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Optical signatures of thiolate/Cu(110) and S/Cu(110) surface structures

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The optical properties of thiolate/Cu(110) and S/Cu(110) surfaces created by the adsorption of methanethiol and L-cysteine are investigated using reflection anisotropy spectroscopy (RAS). We find that characteristic optical signatures are obtained from these systems. The experimental RAS profiles are simulated using a four-phase model consisting of vacuum, anisotropic overlayer, anisotropic surface, and isotropic substrate. The results of the simulations suggest that a broad optical transition at 3.8 eV is associated with the thiolate/Cu(110) interface, consistent with recent first-principles calculations [S. D'Agostino *et al.*, Phys. Rev. B **75**, 195444 (2007)].

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I. INTRODUCTION

The adsorption and self-assembly of organic molecules into two-dimensional monolayers (ML) is a key step in the nanoscale engineering of chemically functionalized surfaces with applications ranging from those in biosciences to molecular electronics. Of fundamental interest is the interplay between molecule-surface and molecule-molecule interactions and whether the surface structure of the substrate imposes order on the molecular layer[1,2] or if the adsorbate induces local restructuring of the substrate.[3] When the molecule contains more than one functional group, the ability to determine which groups are involved in bonding to the surface becomes important. The thiolate-metal surface bond is a key interaction that finds widespread use in the attachment of alkanethiols and thiol-derivatized molecules to metal surfaces.[4–6] This linkage is important for its ability to functionalize surfaces under aqueous or ultrahigh vacuum (UHV) environments with simple or complex molecules.

In the work reported here, we characterize the optical properties of thiolate/Cu(110) and S/Cu(110) surfaces created by the adsorption of (i) the simplest alkanethiol, methanethiol [CH_3SH] and (ii) the amino acid L-cysteine [HS-CH_2-CH(NH_2)-COOH]. We use the linear optical technique of reflection anisotropy spectroscopy (RAS) (Refs. 7 and 8)—a versatile and widely used probe belonging to the *epioptics* family of techniques designed for the study of surfaces and interfaces.[9] RAS has been used to investigate carboxylate/Cu(110) surfaces[1,10–12] and the bonding interaction at this interface.[11] We find that characteristic optical signatures are obtained from thiolate/Cu(110) and S/Cu(110) surface structures, and simulations suggest that a broad optical transition at 3.8 eV is associated with the thiolate/Cu(110) interface, as a result of the thiolate-Cu bonding.

II. EXPERIMENTAL PROCEDURE

The experiments were performed in an UHV environment at a base pressure in the 10^{-10} mbar region. Clean Cu(110) surfaces (crystals oriented to 0.1°, SPL Netherlands) were prepared by cycles of Ar ion bombardment (500 eV, 300 K, 15 min) and annealing to 800 K. Surface order was confirmed by low-energy electron diffraction (LEED) and cleanliness monitored using x-ray photoelectron spectroscopy (XPS). Methanethiol (99.5+%) and L-cysteine (99%) were used as received from Aldrich. Exposures took place with the Cu crystal at room temperature and are measured in Langmuir ($1\ \text{L}=10^{-6}$ Torr s). Coverage θ is reported as the ratio of adsorbate concentration to the number of Cu atoms in a complete (1×1) layer. RAS (Refs. 7 and 8) probes the linear optical response of a surface as a function of photon energy by measuring Δr, the difference in reflectance of normal incidence linear polarized light for orthogonal linear polarizations, normalized to the mean reflectance r. For Cu(110) the difference between the two orthogonal surface directions $[1\bar{1}0]$ and $[001]$ is measured

$$\frac{\Delta r}{r} = \frac{2(r_{[1\bar{1}0]} - r_{[001]})}{r_{[1\bar{1}0]} + r_{[001]}}, \tag{1}$$

where r_x represents the complex Fresnel reflection amplitude for x polarization. The real part of the complex RA is measured.

III. EXPERIMENTAL RESULTS

A. Methanethiol/Cu(110)

The adsorption of methanethiol, also known as methyl mercaptan, on Cu(110) at room temperature has been studied by Carley *et al.*[13–15] using scanning tunneling microscopy (STM) and XPS. Their XPS results show that upon adsorption the S-H bond is broken and the molecule adsorbs as methanethiolate (CH_3S).[13] We note that at room temperature, methanethiol adsorbs as CH_3S on Cu(111) (Ref. 16) and dodecanethiol[17] and heptanethiol[18] adsorb as thiolates on Cu(110). STM data[13,15] have revealed a significant restructuring of the Cu(110) surface morphology upon exposure to CH_3SH at room temperature. Below 0.28 ML, high surface mobility prevents STM imaging. When the coverage reaches ~0.3 ML, small islands of $c(2\times 2)$ structure are found on the terraces and a large number of step edges are observed which show a tendency to be decorated. The islands, which

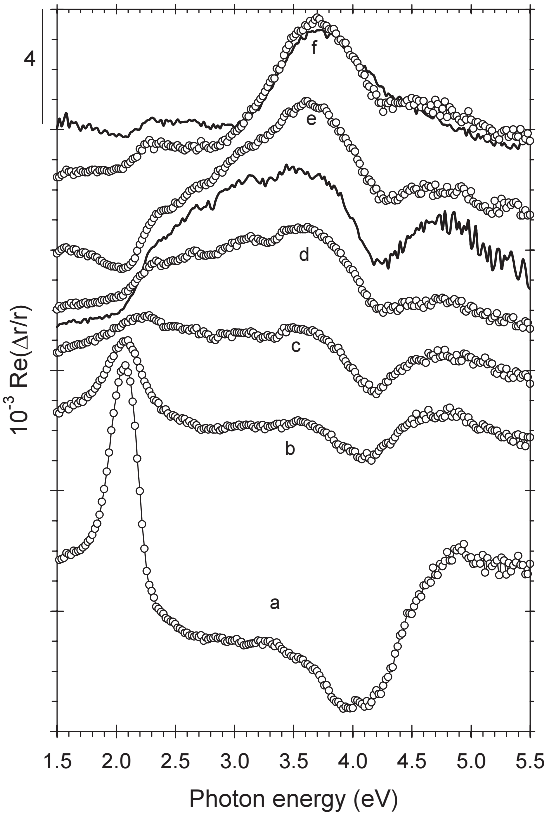

FIG. 1. RA spectra of (a) the clean Cu(110) surface, [(b)–(f)] increasing exposure to methanethiol. Solid lines show the effect of heating the surfaces (d) and (f). Successive spectra are offset on the vertical axis for clarity.

contain two CH_3S molecules per $c(2\times2)$ unit cell, reside on narrow (10–15 Å width in [001]) terraces.[13] With further exposure the islands grow to completely cover the Cu surface at $\theta=0.5$ ML.

RA spectra recorded during exposure of Cu(110) to methanethiol are shown in Fig. 1. The spectrum of the clean surface [Fig. 1(a)] is characterized by an intense positive peak at 2.1 eV, a negative structure around 4 eV and a positive peak at 4.9 eV. The dominant contribution to the 2.1 eV RAS peak arises from transitions between two surface states located near the Fermi level (E_F) at the $\bar{Y}$ point of the surface Brillouin zone.[19,20] Transitions between bands near E_F at the L point, that are modified by the anisotropic surface, contribute to the RA response: the peaks observed at 4.2 and 4.9 eV have been assigned[21] to the optical transitions $E_F \rightarrow L_1^u$ and $L_2' \rightarrow L_1^u$, respectively. Equivalent transitions have been associated with peaks observed in the RA spectrum of Au(110) (Ref. 22) and Ag(110).[23] First-principles calculations have also indicated that the RA response between 3.0 and 5.5 eV is associated with transitions involving bulk bands.[24–27]

With increasing exposure to methanethiol the 2.1 eV RAS peak is quenched (Fig. 1)—indicating the loss of the transitions between the surface states at $\bar{Y}$—and a shoulder profile centered at 2.2 eV is observed. The RAS structure at ~4 eV is reduced in magnitude and the growth of a large positive peak at 3.7 eV is observed [Fig. 1(f)]. The RAS profile of Fig. 1(d) is obtained following exposure of ~3 L [corresponding to $\theta\sim0.3$ ML (Ref. 15)] where LEED results show a $c(2\times2)$ pattern with broad diffuse spots at the half-order positions [Fig. 2(a)]. We note that a similar LEED pattern was observed for $H_2S/Cu(110)$ that was related to the growth of small $c(2\times2)$ islands separated by uncovered surface.[28]

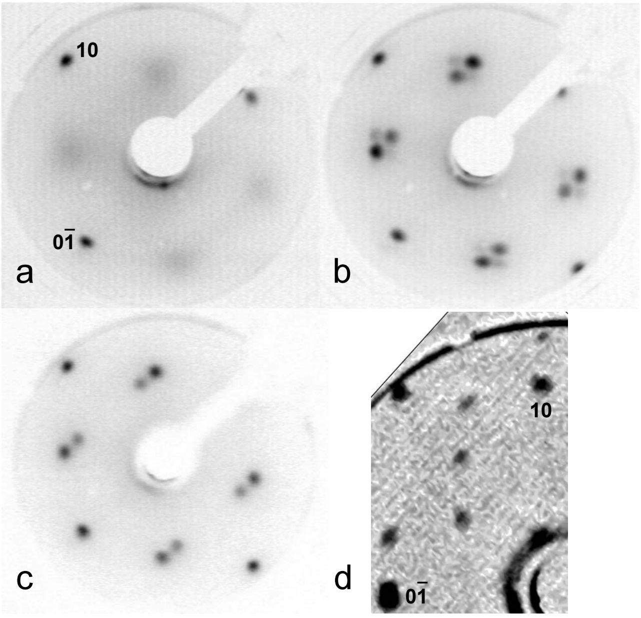

FIG. 2. LEED patterns. $CH_3S/Cu(110)$ surface structures for exposures of (a) 3 L (74 eV), (b) 12 L (76 eV), and (d) 40–70 L (91 eV). The S/Cu(110) surface structure following heating of the 3 L exposed surface is shown in (c) (74 eV).

The RA spectrum of Fig. 1(e) is obtained following ~12 L exposure where a $c(2\times2)$ LEED pattern is observed with the half-order spots split into two orthogonal doublets [Fig. 2(b)]. The RAS profile of Fig. 1(f) is obtained from exposures between 40–70 L and showed no change in this range. The LEED pattern of this surface was of an incomplete $c(8\times2)$-type pattern [Fig. 2(d)]. We will refer to this structure as a "$c(8\times2)$ type" to distinguish it from a complete $c(8\times2)$. The LEED patterns of Figs. 2(b) and 2(d) are very similar to those reported by Domange and Oudar for Cu(110) following exposure to H_2S.[29]

Considering the simple structure of methanethiol, and that the highest occupied to lowest unoccupied molecular orbital gap is ~4.5–5.5 eV,[30,31] it is likely that RAS is probing the thiolate/Cu(110) interface and that the methyl group has relatively little effect on the RAS signal. To evaluate this view, the methyl group can be removed by heating: Carley *et al.*[13,14] have shown that heating $CH_3S/Cu(110)$ surfaces above 400 K results in the decomposition of the adsorbate to leave only a chemisorbed S adlayer, which appears to be identical to that prepared from the exposure of clean Cu(110) to H_2S.[14] RAS is sensitive to both the bonding interaction and the spatial arrangement of adsorbates at the interface and so to evaluate the contribution from the methyl group, and any difference between thiolate-Cu and S-Cu bonding, the surface structure following the heating process must be similar to that before.

First, an example of a combined change in adsorbate species and surface structure is provided by heating the 0.3 ML surface to 580 K and allowing to cool to room temperature. The resulting RA spectrum changes from the open circles to the solid line of Fig. 1(d) and the LEED pattern changes from Figs. 2(a)–2(c). The doublets split along the [001] real-space direction [Fig. 2(c)] are similar to those observed for H_2S on Cu(110) and in agreement with Carley *et al.*[14] we find that heating $CH_3S/Cu(110)$ results in an ordered S adlayer structure, as would have been obtained from exposure of the clean surface to H_2S. The doublets indicate the formation of antiphase boundaries along the [001] direction separating adjacent $c(2\times2)$ domains.[28] The change in the RAS profile is due to the combination of the change in the structure of the interface and any contribution due to the change in adsorbed species from CH_3S to S. Simulations performed later will provide some insight into these contributions.

We find that a change in adsorbate species, but with no change in surface structure, is provided by heating the high coverage $CH_3S/Cu(110)$ surface [open circles, Fig. 1(f)] at 450 K and then allowing to cool to room temperature. No change is observed in the LEED pattern of the high coverage surface [Fig. 2(d)] following the heating procedure, which changes the adsorbed species from CH_3S to S. A similar RA spectrum is observed to that before the heating process [Fig. 1(f)]. The similarity between the RA spectrum of CH_3S/Cu [open circles, Fig. 1(f)] and that of S/Cu [solid line, Fig. 1(f)] indicates that RAS is sensitive to the S/Cu interface and that the RAS profile of Fig. 1(f) is an optical signature of the S/Cu-$c(8\times2)$-type structure. While the shape of the RAS profile is similar, there is a notable difference in RAS intensity below 3 eV between the two surfaces in Fig. 1(f). This increase in RAS response going from CH_3S/Cu to S/Cu implies there is an increase in $r_{[1\bar{1}0]}$ and/or a decrease in $r_{[001]}$, from Eq. (1). This difference could be attributed to the presence or absence of the methyl group, however, the results of L-cysteine/Cu(110) in the next section suggest an alternative interpretation is necessary.

B. L-cysteine/Cu(110)

We now turn to L-cysteine, a molecule containing three groups (amine, carboxylic acid, and thiol) all of which have the potential to interact with the Cu surface. The RAS profile of the L-cysteine saturated Cu(110) surface is shown in Fig. 3(a). This spectrum is very similar to the spectrum shown in Fig. 1(d) for $CH_3S/Cu(110)$, which is plotted again in Fig. 3 for comparison. The similarity indicates a similar bonding interaction and surface structure for L-cysteine/Cu(110) and $CH_3S/Cu(110)$. Indeed, similar to the methanethiol results, a $c(2\times2)$ LEED pattern develops as L-cysteine is deposited with the half-order spots split into doublets. For L-cysteine the splitting occurs along the real-space $[1\bar{1}0]$ direction and again suggests the presence of domains. The RAS response at 4.2 eV for L-cysteine shows a well-defined peak that is different from the response observed for methanethiolate at the same energy [Fig. 3(a)]. The peak indicates the presence of a carboxylate interaction for L-cysteine/Cu(110), as the carboxylate-Cu interaction was found to contribute a characteristic RAS intensity at 4.2 eV.[11] The RAS data of Fig. 3(a) indicate that L-cysteine is interacting with the Cu surface via a thiolate and a carboxylate linkage. Mateo Marti *et al.*[32] have investigated the adsorption of S-cysteine on Cu(110) using reflection absorption infrared spectroscopy and XPS. Their results indicate that the molecule interacts with the Cu surface via a thiolate and a carboxylate linkage, consistent with our RAS results.

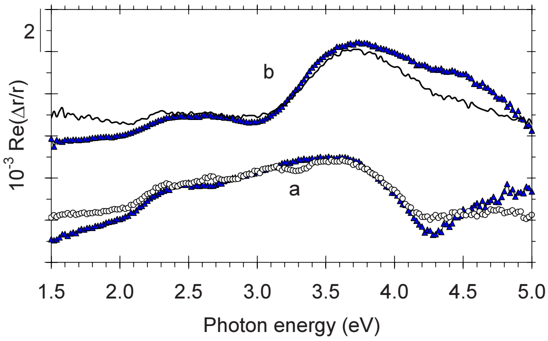

FIG. 3. (Color online) RA spectra of (a) L-cysteine/Cu(110) saturated surface (triangles) and $CH_3S/Cu(110)$ of Fig. 1(d) (circles), (b) following heating of L-cysteine/Cu(110) to create a S/Cu(110)-$c(8\times2)$-type structure (triangles), and equivalent structure formed from heating $CH_3S/Cu(110)$ (solid line). Pairing of spectra for comparison is achieved by offsetting in the vertical axis.

We find that by flashing the L-cysteine saturated surface to ~800 K and cooling to room temperature, an incomplete $c(8\times2)$ LEED pattern is observed that appears identical to that found for the corresponding S/Cu(110) results obtained via heating $CH_3S/Cu(110)$ [Fig. 2(d)]. The RA profiles of the two surfaces are similar, as shown in Fig. 3(b). XPS results of the L-cysteine heated surface show a shift of 2 eV to higher kinetic energy of the S 2*p* peak, consistent with the XPS results of heating $CH_3S/Cu(110)$ (Ref. 13) which leaves only chemisorbed S on the surface. We conclude that heating L-cysteine results in the decomposition of the adsorbate, and an ordered S adlayer is formed that is similar to the methanethiol results. This result supports the conclusion that the RAS profile of Fig. 1(f) [and Fig. 3(b)] is an optical signature of S-Cu bonding with the S atoms arranged in the $c(8\times2)$-type structure.

The small difference in RAS intensity below 2.5 eV between the two S/Cu-$c(8\times2)$-type surfaces in Fig. 3(b) is similar to the difference in the RAS profiles of the $c(8\times2)$-type surfaces of CH_3S/Cu and S/Cu [Fig. 1(f)]. This observation suggests that the difference in Fig. 1(f) is not directly due to the presence/absence of the methyl group. Instead, the difference in RAS could be due to subtle differences in the structure of the S/Cu-$c(8\times2)$-type surface resulting from the different routes taken to produce this structure (heating CH_3S/Cu or L-cysteine/Cu).

IV. SIMULATING THE RAS DATA

RA spectra of surfaces and interfaces derive from a combination of morphological and electronic effects and can therefore be difficult to interpret. A common method that is used to simulate clean surfaces, developed from Fresnel theory by McIntyre and Aspnes,[33] is to simplify the system

TABLE I. Values used to simulate the RAS data (Fig. 4) over the photon energy range 2.5–5.5 eV. Values used to simulate the region 1.5–2.5 eV are shown in brackets.

Structure	ΔE_g (eV)	$\Delta\Gamma$ (eV)	ω_t (eV)	S	γ (eV)
Thiolate/Cu-$c(2\times2)$	0.01(0)	0.03(0.01)	3.8	0.7	1.0
S/Cu-$c(2\times2)$	0.03(0)	0.03(0.03)	3.8	0.8	1.0
Thiolate/Cu-$c(8\times2)$ type	−0.01(0)	0.03(0.01)	3.9	0.9	1.0

under investigation to that of a three-phase system. Each phase has its own complex dielectric function ϵ, i.e., vacuum ($\epsilon_v=1$), a biaxial anisotropic surface ($\Delta\epsilon_s=\epsilon_s^x-\epsilon_s^y$, where x and y are orthogonal in-plane directions aligned along x and y polarizations) and an isotropic bulk (ϵ_b). The vacuum and bulk phases are semi-infinite whereas the surface phase has a thickness $d_s \ll \lambda$ the wavelength of light to satisfy the thin-film limit.[33] The reflection coefficients and $\Delta r/r$ for normal incidence reflection from the stacked three-phase system are then determined. To simulate the RAS of clean Cu(110) between 3.0 and 5.5 eV, the region dominated by transitions near L, $\Delta\epsilon_s$ is based on the energy derivative of the bulk dielectric function, $d\epsilon_b/dE$.[34] The anisotropic Cu(110) surface is assumed to perturb the electronic structure of the subsurface region, causing different band narrowing along $[1\bar{1}0]$ and $[001]$ leading to differences in gap energies ΔE_g and linewidths $\Delta\Gamma$ of interband transitions at L between x and y polarizations. Values of $\Delta E_g=0.1$ and $\Delta\Gamma=0$ produce a simulated spectrum that is in good agreement with experiment with peaks at 4.2 and 4.9 eV occurring close to the experimentally observed peaks.[21,35]

For adsorbate systems it becomes desirable to extend the three-phase model to incorporate an adsorbate overlayer phase. While the three-phase equations of McIntyre and Aspnes are ubiquitous, it does not appear to be widely recognized that the thin-film limit provides considerable simplification for multilayer systems. For n isotropic phases (here, layers 1 and n being the semi-infinite vacuum and substrate, respectively) the normal incidence Fresnel reflection coefficients take the form

$$\frac{r_{123,\ldots,n}}{r_{1n}} \approx 1 + \frac{4\pi i\sqrt{\epsilon_1}}{\lambda(\epsilon_n-\epsilon_1)}\sum_{j=2}^{n-1} d_j(\epsilon_j-\epsilon_n). \tag{2}$$

When the layers between 1 and n are anisotropic the RAS response of the system can be expressed as

$$\frac{\Delta r}{r} = \frac{4\pi i\sqrt{\epsilon_1}}{\lambda(\epsilon_n-\epsilon_1)}\sum_{j=2}^{n-1} d_j\Delta\epsilon_j. \tag{3}$$

Thus RAS spectra of multilayer systems are additive, in the thin-film approximation.

To simulate our thiolate/Cu(110) and S/Cu(110) results, a four-phase system is used that incorporates a biaxial overlayer ($\Delta\epsilon_o=\epsilon_o^x-\epsilon_o^y$) of thickness d_o on top of the anisotropic Cu surface ($\Delta\epsilon_s \propto d\epsilon_b/dE$) of thickness d_s. The overlayer phase represents the adsorbate (CH_3S or S) on top of the Cu surface. This approach has the advantage of retaining the derivative Cu surface phase that is effective for simulating the clean Cu surface. Applying Eq. (3) to this system, the RAS response is given by

$$\frac{\Delta r}{r} = \frac{4\pi i}{\lambda}\left[\frac{d_s(\Delta E_g - i\Delta\Gamma)}{\epsilon_b-1}\frac{d\epsilon_b}{dE} + \frac{d_o\Delta\epsilon_o}{\epsilon_b-1}\right]. \tag{4}$$

The real part of Eq. (4), using $\epsilon=\epsilon'-i\epsilon''$, is used to simulate the experimental RAS results $[\mathrm{Re}(\Delta r/r)]$. The overlayer phase $\Delta\epsilon_o$ is based on a single oscillator of energy ω_t, strength S, and width γ occurring for one of the RAS polarizations. It is found that an oscillator for y polarization gives simulated RAS profiles with sign in agreement with experiment. For this case, the oscillator is described by[36]

$$\epsilon_o^y = 1 + \frac{S/\pi}{\omega_t-\omega+i\gamma/2}; \quad \epsilon_o^x = 1. \tag{5}$$

Thicknesses d_o and d_s are both set to 1 nm, leaving ω_t, S, and γ of the oscillator and ΔE_g, $\Delta\Gamma$ of the surface as variables. The dielectric properties of Cu(ϵ_b) are obtained from tabulated data below 2.5 eV,[37] and above 2.5 eV higher resolution data on single-crystal Cu is available.[38]

RA spectra of the methanethiolate/Cu-$c(2\times2)$ surface [open circles, Fig. 1(d)], S/Cu-$c(2\times2)$ surface [solid line, Fig. 1(d)], and the thiolate/Cu-$c(8\times2)$-type structure [Fig. 1(f)] are simulated using the values listed in Table I and the results are shown in Fig. 4. A three-phase derivative model, obtained by setting $d_o\Delta\epsilon_o=0$ in Eq. (4) and only dependent on ϵ_b and its energy derivative, is sufficient to simulate the RAS from 1.5 to 2.5 eV. The values of ΔE_g and $\Delta\Gamma$ used in these simulations are listed in brackets in Table I. A separate simulation below 2.5 eV is valid as in this energy region we are dealing with a different critical point (X rather than L) with its own values of ΔE_g and $\Delta\Gamma$.[21,34,39] Above 2.5 eV, the four-phase model is used with values listed in Table I. Figure 4 shows that the simulated profiles reproduce the main features of the experimental spectra. The blue (dark) and red (light) lines show the contribution from the first (surface) and second (overlayer) terms of Eq. (4), respectively.

The simulations reveal that a single overlayer transition at $\omega_t=3.8$ eV reproduces the broad RAS profile for the $c(2\times2)$ symmetry structures of both thiolate/Cu and S/Cu [Figs. 4(a) and 4(b)]. For the incomplete thiolate/Cu-$c(8\times2)$ structure, ω_t shifts to 3.9 eV [Fig. 4(c)]. The similarity in experimental spectra between thiolate/Cu-$c(8\times2)$ and S/Cu-$c(8\times2)$ type [Fig. 1(f)] means that these surfaces can be simulated using similar values. The single overlayer transition of

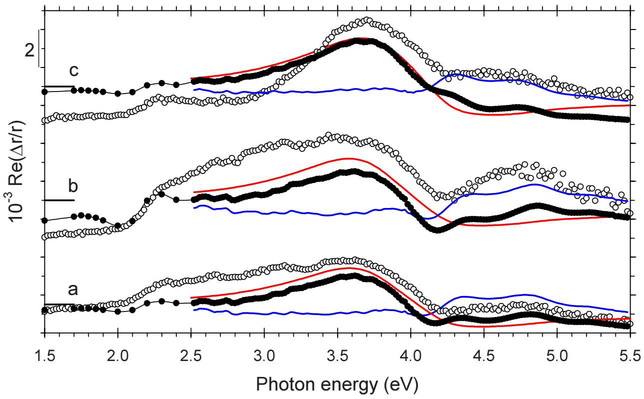

FIG. 4. (Color online) Simulated (filled circles) and experimental (open circles) RA spectra: (a) thiolate/Cu(110)-$c(2\times 2)$, (b) S/Cu(110)-$c(2\times 2)$, and (c) thiolate/Cu(110)-$c(8\times 2)$ type. Blue (dark) and red (light) lines correspond to contributions from the first and second terms of Eq. (4), respectively. The zero RAS level for each simulation is marked and experimental spectra are offset in the vertical axis relative to the simulated spectra for clarity.

similar energy for all the simulations implies a common origin, i.e., the bonding interaction at the interface.

The $c(8\times 2)$ structure can be obtained by a contraction of the distance between S atoms along the $[1\bar{1}0]$ rows of the $c(2\times 2)$ structure[14] and this contraction has been proposed to account for the various high coverage surface structures observed for S/Cu(110).[14,29,40] Carley *et al.*[14] have proposed a "surface buckling" model where the S atoms, occupying the twofold hollow sites, compress along $[1\bar{1}0]$ with the amount of compression determining the structure observed: either $p(5\times 2)$, $p(3\times 2)$, or $c(8\times 2)$. It is likely that surface buckling will have an influence on the RAS data and we speculate that buckling could account for the change in ΔE_g with increasing coverage, although $\Delta\Gamma$ does not appear to be influenced by the surface structure (Table I). The same value of $\Delta\Gamma$ appears in all the simulations of the region 2.5–5.5 eV (Table I) and suggests a similar broadening of the transitions at the L point. We note that a nonzero $\Delta\Gamma$ term has been used to simulate the effects of ion bombardment on the (110) surfaces of Cu, Ag, and Au (Ref. 23) where changes in surface morphology introduce the broadening effect.

The four-phase model simplifies a complex interface into two discrete phases: surface and adsorbate overlayer. In the thin-film limit the contributions of these phases are additive and as the optical axes of the two phases are aligned with each other and with the polarization axes, similar results would be obtained by incorporating the oscillator directly into the surface phase of a three-phase model, as the form of Eq. (4) suggests. Thus it can be difficult to distinguish between an anisotropy originating in the adsorbate overlayer and an anisotropy induced into the surface layers by the adsorbate interaction (via a change in surface electronic structure, strain, etc.). An oscillator of the form of Eq. (5) is typically used in simulating transitions localized at the interface, e.g., transitions between surface states,[36] and adsorbate-induced effects in the surface layers generally produce derivativelike RA spectra. Our resulting simulations with these assumptions show good agreement with experiment (Fig. 4). However, these assumptions may not always be valid and as such we cannot unambiguously assign the 3.8 eV transition of the simulations directly to the thiolate-Cu bond. The possibility remains that this transition could arise from an anisotropy induced in the Cu surface layer by the adsorbate bonding. In any case, the resultant effect is a characteristic optical signature of the system which originates in the interfacial region of the topmost Cu layers and the adsorbate overlayer.

Finally, we consider the results of first-principles calculations performed by D'Agostino *et al.*[41] on the structural and electronic properties of $CH_3S/Cu(110)$-$c(2\times 2)$. The results of the calculations show that the bonding involves a strong hybridization between p orbitals of the molecular S and d states of the Cu surface. This leads to an increase, relative to the clean Cu surface, in the density of states in the Cu surface layer of the CH_3S/Cu interface between 3 and 4 eV binding energy.[41] In particular, a bonding state is found at ~3.5 eV binding energy. Our simulations which use a broad transition at 3.8 eV are consistent with the theoretical results of D'Agostino *et al.*[41]

V. CONCLUSIONS

We have investigated the optical properties of $CH_3S/Cu(110)$ and L-cysteine/Cu(110) surfaces and found that RAS is sensitive to ordered surface structures utilizing thiolate-Cu and S-Cu bonding. Simulations of the experimental data indicate that a broad optical transition at 3.8 eV is associated with the thiolate/Cu(110) interface, as a result of thiolate-Cu bonding. This result is consistent with the results of recent first-principles calculations.[41] Characterizing bonding interactions in UHV provides a basis for the interpretation of RAS results at the solid/liquid interface[42] and we anticipate that the thiolate-Cu(110) RAS results presented here will provide a similar foundation for further work involving the assembly of thiol-derivatized molecules at metal/liquid interfaces.

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