

Creating a functionalized surface: The adsorption of terephthalic acid onto Cu(110)D. S. Martin^{1,2,*} R. J. Cole,³ and S. Haq²¹*Department of Physics, University of Liverpool, Liverpool, L69 3ZE, United Kingdom*²*Surface Science Research Centre, University of Liverpool, Liverpool, L69 3BX, United Kingdom*³*Department of Physics, University of Edinburgh, Edinburgh, EH9 3JZ, United Kingdom*

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We investigate the adsorption of terephthalic acid onto the Cu(110) surface using a variety of surface-sensitive techniques including optical-based probes. The nature of the adsorbate-Cu surface bonding, the adsorbate orientation, and the two-dimensional order are determined. The molecule adsorbs as a monoterphthalate species, bonding via the carboxylate group, to form a saturated layer of upright molecules that are terminated by acid groups—a functionalized surface. These acid groups are available for chemical interactions with additional adsorbates. Further deposition of the acid onto the first layer results in multilayer growth consisting of broadly flat-lying, hydrogen-bonded molecules.

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I. INTRODUCTION

The adsorption of simple monocarboxylic acids on Cu(110) has previously been studied using a variety of surface sensitive experimental probes and details of the adsorption process, including the bonding mechanism, have been determined. Generally, adsorption leads to the deprotonation of the acid group into the carboxylate functionality and this species bonds to the Cu(110) surface in an upright configuration with the carboxylate plane aligned along the Cu close-packed atomic rows and with the O atoms on top of the Cu atoms.^{1–4} In this work we investigate the interaction of a dicarboxylic acid with the Cu(110) surface. The additional acid group on this molecule introduces a significant complication to the competition between surface-adsorbate and adsorbate-adsorbate interactions. It is possible that (i) the diacids adsorb in a fashion broadly similar to the monoacids, (ii) the formation of the dicarboxylate species could tether the molecules to the surface with flat-lying geometry, or (iii) intermolecular attraction via hydrogen bonding could suppress Cu-carboxylate bonding. In principle the understanding and control of these effects in Cu-carboxylate systems will provide a flexible route to nanoengineering surface properties, a key enabling technology in the nanoscience revolution. In case (i) a diacid has the potential to form a surface species of upright monocarboxylates terminated with an acid group at the vacuum interface that would be available for chemical interactions. Such a chemically functionalized surface would have wide-ranging applications including the immobilisation of biomolecules, molecular recognition, biosensors, molecular electronics, and molecule-based magnetic materials.

In the present work we investigate the adsorption of terephthalic acid (TPA, HOOC-C₆H₄-COOH), a highly symmetric planar molecule, onto the Cu(110) surface. To determine the nature of the dicarboxylic acid-Cu bonding, the molecular orientation and the two-dimensional order we have used a combination of techniques. Reflection absorption infrared spectroscopy (RAIRS) distinguishes functional groups by their vibrational signatures and can determine their orientation by exploitation of the surface selection rule:

only modes with a significant component of the dynamic dipole moment directed perpendicular to the surface are observable.⁵ Low-energy electron diffraction (LEED) is used to determine ordering and temperature programmed desorption (TPD) reveals how molecules desorb from the surface, in terms of mass fragments, as a function of temperature.

We also investigate the effect of molecular adsorption upon the optical properties of the surface using reflection anisotropy spectroscopy (RAS). This is an optical probe of surfaces⁶ that has been shown to be sensitive to adsorbate orientation using the system 3-thiophene carboxylic acid (3TC) on Cu(110).⁷ Since RAS and RAIRS detect optical anisotropy in the plane of the surface and transition dipoles perpendicular to the surface, respectively, these techniques are highly complementary. Both optical techniques are surface sensitive probes capable of determining adsorbate orientation *in situ* and are not constrained to operation in a vacuum.

II. EXPERIMENTAL PROCEDURE

The experiments were carried out in an ultrahigh vacuum (UHV) environment at a base pressure in the 10⁻¹⁰ mbar region. The Cu(110) single crystal aligned to better than 1° was mechanically polished to produce a mirror smooth surface before introduction into the vacuum chamber. A clean Cu(110) surface was prepared in UHV by cycles of Ar ion bombardment (10 μA, 500 eV, 300 K, 20 min) and subsequent annealing to 860 K for 60 min. Surface order was confirmed by a sharp (1 × 1) low-energy electron diffraction (LEED) pattern and cleanliness was monitored using x-ray photoelectron spectroscopy (XPS). The clean surface generated a RA spectrum in agreement with the well known Cu(110) RA profile.^{7–9} This standard cleaning procedure produces a variable surface morphology.¹⁰ A roughening transition on Cu(110) is known to occur at a temperature of ~1000 K and is characterized by the proliferation of monoatomic steps across the surface.⁹ In a previous study combining the results of RAS and scanning tunneling microscopy (STM) we showed the potential of the roughening transition as a method for the creation of a more well-defined metal

surface morphology.⁹ Such a surface was preferred for the present RAS work and was prepared by heating the clean surface from 860 to 1030 K over a period of 30 min and remaining at 1030 K for a further 10 min. This method when applied to our crystal was observed by STM to produce a stepped surface morphology consisting of terraces of 5 to 15 nm in width in the $[1\bar{1}0]$ direction that were terminated by monoatomic steps aligned along the $[001]$ direction.

Terephthalic acid (TPA, purity 99%) was used as received from Aldrich. Dosing of the acid was conducted by placing the acid in a small glass vessel separated from the main vacuum chamber by a gate valve and differentially pumped by a turbo-molecular pump. Sublimation was performed by heating the glass vessel. Before deposition onto the Cu(110) specimen the acid was outgassed with the gate valve closed. Unless otherwise stated, deposition occurred with the specimen held at a constant temperature of 300 K for RAIRS experiments and 340 K for RAS experiments.

The RA spectrometer of the Aspnes design¹¹ was operated external to the UHV chamber and utilized a Xe photon source to project light through a low-strain window on the UHV system. RAS probes as a function of energy the optical anisotropy of a surface by using linearly polarized light to illuminate the surface and by measuring the difference in normal incidence reflectance of two perpendicular directions (Δr) normalized to the mean reflectance (r)

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

where the r are complex Fresnel reflection amplitudes. Spectra of the real part of the complex RA were taken over a photon energy range of 1.5 to 5.5 eV. Experimental artifacts were removed from the spectra using a correction function determined by measuring RAS spectra with the specimen aligned in two orthogonal orientations. RA spectra were recorded continuously during dosing and during thermal desorption.

RAIRS measurements were recorded continuously during dosing as sample single-beam infrared spectra and ratioed against a reference background single-beam spectrum obtained from the clean Cu(110) surface, thus measuring the change in grazing-incidence reflection due to adsorption $\Delta R/R_0$. The RAIR spectrometer was located outside the UHV chamber and operated over a spectral range of 650–4000 cm^{-1} . Spectra were recorded at a resolution of 4 cm^{-1} with the coaddition of 256 scans. The spectrometer was coupled to the UHV system via KBr optics and windows. In some spectra, a doublet structure was observed at around 2350 cm^{-1} due to CO_2 absorption occurring during the optical path through the atmosphere. A quadrupole mass spectrometer was used to monitor molecular mass fragments both during deposition and on performing TPD experiments on the prepared films.

III. RESULTS AND DISCUSSION

A. Surface saturation

A coverage dependent LEED study of the deposition of TPA showed a progression from the (1×1) pattern of the

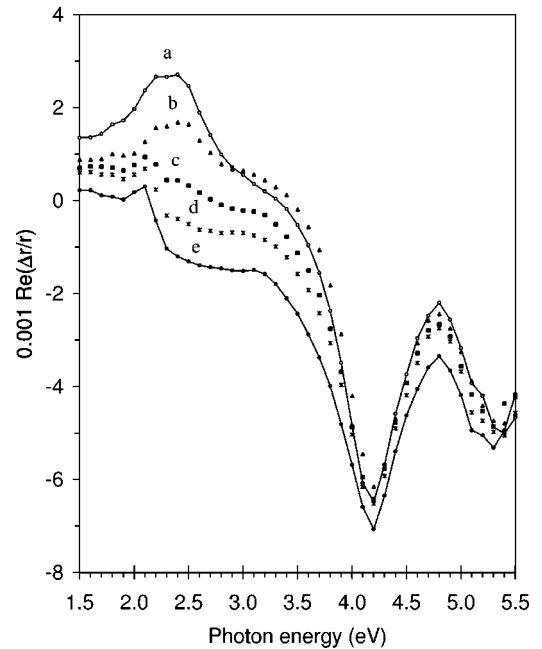


FIG. 1. RA spectra of (a) clean thermally roughened Cu(110) surface, (b-e) increasing coverage with TPA at a substrate temperature of 340 K.

clean Cu(110) surface to a LEED pattern of (10×2) symmetry. While there was an absence of significant intensity in the $(\pm n^{\text{odd}}/10, k^{\text{even}}/2)$ positions, the observation of diffraction spots with both odd and even n values for odd k eliminates the possibility of a centred unit cell. We therefore assign the observed pattern to a $p(10 \times 2)$ structure. With further coverage, the pattern developed into a $p(2 \times 1)$ phase with diffuse half-order spots and a diffuse background of low intensity.

RA spectra taken *in situ* during growth of the saturated adlayer of TPA onto the clean, thermally roughened Cu(110) surface are shown in Figs. 1(a)–1(e). The RA spectrum of the clean, thermally roughened Cu(110) surface shown in Fig. 1(a) is in agreement with previous work.⁹ The absence in Fig. 1(a) of the intense RA peak observed at 2.1 eV for the clean nonroughened surface^{7–9} has been attributed to the depopulation of the occupied surface electronic state at the \bar{Y} point of the surface Brillouin zone.⁹ The shoulder observed at 2.2 eV in Fig. 1(a), a residual structure observable upon the quenching of transitions involving the surface state at \bar{Y} , has been assigned¹² to the surface local-field effect¹³ and the large response at 4.2 eV has been attributed to the anisotropic step morphology⁹ of the thermally roughened surface. Significant changes in the RA profile over the region 1.5 to 4.0 eV occurred upon dosing with TPA [Figs. 1(a)–1(e)]. With increasing coverage the shoulder at ~ 2 eV that is a characteristic feature of the clean roughened surface [Fig. 1(a)] was reduced to nearly zero anisotropy [Fig. 1(c)] and with further coverage developed into a sharp edge structure centered at 2.2 eV [Fig. 1(e)] at the completion of the first molecular layer.

Changes in the RA response at 4.2 eV were also observed. A small decrease in intensity at 4.2 eV occurred for very low

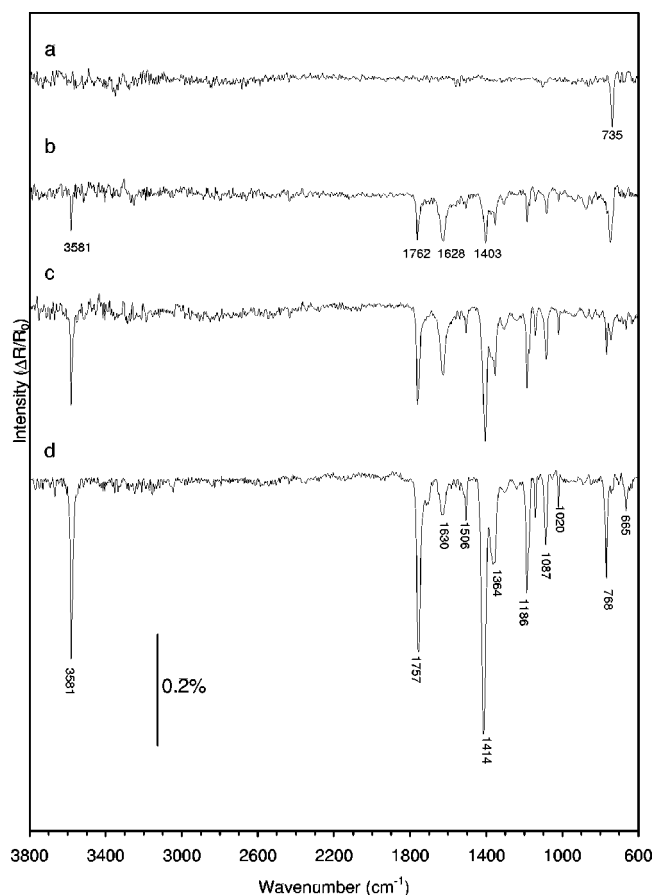


FIG. 2. RAIRS data for increasing coverage of TPA on Cu(110) up to surface saturation.

coverage [Fig. 1(b)], however, the intensity recovered with further coverage and increased negatively to beyond that of the clean surface [Fig. 1(e)]. The RA spectrum of Fig. 1(e) resembled the RA spectrum measured from the monocarboxylic acid, 3-thiophene carboxylic acid (3TC) on Cu(110)⁷—particularly in the region 1.5 to 3.5 eV. The behavior of the intensity of the RAS signal at 4.2 eV as a function of TPA coverage was similar to that observed for 3TC.⁷ The RA response at ~ 4 eV is thought to be sensitive to the Cu-carboxylate bond and a negative-going increase in intensity observed for 3TC/Cu(110) relative to clean Cu(110) was attributed to upright carboxylate species bonding along the Cu $[1\bar{1}0]$ rows.⁷

RAIR spectra taken during dosing the Cu(110) surface with TPA up to a coverage of the first saturated adlayer are plotted in Fig. 2 and the major absorptions are summarized in Table I together with their vibrational assignments. These assignments have been made with reference to previous related work including infrared absorption studies of aqueous bi-terephthalate (TPA²⁻),¹⁴ solid TPA,¹⁵ and the benzoate/Cu(110) system.^{2,16}

The first absorption peak to develop upon dosing the Cu(110) surface with TPA was located at 735 cm^{-1} [Fig. 2(a)]. To assign this band, we note that bands at 739 and 740 cm^{-1} have been observed for TPA²⁻ and for benzoate/Cu(110), respectively. The former absorption was assigned to

a vibration out of the plane of the molecule (out-of-plane) of the carboxylate (OCO) group¹⁴ and the latter absorption was assigned to an out-of-plane $\gamma(\text{CH})$ mode.¹⁶ The peak observed in Fig. 2(a) may then be attributed to two contributions, however, the discussion that follows is consistent with either or both of these assignments of this band since they are both out-of-plane vibrational modes. Considering the dipole selection rule, the observation of the out-of-plane vibration at 735 cm^{-1} means that there must be a significant component of the dipole moment of this vibration that is perpendicular to the surface plane. This condition indicates that this species must be oriented parallel to the surface, that is, lying flat on the surface and this deduction is supported by the absence of any other peaks—in particular the $\nu(\text{C}=\text{O})$ and $\nu_s(\text{OCO})$ stretches—in Fig. 2(a). With increasing coverage the band at 735 cm^{-1} decreased significantly in intensity leaving only a very small, broad absorption [Fig. 2(d)], suggesting reorientation of the adsorbed species towards the surface normal.

The single peak at 735 cm^{-1} dominated the spectrum for several minutes before additional adsorption peaks were first observed [Fig. 2(b)] some of which were identified with absorptions characteristic of the carboxylate functionality (Table I). It is known that monocarboxylic acids deprotonate readily upon adsorption on Cu(110) with the carboxylate group providing a strong bonding interaction with the Cu(110) surface.¹⁻⁴ The band observed at 1403 cm^{-1} in Fig. 2(b) resembles that at 1404 cm^{-1} for TPA adsorbed on an evaporated silver film and assigned to an in-plane carboxylate symmetric stretching mode $\nu_s(\text{OCO})$ (Ref. 14) confirming deprotonation of the TPA molecule upon adsorption. With increasing coverage this band was observed to grow in intensity [Figs. 2(b)–2(d)] indicating the reorientation of the carboxylate group from flat-lying to upright. A broad peak at $\sim 1628\text{ cm}^{-1}$ in Figs. 2(b)–2(d), assigned to the asymmetric $\nu_{as}(\text{OCO})$ mode,¹⁵ exhibited a relatively large intensity at low coverage [Figs. 2(b)–2(c)] indicating the presence of asymmetrically bound carboxylate groups oriented out of the surface plane and tilted so that one oxygen atom of the carboxylate is nearer to the Cu surface than the other. The intensity of this band decreased rapidly with increasing the coverage to surface saturation [Figs. 2(c)–2(d) and Fig. 3(a)] implying the adsorbate adopts an upright, symmetrically bound orientation upon surface saturation. Further evidence for the reorientation of the adsorbate from flat-lying to upright with increasing coverage is the observation in Fig. 2(b) of the $\nu(\text{C}=\text{O})$ stretch at 1762 cm^{-1} and an equally strong absorption at 3581 cm^{-1} that is generated by the $\nu(\text{O}-\text{H})$ stretch. These peaks increase in intensity in Figs. 2(c) and 2(d). Both these bands would be expected to be observed for the COOH functionality and indicate the presence of intact acid groups oriented out of the surface plane and towards the normal to the Cu surface. Figures 2(b)–2(d) show the presence of both acid and carboxylate groups implying there is either a coexistence of diacid molecules and dicarboxylate molecules at the surface, or that molecules at the surface exist as a monocarboxylate species retaining the acid functionality at one end. To determine whether dicarboxylate molecules are present at the surface we note that the RAIRS

TABLE I. RAIRS data for TPA deposited onto Cu(110) at 300 K and comparison with solid TPA and aqueous TPA²⁻.

Saturation [Fig. 2(d)]	Wave number cm ⁻¹		Assignment ^a
	Multilayer [Fig. 3(c)]	TPA (s) (Ref. 15) [TPA ²⁻ (aq)] (Ref. 14)	
665			$\delta(\text{OCO})$
735	736	(739)	$\gamma(\text{OCO})^b$ or $\gamma(\text{CH})^b$
768			
	883	850	(C-H) ^b
	951	944	(C-H) ^b
1020	1020	(1015) 1019	$\beta(\text{C-H})$
1087	1087		carboxylate-ring
1142	1142	1136	carboxylate-ring
1174	1174	1168	$\beta(\text{C-H})$
1186	1186		$\beta(\text{C-H})$
1290	1291	1289	$\nu(\text{C-O})$
1364	1370		$\nu^{acid}(\text{C-O})$
1414	1421	(1378)	$\nu_s(\text{OCO})$
1506	1506	(1504) 1509	$\nu(\text{C-C})$ ring
1630	1617	(1562) 1630	$\nu_{as}(\text{OCO})$
	1706		$\nu(\text{C=O})$
1757	1741		$\nu(\text{C=O})$
3581	3515		$\nu(\text{O-H})$

^aAssignments made with reference to Refs. 2,14–16.^bOut-of-plane vibrations.

data of Table I show that the symmetric $\nu_s(\text{OCO})$ and asymmetric $\nu_{as}(\text{OCO})$ absorptions for TPA deposited onto Cu(110) are at significantly different wave numbers from those of the TPA²⁻ dicarboxylate values observed in solution. Indeed, no peaks were observed at the wave numbers expected for the $\nu(\text{OCO})$ modes of the bi-terephthalate species. These observations indicate that the carboxylate group observed in the RAIRS data is chemically bound to the Cu(110) surface. The observation of only one narrow component at each of the $\nu(\text{OCO})$ wave numbers [Fig. 2(d)] indicates that the bound carboxylate is the only such species at the interface. The absence of vibrational modes corresponding to an unbound carboxylate group permits the rejection of the presence of dicarboxylate molecules at the surface. We conclude that we have an upright monoterephthalate species adsorbed at the surface.

A $p(2 \times 1)$ LEED pattern was observed from the surface corresponding to the RAIRS spectrum of Fig. 2(d). Considering the bonding geometry and upright orientation of the terephthalate molecule as deduced from the RAIRS data, the observation of $p(2 \times 1)$ symmetry suggests the deposition of a complete layer of upright adsorbates with surface saturation occurring when each terephthalate molecule occupies two Cu atoms.¹

The completion of the first layer in the RAIR spectrum of Fig. 2(d) is confirmed by the occurrence here of the maximum intensities of the $\nu(\text{C=O})$ and $\nu(\text{O-H})$ peaks and by the sharpness of both of these bands together with the intensity and sharpness of the $\nu_s(\text{OCO})$ band. The majority of peaks listed in Table I for surface saturation result from vi-

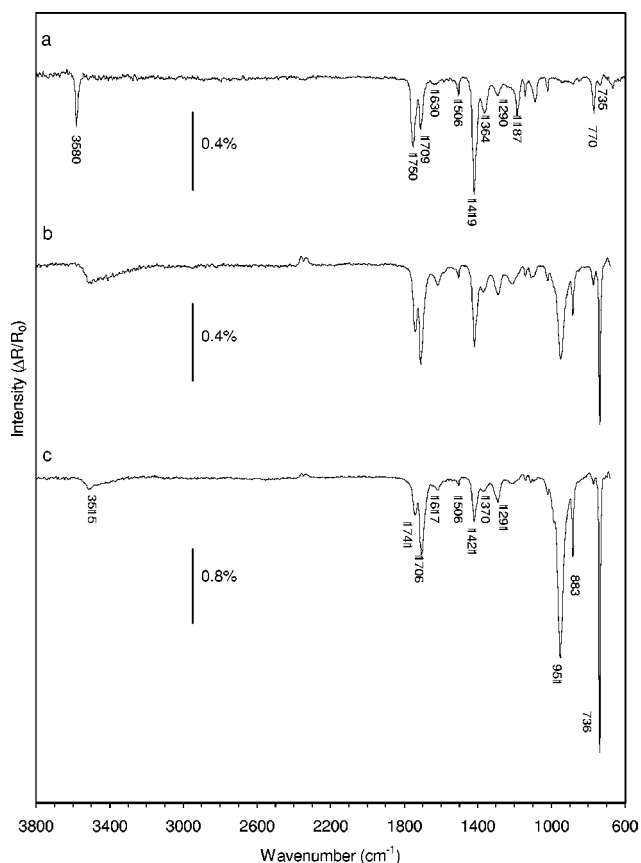


FIG. 3. RAIRS data of multilayer growth of TPA on Cu(110).

brations in the plane of the molecule and are observable in RAIR spectra for an upright molecular geometry. At this coverage the RAIRS and LEED data show that the carboxylate functionality is upright and aligned along the close-packed copper $[1\bar{1}0]$ rows. The data are consistent with the view of the short-bridge bonding arrangement with O atoms located on top of Cu atoms.¹⁻⁴

A characteristic signature of the occurrence of hydrogen bonding interactions involving the acid group is the lowering of the $\nu(\text{O-H})$ and $\nu(\text{C=O})$ stretches and increasing the $\nu(\text{C-O})$ vibrational frequencies as a consequence of the lengthening and weakening of these covalent bonds when involved in hydrogen bonding. In Fig. 2(d), the intensity, sharpness, and relatively high wave number of the $\nu(\text{O-H})$ band at 3581 cm^{-1} —a wave number identical to that of acetic acid vapor¹⁷—indicate an (OH) species that is not under significant influence of hydrogen bonding and oriented perpendicular to the Cu(110) surface. The intensity and wave number 1757 cm^{-1} of the $\nu(\text{C=O})$ stretch also indicates a lack of significant hydrogen bonding between acid groups in the first adlayer.

The RAIRS data show little influence of hydrogen bonding on the acid group in the $p(2\times 1)$ structure—a surprising result considering the close proximity of nearest neighbors in this structure. However, with an upright geometry and with the (O-H) group perpendicular to the surface, the influence of hydrogen bonding interactions on absorption modes that are observable with RAIRS will be limited. Hydrogen bonding interactions have been found to be crucial to the formation of ordered superstructures of tartaric acid on Cu(110),¹⁸ however, this molecule has additional OH groups which participate in intermolecular interactions. At this coverage, we can exclude the possibility of significant interactions between the acid group and additional TPA molecules due to the absence of change in the $\nu(\text{O-H})$ and $\nu(\text{C=O})$ absorption bands as will be seen later for further coverage. In summary, the deposition of TPA on Cu(110) leads to a densely-packed $p(2\times 1)$ ordered saturated surface of upright monoterephthalate species terminated with acid groups at the vacuum interface.

B. Multilayer growth

The surface of the saturated adlayer of upright terephthalate molecules is terminated by (C=O) and (O-H) groups and it is these bonds that will be most sensitive to further adsorption. RAIR spectra for TPA coverage beyond the saturated surface adlayer are shown in Fig. 3 and suggest multilayer formation. With increasing coverage the $\nu(\text{C=O})$ band at 1757 cm^{-1} of the monolayer in Fig. 2(d) splits into two distinct peaks at 1709 and 1750 cm^{-1} [Fig. 3(a)]. This observation indicates that there are now two discrete environments of the (C=O) group at this coverage. It is likely that the two environments are a result of the absence, and influence of, hydrogen bonding on the carboxyl group. There appears to be a lack of published IR data of TPA in this frequency region, however, in aqueous acetic acid (CH_3COOH) where hydrogen bonding is prevalent the $\nu(\text{C=O})$ stretch is found¹⁹ at 1709 cm^{-1} . The peak at 1706 cm^{-1} for TPA on Cu(110) thus reflects the presence of

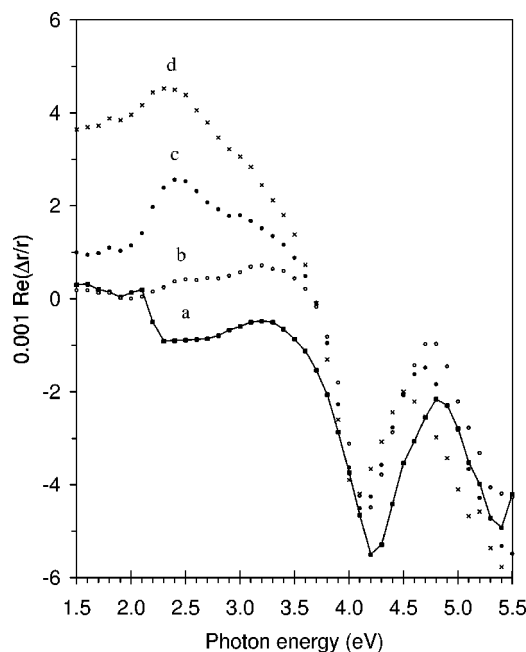


FIG. 4. RA spectra of the thermal desorption of TPA with spectra at temperatures of (a) 300 K, (c) ~ 580 K, and (d) ~ 620 K.

significant intermolecular hydrogen bonding—a view also supported by the increase in intensity of this peak with the build-up of the multilayer [Figs. 3(a)–3(c)]. The intensity of the peak at 1750 cm^{-1} remains approximately constant with increasing coverage [Figs. 3(a)–3(c)] and the similar wave number to that of the single layer result [Fig. 2(d)] indicates that this signal originates from the single layer and is unchanged with further coverage. Thus the two signals from the (C=O) group originate from the first layer, and from the second and subsequent layers. LEED of the multilayer showed no ordered adsorbate structure, only a poor (1×1) pattern originating from the substrate. Small differences in the 2.5 to 3.5 eV region between the RA spectra of the ordered first layer [Fig. 1(e)] and the multilayer [Fig. 4(a)] indicate optical anisotropy and hence a degree of at least short-range order in the multilayer.

The absorption at 3515 cm^{-1} in Figs. 3(b), 3(c) is assignable to the $\nu(\text{O-H})$ vibration, however, in contrast to the sharp $\nu(\text{O-H})$ peak in Fig. 3(a) the reduced wave number and broadness of the peak in Fig. 3(c) are features that are indicative of the presence of significant intermolecular hydrogen bonding between neighboring TPA molecules in the multilayer. The $\nu(\text{O-H})$ stretching frequency is dependent upon the degree of hydrogen bonding, which increases the (O-H) bond distance and hence lowers its vibrational frequency. In the same way, hydrogen bonding is responsible for the reduced frequency of the $\nu(\text{C=O})$ group and the raising of the $\nu(\text{C-O})$ frequency (Table I). The presence of $\nu(\text{C=O})$ and $\nu(\text{O-H})$ vibrations in Fig. 3 together with the absence of any change observed in the bands associated with the carboxylate group indicates that (i) the upright molecules in the first layer retain the acid group upon interaction with adsorbing TPA molecules and (ii) adsorption in this growth

regime occurs with the adsorbate in the acid form, as TPA, with no deprotonation into isolated carboxylate species upon adsorption.

The observation in the RAIRS data of Fig. 3 of a continued signal from a free $\nu(\text{C}=\text{O})$ bond from the saturated surface layer and the clear change in the $\nu(\text{O}-\text{H})$ signal shows that the interlayer hydrogen-bonding interaction is limited to occurring between the acid group of the adsorbing TPA and the (O-H) group of the upright mono-terephthalate species at the Cu surface.

A very strong absorption was observed in Figs. 3(b)–3(c) at 736 cm^{-1} due to the out-of-plane mode [either $\gamma(\text{OCO})$ or $\gamma(\text{CH})$] as found in the case of very low coverage [Fig. 2(a)]. The considerable increase in intensity of this band with increasing coverage combined with the clear indications of hydrogen bonding involving the acid group indicates that the growth of the film proceeds with the deposition of hydrogen bonded molecules broadly aligned parallel to the surface. This view would favor the assignment of the 736 cm^{-1} peak to the $\gamma(\text{CH})$ mode since there are no new carboxylate groups present in this deposition regime. The peak observed at 883 cm^{-1} [Fig. 3(c)] is assigned to out-of-plane ring vibrations for the bisubstituted benzene ring^{14,15} and this vibration is another indication of a flat-lying molecular configuration. Thus the RAIRS data of Fig. 3 indicate the presence of a single layer of upright monoterephthalate molecules at the Cu interface and subsequent flat-lying hydrogen-bonded TPA layers. The strong RAIRS peaks that are observed exclusively for the multilayer cannot be assigned to any in-plane modes² and so these absorptions do not result from an upright orientation of molecules. The peak at $\sim 770\text{ cm}^{-1}$ was found to increase in intensity with the build-up of the first layer (Fig. 2) and subsequently decreased in the multilayer growth regime (Fig. 3) suggesting that this band results from an upright vibrational mode of bonds associated with the acid group.

In contrast to the upright orientation found in the saturated surface adlayer where the influence of any hydrogen bonding on the RAIRS data was minimal, hydrogen bonding interactions present in the multilayer, as determined from the RAIRS data, will be enhanced significantly if the adsorbed molecules are in a flat-lying geometry with hydrogen bonds being readily formed in this plane between neighboring molecules. Beyond the first layer, the influence of the Cu surface appears to be significantly reduced and adsorbate-adsorbate interactions now dominate the growth. The RAIRS data eliminate the possibility of layers of upright hydrogen-bonded dimers stacked on top of each other since terephthalate dimers oriented vertically at the surface would be expected to generate a broad absorption region¹⁵ with peaks between $2500\text{--}3000\text{ cm}^{-1}$ and no such absorptions were observed in Fig. 3.

C. Desorption

Thermal desorption of the TPA-dosed Cu(110) surface was studied *in situ* using RAS and TPD. The RAS results are shown in Figs. 4(a)–4(d). RAS experiments involving increasing exposure of the Cu(110) crystal to TPA combined

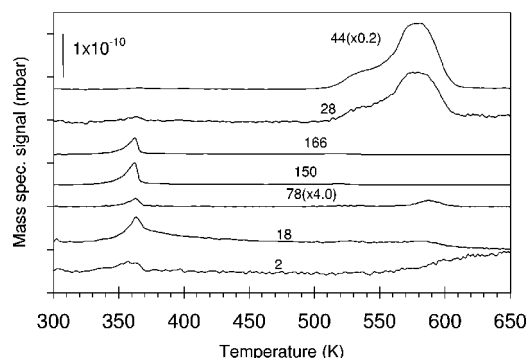


FIG. 5. TPD results of the TPA-dosed Cu(110) surface.

with LEED and RAIRS results indicate that the spectrum of Fig. 4(a) corresponds to multilayer coverage. Desorption was induced by heating the specimen and monitoring with RAS. During the desorption procedure the RA profile of the TPA-dosed surface lost its distinctive edge structure [Fig. 4(a)] and proceeded to pass through zero anisotropy in the region 1.5 to 3.5 eV [Fig. 4(b)] and subsequently to recover the profile characteristic of the clean roughened surface at elevated temperature [Fig. 4(c)]. The position of the $\sim 4\text{ eV}$ RA minimum was found to shift to lower photon energy by 0.1 eV during the desorption procedure [Figs. 4(a)–4(d)] and this change can be attributed purely to the increase in temperature of the specimen.⁹ Upon cooling of the surface to room temperature following the thermal desorption procedure, the RA profile was similar to that of the clean Cu(110) surface before deposition [Fig. 1(a)]. However, some difference in the RA profile below 3 eV was observed following treatment with TPA in the form of a lower intensity in this region and a shift to higher photon energy of the shoulder feature by $\sim 0.2\text{ eV}$. The observation of a similar intensity of the feature at 4.2 eV combined with the known sensitivity of the RA response around 4 eV to surface morphology⁹ indicates a surface morphology following desorption that is similar to the original clean surface structure.

The TPD results shown in Fig. 5 show the multilayer to be stable up to around a temperature of 350 K. Above this temperature, the increase in the mass spectrometer signal at masses 18 (H_2O), 78 (benzene), 150, and 166 (TPA) indicate TPA desorbs intact from the multilayer. The maxima of these desorption peaks all coincide at 360 K. The lower mass fragments observed are cracking fragments by the mass spectrometer of the parent ion. This result is consistent with an experiment where we heated the multilayer to 370 K and observed a RAIRS spectrum very similar to the monolayer spectrum [Fig. 2(d)]. This observation supports the view of an interfacial layer of bound, vertically aligned molecules with subsequent layers of parallel orientation that are relatively weakly adsorbed through hydrogen bonding. The evolution of CO_2 and CO began at 510 K and peaked at a temperature of 580 K with a relatively large amount of CO_2 desorbing (Fig. 5). The TPD results indicate that the molecules in the multilayer desorb intact at $\sim 360\text{ K}$. However, the terephthalate molecules in the first layer decompose prior to desorption. The evolution of predominantly CO_2 is consistent with the thermal decomposition proceeding via a de-

carboxylation mechanism, as previously observed for benzoate on Cu(110). In regard to the RAS desorption data, the RA profile of Fig. 4(b) corresponds to the surface following the desorption of large mass fragments (≥ 360 K) and Fig. 4(c) is in the region of CO₂ and CO evolution (500–600 K). The spectrum of Fig. 4(d) corresponds to the clean surface regime following desorption at ~ 620 K.

IV. SUMMARY

In common with a number of previously studied monocarboxylic acids, TPA adsorbs to the Cu(110) surface as a monocarboxylate following deprotonation of an acid group. The flat-lying geometry of the terephthalate species at low coverage allows both carboxylate and phenyl ring interactions with the Cu surface. The perpendicular orientation observed at higher coverage with the loss of the π interaction between the ring and Cu surface is easily compensated for by the adsorption energy of additional carboxylates, and by increasing intermolecular interactions between upright molecules with increasing coverage. Carboxylate bonding along the $[1\bar{1}0]$ direction implies the plane of the aromatic ring of the monoterphthalate species is also aligned along this direction. For subsaturation coverages steric repulsion between the terephthalate molecular tails can be accommodated. The $p(10\times 2)$ periodicity observed is presumably determined by the detailed adsorbate-adsorbate interactions, as discussed by Frederick *et al.*²⁰ who observed an ordered structure for the monocarboxylate 3TC/Cu(110) system. In that case a $c(4\times 8)$ adlayer structure of upright molecules developed into a densely packed $p(2\times 1)$ phase upon surface saturation²⁰ by the adsorption of additional molecules into the spaces between existing adsorbates in the $c(4\times 8)$ structure. For the system TPA/Cu(110) the $p(10\times 2)$ structure with an appropriate population, both number and location, of molecules within the unit cell can also act as a template for the formation of the $p(2\times 1)$ phase. The $p(10\times 2)$ unit cell is determined from the LEED results, however, the exact number and location of molecules within the unit cell requires STM studies. While we have no direct experimental evidence, it is clear from steric considerations that (2×1) periodicity for the TPA/Cu(110) adsorption system requires the rotation of the terephthalate ring away from the $[1\bar{1}0]$ direction, as previously observed by STM for the 3TC/Cu(110) system.²⁰

While RAS is proving to be of great value in the study of

surfaces, particularly in nonvacuum environments,²¹ an established methodology for detailed spectral analysis has not yet been achieved. The present study, in combination with previous work on a related adsorption system,⁷ affords the opportunity to correlate RA spectra with the chemical and structural information provided by the corresponding RAIRS and LEED measurements. A clear similarity between Fig. 1(e) and the RA spectrum of the Cu(110) surface saturated with upright 3TC adsorbates⁷ suggests that these spectra are signatures of the Cu-carboxylate bond, which is identical in both cases. Further similarity with the previous 3TC study is the evolution of the RA response at 3.3 and 4.2 eV during deposition. As determined previously,⁷ we associate these changes with the reorientation of the monocarboxylate adsorbates from flat-lying to upright geometry since *ab initio* electronic structure calculations⁷ indicate Cu-carboxylate bonds contribute to RA spectra at a photon energy of ~ 4 eV.

The coverage-dependent behavior of the molecular orientation and the saturation of the Cu(110) surface with an ordered structure by the diacid TPA is clearly advantageous for the creation of an acid-functionalized surface. The data show that RAS is sensitive to the formation of the carboxylate-Cu bond and RAIRS can monitor the completion of the layer. Both techniques are sensitive to molecular orientation at surfaces.

V. CONCLUSION

The adsorption of TPA onto Cu(110) has been studied using surface-sensitive optical probes. The molecule adsorbs as a monoterphthalate species, bonding via the carboxylate group, to form a $p(2\times 1)$ layer of upright molecules at surface saturation—here we have created upright acid groups at the vacuum interface to form a chemically functionalized surface. Further deposition of TPA results in multilayer growth consisting of broadly flat lying, hydrogen-bonded molecules. By comparison with previous work, we find that the Cu-carboxylate bond gives rise to a characteristic RAS signature that is sensitive to reorientation from flat lying to upright bonding geometry.

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