Surface Structure and Chemical Switching of Thioctic Acid Adsorbed on Au(111) as Observed Using Near-Edge X-ray Absorption Fine Structure

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January 8, 2004

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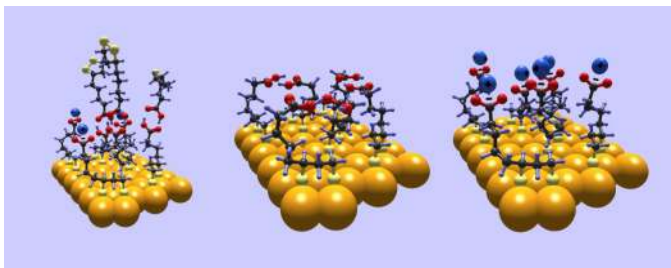
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thioctic acid

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Abstract

Thioctic acid (alpha-lipoic acid) is a molecule with a large disulfide-containing base, a short alkyl-chain with four CH_2 units, and a carboxyl termination. Self-assembled monolayer (SAM) films of thioctic acid adsorbed on Au(111) have been investigated with near-edge x-ray absorption fine structure (NEXAFS) spectroscopy and x-ray photoelectron spectroscopy (XPS) to determine film quality, bonding and morphology. Using standard preparation protocols for SAMs, that is, dissolving thioctic acid in ethanol and exposing gold to the solution, results in poor films. These films are highly disordered, contain a mixture of carboxyl and carboxylate terminations, have more than monolayer coverage, and exhibit unbound disulfide. Conversely, forming films by dissolving 1 mmol thioctic acid into 5% acetic acid in ethanol (as previously reported with carboxyl-terminated alkyl-thiols) forms ordered monolayers with small amounts of unbound sulfur. NEXAFS indicates tilted over endgroups with the carboxyl group normal on average 38° from the surface normal. Slight dichroism in other features indicates alkyl chains statistically more upright than prostrate on the surface. Reflection-absorption Fourier transform infrared (RA-FTIR) spectra indicate hydrogen bonding between neighboring molecules. In such well-formed monolayers, a stark reorientation occurs upon deprotonation of the endgroup by rinsing in a KOH solution. The carboxylate plane normal is now about 66° from sample normal, a much more upright orientation. Data indicate this reorientation may also cause a more upright orientation to the alkyl portion of the molecules.

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Introduction

Surface modification by using ω-functionalized self-assembled monolayers (SAMs) on gold or other noble metals is the simplest way to create flat, chemically- or biologically-functionalized surfaces. Although alkyl-thiols are often used for carboxyl terminated SAMs, thioctic acid has distinct advantages for surface modification. The disulfide-containing base gives added stability, and yields two gold-sulfur bonds per molecule in surface-attached species.

Potential uses for thioctic acid monolayers include bio- and immuno- sensors[1-5], components in molecular electronic applications[6], and molecular anchors for surface-attachment of catenanes and rotaxanes[7-9]. Our group is thus currently pursuing thioctic acid as a means of providing superior gold surface attachment for functionalized and molecular electronic interlocking molecules[10,11]. A thorough understanding of the binding and orientation is necessary for further use of thioctic acid to ensure claims that conformational and chemical changes lead to observed phenomena in molecular electronic and interlocking molecule applications[12]. Although previous studies have characterized thioctic acid layers electrochemically for layer stability and an indication of packing[13-17], to our knowledge, no direct morphological characterizations of this molecule exist to date.

The surface structure of thioctic acid is intriguing compared to thiol based, long alkyl-chain, carboxyl-terminated SAMs. For example, SAM ordering, substrate binding and surface attachment has been extensively studied for mercaptohexadecanoic acid[18-21]. This molecule has 15 CH_2 units encouraging order through intermolecular interactions, a small-footprint thiol for attachment, and a carboxyl termination. Conversely, thioctic acid (Figure 1) has a very short alkyl-chain (four CH_2 units) with weak van der Waals interactions between neighboring molecules. The disulfide base has a larger footprint than a thiol, which intuitively should further

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hinder self-assembly. These differences in thioctic acid allow a more focused study on the carboxyl endgroup and the role it plays in organic monolayer film structure.
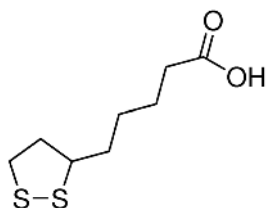

Figure 1. Thioctic acid, the adsorbed molecule studied in this work.

In this paper, we quantitatively investigate substrate binding, monolayer formation, and chemical switching of film morphology for thioctic acid on Au(111) using NEXAFS and XPS for the first time. This work explores films derived from three preparation conditions. The first consists of dissolving 1mmol thioctic acid in ethanol only, exposing gold to this solution, and then rinsing with ethanol only, which is found to result in disordered films of more than one monolayer in thickness. The second method, using 1 mmol thioctic acid dissolved in 5% acetic acid in ethanol for both SAM formation and rinsing is analogous to a successful method for producing reproducibly well-ordered monolayers of carboxyl-terminated alkyl-thiols[19]. Using this method yields thioctic acid monolayers with tilted-over, hydrogen-bound endgroups and alkyl chains statistically more upright than prostrate on the surface. In the third case, where well-prepared thioctic acid molayers via the second method are exposed to KOH for deprotonation, the carboxylate endgroups exhibit a strong reorientation to an upright position, similar to changes observed in alkyl-thiols[18]. The more thorough understanding of the switchable morphology and substrate binding thus provided should aid the emerging applications requiring surfaces modified with thioctic acid.

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Experimental Details

Reagents and Materials

Reagents were purchased from commercial sources and used as received. Thioctic acid (98%) was purchased from Aldrich. Ethanol (200 proof, USP) was purchased from Aaper. Acetic acid (HPLC grade, 99.7%) was purchased from VWR. Au(111) substrates were formed by evaporating 5 nm Ti and then 100nm Au on Si(100) under high vacuum. All gold substrates were hydrogen-flame annealed immediately before use[22].

Sample Preparation

Thioctic acid solutions were prepared similarly to previously reported carboxyl-terminated alkyl-thiols[19] by dissolving thioctic acid into into either pure ethanol or 5% (by volume) acetic acid in ethanol at concentrations of approximately 1mmol. Gold substrates were immersed and stored in these solutions for 24-36 hours. Under these conditions, disulfide-containing thioctic acid molecules adsorb to the gold surface through gold-sulfur bonds as in thiol containing molecules[23]. Each sample was then removed, rinsed with its corresponding pure solvent – pure ethanol or 5% acetic in ethanol. Samples were then immediately transferred into ultra-high vacuum for analysis.

Instrumentation

X-ray absorption spectroscopy (XAS) measurements were acquired at VUV BL 8.2 of The Stanford Synchrotron Radiation Laboratory (SSRL,SPEAR II) at the Stanford Linear Accelerator Center. This beamline uses bend magnet radiation and a spherical grating monochromator[24]. XAS experiments were conducted with an energy resolution of

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approximately 0.2 eV at the carbon K-edge. Absorption spectra were recorded simultaneously using both total electron yield (TEY) and auger electron yield (AEY). While the measured total current leaving the sample constitutes the TEY signal, AEY measurements consist of measuring the intensity of the appropriate auger electron at a given fixed analyzer kinetic energy with large pass energy while scanning the X-rays through the absorption edge.   Both currents were normalized to the incident photon flux via the current from a clean transmissive grid with a freshly evaporated gold coating. X-ray flux was carefully limited in order to minimize sample damage during data collection[25].   All spectra were recorded at a base pressure of less than 1 x 10^{-9} torr. The degree of linear polarization was measured with highly-oriented pyrolytic graphite (HOPG) by rotating about two different axes and using the intensity of the C 1s to π^* feature in the C K-edge spectra[18].   In conjunction with these measurements, this method measured the linear polarization at about 88% in the plane of the storage ring. The energy scale of carbon XAS spectra were calibrated to the π^* resonance of HOPG which was taken to be 285.38 eV[26].

X-ray photoelectron spectra were obtained at SSRL using a PHI 15-255G Cylindrical Mirror Analyzer (CMA) and associated PHI electronics. The pass energy was set to 25 eV for XPS spectra, while for Auger electron yield absorption, the pass energy was set to 200 eV. XPS measurements have an overall estimated resolution of 0.4 eV. S 2p spectra were obtained at a photon energy of 280 eV or 400 eV; C1s spectra were obtained at a photon energy of 400 eV. Au 4f spectra of the substrates were taken immediately after each sulfur and carbon spectrum to calibrate the binding energy scales. The Au $4f_{7/2}$ photoelectron at 84.01 +- 0.05 eV was used to convert the kinetic energy scales to binding energy scales.

FTIR spectra were obtained using a Nicolet 560 FTIR with an MCT detector and a reflecting grazing incidence accessory.   The largest aperture was used (1.7cm x 2.7cm) for

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analysis. Flame annealed and/or SAMs consisting of undecanethiol on gold were used as a background references for the carbonyl / carboxylate region (1900 cm^{-1} to 1300 cm^{-1}).

Analysis

NEXAFS quantitatively investigates the orientation of bonds through polarization dependencies of various resonances. The intensity of a transition from a 1s core level into an unoccupied orbital is proportional to the dot product of the incident electric field and the transition dipole moment. Varying the incidence angle changes the electric field from nearly orthogonal to the substrate at grazing incidence to within the surface plane at normal incidence. One can thus determine the orientation of the alkyl chains and the terminal carboxyl groups in monolayers derived from thioctic acid. For these films, the Au(111) substrate has threefold azimuthal symmetry. The transition dipole moment can be modeled as a vector in the case of the C-C σ* molecular orbitals along C-C backbone of the alkyl chain or the π* orbital whose transition dipole moment vector is perpendicular to the O=C-O plane. One can also model the transition dipole moment as a number of resonances in a given plane with (C-H σ*-like) Rydberg R* resonances[27] or the two C-O σ * bonds in the O-C=O plane of the carboxyl group. The R* and carboxyl π* resonances are highly convoluted. In order to isolate contributions for each of these states, peakfitting of all spectra and difference spectra were simultaneously performed to advantageously use position and width information within spectra, and polarization dependence within differences[18]. To remove proportionality, and to greatly simplify analysis, intensities are compared as ratios and left as functions of cosine squared. P is the degree of linear polarization, θ is the angle between the incident radiation and the surface, α is the angle between the surface normal and the transition dipole moment vector, and λ is the angle between the

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normal to the transition dipole moment plane and the normal to the surface. With $\Theta = \cos^2 \theta$, $A = \cos^2 \alpha$, and $\Gamma = \cos^2 \gamma$ the intensities from references [27, 28] become:

$$\frac{I_v(\Theta_i, A)}{I_v(\Theta_j, A)} = \frac{P(3A-1)\Theta_i - A + 1}{P(3A-1)\Theta_j - A + 1} \tag{1}$$

and

$$\frac{I_p(\Theta_i, \Gamma)}{I_p(\Theta_j, \Gamma)} = \frac{P(3\Gamma-1)\Theta_i - \Gamma - 1}{P(3\Gamma-1)\Theta_j - \Gamma - 1} \tag{2}$$

These two equations are linear in Θ_i. A linear regression is then obtained from all spectra acquired at Θ_i vs. each incidence spectrum taken at Θ_j. One can then solve for α or γ as a function of the slopes and as a function of the offsets.

Another common method of determining orientation of bonds is through taking the difference of spectra taken at various incidence angles and comparing to a sample of a known orientation[28]. As a function of $\cos^2 \theta_i - \cos^2 \theta_j$ (or $\Theta_i - \Theta_j$) these equations are also linear:

$$I_v(\Theta_i, A) - I_v(\Theta_j, A) = SP\left(\frac{3}{2}A - \frac{1}{2}\right)(\Theta_i - \Theta_j) \tag{3}$$

and

$$I_p(\Theta_i, \Gamma) - I_p(\Theta_j, \Gamma) = SP\left(-\frac{3}{2}\Gamma + \frac{1}{2}\right)(\Theta_i - \Theta_j) \tag{4}$$

so linear regressions of all difference spectra taken at Θ_i and Θ_j can be made to determine angles relative to a sample with a known orientation. A reference sample with known orientation is needed to determine S, the transition dipole moment cross section, and P the polarization[28]. Using regressions on a number of spectra, one can obtain a high degree of precision. Typical

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error bars for precision are less than 1°; however, these values of precision do not include a number of other sources of systematic errors which lead to an estimated accuracy of 4-5°.

Results and Discussion

Carbon NEXAFS spectra can be used to derive both the chemical nature and orbital orientation within the thioctic acid films. The raw data from our study is shown in Figure 2, Figure 3, and Figure 4 for thioctic acid deposited from solution on Au(111) using the three methods described above, respectively. The spectra in upper panes are all normalized to the absorption step edge with the pre-edge set to 0 and the absorption step height set to 1 at about 320eV. Spectra were acquired at various angles from normal incidence (90 degrees) to grazing (20 degrees.) The lower panes consist of the difference between each spectra and the scan acquired at 20 degrees to emphasize polarization dependent peaks. Visible spectral features include a shoulder at 287.8eV from resonances into (C-H σ^* - like) R* resonances from alkyl portions of the molecule[27]. The pronounced, sharp feature at 288.7eV is from C1s transitions into the π^* orbital of the carboxyl group. These R* and π^* resonances are highly convoluted, but intensities of each can be determined through the peakfitting procedure described above. Beyond the edge, two broad resonances appear at around 293.5eV and 298.5eV primarily due to C-C σ^* resonances. The variation in intensity of these features determines order and orientation on the surface.
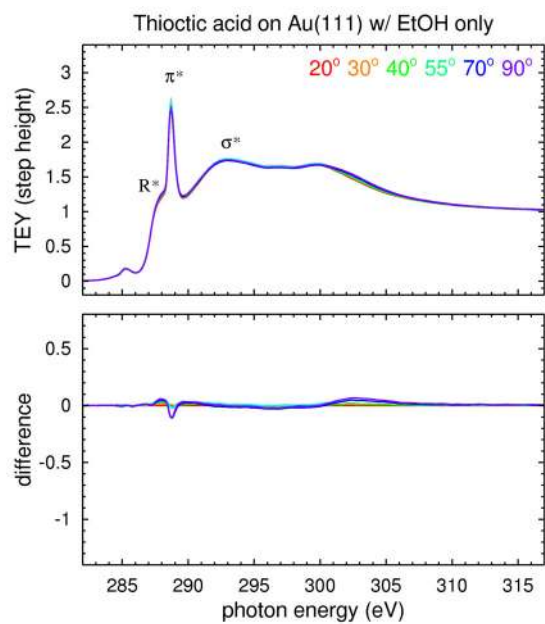
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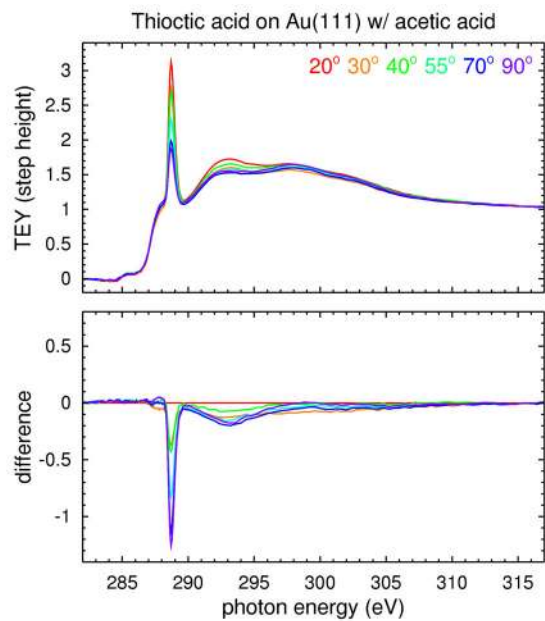**Figure 2. Carbon NEXAFS of thioctic acid on Au perpared with EtOH only**

Figure 3. Carbon NEXAFS of thioctic acid prepared with 5% acetic acid in EtOH.
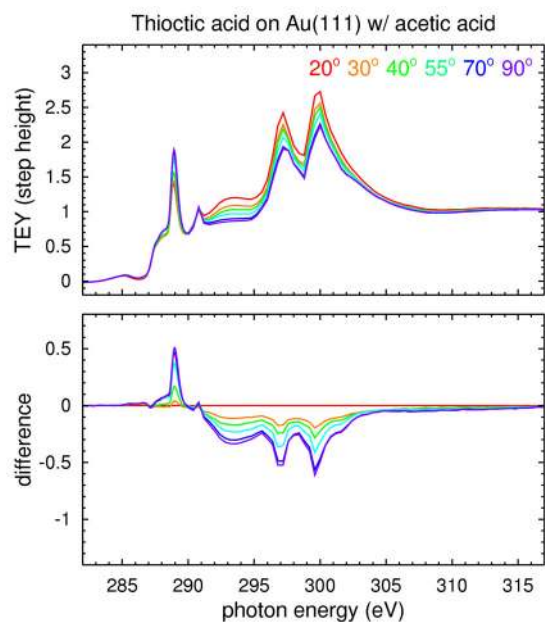
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Figure 4. Thioctic acid on Au, subsequent rinsing in KOH.

Thioctic acid layers prepared using only ethanol (Figure 2) show very little polarization dependence. This is interpreted as a film with a high degree of disorder. The nature of this film is further investigated with other techniques.

Conversely, and surprisingly, the film prepared with acetic acid (Figure 3) has a π^* feature with a strong polarization dependence. Using the intensities of this resonance at each angle through equations (1) and (2) the carboxyl plane normal is on average 38° from the surface normal. Polarization dependence in σ^* features above the absorption edge yield 53.5°, a degree less than the magic angle. The R* features, considering high convolution with the carboxyl π^* feature, return 51.5°. Although indicative of a disordered film, both resonances show an upright tendency of the alkyl portion of the molecules.

As noted previously, films prepared in acetic acid were also later rinsed in a KOH solution in order to deprotonate the carboxyl groups. NEXAFS spectra of such SAMs (Figure 4)

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reveal additional features that are not due to carbon. The first, at 291 eV, is presumably due to contaminant Na in our KOH solution. This K-edge, which arises from synchrotron light of higher order, is strong in samples rinsed in NaOH, and is absent in Auger-yield spectra that are more sensitive to only the carbon in the sample (see supplemental information.) Features at 297eV and 300eV are due to the potassium L-edge from the counterions that now decorate the surface. Endgroup NEXAFS features have opposite polarization dependence compared to protonated carboxyl groups, indicating a strong orientational change. With consideration of difficulties in normalization due to Na and K features in the spectra obscuring the step edge normalization, the carboxyl plane normal on average is roughly estimated to be about 66° from the surface normal. Along with the change in endgroup orientation, which is confirmed with oxygen NEXAFS, σ^* features due to alkyl-units return angles about 5° less than in the acetic rinsed case, while little change occurs in the highly convoluted R* features. All derived angles from C K-edge NEXAFS are summarized in Table 1.

Table 1: Thioctic acid angles derived from C K-edge NEXAFS spectra

Sample	carboxyl π^*	R* (C-H σ^*)	C-C σ^*
acetic acid / ethanol prep.			
slopes	37.9 +/- 0.8	51.2 +/- 0.1	53.5 +/- 0.1
offsets	38.2 +/- 0.8	51.8 +/- 2.9	53.6 +/- 1.6
KOH rinsed			
slopes (a)	66.0 +/- 0.3	51.1 +/- 0.1	48.5 +/- 0.3
offsets (a)	65.4 +/-1.1	51.7 +/- 0.9	48.7 +/- 0.8

(a)   K photoelectron peaks may introduce systematic errors
Errors presented in this table are standard deviations from results obtained using slopes and offsets from equations 1 and 2 at each incidence angle.

Oxygen K-edge spectra (Figure 5)) were acquired using AEY for better signal to background and enhanced surface sensitivity. However, Auger-yield has disadvantages in a lower signal to noise ratio, and the possibility that low binding-energy photoelectrons could

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sweep through the kinetic energy window of the analyzer and hence, exist in the spectra. All spectra show pre-edge features due to excitations from the Oxygen 1s into the carboxyl π^*, and broad σ^* features due to C-O bonds.

The left panes present O K-edge NEXAFS of thioctic acid monolayers prepared with acetic acid in ethanol. The top spectra are normalized to the foot and step acquired at 90°, 55°, and 20°. The lower panes contain differences between spectra. Polarization dependencies, with the π^* resonance most intense grazing incidence and O-C σ^* most intense at normal incidence, confirm carbon results – the carboxyl group plane is tilted towards the surface plane.

For the KOH rinsed sample, in the right panes, polarization dependence indicates that the endgroup is much more upright on the surface. The π^* resonance is now most intense at normal incidence. The O-C σ^* is now somewhat obscured due to an extra feature not due to endgroup oxygen at about 545 eV. This feature is likely due to K 3s photoelectrons (33 eV) entering the analyzer window, and/or water present on the surface.
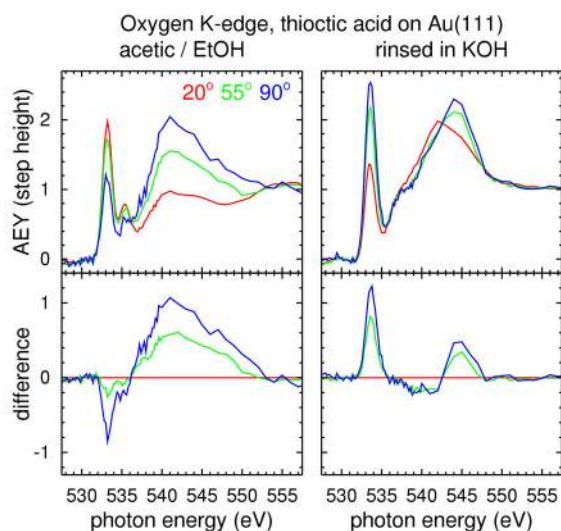

Figure 5. Oxygen K-edge spectra (top) and difference spectra (bottom) for SAMs prepared and rinsed with 5% acetic acid in EtOH (left) and SAMs prepared and then rinsed in KOH (right).

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RA-FTIR spectra (Figure 6) show differences in the endgroup chemical nature. The layers show clear carbonyl stretches from 1740-1700cm^{-1}. These have been previously shown to be from single, non-hydrogen bound carboxyl groups at 1740cm^{-1}, carboxyl groups hydrogen bound with one hydrogen bond or hydrogen bonds to two different neighboring molecules at 1720cm^{-1}, and completely dimerized carboxyl groups with two hydrogen bonds to one neighboring molecule at 1700cm[-1][19, 21, 29]. The acetic-formed thioctic layers show a mixture of dimerizations. In the case where the film is formed with only ethanol as the solvent, the peak associated with single carboxyl groups is greatly reduced, the middle peak is reduced, and intensity at 1740 for fully dimerized pairs increases. The carboxylate band (1450cm^{-1}) is much larger, while one associated with water (1600cm^{-1}) also appears. This indicates that the ethanol-only sample carboxyl groups exist as both highly dimerized carboxyl pairs and carboxylates. To further investigate endgroup nature, carbon x-ray photoelectron spectroscopy was employed.
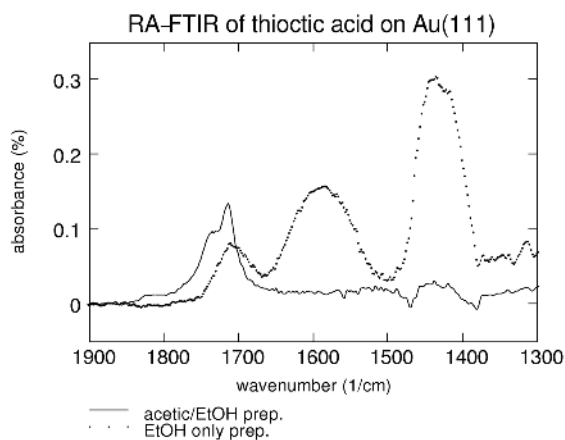

Figure 6. FTIR spectra of thioctic acid films produced with and without acetic acid

Carbon 1s spectra (Figure 7) show chemical differences between thioctic acid layers adsorbed on Au. For those formed with acetic acid, (bottom trace) a sharp carboxyl feature at thioctic acid

289 eV and a larger feature due to the remaining aliphatic carbon in the molecule at 284.4eV[30]. For adsorbates solution deposited without acetic acid, the carboxyl/carboxylate peak is broadened (1.4eV compared to 1.15eV) and shifted to slightly lower binding energy relative to the gold substrate. This indicates that without acetic acid, some of the endgroups are deprotonated in the final film. The alkyl peak is also slightly broadened, shifted to higher binding energy, and has a slightly different shape.   This is due to different chemical environments of the deprotonated carboxylate groups. The relative carboxyl to alkyl peak intensity is also weaker in this case, which could be due to a combination of a short mean-free-path of the photoelectrons and more than a monolayer on the surface, and a small amount of acetic acid still on the surface in the acetic acid / ethanol case. This possibility and substrate bonding are resolved with sulfur photoemission.
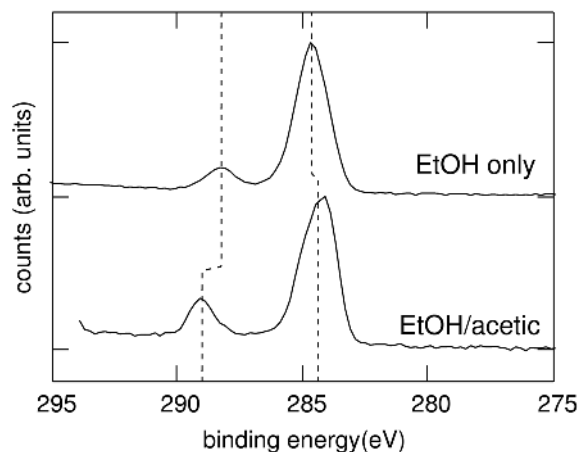

Figure 7. Carbon 1s photoelectron spectra for thioctic acid layers on Au prepared with and without acetic acid in solution when layer was formed

Sulfur 2p spectra indicate the degree of bonding to the substrate(Figure 8). The spectra can be deconvoluted using the S 2p doublet with branching ratio about 2:1 and energy difference thioctic acid

about 1.2eV. Two species are predominant on the surface: gold bound thiolate, with S $2p_{3/2}$ (S $2p_{1/2}$) at 161.9eV (163.1eV) and unbound disulfide, with S $2p_{3/2}$ (S $2p_{1/2}$) at 163.3eV (164.5eV)[31]. As with carboxyl terminated SAMs, no sample is completely free from unbound molecules. This is due to prevailing carboxyl dimers even with acetic acid, and does not eliminate the possibility that some molecules may be attached to the substrate through the carboxyl end. However, additional XPS spectra indicate unbound sulfur atoms are not near the gold interface with samples prepared in this manner (see supplemental information.) In any case, with the ultra-high surface sensitivity of photoelectron spectroscopy with electron kinetic energies just over 100eV, the top spectrum shows the majority of the molecules using acetic acid in solution are bound to the substrate through gold-thiolate bonds.
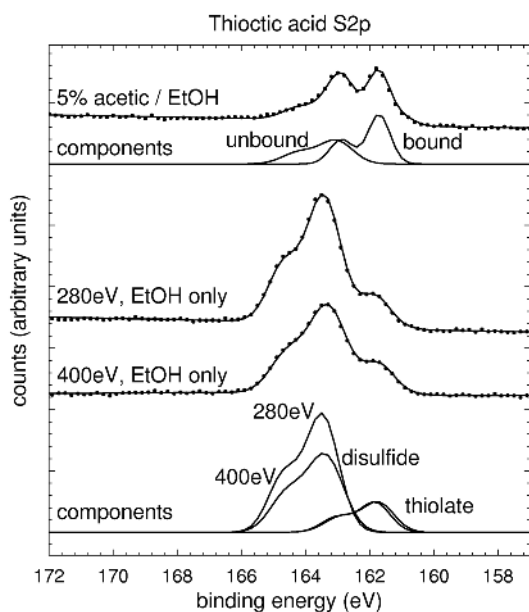

Figure 8. Sulfur 2p photoemission of the thioctic acid films formed with and without acetic acid in solution.

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For the ethanol only case, a very large disulfide component exists. To estimate the position within the layer of this extra disulfide, spectra at photon energies of 280eV and 400eV were acquired. Based on differences in mean-free paths of S 2p photoelectrons from two photon energies and the exponential decrease of photoelectron intensity with overlayer thickness[32-35], we estimate the unbound disulfide is on average 9 +/- 4 Ångströms above the Au-S interface. This indicates carboxyl group dimerization, in some instances with one molecule anchored to the surface, and a second molecule attached through carboxyl groups with disulfide near the layer-vacuum interface. Additional results show that this monolayer is 3-5 Ångströms thicker than the sample prepared with acetic acid (see supplemental information.)

Combining NEXAFS, XPS and FTIR results, a model of thioctic acid under three different preparation conditions is roughly depicted in Figure 9. Using only ethanol to prepare and rinse samples leads to disordered, more than monolayer films as seen in Figure 9 a). Unbound disulfide exists about 9 Å above the gold-sulfur interface, and the endgroups are a mixture of highly dimerized carboxyl groups and carboxylate. Preparing and rinsing thioctic acid SAMs using 5% acetic in ethanol gives well (although not completely) bound monolayers with a high degree of interaction and hydrogen bonding between carboxyl groups as depicted in Figure 9 b). NEXAFS results indicate carboxyl group planes are statistically 38° from the surface plane. Similar tilting in the endgroups of SAMs have been seen in other types of polar molecules, due to the energy minimization of the electric dipoles[36]. Although this effect may contribute to the tilting of the headgroups, especially in partially dimerized films, we believe the primary cause to be hydrogen bonding between endgroups as seen in FTIR spectra. The remainder of the molecular film has a slight upright tendency with polarization dependence in σ^* and R* features yielding angles from 51.5°-53.5°, a few degrees less than the magic angle. This

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underestimates the upright nature of these films considering the variation in orientation of aliphatic carbon at the ring-like base of the molecules driving derived angles toward the magic angle. Rinsing these well-formed monolayers in KOH for deprotonation causes a reorientation of the endgroups to a much more upright orientation as seen in Figure 9 c). The carboxylate plane normal is now 66° from the surface normal. Angles derived from the highly convoluted R* features do not change significantly. However, alkyl portions of these films may also have a more upright nature as σ* features indicate a 5° degree change in the average orientation of the alkyl units.
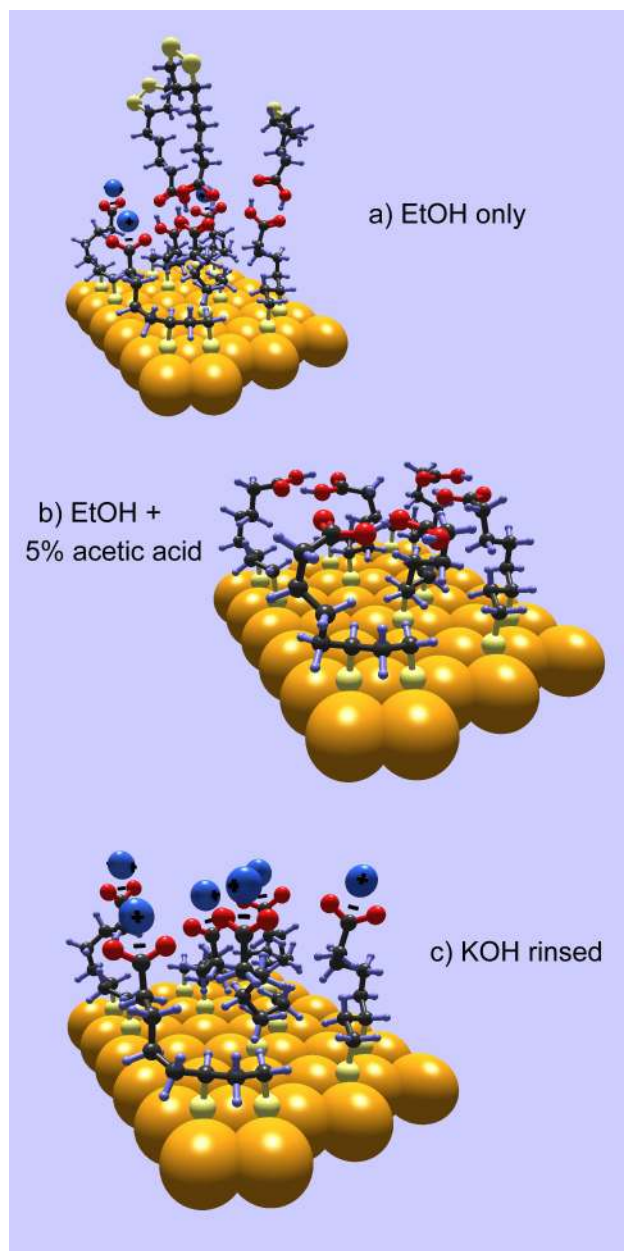
thioctic acid

Figure 9. Three dimensional rough model of thioctic acid on Au(111). a) prepared with 1mmol thioctic acid in EtOH and rinsed in EtOH. b) prepared with 1mmol thioctic acid in 5% acetic acid in EtOH, rinsed in 5% acetic acid in EtOH. c) sample prepared as in b, but then rinsed in KOH solution.

thioctic acid

Conclusion

The extent of substrate binding, endgroup chemical nature, and orientational structure of thioctic acid films adsorbed on gold were investigated with NEXAFS, XPS and RA-FTIR. Depending upon the solvent and rinsing step, various configurations exist.

Using ethanol only, thioctic acid forms a completely disordered, more-than-monolayer film of molecules. Many of the endgroups are deprotonated to carboxylate.

Using 5% acetic acid in ethanol for the formation solution, thioctic acid surprisingly forms ordered films. Carboxyl-carboxyl interaction plays heavily on film structure as carboxyl group planes are tilted towards the surface as the NEXAFS angle between the group normal and surface normal is 38°. The bases of the molecules are also statistically more upright than prostrate with a tilt angle a few degrees less than the magic angle.

Upon deprotonation to carboxylate by rinsing in KOH, the carboxylate groups change orientation indicating a chemically driven conformational switching. They are upright with respect to the surface, with carboxylate plane normal 66° form the surface normal. This may also induce alkyl chains to exhibit a more upright orientation, with the tilt angle decreasing by 5° in C-C σ* NEXAFS features.

These results allow for better understanding of self-assembly process in carboxyl terminated films. In this case, when alkyl-chain interactions are minimized, carboxyl group interactions tend to form tilted-over dimers. To date, the best films are formed using a process similar to that used in carboxyl terminated alkyl-thiols by adding acetic acid to ethanol solutions to form and rinse films. In addition, this quantitative characterization of thioctic acid monolayers adsorbed on Au builds a foundation for the use of these films in biological and chemical sensor applications and for surface-attached macromolecules.

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Acknowledgements

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Supplemental Information

Surface Structure of Thioctic Acid Adsorbed on Au(111) as Observed Using NEXAFS

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Table 1 presents calculated tilt angles from C K-edge TEY NEXAFS spectra. These results were obtained by fitting the 6 NEXAFS spectra and all 15 combinations of difference spectra simultaneously, keeping positions and widths of peaks the same while allowing intensities to vary for each spectra or difference independently. This assists deconvolution of overlapping resonances. Errors presented are simply the standard deviation of the 6 values returned from slopes, and 5 values returned from offsets. For the difference spectra, values from the acetic rinsed are used as references, while the errors are based on the 95% confidence limit of the regression slope. Changes in derived angles between the acetic-rinsed and KOH-rinsed samples are also presented.

In the table, for the π^* resonance, one can see the strong reorientation upon deprotonation from about 38 to 66 degrees. The R* region also shows a small deviation of a few degrees from the magic angle (54.7 degrees) indicating the alkyl portions of the molecule are statistically more "upright" than "lying down." This is also seen in the C-C σ^* region, especially when statistical outliers using the less accurate offset method are removed (e.g. 63.3 degrees calculated using the intercept from the 70 degree spectra.) For the KOH rinsed sample, the σ^* region must be treated with care due to the superimposed K L-edge, but may indicate a more upright orientation of the alkyl portion of the molecule by a few degrees using both ratio and difference methods. The R* region shows little change from the acetic-rinsed sample, but is highly convoluted with the π^* region.

Table 1: Thioctic acid tilt angles derived from C K-edge NEXAFS spectra

all spectra vs.:	20	30	40	55	70	90	avg.	stdev.
acetic acid / ethanol prep.								
carboxyl π*								
slopes	38.92	36.35	38.59	37.87	37.57	37.91	37.87	0.82
offsets	37.32	38.88	37.32	37.97	39.41		38.18	0.84
R* (C-H σ*)								
slopes	51.23	51.04	51.23	51.13	51.07	51.20	51.15	0.07
offsets	53.08	50.78	53.16	51.05	45.12		51.83	2.92
C-C σ*								
slopes	53.65	53.40	53.61	53.53	53.48	53.59	53.54	0.08
offsets	52.11	55.89	52.18	54.34	63.31(a)		55.5(a)	4.1
KOH rinsed								
carboxyl π*								
slopes	65.94	66.33	66.04	65.61	65.93	66.33	66.03	0.25
offsets	65.84	66.79	66.08	63.73	64.62		65.41	1.09
difference					(Δ=+27.13)		65.0	0.5
R* (C-H σ*)								
slopes	51.16	51.07	51.09	51.21	51.17	51.06	51.13	0.06
offsets	50.82	50.14	50.39	53.05	54.09		51.70	1.58
difference					(Δ=+.45)		51.6	0.4
C-C σ* (b)								
slopes	48.9	48.2	48.3	48.6	48.5	48.6	48.5	0.3
offsets	47.6	49.5	49.4	48.1	49.0		48.7	0.8
difference					(Δ=-1.84)		51.7	0.2

(a) The value 63.31 is essentially a statistical outlier. Without this value, the average
      is 53.6 +/- 1.6. This value is presented in the main paper.
(b) K photoelectron peaks may introduce systematic errors

Tilt angle calculations from Oxygen K-edge are not presented due to underlying photoemission structure in auger yield spectra. The resonances also seemed to vary in intensity as a function of the kinetic energy window of the analyzer. Oxygen K-edge results varied from about 38-46 degrees from the oxygen spectra.

Other basic solutions were attempted for the deprotonation of the carboxyl group in long chain alkyl-thiols and thioctic acid. NaOH was successful, but strong Na features appear from higher order light in the beamline just above the π* feature. Organics such as ammonia were attempted and seem to show carboxylate formation in immediate IR measurements, but in NEXAFS and XPS measurements, in UHV and an hour or two after rinsing, Nitrogen is below detection limits, and the sample appears as an acetic prepared sample.

Figure 1 presents spectra acquired from mercaptohexadecanoic based SAMs and one spectrum from the KOH rinsed thioctic-based monolayer from the text. One can see that the feature at 291eV appears very strongly in the SAM rinsed in NaOH, but also

appears in monolayers rinsed in KOH. We thus infer that this feature is due to contaminant Na (K-edge) from higher order radiation in the beamline.
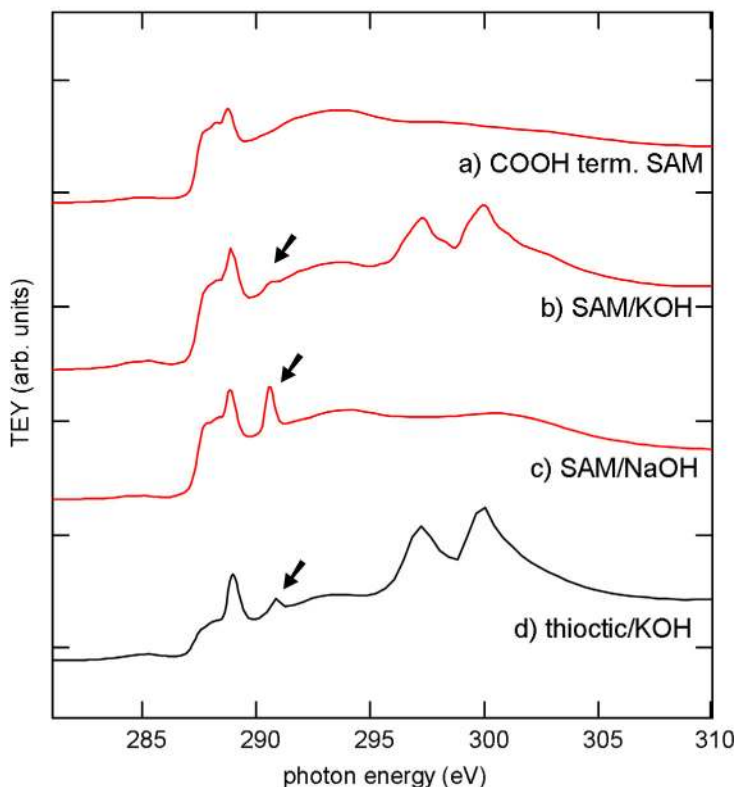

Figure 1. Comparison of carboxyl terminated SAMs a) rinsed in acetic acid, b) rinsed in KOH, c) rinsed in NaOH, and d) thioctic acid monolayer rinsed in KOH. The feature indicated appears most strongly in the NaOH rinsed case and is presumably from the Na K-edge from higher order light in the beamline.

S 2p spectra reveal details about the film formed with only ethanol. The integrated intensities for the bound thiolate and unbound dithiol give:

      280eV: 19.6% bound, 80.4% unbound

      400eV: 26.3% bound, 73.7% unbound

It is interesting to note that in the sample prepared using acetic acid, these give:

      280eV: 59.4% bound, 40.6% unbound

      400eV: 64.3% bound, 35.7% unbound

This indicates that the unbound disulfide in the well-formed monolayer is also primarily near the top of the layer. Although this supports gold-sulfur binding involving both sulfur atoms, it is not proof that all molecules do not bind through only one atom. Another interesting issue is that upon cleavage of the sulfur-sulfur bond, relaxation in the base through rotation about carbon-carbon bonds easily accommodates the gold-gold distance, thus binding in equivalent sites is quite likely, but beyond our investigations in this work.

We also present XPS spectra acquired on a PHI Quantum 2000 laboratory system using monochromatized Al Kα radiation. Figure 2 presents survey spectra of an additional set of thioctic monolayers on gold. The top, red spectrum is from a thioctic acid monolayer prepared and rinsed in ethanol only. The middle, blue spectrum is of thioctic acid prepared and rinsed in 5% acetic acid in ethanol. The lower, green spectrum is a reference SAM of hexadecanethiol on gold.
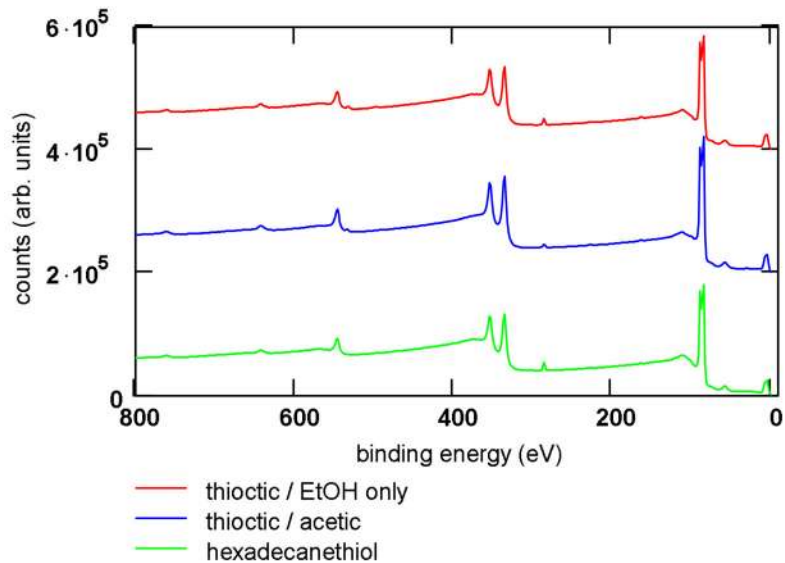

Figure 2. survey XPS of monolayers. Top: thioctic acid prepared in EtOH only. Middle: thioctic acid prepared with acetic acid. Bottom: Hexadecanethiol on gold reference.

Film thicknesses can be estimated through the relative intensities of carbon photoelectron peaks presented in Figure 3. We use integrated intensities of all photoelectron peaks and assume a monolayer thickness of about 17 Ångströms for the hexadecanethiol-based monolayer. The thioctic / acetic layer is about 8 Ångströms thick while the thioctic monolayer prepared with ethanol only is estimated to be about 11 Ångströms in thickness. The attenuation in gold photoelectron peaks through the monolayer can also be used to estimate thickness. Using attenuation equations form Lamont and Wilkes (Langmuir 1999, 15, 2037-2042) and the integrated intensities for gold photoelectron peaks (Figure 4) the thioctic acid / EtOH monolayer is about 11.5 Ångströms thick while the thioctic acid / acetic sample is about 6.5 Ångströms thick. These estimates have an error of about +/-3 Ångströms.
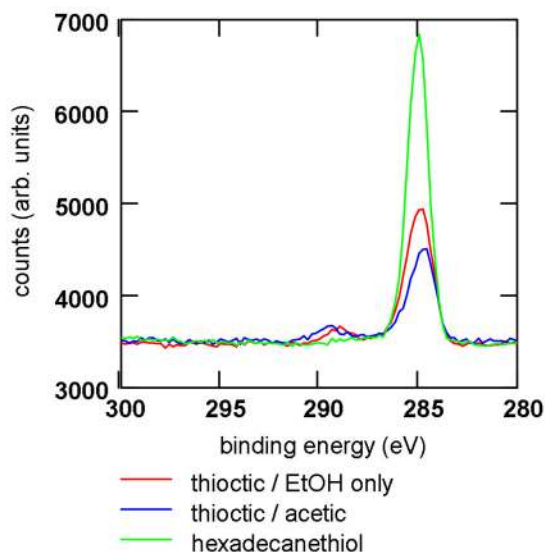
Figure 3. Carbon XPS of the layers indicated. Hexadecanethiol is the most intense, followed by thioctic / EtOH and thioctic / acetic.
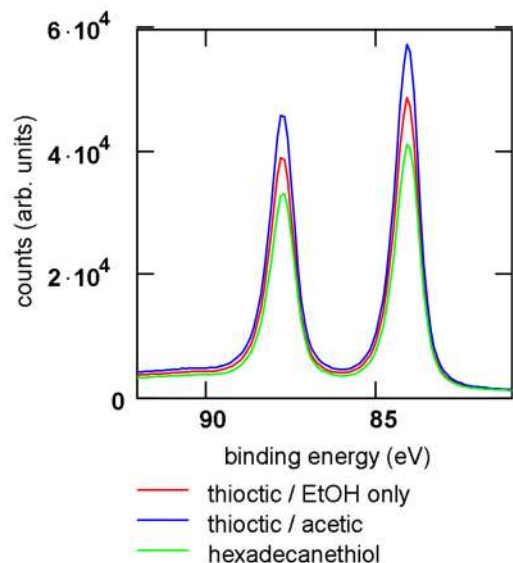

Figure 4. Gold 4f XPS of the monolayers. Thioctic / acetic is most intense, followed by thioctic / EtOH and hexadecanethiol.

Sulfur XPS acquired with hv=1486.6eV are presented in Figure 5. Although this is a separate set of samples, one would expect relative ratios of bound to unbound sulfur to be similar to the text. With the much longer mean free path of the photoelectrons in this case, expecially for the thioctic / EtOH case, the unbound to bound intensity is much lower as expected if the unbound disulfide is near the top of the layer.
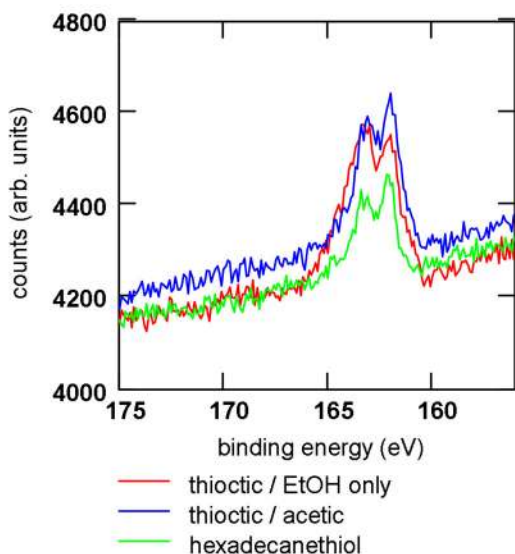
Figure 5. Sulfur 2p XPS of monolayers.

Thioctic acid FTIR in the C-H stretch region also may show curious results(Figure 6). For a mercaptohexadecanoic acid, a carboxyl-terminated, long-chain alkyl-thiol molecule, the bottom trace shows sharp CH stretching peaks at 2918 cm^{-1} and 2850 cm^{-1} indicating a crystalline, well packed monolayer. Conversely, the peaks for thioctic acid layers are broadened significantly and at higher wavenumber. For alkanes, a shift to a few cm^{-1} is interpreted as alkyl groups which are not well packed nor crystalline, however, for thioctic acid, the shifts are 10's of cm^{-1} and the broadening is significant.
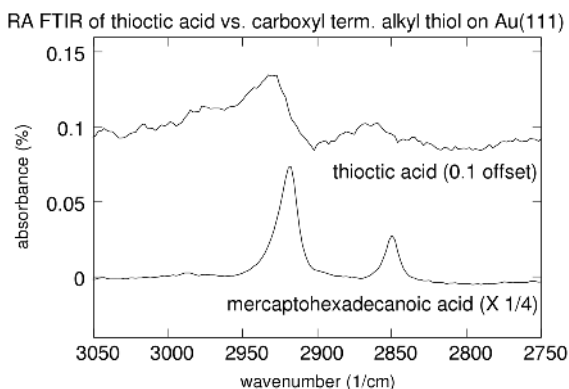

Figure 6. RA-FTIR for the C-H stretch region for thioctic acid, and for mercaptohexadecanoic acid (a carboxyl-terminated, long-chain alkyl-thiol) on Au(111)