

Molecular orientation with visible light: Reflectance-anisotropy spectroscopy of 3-thiophene carboxylate on Cu(110) surfaces

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(Received 7 October 1997)

We present reflectance-anisotropy spectroscopy data for the adsorption of 3-thiophene carboxylic acid on the clean and O(2×1)/Cu(110) surfaces, which demonstrates the sensitivity to orientation parallel and perpendicular to the surface. Electronic structure calculations were performed to clarify the bonding and assign RAS transitions. [S0163-1829(98)00739-5]

I. INTRODUCTION

Reflectance-anisotropy spectroscopy (RAS) is a technique developed originally for real-time, *in situ* monitoring of semiconductor growth,¹ in which the normalized difference in reflectivity along two orthogonal directions is measured. Despite a relatively large database of experimental information on semiconductor systems, the theoretical calculation of RA spectra is still a formidable problem.^{2,3} Only recently has the technique been applied to metal single-crystal surfaces⁴ and chemisorption processes; many aspects of the interpretation remain open. Pemble *et al.*^{5,6} were the first to report single wavelength RA results for chemisorption of oxygen, formate, and benzoate on Cu(110), which demonstrated that the signal at 1.98 eV can provide a real-time measure of the adsorption of molecular species. The response was ascribed to the quenching of a well-known transition between two surface states at \bar{Y} . Subsequent spectroscopic measurements reported by Hofmann *et al.*⁷ agreed with this assignment and showed that two, bulk-derived, *d-sp* interband transitions at 3.8 and 4.2 eV respond differently to oxygen and CO adsorption; one is quenched by adsorption while the other is rather surface insensitive. Recent work by Jin *et al.*¹⁰ have utilized the quenching of the 2 eV feature to quantify CO coverage during adsorption and desorption processes, leading to a revised interpretation of the kinetics. However, questions regarding the sign of the anisotropy and the relationship between coverage and the RA signal remain open. Scholz *et al.*¹¹ have also utilized RAS to follow reactions of H₂ and O₂ on Rh(110).

While the studies reported here indicate the potential of RAS to follow orientational changes of molecules on metal surfaces, a number of fundamental questions need to be resolved. Theoretical interpretation has so far been limited to symmetry-based arguments invoking dipole selection rules and examination of known band structures for transitions that would lead to large maxima in the joint density of states. The orientational information obtained has been limited to the molecule surface bonding region, since in the visible region accessible, organic molecules are generally transparent. The design of the measurement as a difference technique

implies that random azimuthally oriented adsorption may be indistinguishable from no adsorption. Thus, correlated or simultaneous measurements using another absorption spectroscopy, such as reflection absorption infrared spectroscopy (RAIRS) or high-resolution electron-energy-loss spectroscopy (HREELS), may be necessary to provide sufficient information to uniquely interpret molecular orientation changes. Additionally, the question of whether a molecule-induced dipole transition induces an increase or decrease in reflectivity depends upon the optical properties of the substrate and is critical to the assignment of molecular orientation.¹² The relationship between coverage and RA signal may depend on the substrate, adsorbate, and bonding, and is, however, not yet established for the general case.

In this paper, we report spectroscopic RA results for 3-thiophene carboxylate chemisorption on clean and oxygen preadsorbed Cu(110), since in correlated HREELS and STM work^{14,15} the coverage dependence reveals reorientation from a flat-lying to upright geometry, which is initially azimuthally aligned and then decays with additional adsorption leading to a rotation of the thiophene ring away from the high symmetry direction. The insensitivity of the RA signal to the rotation of the ring shows that little information regarding conformational changes of nonbonding functionalities of the molecules could be obtained, but the information, derived from interface-related states, allows sensitivity to a buried interface. Electronic structure calculations were performed to clarify the bonding and assign RAS transitions.

II. EXPERIMENT

The results were obtained in two different UHV systems. The Cu(110) samples were mechanically and electrochemically polished and then cleaned in UHV by repeated cycles of sputtering and annealing at 800 K until a sharp LEED pattern with low diffuse background was obtained. In HREELS (VSW HIB 1000 double pass spectrometer¹⁶), cleanliness was assessed by the appearance of the dipole active, surface phonon resonance¹⁷ at 160 cm⁻¹ and the absence of any other losses, while in RAS cleanliness was verified by the appearance of an intense ($>6 \times 10^{-3}$) feature at

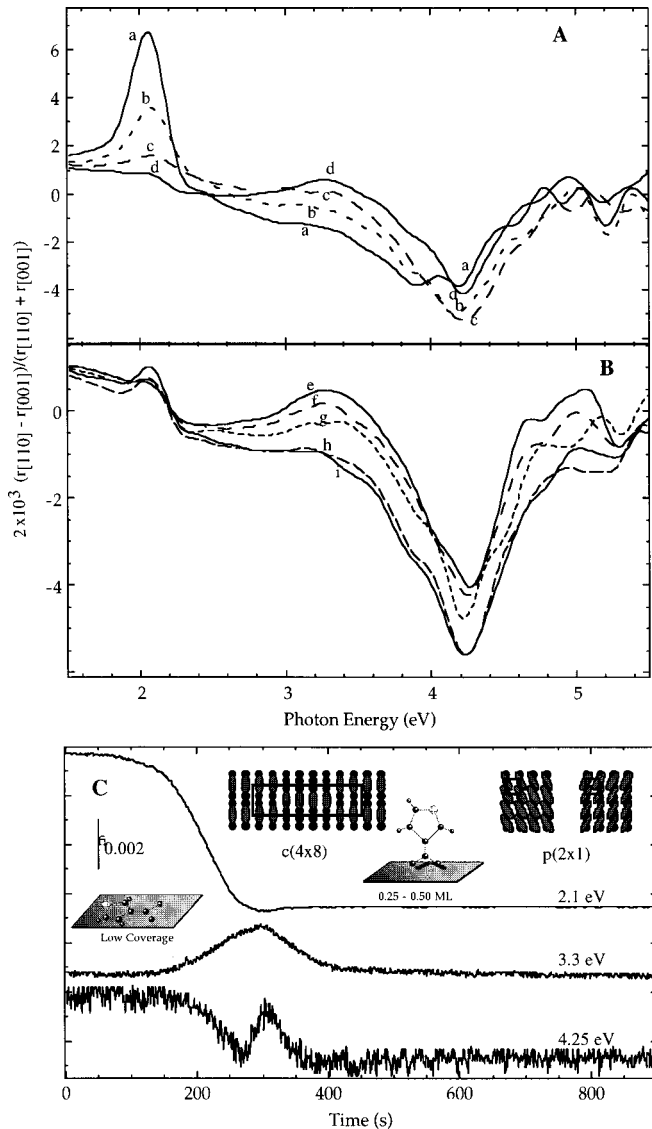


FIG. 1. (a),(b) Representative RAS data with increasing coverage (curves *a-i*) for exposure of 3-thiophene carboxylic acid onto the clean Cu(110) surface. (c) Single wavelength RA data acquired while dosing at several photon energies as indicated.

2.1 eV, characteristic of the clean surface.⁷ The organic solid, 3-thiophene carboxylic acid (Aldrich 99%) was dosed as described previously¹⁸ with the Cu(110) sample held at 340–350 K. The RAS spectrometer,^{19,20} based on a design by Aspnes,²¹ was attached to a strain-free window on the UHV system. Experimental artifacts were removed from the raw data using a correction function determined by measuring RAS spectra with the sample aligned in two orthogonal orientations at 45° to the [110] direction of the crystal.

III. ADSORPTION OF 3-THIOPHENE CARBOXYLATE ON CLEAN Cu(110)

A. RAS measurements of clean Cu(110)

The spectrum of the clean surface, Fig. 1(a), curve *a*, is in good agreement with that of Hofmann *et al.*,⁷ with reso-

nances at 2.1 eV and a doublet at 3.8 and 4.2 eV. However, we assign the sense of the anisotropy opposite to that due to Hofmann *et al.*⁷ Although there is consensus that the transition between the two surface states at \bar{Y} is allowed only for light polarized along $\langle 001 \rangle$,^{5–7} whether the transition induces an increase or decrease in reflectivity has not been clarified. In a separate publication,¹² we have examined the optical response of a range of materials within a three-layer dielectric theory model. Solution of the Fresnel equations shows that, for an isotropic copper substrate, a transition near 2 eV in the overlayer (surface region) leads to a *decrease* in reflectivity, as assigned in Fig. 1(a), curve *a*. Furthermore, this simplistic model also shows features near 4 eV that resemble the measured spectrum. Within the Fresnel description, the response at 4 eV is not due to structure in the overlayer, *per se*, but derives from the optical response of the substrate. This view is consistent with both the sign and, qualitatively, the interpretation for Ag(110) and Au(110) by Mochan *et al.*⁹ Additionally, we have recently shown²² that Fresnel calculations correctly predict the azimuthal orientation of a molecule from the RA response of an intramolecular electronic transition, for the case of 9-anthracene carboxylate adsorbed on $p(2 \times 1)O/Cu(110)$. Therefore, we reassign the sense of the anisotropy of the clean surface.

In recent work on the Ag(110) surface, the corresponding transition between the filled and unoccupied surface states at \bar{Y} , expected near 1.7 eV, was not clearly identified,⁸ which suggested that the 2-eV transition on Cu(110) may involve a significant contribution from *d-sp* interband transitions near the absorption edge, based on theoretical calculations by Mochan *et al.*⁹ for Ag(110) and Au(110). The sense of the weak feature near 1.7 eV was opposite to that on Cu(110),⁷ consistent with our reassignment. Possible reasons for the weak intensity suggested⁸ were differences in the bulk optical response and a smaller density of states in the Ag(110) surface states at \bar{Y} . We find¹² that the substrate optical response function, $A(\omega)$, for Cu is $A(2.1 \text{ eV}) = 0.106$, while for Ag it is $A(1.7 \text{ eV}) = 0.042$. While the bulk response involved in the RA is weaker by a factor of two on Ag compared to Cu, the strength of the optical transition between the \bar{Y} surface states on Ag is apparently also weaker than on Cu, which could be due to differences in factors such as density of states and the magnitude of the transition dipole. For Au(110), the corresponding \bar{Y} transition is about 0.5 eV,²³ which is not within the current spectrometer's range.

The coverage dependent quenching of the surface state transition in the RA signal at 2 eV on Cu(110) behaves similarly for the adsorption of thiophene carboxylate, show in Fig. 1(c), as for the adsorption of oxygen,^{5–7} formate,^{5,6} and benzoate.^{5,6} Jin *et al.*¹⁰ have found the RA response to be linearly related to coverage, as determined from thermal desorption measurements for the CO/Cu(110) system. As a first approximation, the RA intensity is given by the joint density of states, $D^e(E, \theta) \otimes D^h(E, \theta)$. If the feature at 2 eV is dominated by a transition between electron and hole surface states at \bar{Y} , then the coverage-dependent change in $D^e(0.15 \text{ eV}, \theta)$ and $D^h(1.85 \text{ eV}, \theta)$, both of which decay more rapidly than linear in coverage, θ , for H/Cu(110) from photoemission and inverse photoemission,¹³ leads to the expectation of a non-linear decay in the RA signal with coverage. For the CO/

Cu(110) system, the \bar{Y} surface state in inverse photoemission²⁴ is obscured by the CO derived levels²⁵ and the coverage dependent decay of the surface state has not been reported. Although many body effects have been shown to be important in the theoretical description of RA spectra,²⁶ it is not clear how including such effects would lead to a linear decay with θ . Thus, the explanation of the coverage dependence remains open.

B. RAS measurements of 3-thiophene carboxylate/Cu(110)

We now correlate the RAS measurements for the adsorption of 3-thiophene carboxylate (3-TC) on the clean Cu(110) surface with molecular reorientation determined previously from HREELS and STM.^{14,15} The coverage-dependent changes involve a single flat-lying orientation converting to an upright, azimuthally aligned orientation at a coverage of $\theta=0.25$ ML with a $c(4\times 8)$ periodicity. As the coverage increases to saturation, at $\theta=0.5$ ML, the structure changes to a $p(2\times 1)$ periodicity in which the thiophene ring rotates approximately 30° away from $\langle 110 \rangle$; however, the carboxylate is presumed to remain aligned along $\langle 110 \rangle$ in the short bridge site.

In the initial adsorption of the flat-lying species, the features at both 2.1 and 3.8 eV decay. The time-dependent change of the signal at 2.1, 3.3, and 4.24 eV is shown in the single-wavelength mode in Fig. 1(c). The decrease in the 2.1-eV signal is similar to that found previously,⁵ including a small but measurable recovery before stabilizing. As the feature at 2.1 eV decays [Fig. 1(a), curves *a-d*], the magnitude of the peak at 3.8 eV also decreases, but changes occur over the entire 2.5–4-eV range, indicating that the anisotropy of the Cu(110) surface-sensitive *d* to *sp* band transition, or Fermi surface to image state band favored by Hofmann *et al.*,⁷ extends over quite a broad spectral range. The change in the anisotropy at 3.3 eV maximizes simultaneously with the minimum in the 2.1-eV feature; however, the magnitude of the anisotropy at 4.2 eV increases (negatively) by 25% and then recovers to nearly its original value [Fig. 1(a) curves *a-d* and Fig. 1(c), 200–300 s] at this stage.

As the coverage increases and the molecules flip upright [Fig. 1(b), curves *e-i* and Fig. 1(c), 300–400 s], the broad band between 2.5 and 4 eV returns to essentially the clean surface value while the magnitude of the anisotropy at 4.24 eV continues to increase (negatively). Fig. 1(b), curve *i*, corresponds to the $c(4\times 8)$ periodicity structure,¹⁵ shown schematically in Fig. 1(c), in which the thiophene carboxylate plane is aligned parallel to $[110]$. With further dosing, the structure converts to the $p(2\times 1)$ surface in which the rings rotate away from $[110]$. The RA spectrum of the $p(2\times 1)$ structure is not shown since it is not significantly different from that of the $c(4\times 8)$ structure, Fig. 1(b), curve *i*, at least within the 1.5–5.5-eV photon range and measured signal to noise. This is consistent with the assumption that the copper-carboxylate bonding does not change despite the rotation of the thiophene rings away from the high symmetry direction. The conformational changes associated with the thiophene ring were not detected within the spectral range and signal-to-noise ratio of our measurements.

C. LDA-DFT calculations of $p(2\times 1)$ 3-thiophene carboxylate/Cu(110)

To clarify the nature of molecule-substrate bonding, we performed *ab initio* calculations for a 25-atom slab supercell in the maximum coverage, $\theta=0.5$ ML, regime, based on the $p(2\times 1)$ structure proposed previously.¹⁵ The Cu(110) unit cell contains two surface Cu atoms, both bonded to oxygens from the same molecule. Since eleven atoms belong to the latter, our calculation then contains seven Cu layers, with the shallowest three Cu layers allowed to relax and the remaining four kept fixed at bulk geometry.

The electronic structure calculations were performed using the Gaussian-based density-functional pseudopotential code QUEST (quantum electronic structure). The LDA to density functional theory^{27,28} yields excellent geometries and relative energies for many systems. We use the Perdew-Zunger LDA parametrization²⁹ of the Ceperley-Alder electron gas results,³⁰ and employ the generalized norm-conserving pseudopotentials of Hamann.³¹ We did not use the generalized gradient approximation³² (GGA) because several workers have now reported that it can lead to inferior geometries^{33–35} and our aim does not include calculating the heat of chemisorption. The basis sets for all atoms consisted of two contracted bases per atomic valence orbital plus optimized polarization functions, i.e., “double zeta plus polarization.”³⁶ In order to achieve near-linear scaling, QUEST employs an algorithm due to Feibelman.^{37,38} Geometric relaxation was done through an iterative Broyden scheme developed by Johnson,³⁹ using accurately computed interatomic forces.⁴⁰

The nature of the Cu-O bonds appears to depend on coverage only to a very limited extent, as confirmed by our calculations at a coverage of 0.25 ML, i.e., using a (4×2) unit cell containing only two 3-thiophene carboxylates in adjacent short bridge sites along $\langle 001 \rangle$. This establishes that the Cu-O bond is unaffected by the orientation of the carbon ring(s). Our relaxed geometry at maximum coverage, $\theta=0.5$ ML, gave 1.28 Å, 1.95 Å, and 126.5° for the basal C-O and O-Cu distances and the O-C-O angle, respectively. These values are the same as those found for surface carboxylate species on Cu(100).⁴¹ The latter were 1.29 Å, 1.95 Å, and 126° , respectively, as obtained from an all electron calculation of a $(\text{HCOO})\text{Cu}_{60}$ cluster,⁴¹ with the carboxylates in the short bridge site in the ground-state geometry. It should be noted that this agreement shows the accuracy of the pseudopotentials used in our calculations. Results for the (4×2) , $\theta=0.25$ ML coverage, system show that the adsorbate induces a slight buckling of the Cu atoms bonded to the molecule.

Results for the local density of states (LDOS) at Cu, O, and basal C atoms are shown in Fig. 2(a), with the vertical line denoting the Fermi energy. Two features in the DOS curves should be noted. The first (at about -6 to -8 eV) pertains to the C-O bond, while the second (at about -1 to -3 eV) superficially suggests possible Cu_{3d} bonding. The nature of these features is clarified by examining the cross terms (and their integrals up to the Fermi energy) of the density matrix, $\rho_{ll'}^{AA'}$ where *A* and *l* denote respectively atom and angular momentum components; these terms (actually $\rho_{ll'}^{AA'} + \rho_{l'l}^{A'A}$) are reported in the inset of Fig. 2(a) for the

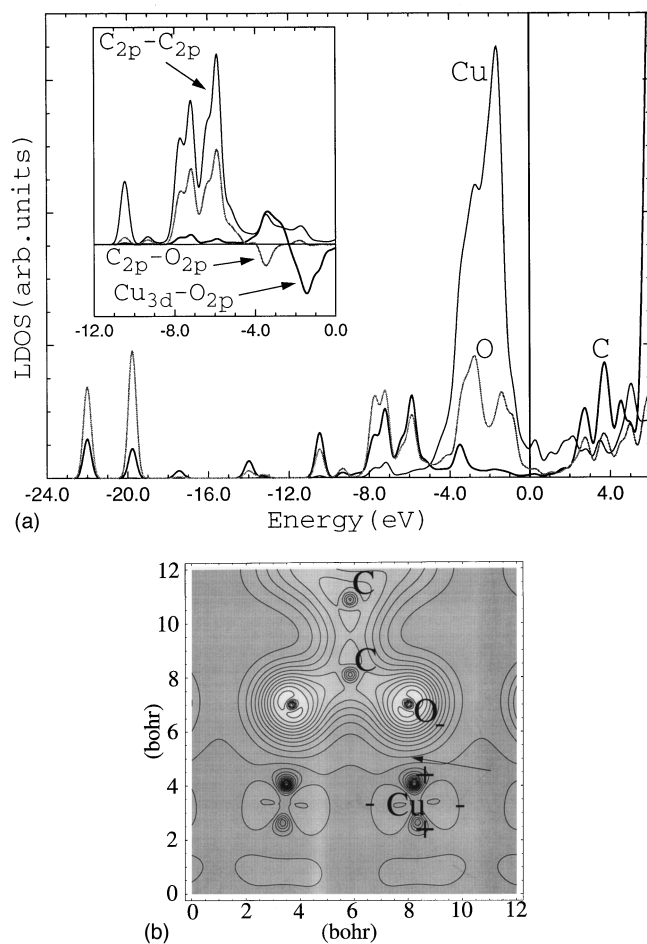


FIG. 2. (a) The local densities of states for the Cu nearest the adsorbed molecule and for the carboxylate O and C atoms (closest to the surface). The irregular portion of the Cu LDOS in the $4s$ band near the Fermi level is due to k -point sampling. The inset shows on the same energy scale the cross terms of the density matrix, indicative of bonding-antibonding behavior (see also main text). (b) The logarithm of the charge density difference made by subtracting the bare Cu slab from the adsorbate covered one (i.e., above the metal the total charge density is shown; below the molecule a difference is shown). A small uniform density was added to make all values positive before the logarithm was taken; the scale is in Bohr. The metal shows a small loss of $3d_{z^2}$ charge and image charge formation below the Cu atoms. Note the separation of the $3d$ orbitals from the oxygen atoms.

Cu-O, $l=2$, $l'=1$ ($\rho_{3d-2p}^{\text{Cu-O}}$) and the C-O, $l=l'=1$ ($\rho_{2p-2p}^{\text{C-O}}$) bonds. The diagonal element $\rho_{2p-2p}^{\text{C-C}}$ is also shown for orientation. Clearly, the integrated areas of the cross terms show there is negligible (versus *significant*) net bonding for the Cu_{3d} -O (versus C-O) orbitals; in addition, the values of the energy integrated LDOS indicate strong electron transfer from C to O, but negligible electron transfer (<0.1 electron) from the Cu $3d$ shell to O. Since the two O features in the -3 eV region show little overlap with both Cu and C orbitals, we assign them to the lone-pair oxygen electrons, and note that their degeneracy with the Cu_{3d} is accidental in the sense that it is not indicative of bonding. The presence of a $2p$ lone pair on the basal oxygens was also noted in Ref. 41, and the atom-substrate bonding was examined. However, in

Ref. 41, only molecular orbitals with significant energy changes for different adsorption geometries were considered, whereas it is the integrated cross terms, to which all occupied levels contribute, which ultimately determine bonding.

All Cu-O cross terms ($l=s,p,d$; $l'=s,p$) were examined to establish the nature of the molecule-surface bond; a similar analysis was performed for comparison to the O-C bond. Strictly, such a procedure is quantitatively not reliable; however, it may offer insight in relative terms. While the sum of the cross terms for the C-O bond gave an indication of a robust covalent bond (obviously, of sp^2 type), a similar sum for the Cu-O one resulted in an off diagonal “bonding” density about ten times smaller, indicating the weakness of such a bond (in fact such a small density can be a basis set artifact).

Due to the weak charge transfer from both Cu $4s$ and $3d$ orbitals, and the small Cu-O cross terms, the molecule-substrate bond is apparently mainly of electrostatic character, with the Cu surface layers providing image charge screening in response to the negatively charged (≈ -0.5 electron) O atoms. Charge density is a physical observable, and provides a clear way to evaluate this statement. In Fig. 2(b), we report a charge density difference plot made by comparing the molecule+metal system and the substrate-only system. The sign of the charge difference is also shown. This unusual type of plot is especially advantageous (instead of, for example, a plot of the molecule+metal system minus the substrate-only + free molecule), since it shows the changes induced by the molecule in the substrate, and the molecular region shows the nature of the molecular charge and bonds. Figure 2(b) reveals the covalent nature of the C-O and C-C bonds. In passing, we note that the asymmetry in the upwards charge lobes of the topmost C in the figure is due to the presence of one sulphur atom in the carbon ring. The charge along C-O and C-C bonds distributes very differently from the one in the Cu-O region. In the former, we see the axial increase in density typical of covalency, while in the latter we see a nodal structure between Cu and O. In fact the (negative) charge around the O shows a spatial compression in the region above the substrate (the arrow in the figure). This is a clear indication of the electrostatic nature of the Cu-O bond and that the (negative) O charge is being compressed in order to get the molecule closer to the surface. The sign and shape of the substrate charge, on the other hand, is typical of a surface image charge distribution.

The nature of the LDOS also gives some indications of the optical properties of the system. For the clean surface, the optical response at 3.8 and 4.2 eV is mainly ascribed to the d -to- sp interband transitions.⁷ Our results here show that while such transitions are still energetically allowed, a new 4 eV substrate-induced transition may occur between Cu-O filled states near -2 eV and carboxylate C-O empty states near $+3$ eV. The comparison of our DF-LDA results for the transition energy (5 eV) with the experimental one (4 eV) is suggestive of good agreement, since the 1-eV discrepancy could be ascribed to the omission of final-state electron-hole correlation, excluded by the DF-LDA scheme. On the other hand, while appropriate to metallic systems, DF-LDA is well known to underestimate gap energies in semiconductors and insulators, and here we have in principle a “mixed” system: i.e., a metallic substrate interacting with a molecule with a

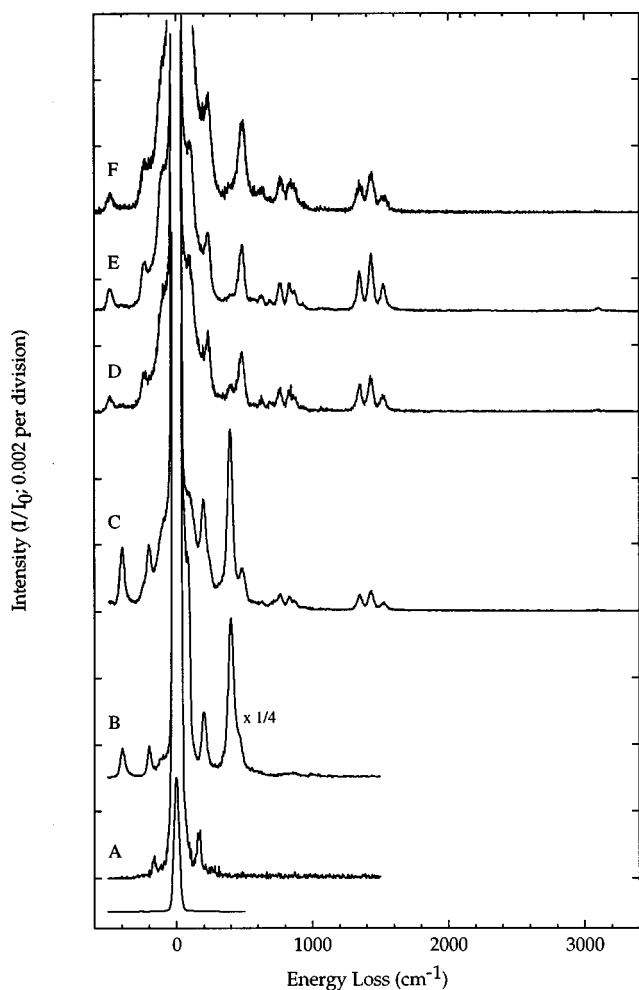


FIG. 3. Coverage-dependent HREELS spectra measured on specular at 2.01 eV ($\theta=60^\circ$) for (a) the clean Cu(110) surface; (b) after saturation of the $p(2\times 1)\text{O}/\text{Cu}(110)$ structure; and following cumulative doses of 3-thiophene carboxylic acid onto the O/Cu(110) surface for (c) 15 min; (d) 30 min; (e) 45 min; and (f) 60 min.

finite energy difference between HOMO and LUMO. So, while quantitative agreement is possibly not excluded, a caveat concerns the lack of self-energy corrections beyond LDA. This also explains why our focus was intentionally on ground state (i.e., structural and bonding) properties rather than on excited states. However, to assess the relative role of intra-atomic O and Cu transitions would require a dipole matrix element analysis, which is beyond the scope of the present paper.

IV. ADSORPTION ON $p(2\times 1)\text{O}/\text{Cu}(110)$

The adsorption of 3-TC on the oxygen predosed surface is simpler than on the clean surface, as indicated by the on-specular HREELS data shown in Fig. 3. The clean surface shows only the surface phonon resonance¹⁷ at 160 cm^{-1} while after completion of the $p(2\times 1)\text{O}/\text{Cu}(110)$ reconstruction, two bands appear at 400 cm^{-1} due to $\nu(\text{Cu-O})$ and at 200 cm^{-1} associated with an adsorbate-induced dipole active

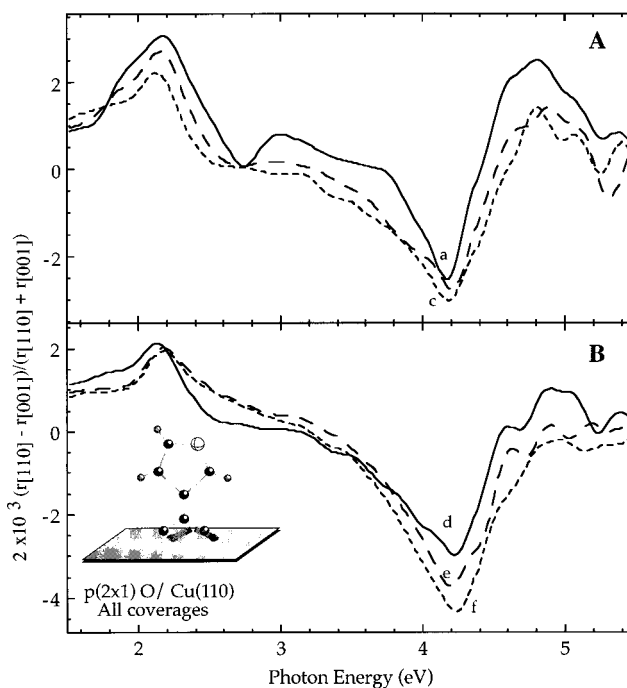


FIG. 4. (a) and (b) Representative RAS data (a-f) with increasing coverage while dosing 3-thiophene carboxylic acid onto a saturated $p(2\times 1)\text{O}/\text{Cu}(110)$ surface.

phonon at \bar{X} . As the surface is exposed to the carboxylic acid, the oxygen metal stretch decreases in intensity and new features associated with 3-TC appear. Comparison with Ref. 14 shows clearly that the bands are attributable to the in-plane A' modes and therefore the species are oriented perpendicular to the surface at all coverages. The reaction of the acid with the oxygen pre-dosed surface is expected to titrate one oxygen atom per two incident acid molecules by reaction to form H_2O , which desorbs and effectively reduces the $\nu(\text{Cu-O})$ intensity. However, at a maximum 3-TC coverage of 0.5 ML, we would expect roughly 0.25 ML of oxygen to remain on the surface. No ordered structures have been observed to date for adsorption of 3-TC on the oxygen pre-dosed surface. Although no change in orientation perpendicular to the surface occurs, the low barrier to rotation of the thiophene ring, estimated at 175 meV ,¹⁵ suggests that any azimuthal orientation associated with the thiophene ring induced by the carboxylate bonding could easily be lost due to thermal excitation of ring torsion or rotation at low coverage, but might grow in at higher coverage due to steric restrictions. Measurements of the RA associated with intramolecular transitions involving the thiophene ring would clearly provide novel insight into the role of intermolecular interactions and local order in this system, but these are anticipated to occur above 5 eV.

The RA spectra acquired during dosing of 3-TC onto a saturated $p(2\times 1)\text{O}/\text{Cu}(110)$ surface are shown in Fig. 4. The time-dependent decay of the feature at 2.1 eV while dosing oxygen showed a minimum and small recovery as reported previously,⁵ similar to the behavior of 3-TC on the clean surface [Fig. 1(c)]. The resulting spectrum, Fig. 4(a), curve a is in good agreement with that reported by Hofmann *et al.*⁷ With exposure to the acid, the feature at 2.1 eV is

quenched further. Comparison of Fig. 4(a) with Fig. 1(a) curve *a*, shows that the changes in the 2.5–4-eV range largely reverse the quenching of the surface sensitive broad band anisotropy, which occurred with formation of the $p(2 \times 1)$ structure. By spectrum *c* in Fig. 4(a), the anisotropy in this range is similar to that of the clean surface and the intensity in the region of 3.8 eV, while not as well resolved as on the clean surface, has nearly recovered. The intensity of the 4.2-eV feature becomes continuously stronger with adsorption (curves *a–f*), which is consistent with the clean surface data where an increase in anisotropy (negatively) was observed when the molecules reorient perpendicular to the surface. This change in anisotropy can be attributed again to a Cu-O to C-O intramolecular transition (see Sec. III B), which acts in a direction opposite to that of the oxygen reconstruction. At higher coverage there is a shift and broadening of the feature near 2.1 eV, so that in the 2.5–3.5-eV range the anisotropy first decreases and then increases again. Comparison of the saturated surface spectrum, Fig. 4(b), curve *f*, with that for the $p(2 \times 1)$ surface of 3-TC, Fig. 1(b), curve *i*, shows that the bonding of the carboxylate functionality must be rather similar.

V. CONCLUSIONS

The correlation of the HREELS data with RAS measurements shows that the effect of molecular reorientation from a flat-lying to upright species produces significant changes in the anisotropy near 4.2 eV, related to a transition involving copper-carboxylate states. The copper-carboxylate bonding is similar for the upright species on the clean and oxygen reconstructed surfaces and during adsorption induces time-dependent changes that demonstrate the potential for following kinetic processes in real time.

ACKNOWLEDGMENTS

We gratefully acknowledge support from the EPSRC. Q.C. thanks the British Council for financial support. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract No. DE-AC04-94AL85000.

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¹D. E. Aspnes, *Surf. Sci.* **307-309**, 1017 (1994).

²L. Kipp, D. K. Biegelsen, J. E. Northrup, L. E. Swartz, and R. D. Bringans, *Phys. Rev. Lett.* **76**, 2810 (1996).

³S. J. Morris, J. M. Bass, C. C. Mathai, V. Milman, and M. C. Payne, *J. Vac. Sci. Technol. B* **12**, 2684 (1994).

⁴Y. Borensztein, W. L. Mochan, J. Tarriba, R. G. Barrera, and A. Tadjeddine, *Phys. Rev. Lett.* **71**, 2334 (1993).

⁵M. E. Pemble, N. Shukla, A. R. Turner, T. Bitzer, B. G. Frederick, K. J. Kitching, and N. V. Richardson, *J. Chem. Soc., Faraday Trans.* **91**, 3627 (1995).

⁶M. E. Pemble, N. Shukla, A. R. Turner, J. M. Fernandez, B. A. Joyce, J. Zhang, A. G. Taylor, T. Bitzer, B. G. Frederick, K. J. Kitching, and N. V. Richardson, *Phys. Status Solidi A* **152**, 61 (1995).

⁷P. Hofmann, K. C. Rose, V. Fernandez, A. M. Bradshaw, and W. Richter, *Phys. Rev. Lett.* **75**, 2039 (1995).

⁸V. Fernandez, D. Pahlke, N. Esser, K. Stahrenberg, O. Hunderi, A. M. Bradshaw, and W. Richter, *Surf. Sci.* **377**, 388 (1997).

⁹W. L. Mochan, R. G. Barrera, Y. Borensztein, and A. Tadjeddine, *Physica A* **207**, 334 (1994).

¹⁰X. F. Jin, M. Y. Mao, S. Ko, and Y. R. Shen, *Phys. Rev. B* **54**, 7701 (1996).

¹¹S. M. Scholz, F. Mertens, K. Jacobi, R. Imbihl, and W. Richter, *Surf. Sci.* **340**, L945 (1995).

¹²R. J. Cole, B. G. Frederick, and P. Weightman, *J. Vac. Sci. Technol. A* (to be published).

¹³P. Sandl, U. Bischler, and E. Bertel, *Surf. Sci.* **291**, 29 (1993).

¹⁴B. G. Frederick and N. V. Richardson, *J. Electron Spectrosc. Relat. Phenom.* **73**, 149 (1995).

¹⁵B. G. Frederick, C. Qiao, S. M. Barlow, N. G. Condon, F. M. Leibsle, and N. V. Richardson, *Surf. Sci.* **352-354**, 238 (1996).

¹⁶H. Ibach, *Electron Energy Loss Spectrometers: The Technology of High Performance*, Springer Series in Optical Sciences Vol. 63 (Springer-Verlag, Berlin, 1991).

¹⁷J. A. Stroscio, M. Persson, S. R. Bare, and W. Ho, *Phys. Rev. Lett.* **54**, 1428 (1985).

¹⁸B. G. Frederick, Q. Chen, F. M. Leibsle, M. B. Lee, K. J. Kitching, and N. V. Richardson, *Surf. Sci.* (to be published).

¹⁹S. M. Scholz, A. B. Mller, W. Richter, D. R. T. Zahn, D. I. Westwood, D. A. Woolf, and R. H. Williams, *J. Vac. Sci. Technol. B* **10**, 1710 (1992).

²⁰J. R. Power, T. Farrell, P. Gerber, S. Chandola, P. Weightman, and J. F. McGilp, *Surf. Sci.* **372**, 83 (1997).

²¹D. E. Aspnes, J. P. Harbison, A. A. Studna, and L. T. Florez, *J. Vac. Sci. Technol. A* **6**, 1327 (1988).

²²B. G. Frederick, J. R. Power, R. J. Cole, C. C. Perry, Q. Chen, S. Haq, Th. Bertrams, N. V. Richardson, and P. Weightman, *Phys. Rev. Lett.* **80**, 4490 (1998).

²³R. A. Bartynski and T. Gustafsson, *Phys. Rev. B* **33**, 6588 (1986).

²⁴W. Jacob, V. Dose, U. Kolac, T. Fauster, and A. Goldmann, *Z. Phys. B* **63**, 459 (1986).

²⁵J. Rogozik, H. Scheidt, V. Dose, K. C. Prince, and A. M. Bradshaw, *Surf. Sci.* **145**, L481 (1984).

²⁶C. H. Patterson and D. Herrendrfer, *J. Vac. Sci. Technol. A* **15**, 3036 (1997).

²⁷P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).

²⁸W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).

²⁹J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).

³⁰D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).

³¹D. R. Hamann, *Phys. Rev. B* **40**, 2980 (1989).

³²J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992).

³³D. R. Jennison, E. B. Stechel, A. R. Burns, and Y. S. Li, *Nucl. Instrum. Methods Phys. Res. B* **101**, 22 (1995).

³⁴I. Frank, D. Marx, and M. Parrinello, *J. Chem. Phys.* **104**, 8143 (1996).

³⁵Y. Yourdshahyan, U. Engberg, L. Bengtsson, B. I. Lundqvist, and

- B. Hammer, Phys. Rev. B **55**, 8721 (1997).
- ³⁶Contact P. A. Schultz, Sandia National Laboratories, Albuquerque, NM 87185-1111; paschul@cs.sandia.gov. See also P. J. Feibelman, Phys. Rev. B **38**, 1849 (1988).
- ³⁷P. J. Feibelman, Phys. Rev. B **33**, 719 (1986).
- ³⁸P. J. Feibelman, Phys. Rev. B **35**, 2626 (1987).
- ³⁹D. D. Johnson, Phys. Rev. B **38**, 12 807 (1988).
- ⁴⁰P. Pulay, Mol. Phys. **17**, 197 (1969).
- ⁴¹M. Sambì, G. Granozzi, M. Casarin, G. A. Rizzi, A. Vittadini, L. S. Caputi, and G. Chiarello, Surf. Sci. **315**, 309 (1994).