approached. Vibrationally resonant sum frequency generation has been used to investigate numerous properties and dynamics of interfacial systems including adsorbate vibrational relaxation<sup>12-15</sup>, surface reactions<sup>16</sup>, molecular order<sup>17, 18</sup>, coverage<sup>19</sup> and tilt angle<sup>20</sup> of adsorbed layers. Tremendous control of the particular elements of the nonlinear susceptibility tensor is achieved by changing the polarization of each of the two input beams to either  $p$  (parallel to the plane of incidence) or  $s$  (perpendicular to the plane of incidence) and selecting either  $p$  or  $s$  output polarizations. Proper selection of input and output polarizations, can therefore be used to quantify and compare select elements for different systems.

Stearic acid and octadecane thiol, shown below, attach to a gold surface with very different interactions. ODT has been shown to form very well ordered layers on metals

by the self-assembly process<sup>21, 22</sup>,. ODT binds very strongly to the gold surface through the oxidation of gold to form a gold-sulfur bond (bond strength of approximately 28.kcal)<sup>23, 24</sup>. Stearic acid has been shown to form chemisorbed layers on metal surfaces such as gold and silver<sup>25</sup> through dipole-induced dipole interactions.



In the case of these layered systems, the nonlinear susceptibility tensor  $\chi^{(2)}$  can be expressed to a first order approximation as:

$$\chi_{total}^{(2)} = \chi_{surface}^{(2)} + \chi_{adsorbate}^{(2)} + \chi_{interaction}^{(2)} \quad (4)$$

The first term is the susceptibility due to the gold surface alone. This term can be particularly large for gold at 532 nm, where it is on the edge of a bulk interband transition. The second term is due to the adsorbate layer alone and is negligible unless it is resonant with one of the incident frequencies. In this case, polarization conditions can be selected to probe the total susceptibility in the presence and absence of resonance to isolate the contribution from methyl resonances. The third term, the interaction term, will reflect only specific close-range interactions between the adsorbate and the surface such as metal bonds. Therefore it is expected that this term will emerge at low coverage levels, most likely with the first added layer and stay somewhat constant with the addition of subsequent layers. Using this expression and the predicted features of each term, we can characterize the nonlinear response from this system.

## II. Experimental

### A. Sample Preparation

Gold crystals were obtained from Monocrystal, cut to the (111) face, as determined by Laue patterns, bulk cleaned, and hand polished with diamond paste from

6 $\mu$  down to 0.25  $\mu$ . Electropolishing was done in a cyanide bath as previously described<sup>26</sup>. The crystals were flame annealed three times in a methane flame before the initial deposition of the films.

Octadecane thiol and stearic acid were obtained from Aldrich and were used as received. Langmuir-Blodgett films were deposited using a KSV model 5000 minitrough. Water with a resistivity of 17.9 M ohms was used as the subphase and the monolayers were spread by applying a 1mg/ml of the layering molecule in chloroform to the surface with a microsyringe. After determination of the proper deposition pressure from the recorded isotherm, layers were deposited at a rate of 2 mm/ min. Layer deposition was confirmed from transfer ratio measurements. Layers were deposited using a withdrawal direction parallel to the  $2\bar{1}\bar{1}$  direction of the gold crystal. Langmuir-Blodgett layer numbers (cumulative transfer) are calculated from the computed transfer ratios obtained from dipping parameters, yielding a more precise estimate of the total deposited material.

### B. Pressure-Area Isotherms

The recorded isotherms for SA and ODT are shown in Figure 1. Surface isotherms are a common method for characterizing monolayer strength and stability. Monolayer collapse, as denoted by the fall off of the surface pressure as the area of the monolayer is reduced, for these two molecules occurs at significantly different surface pressures. SA, which is known to form very stable monolayers, collapses at a surface pressure near 25 mN/m whereas ODT monolayers on water collapse at about 10 mN/m. Monolayer strength and stability are determined by molecule-molecule interactions as well as head group interactions with the surface of the subphase. The molecule-molecule interaction energy will be determined by:

$$E_{total} = E_{head-head} + E_{tail-tail} \quad (5)$$

In the case of stearic acid and octadecane thiol, the tail-tail interaction energy will be comparable for the two 18 carbon chains. For the head groups however, one expects a weaker interaction between neighboring thiol groups than between the hydrogen bonding

carboxylic acid groups. In addition the interaction of these head groups with the water surface can add stability to the monolayer and hinder collapse.

Rotational anisotropy measurements of the sum frequency signal were made with the laser set up described below. Briefly, a QuantaRay DCR 11 Nd:YAG laser is used to generate 1064 nm pulses of 12 ns in duration at 10 Hz repetition rate. This beam serves to pump a LiNbO<sub>3</sub> optical parametric oscillator to generate the mid range infrared beam of tunable pulses between 3.2 and 3.9 microns and between 0.75-1.5 mJ in intensity. The 532 nm visible beam is generated from the remaining 1064 output in a KDP crystal to produce powers of 2-6 mJ. The beams are sent to the sample in a counterpropagating geometry with the IR beam and visible beams 55° and 50° from the normal, respectively as shown in Figure 2. The electric field vectors for the input visible beam are shown for *p* and *s* polarization. The sum frequency signal emerging at 37° is sent through interference and glass filters to a PMT, boxcar and computer interface. Each data point is the average of between 200 and 400 shots.

### III. Results and Discussion

#### A. Sum Frequency Spectra

The sum frequency spectrum of 6 multilayers of ODT on a gold crystal (111) face is shown in Figure 3a. The resonance with the asymmetric stretch of the terminal methyl group of the alkyl chain shows a strong enhancement in the sum frequency signal at the corresponding wavelength, 2960 cm<sup>-1</sup>. The polarizations for this data were *p* for sum frequency, *p* for IR and *p* for the visible. Shown with the solid line is the fit to this resonance by the following equation:

$$I_{SF}(\omega) \propto |\chi^{(2)}(\omega) \cdot E_{IR}(\omega) \cdot E_{vis}|^2 \quad (6)$$

where  $I_{IR}$  and  $I_{vis}$  are the respective light intensities and  $\chi^{(2)}$  is the nonlinear susceptibility tensor:

$$\chi^{(2)}(\omega) = \frac{\chi^{(2)}_{avg}}{(\omega - \omega_{res} - i\Gamma_{\omega})} \quad (7)$$

Although the transition dipole for this stretch is perpendicular to the molecular axis, it has intensity along the surface normal axis due to the tilt of the molecules on the gold surface of approximately  $38^\circ$ <sup>27</sup>. All subsequent rotational anisotropy measurements are performed at this wavelength allowing the examination of the effect that this resonance for each of these two different molecules may have on the optical properties of the surface.

### B. SFG Rotational Anisotropy Measurements

Measurement of the sum frequency signal as a function of the azimuthal angle of the sample can reveal considerable detail about the surface crystalline and electronic structure. To fully investigate the sum frequency response as a function of angle, it is necessary to consider the elements of the nonlinear susceptibility tensor  $\chi$ . The nonlinear susceptibility tensor, consisting of 27 elements for the totally nonsymmetric system, reduces to 5 independent non-zero elements for the case of  $C_{3v}$  symmetry:  $\chi_{zzz}$ ,  $\chi_{xxx}$ ,  $\chi_{zxx} = \chi_{zyy}$ ,  $\chi_{xxz} = -\chi_{yyz}$ ,  $\chi_{xzx} = -\chi_{yzy}$ . Although the system examined here consists of a  $C_{3v}$  surface with an overlayer of  $C_s$  symmetry, the response is dominated by the  $C_{3v}$  symmetric contribution. The nonlinear response will result from the sum of all induced dipoles in a unit cell. The large polarizability of the gold metal of  $C_{3v}$  symmetry clearly dominates the response suggesting that the contribution to the polarizability of the overlayers is relatively small. The system will be discussed below in terms of the parameter fits for  $C_{3v}$  symmetry which were obtained in the presence and absence of the absorption contribution.

Although the symmetry of the response will be dominated by that of the metal surface, some residual symmetry of the applied layers may be detectable. One would expect additional symmetry contributions from the ODT and SA layers due to the directional dipping by the LB method. To investigate the symmetry of these films on gold, it is necessary to measure the rotational anisotropy of these layered systems on an isotropic sample, such as polycrystalline gold. The result of such an experiment with

ODT multilayers is shown in Figure 4a. With one reflection plane perpendicular to the surface, an ordered LB film on an isotropic substrate is believed to possess  $C_s$  (m) symmetry<sup>28</sup> such is the case for ODT as shown in the figure. The resulting intensity curve is fit to:

$$I = |a + c \cdot \cos \varphi|^2 \quad (8)$$

where  $a$  and  $c$  are the isotropic and anisotropic coefficients, respectively and  $\varphi$  is the azimuthal angle. The above equation is the predicted form of the sum frequency signal for a system possessing this symmetry<sup>29</sup>. Alignment of the methyl group transition dipoles along the direction of film deposition allows the observation of this anisotropy in the resonant sum frequency signal. It is also possible that addition of these films can cause an anisotropy in the metal surface response due to an anisotropic interaction of the oriented head groups of the molecules with the metal atoms. Rotational anisotropy measurements using  $s$  polarized IR light show that this anisotropy is indeed from the resonant component of the response, since it shows no anisotropy. These results confirm that there exists a well-ordered film with well oriented transition dipoles on the substrate.

The following experiments are labeled based on the polarizations chosen for the sum frequency, IR input and visible input beams, respectively. For example,  $ssp$  denotes the experiment in which the output light is  $s$  polarized the IR beam is  $s$  polarized and the visible beam is  $p$  polarized. Table 1 below shows that contributing tensor elements of the sum-frequency response for several polarization experiments. Of particular note is the comparison of the  $sps$  and the  $ssp$  polarization combinations. For the  $ssp$  polarization experiment, the infrared beam is  $s$  polarized and forms no electric field at the surface of the metal and thus cannot show any resonant enhancement by the adsorbate methyl groups<sup>6</sup>. Any SFG signal obtained with this polarization combination must be attributed to nonlinear polarization of the metal surface itself and not from adsorbates on top of the surface. In contrast, the  $sps$  polarization combination has a constructive interaction upon reflection at the gold surface and therefore forms a large electric field on the metal

surface capable of causing a resonant enhancement by the adsorbate methyl group. By comparing the results of these two polarization experiments, it is possible to quantify the resonant and the non-resonant components of the response.

The rotational anisotropy measurements of the bare gold (111) crystal surface for the *ppp* polarization combination at  $2960 \text{ cm}^{-1}$  is shown in Figure 4b. There are several important features of this data that should be noted. First, the signal shows distinct contributions from the anisotropic and isotropic components which are of different phase and show interference that leads to the unique shape of the angular response, as has been previously observed. Fits to this data show a phase angle of  $47^\circ \pm 5^\circ$  and a magnitude ratio for  $|c//a|$  of  $1.2 \pm 0.1$ . Second, the response of three large and three small peaks reflects the 3-fold symmetry of the surface. Comparison of changes in experimental signal levels from the experiments for polycrystalline gold with multilayers (Figure 4a) and for polycrystalline gold without multilayers (not shown) indicates that the gold nonlinear response is approximately an order of magnitude larger than the nonlinear response due to the adsorbate layers, and therefore it is expected that the threefold symmetry will dominate the response. This is in fact observed in the rotational anisotropy measurements from gold (111) with layers of SA and ODT (not shown) which qualitatively resemble that obtained for the bare gold (111). This indicates that the measurements that follow are mainly probing the different components of the metal response. From fits to these data, phase angle and anisotropic and isotropic component ratios can be examined and compared later as layers are added.

The phenomenological forms of the rotational anisotropies for output, IR and visible light are shown below:

$$I_{p_{out},p,p} \propto \left| F_z \chi_{zzz} f_z f_z - F_z \chi_{zxx} f_x f_x - F_x \chi_{xzx} f_z f_x - F_x \chi_{xxx} f_x f_x \cos 3\phi \right|^2 \quad (9)$$

$$I_{s_{out},p,s} \propto \left| F_y \chi_{zyz} f_z f_y - F_y \chi_{yxy} f_x f_y \cos 3\phi \right|^2 \quad (10)$$

$$I_{S_{out},s,p} \propto |F_y \chi_{yyz} f_y f_z - F_y \chi_{yyx} f_y f_x \cos 3\phi|^2 \quad (11)$$

where  $F_x$ ,  $F_y$  and  $F_z$  are the output fresnel factors and  $f_x$ ,  $f_y$ , and  $f_z$  are the input fresnel factors for x, y and z polarizations, and  $\phi$  is the azimuthal angle. As can be seen from the above equations, the sum frequency intensity for each of these polarization experiments can be expressed in terms of an anisotropic and isotropic component. All data are fit to the equation:

$$I = |a + c \cdot \cos 3\phi|^2 \quad (12)$$

where  $\phi$  is the azimuthal angle and  $a$  and  $c$  are complex. From these fits, the parameters  $\gamma$  and  $|c|/|a|$  are obtained where  $\gamma$  is the relative phase between  $a$  and  $c$  and  $|c|/|a|$  represents ratios of the magnitudes. The coefficient  $a$  is the isotropic component and is generally assigned to the out-of-plane response and  $c$  is the anisotropic, in-plane response. The phase angles and magnitude ratios of these coefficients are readily obtained from fits to the experimental data and have been frequently used to characterize metal and semiconductor surfaces<sup>30-33</sup>. From these coefficients, corresponding elements of the susceptibility tensor can be determined from the following equations using appropriate fresnel factors.

$$\begin{aligned} P_{out,p,p} \quad a &= F_z \chi_{zzz} f_z f_z - F_z \chi_{zxx} f_x f_x - F_x \chi_{xzx} f_z f_x \\ c &= F_x \chi_{xxx} f_x f_x \end{aligned} \quad (13)$$

$$\begin{aligned} S_{out,p,s} \quad a &= F_y \chi_{yzy} f_z f_y \\ c &= F_y \chi_{yxy} f_x f_y \end{aligned} \quad (14)$$

$$\begin{aligned} S_{out,s,p} \quad a &= F_y \chi_{yyz} f_y f_z \\ c &= F_y \chi_{yyx} f_y f_x \end{aligned} \quad (15)$$

### C. Phase Angle and Magnitude Ratio Calculations

To see if one can observe a difference in the nonlinear response due to chemisorption or physisorption, the ODT and SA layered systems were examined and compared. Although ODT layers are typically deposited by the self assembly technique,

concern for consistent film structure made the Langmuir-Blodgett technique an excellent choice for deposition of ODT in a more ordered fashion. It has been shown that ODT can form multilayers possibly through the formation of disulfides or sulfonates<sup>34</sup>. Stearic acid forms well ordered multilayers by the LB techniques and provides a good example of a physisorbed system. The results of the phase angle between  $c$  and  $a$  determined from fits to data for ODT and SA layered systems are shown in Figures 5a and 5b obtained from rotational anisotropy measurements at 2960  $\text{cm}^{-1}$ , the methyl asymmetric stretch resonance (not shown). Results from several polarization experiments are shown. The aim in performing these polarization experiments is to attempt to isolate effects due to the resonance of methyl groups, ( $\chi_{adsorbate}^{(2)}$ ), those due to surface bonding ( $\chi_{interaction}^{(2)}$ ), and those due to effects from the gold surface ( $\chi_{surface}^{(2)}$ ).

Specifically, it is expected that the *sps* polarization will reflect surface electronic properties as manifested in the susceptibility due to the additional resonances ( $\chi_{surface}^{(2)}$ ,  $\chi_{interaction}^{(2)}$ , and  $\chi_{adsorbate}^{(2)}$ ), whereas the *ssp* polarization will reflect surface electronic properties in the absence of resonances ( $\chi_{surface}^{(2)}$  and  $\chi_{interaction}^{(2)}$ ). If one first considers the *sps* polarization combination, it is seen that in Figure 5a, a large change (about 50°) in the phase angle takes place upon addition of ODT to the surface. For stearic acid, a smaller (about 30°) change occurs with layering, showing a distinct difference in the effect of layering with these two different molecules. Specifically, the chemisorbed system (ODT) shows a dramatic change in phase angle with the application of just one layer whereas the physisorbed molecule (SA) undergoes a very gradual change in phase angle with adsorbate layer number. The fact that ODT causes a large change in phase angle with the addition of only one layer suggests that the interaction with gold is short range and strong. This is what would be expected for a covalent surface bond. The large change in the phase angle can therefore be attributed to the short range surface bond formed by the thiol as manifested in the  $\chi_{interaction}^{(2)}$  term. For SA, a very different behavior is observed, as would be expected for layers with no covalent surface bonds. In

this case gradual change in phase angle due to the contribution to the nonlinear polarizability by the molecular resonances through the  $\chi_{adsorbate}^{(2)}$  term is observed. This change most likely results from the interference of the surface sum frequency from the  $\chi_{surface}^{(2)}$  term with the resonant sum frequency signal from the  $\chi_{adsorbate}^{(2)}$  term of the adsorbate layers. These changes show that the resonant methyl stretches do in fact interact with the surface in a way to change the phase angle between the anisotropic and isotropic components. In addition, it is interesting to note that the change in phase angle for the physisorbed molecule is opposite in magnitude from that of the chemisorbed molecule suggesting that there is a large difference in the nature of the interaction that a surface bond and methyl group resonances have on the sum frequency signal from a gold surface.

Next the *ssp* polarization is considered, where the IR light is *s* polarized. In this case it is expected that only changes in the electronic properties of the surface and no molecular resonances from methyl groups are probed. It is seen in Figure 5b that stearic acid shows no significant change in phase angle upon layering whereas ODT shows a very significant decrease in phase angle. This suggests that in the physisorbed case, very little effects on the surface electronic properties are present, and in the chemisorbed system a large perturbation of the surface occurs, as would be predicted. Lastly, the *ppp* polarization experiment is considered, which is expected to have a contribution from the  $\chi_{surface}^{(2)}$ ,  $\chi_{interaction}^{(2)}$  as well as  $\chi_{adsorbate}^{(2)}$ . Table 1 shows the contributing tensor elements to this response to be three terms sensitive to changes in surface electronic properties alone ( $\chi_{xxx}$ ,  $\chi_{zxx}$ , and  $\chi_{xxz}$ ) and two terms ( $\chi_{zxz}$  and  $\chi_{zzz}$ ) capable of probing molecular resonances as well as surface electronic properties. Depending on the nature of the specific interaction of the adsorbate with the gold surface, these terms may or may not reflect the  $\chi_{interaction}^{(2)}$  term. From Figures 5a and 5b, it can be seen that no significant change occurs in the phase angle for *ppp* polarization for either ODT or SA. This suggests that the dominant response is not affected by either the  $\chi_{interaction}^{(2)}$  term or

the  $\chi_{adsorbate}^{(2)}$  term. It is well known that the dominant tensor element in nonlinear surface response from a surface is the  $\chi_{zzz}$ <sup>35</sup>. Assuming that our *ppp* signal is dominated by this term, it can be concluded that this term is not strongly affected by the bonding or the resonance.

A similar analysis of the anisotropic to isotropic component magnitude ratios yields more insight into the effects of these layers on the surface. The results of the fits are shown in Figure 6a and 6b. By examination of the *sps* data in Figure 6a, it is seen that the  $|c//a|$  term for *sps* polarization shows a distinct change upon addition of the ODT and virtually no change upon layering of SA. It is clear that for ODT there is a strong interaction with the surface because of the large change in the anisotropic to isotropic magnitude ratio. It is most likely due to a short range interaction effect since the largest change occurs after deposition of one layer. The fact that there is relatively little change in this ratio for the *ssp* polarization might lead one to believe that the large change in the *sps* polarization is due to the addition of resonances. More likely though, it is due to a much larger contribution by  $\chi_{interaction}^{(2)}$  to  $\chi_{yzy}$  and  $\chi_{yxy}$ , the tensor elements key to the *sps* response, than to  $\chi_{yyz}$  and  $\chi_{yyx}$  the tensor elements for the *ssp* polarizations. An increase in  $|c//a|$  reflects a change in the relative magnitudes of the in plane ( $\chi_{yyx}$  and  $\chi_{yxy}$ ) and the out of plane ( $\chi_{yzy}$  and  $\chi_{yyz}$ ) components. An increase upon layering leads to the conclusion that the bonding to the surface causes either an increase in the in-plane or a decrease in the out-of-plane susceptibility. By considering the nature of the Au-S bond, which is thought to be either an sp or an sp<sup>3</sup> hybrid<sup>36</sup> it is reasonable to assume that the  $\sigma$  bond reduces the polarizability of the electrons in the z direction by localizing them through bonding. This has been shown to occur in other metal systems with deposited layers as well<sup>33</sup>.

As previously mentioned, the SA layering shows no effect on the  $|c//a|$  values but does show an observable small change in the phase angle values. Referring to Equations 13-15 which show the constituents of the coefficients, one of two conclusions

can be drawn from this observation about the SA-metal interaction: one, that  $c$  and  $a$  are affected equally or two, that they are affected not at all by  $\chi_{interaction}^{(2)}$  and  $\chi_{adsorbate}^{(2)}$  terms. Since the dipole-induced dipole interaction is somewhat weak, this suggests that there is little contribution from  $\chi_{interaction}^{(2)}$  term. Phase angle calculations have shown that the contribution from  $\chi_{adsorbate}^{(2)}$  for stearic acid is small as well. This being the case, it appears that the phase of the nonlinear response is much more sensitive to resonant components of the adsorbate layers than is magnitude ratio calculations.

It is also worth noting the possibility that this data may be the result of linear absorption of the input IR beam with the addition of layers. To assure that the observed trends are not the result of a reduction in infrared light intensity, the absorption of light by the layers was calculated. A rough estimate of the optical density change per layer yields a decrease in transmission of less than one part in  $10^4$ . Upper estimate of the effect on output sum frequency signals then yields a change of less than 0.01 %. and it can be safely concluded that this is not a linear effect.

Close examination of the phase angle and the magnitude ratios at higher layer number reveals a general tendency in the parameters to return to the original bare metal values. This trend, observed in both types of adsorbed layers, may reflect destruction or disorder induced in the films, most likely from repeated laser irradiation. It has been shown that at temperatures above 453°K, all trans alkane chains undergo irreversible conformational changes<sup>37</sup>. Although minimal laser powers needed to obtain necessary signal levels were used, it is likely that repeated laser irradiation may cause this type of destruction. Because of this, no absolute conclusions can be made about films that are larger than 3 layers for the ODT and larger than 5 layers for SA.

#### IV. Conclusions

It has been shown that the technique of resonant IR-Visible sum frequency is capable of characterizing surface interaction of layered materials on crystalline metals as well as resonance contributions. The primary result from this study is that it is possible to

discern between chemisorbed and physisorbed molecules on the surface of gold. In short, the chemisorbed molecules show a very short range effect on the susceptibility tensor from the strong bonding interaction, and the physisorbed molecules show a much weaker and long range affect due to their molecular resonances. In addition, this technique allows characterization of the surface response in terms of the symmetric and asymmetric components. Future studies will extend this work to semiconductor and insulator surfaces.

## V. Acknowledgments

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## Figure Captions

Figure 1: Pressure-area isotherms for stearic acid and octadecane thiol on a water subphase at 25°C.

Figure 2: Schematic of sum frequency experimental geometry. Polarizations are defined such that p is parallel to the plane of incidence and s is perpendicular to the plane of incidence. The angle  $\phi$  is the azimuthal angle of the sample about which the sample is rotated to obtain rotational anisotropies.

Figure 3: The sum frequency spectrum of 6 ODT layers on gold (111) obtained with p polarized output, p polarized IR light, and p polarized visible light. The solid line is a fit to the data using a bandwidth of  $8 \text{ cm}^{-1}$  and the equations described in the text.

Figure 4A: The rotational anisotropy of 6 ODT LB layers on polycrystalline gold with p polarized output, p polarized IR light, and p polarized visible light. Solid circles are the data and the line is the fit to  $I = |a + c \cdot \cos \phi|^2$ . Data was obtained with

Figure 4B: The rotational anisotropy of clean gold (111) obtained with p polarized output, p polarized IR and p polarized visible light.

Figure 5: Phase angle as a function of layer number for A) octadecane thiol and B) stearic acid Langmuir-Blodgett layers. Phase angles were obtained from sum frequency rotational anisotropy data fits to  $I = |a + c \cdot \cos(3\phi)|^2$  where the phase angle is the relative phase between the coefficients a and c.

Figure 6: Anisotropic isotropic magnitude ratios as a function of layer number for A) octadecane thiol and B) stearic acid Langmuir-Blodgett layers. Magnitude ratios were obtained from sum frequency rotational anisotropy data fits to  $I = |a + c \cdot \cos(3\phi)|^2$

**Table 1: Nonlinear Polarizability Tensor Elements for Various Polarizations**

Sum Frequency polarization	Input IR polarization	Input 532 nm polarization	Contributing Tensor Elements
P( $E_x, E_z$ )	P( $E_x, E_z$ )	P( $E_x, E_z$ )	$\chi_{xxx}, \chi_{xzx}, \chi_{zxx}, \chi_{xxz},$ $\chi_{zzz}$
S( $E_y$ )	P( $E_x, E_z$ ) (resonant)	S( $E_y$ )	$\chi_{yyx}$ (in-plane), $\chi_{yyz}$ (out-of plane)
S( $E_y$ )	S( $E_y$ ) (non-resonant)	P ( $E_x, E_z$ )	$\chi_{yxy}$ (in-plane), $\chi_{yzy}$ (out-of plane)

FIG 1

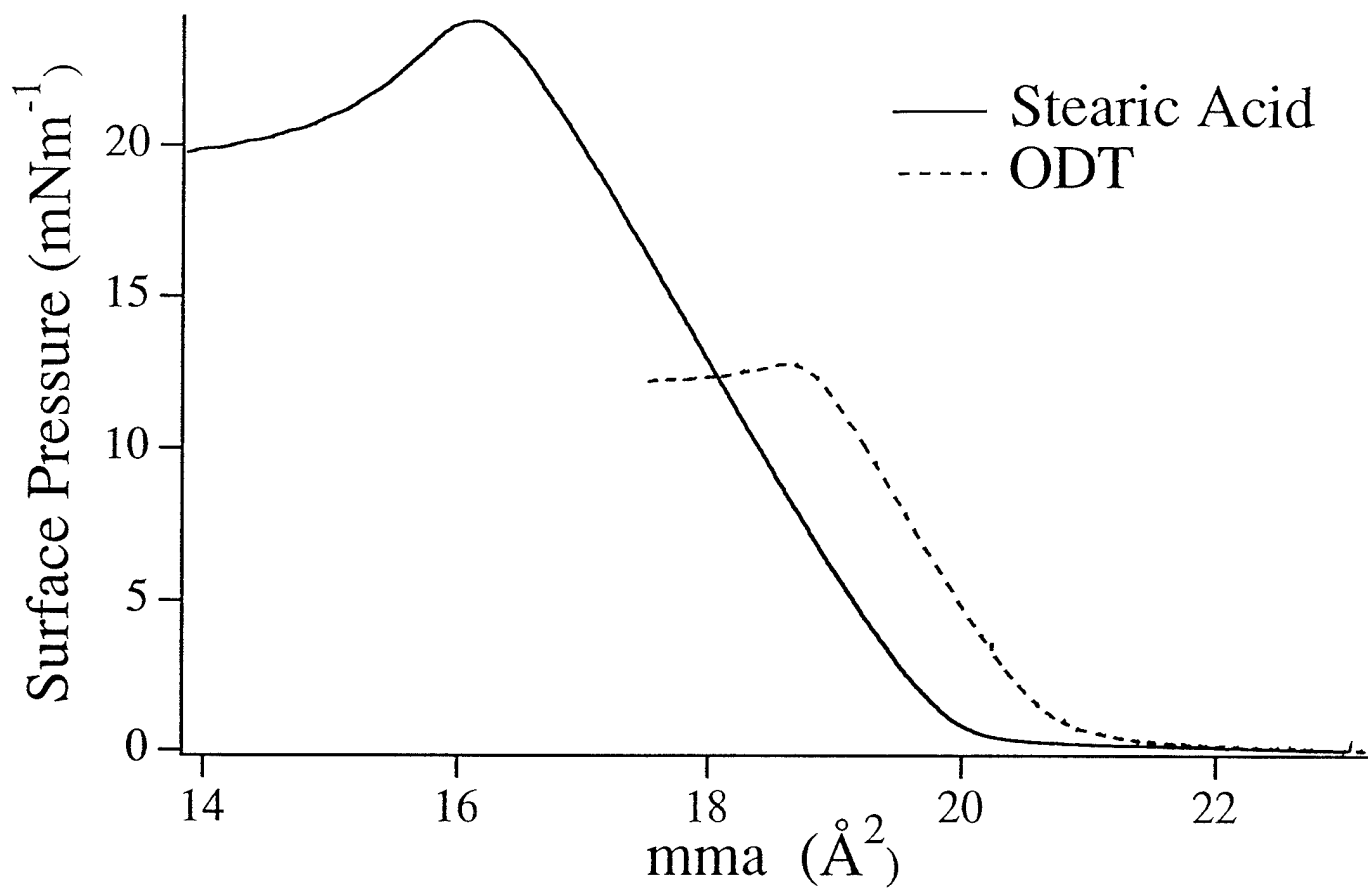


FIG 2

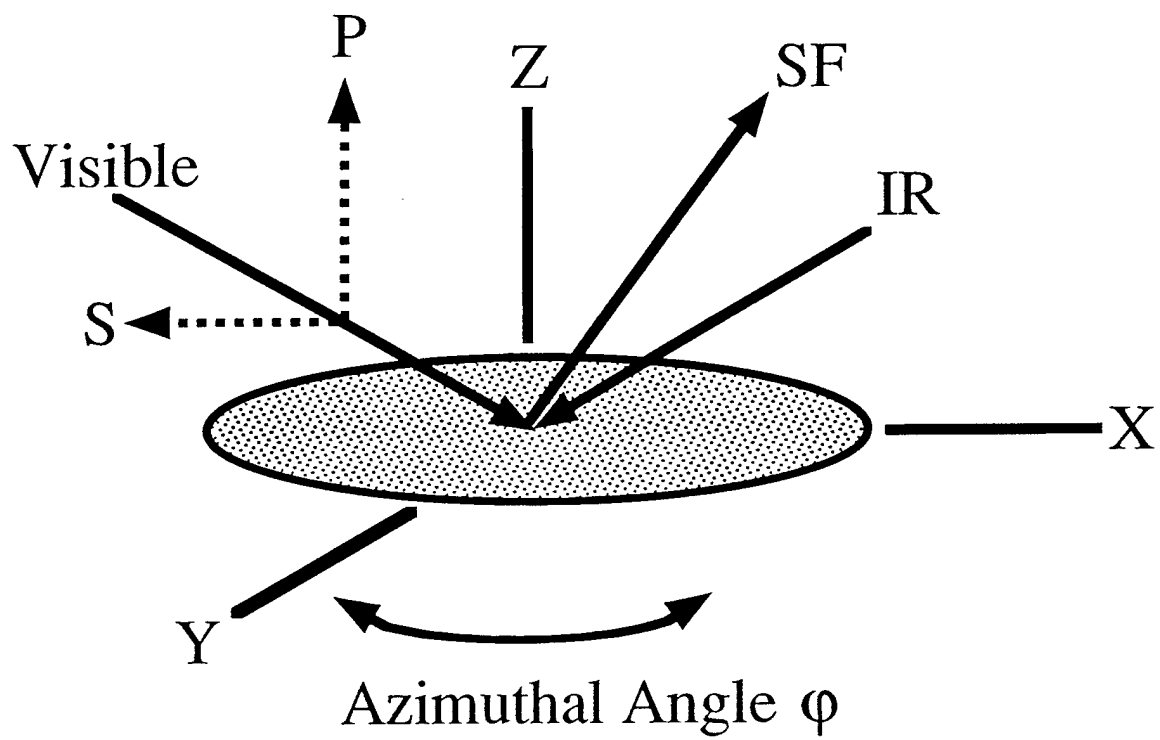


FIG 3

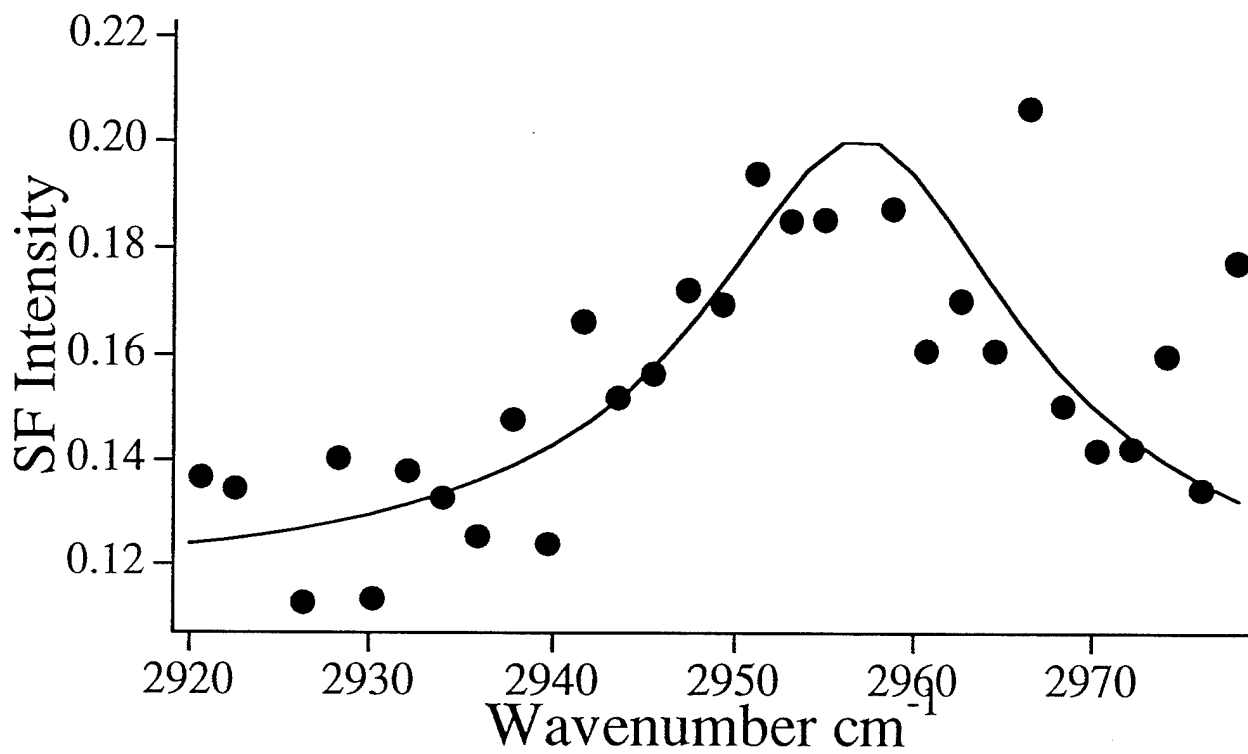


FIG 4

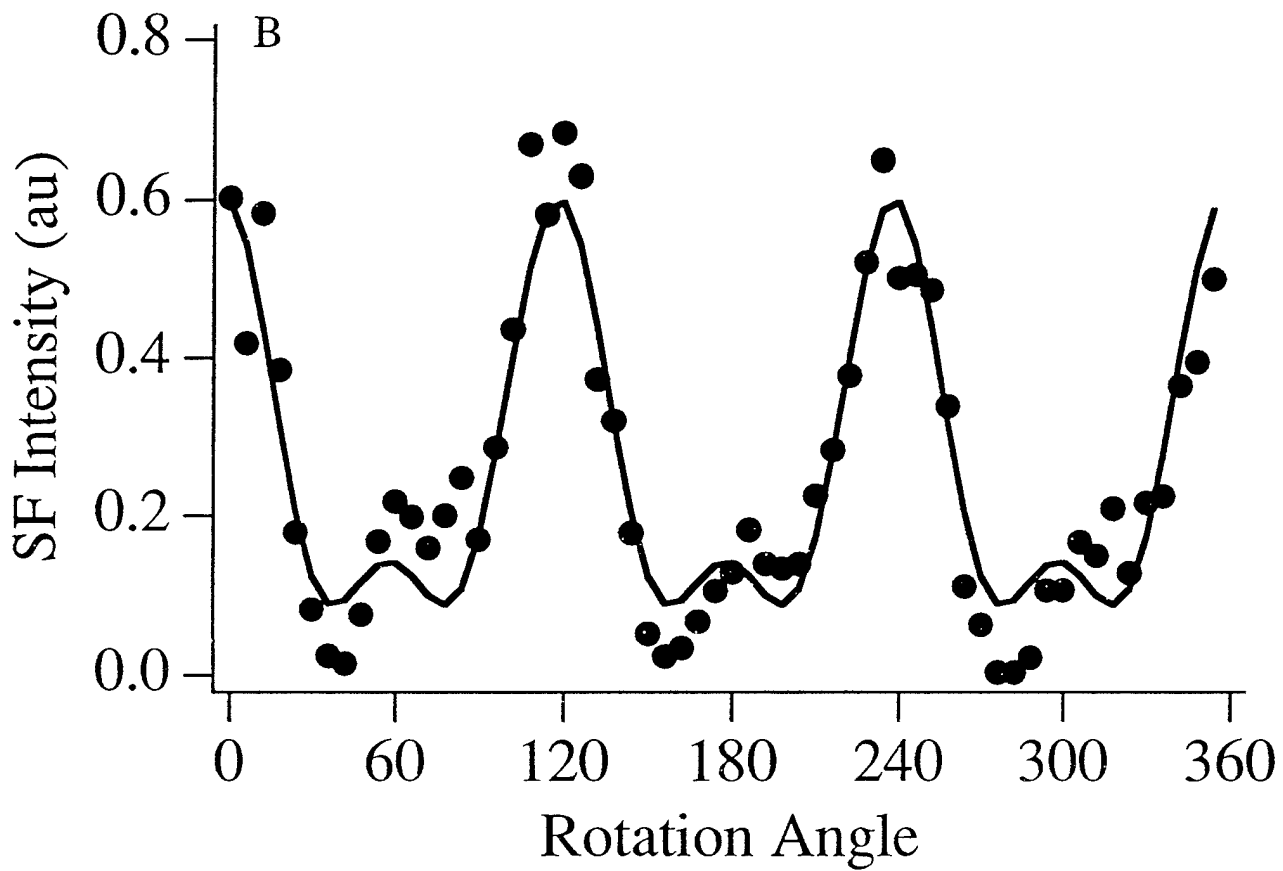
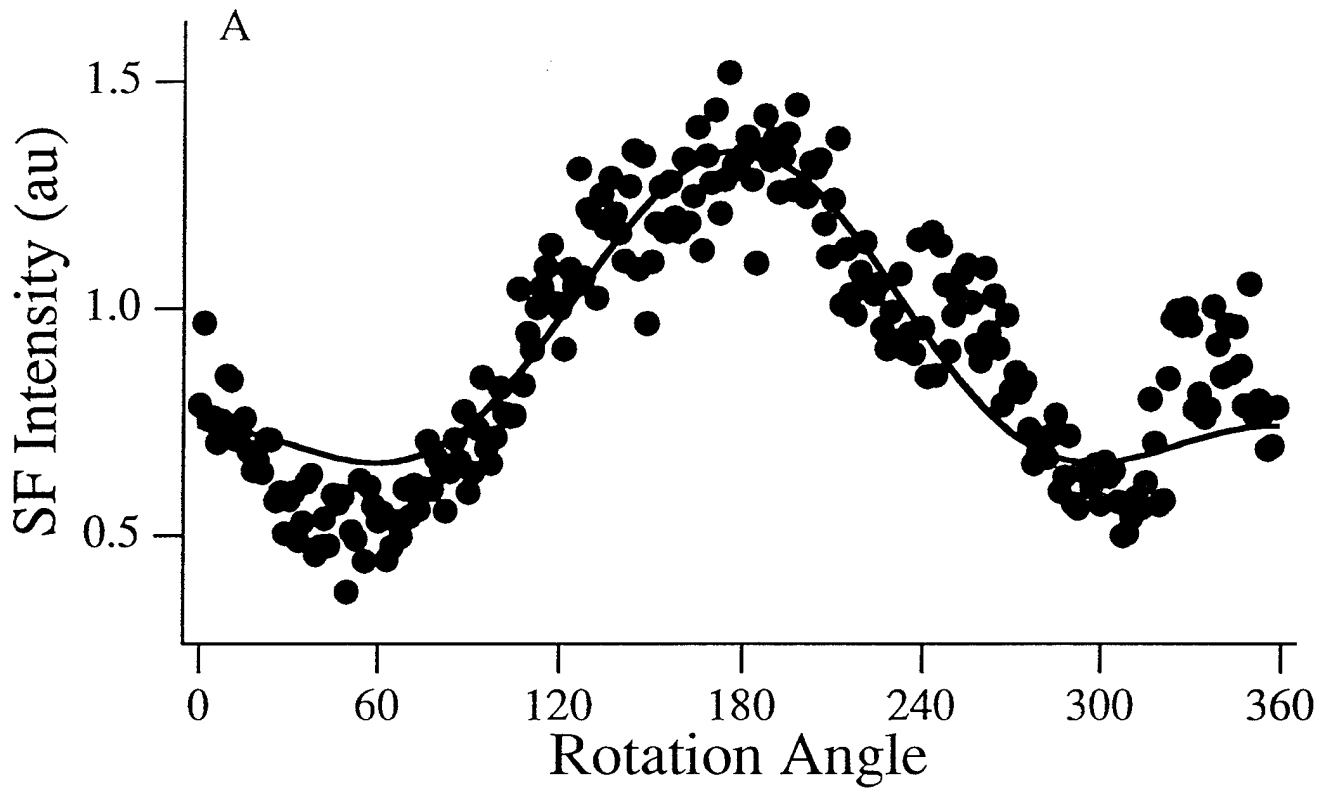


Fig 5

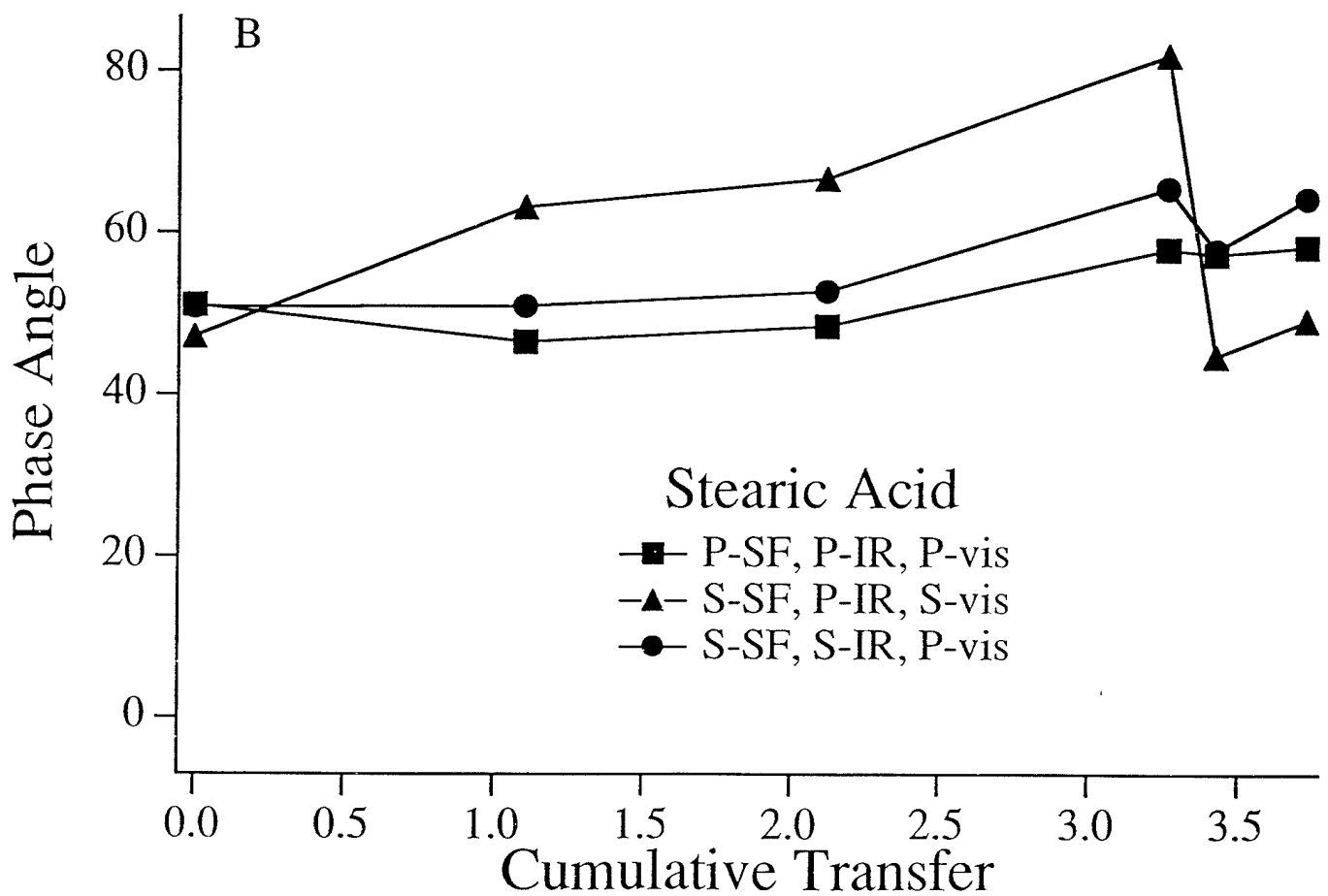
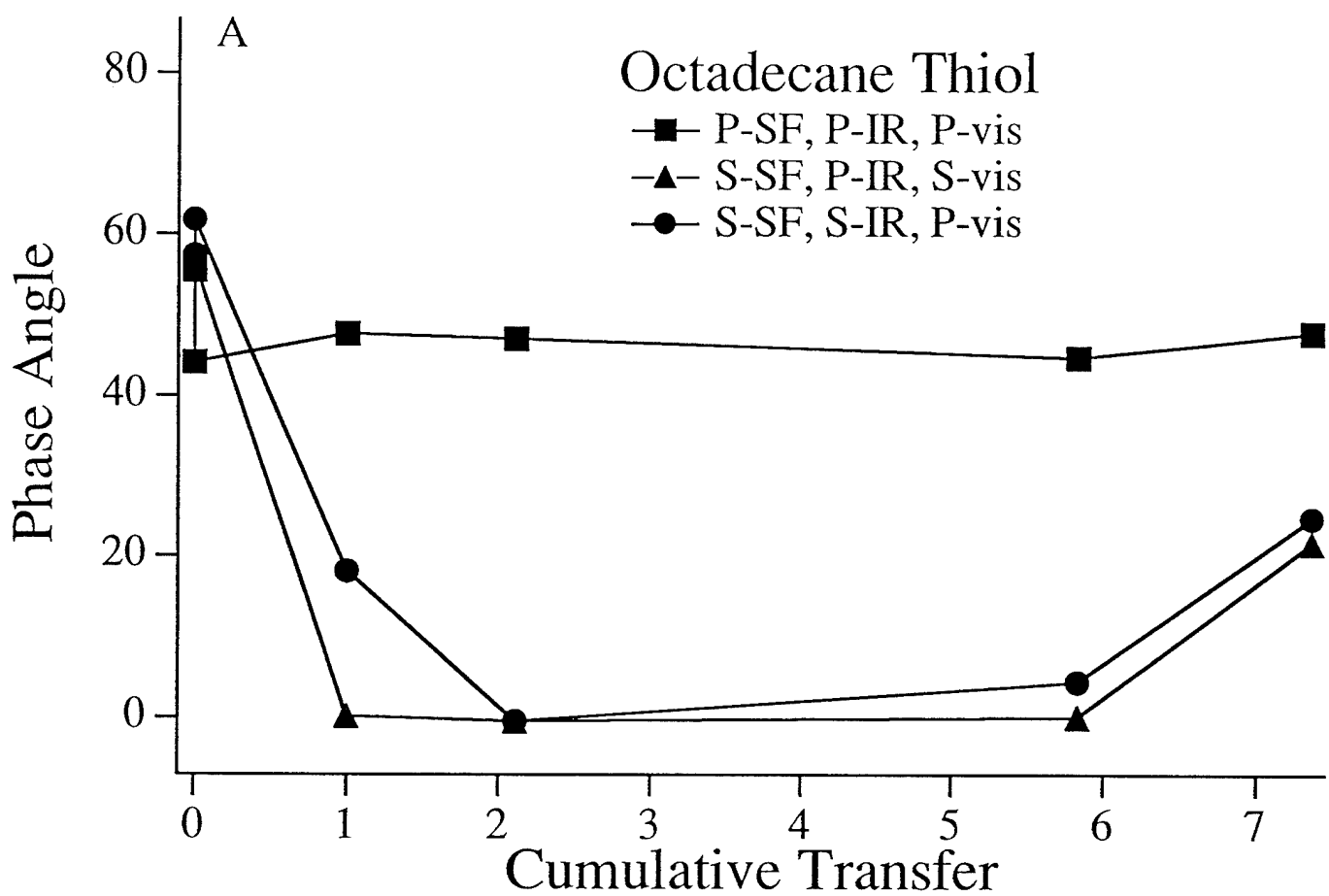


FIG 6

