A momentum space view of the surface chemical bond†

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Well-ordered and oriented monolayers of conjugated organic molecules can offer new perspectives on surface bonding. We will demonstrate the importance of the momentum distribution, or symmetry, of the adsorbate molecules’ π orbitals in relation to the states available for hybridization at the metal surface. Here, the electronic band structure of the first monolayer of sexiphenyl on Cu(110) has been examined in detail with angle-resolved ultraviolet photoemission spectroscopy over a large momentum range and will be compared to measurements of a multilayer thin film and to density functional calculations. In the monolayer, the one-dimensional intramolecular band structure can still be recognized, allowing an accurate determination of orbital modification upon bonding and the relative energetic positions of the electronic levels. It is seen that the character of the molecular π orbitals is largely maintained despite strong mixing between Cu and molecular states and that the lowest unoccupied molecular orbital (LUMO) is filled by hybridization with Cu s,p states rather than through a charge transfer process. It is also shown that the momentum distribution of the substrate states involved and the periodicity of the molecular overlayer play a large role in the final E(k) distribution of the hybrid states. The distinct momentum distribution of the LUMO, interacting with the Cu substrate s,p valence bands around the gap in the surface projection of the bulk band structure, make this system a particularly illustrative example of momentum resolved hybridization. This system demonstrates that, for hybridization to occur, not only do states require overlap in energy and space, but also in momentum.

1. Introduction

The interaction of π-conjugated organic molecules with a metallic surface is important for an understanding of the nature of the bond of partially delocalized and quasi-periodic π states with fully delocalized metallic bands. In this report, the bonding of sexiphenyl (6P), a device relevant, 1,2 π-conjugated molecule, with the Cu(110) surface has been studied using angle-resolved valence band photoemission spectroscopy (ARPES). ARPES allows energy and momentum resolved observation of the π orbitals involved in the bond, revealing not only their electronic level alignment, critical for device function, but also a dependence of the momentum structure of the bond on the geometric details of the first layer of molecules. Often neglected, the importance of momentum overlap for the formation of hybrid states in surface bonding is emphasized by this dependence.

Much of our perspective on bonding at metal surfaces derives from atoms and small molecules. In the standard view of chemisorption 3,4 adsorbate energy levels can interact with both highly delocalized s,p bands and rather localized d bands. In the interaction with the s,p bands, the adsorbate levels broaden in energy and the frontier orbitals are pulled closer together. These effects lead to a reduction of the gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), with a possible partial filling or emptying of these orbitals if they cross the Fermi level. A further modification of splitting into bonding and antibonding combinations occurs for interactions with the more localized d states. This model has been applied successfully to adsorbed atoms and small molecules (e.g. ref. 5), but, considering that the frontier orbitals of molecules with n monomer units will be ≈1/n sharper in k-space than their monomer units, there has been little evidence that it can be generally applied to the bonding of extended π systems to transition metals.

A number of recent studies have looked at the organic–inorganic interface using photoemission 6–15 and scanning tunneling microscopy (STM) 16,17 to explore the filling and dispersion of molecule-metal derived interface states and
resonances. In addition to dispersive molecule-induced states, modifications of metal surface-state occupation and curvature have been observed and used to estimate bond strength.\(^{14,15}\)

Also the amount of filling of the LUMO has been seen to vary with the distance of the aromatic core from the metallic surface.\(^{10,11}\) The question of clearly experimentally identifying the particular molecular states and the extent to which they are modified on bonding has been addressed by resonant photoemission\(^6\) and by utilizing photoemission selection rules.\(^7\)

However, neither the role of the full momentum structure (\(k\)-distribution) of the molecular orbitals (a result of the quasi-periodicity within the adsorbate) nor the effects of the periodicity of the molecular overlayer on the hybridization are generally considered (with a few exceptions, e.g. surface state folding by molecular periodicity\(^8\)).

Photoemission selection rules exploiting symmetry-dependent photoemission cross sections have been used extensively in the past to identify particular states. Applying these rules to small molecules on surfaces has provided evidence with regard to which electronic states are involved in bonding with the surface. These rules entail identifying particular electron emission nodal planes for particular high symmetry orientations of the photon polarization. As we have shown in previous publications\(^18,19\) this simple picture can be refined for molecules with extended structures such as the larger conjugated organic molecules. For the \(\pi\) orbital systems of these molecules, the Fourier transform of the electron distribution of the molecular orbital predicts both the momentum distribution of the orbital and, under certain conditions (cf. ref. 19), the angle-dependent photoelectron intensity distribution of the emitting orbital. A combination of the angle-dependent photoemission intensity and the Fourier transform can be used both to identify the orbitals observed in photoemission spectroscopy and to determine the extent to which the orbital character is maintained or modified upon bonding. Thereby, we have shown that the molecular character is largely maintained in the HOMO and partially filled LUMO of the 6P molecule on the Cu(110) surface.\(^9\) The electron densities derived there are very similar to those of the isolated molecule and might suggest a simple charge transfer to the LUMO. However, deviations from the momentum distribution of an unperturbed molecule can also be observed in the photoemission data which, as we will show here, clearly demonstrate that the filling of the LUMO occurs through a hybridization with metal states.

In this report, we concentrate on these deviations through a detailed examination of the electronic band structure of sexiphenyl on Cu(110) from submonolayer to full monolayer (ML) coverages. In the complete ML, the one-dimensional intramolecular band structure, \(i.e\). the momentum distributions of the orbitals of the individual molecules, is still apparent and allows an accurate identification of the molecular orbital emissions despite the superposition of molecular orbital and strong substrate \(d\) band emission features. A comparison of experimental data to DFT calculations clarifies electronic, and optical properties of organic semiconductors and their interfaces investigated by \(ab\) initio electronic structure methods.

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substrate-induced energetic changes throughout the π band. The nature of the molecule-substrate interaction and the resulting interface states is revealed through a study of the LUMO momentum distribution using 2D constant energy photoemission maps over multiple Brillouin zones in an energy range near the Fermi level ($E_F$). The hybridization of previously unoccupied molecular states with Cu states is proven and shown to depend both on the $E(k)$ distribution of occupied Cu bulk states and on the periodicity of the molecular overlayer.

We begin with the development of geometric structure and photoemission features near $E_F$ with coverage up to the dense 6P ML. Then the photoemission characteristics of the valence band over a wide energy and momentum range are shown for the dense ML to identify changes in deeper-lying orbitals. Next the momentum structure of the partially filled LUMO near $E_F$ is shown in detail and related to the geometric structure of the dense ML. Finally, the significance of the organic ML periodicity for the hybridization between metal and molecular states is discussed.

2. Experimental and computational details

Sexpiphenyl, 6P ($C_{36}H_{36}$) from Tokyo Chemical Industry Co., Ltd. was evaporated in ultra-high vacuum (UHV) from a thoroughly degassed evaporator. The Cu(110) single crystal surface was cleaned by repeated cycles of Ar$^+$-ion sputtering and annealing at 800 K. One ML of 6P refers to the coverage which gave the most densely packed single layer structure and is equivalent to a thickness of 3 Å, assuming the bulk structure. Coverages were determined using a quartz microbalance.

The ARUPS spectra were recorded using a noble gas discharge lamp (unpolarized Helium I radiation, $h\nu = 21.2$ eV) and a VG ADES 400 electron energy analyzer mounted on a single axis goniometer, allowing measurement in the specular plane with an angular resolution of 1°. Low energy electron diffraction measurements were made with an Omicron microchannel plate LEED system in the same UHV chamber. A toroidal electron analyzer was used for the photoemission intensity plots and constant energy maps. The sample holder is on a double goniometer, which allows full azimuthal rotation and rotation in the specular plane. The system was attached to the TGM-4 beamline at the synchrotron light facility BESSY II. The relation between the photoelectron emission angle $\theta$ and the component of the electron wave vector parallel to the surface ($k_x$) is calculated using $k_x = k_{x,F} = \sqrt{2mE_{km}/h^2}$ $\sin \theta$, where $E_{km}$ is the kinetic energy of the photoelectron. Both UHV systems have a base pressure of $1 \times 10^{-10}$ mbar in the measurement chambers.

All calculations are performed within the framework of density functional theory (DFT), exchange and correlation effects are treated with the generalized gradient approximation (GGA). Computations for the 6P monolayer adsorbed on the Cu(110) surface are done with the SIESTA code. We model the surface using 5 Cu-layers in a repeated slab approach and perform a geometry relaxation allowing the two topmost Cu layers as well as all structural degrees of freedom of the 6P molecule to be relaxed. This led to a molecule–surface distance of 2.8 Å. However, it is known that GGA functionals overestimate organic molecule–metal distances due to their lack of van der Waals interactions. To overcome this computational deficiency, we reduced the molecule distance to 2.4 Å and relaxed all other structural degrees of freedom. A value of 2.4 Å is supported by X-ray standing wave (XSW) data for other large organic molecules and data for small molecules such as thiophene on Cu(111). We note, however, that within the range of distances 2.4–2.8 Å, results for the interface dipole magnitudes and density of states are quite similar, and the observed distance dependence would not alter our conclusions. Our approach to project the density of states of the combined 6P/Cu(110) system onto individual molecular orbitals of the isolated 6P system is described elsewhere.

Calculations of the photoemission intensity are performed for an isolated 6P molecule. The ABINIT software package using the norm-conserving Troullier–Martins pseudo potentials with a plane wave cut-off of 30 Ryd. Calculations are performed within a super cell approach with a box size of $160 \times 30 \times 30$ Bohr$^3$ and Γ-point sampling of the Brillouin zone. Details about our approach to simulate photoemission intensities have been published elsewhere.

3. Results

3.1 Electronic and geometric structure development

A series of AREPS spectra were recorded for clean Cu(110), 0.5 ML, 0.75 ML and 1 ML in the Cu $\Gamma$–Y direction perpendicular to the molecular axes. These angular series are shown in Fig. 1 along with the corresponding low energy electron diffraction (LEED) structure obtained at each coverage value. For clean Cu(110) in (a), the surface state is clearly observed centered around the Y point ($\theta = 23^\circ, k_y = 0.82$ Å$^{-1}$) and dispersing roughly 0.3 eV below $E_F$ ($\sim 0$ eV). The s,p band is also visible between binding energies $E_B = -0.5$ and $-1.0$ eV at higher angles.

The LEED of a 0.5 ML coverage on Cu(110) in Fig. 1b indicates that the incomplete ML is poorly ordered at room temperature. Although sharp diffraction spots are absent, a regular spacing can be inferred from the diffuse intensities observed to either side of the 00 reflex and the horizontal stripes at regular intervals. These diffuse intensities suggest a spacing of $\approx 10.8$ Å, equivalent to three protruding Cu rows, and the horizontal stripes a spacing of $\approx 28$ Å, equivalent to the length of a molecule. Low temperature STM measurements (see ref. 32) suggest that the molecules repel each other and form a rather dilute layer with a minimum distance of three Cu rows between the molecules in the Cu [001] azimuthal direction. At the 0.5 ML coverage, the AREPS series becomes somewhat featureless as both the surface state and the s,p bands are suppressed almost completely. What remains is a depression in the photoemission intensity where the surface state had previously existed and an increase in the photoemission intensity around $E_F$ at higher emission angles. The depression can be ascribed to the gap in the bulk s,p bands projected onto the two-dimensional Brillouin zone of the surface that formerly hosted the surface state. The increase in photoemission intensity at higher angular ($k_x$) values in comparison to the
clean substrate can be ascribed to the occupation of the LUMO of the oriented, but sparsely distributed and weakly ordered 6P molecules.

As the coverage is increased to 0.75 ML, the LEED pattern of Fig. 1c still shows significant disorder. Stripes are observed spaced at distances characteristic of the lengths of the molecules, as for the 0.5 ML coverage. Significantly, the broad reflexes of the LEED in a plane containing the surface normal and the 6P long axis have a length 1/2 of the Cu reciprocal lattice vector, the solid arrow 1/3.

Fig. 1d. In the AREPS series, the depression in the photoemission intensity at the bulk s,p band projected gap remains. The parabolic feature observed in the broad intensity increase seen near $E_F$ at 0.75 ML has now become fully developed. It should be noted that the photoemission intensity at $E_F$ inside the parabola is still significant and greater than the intensity observed here for the clean Cu surface.

Beyond one ML, the photoemission features from the strongly bound 6P layer are attenuated by a further layer of molecules which shows no photoemission features in this energy range (see ESI†).

3.2 Monolayer structure

On the Cu(110) surface, the most densely packed first layer structure forms at a nominal deposition depth of 3 Å. LEED measurements of this coverage are shown in Fig. 2a. Sharp diffraction spots due to the 6P overlayer reveal a highly commensurate structure with real space vectors $b_1 = 28.3$ Å and $b_2 = 7.2$ Å separated by $\phi = 82.7$°. This results in an epitaxial matrix $M = (11,1;0,2)$ for Cu(110) surface dimensions $a_1 = 2.55$ Å and $a_2 = 3.6$ Å. The completed ML density suggests that the molecules are lying with their phenyl planes flat, or nearly flat, on the Cu(110) surface. A flat adsorption geometry is confirmed both by the photoemission maps (cf. ref. 19) and by near-edge X-ray absorption fine structure measurements (see ESI†). The registry of the molecules in a diffuse ML, as determined by STM, can be found in ref. 32 and is shown in Fig. 2c.

The overlayer Brillouin zone (BZ) determined from this structure is compared to that of the underlying Cu substrate in Fig. 2b. It can be seen that two overlayer BZs fit into the substrate BZ in the $Y_{Cu}$ direction, while 11 fit in the $X_{Cu}$ direction. For the purposes of the following energy- and momentum-resolved photoemission intensity maps, $k_x$ will refer to momentum in the $\Gamma$–X direction and $k_y$ to the $\Gamma$–Y direction, which correspond to real space directions parallel and perpendicular to the long molecular axis, respectively. At the $Y_{Cu}$, the gap in the Cu bulk density of states projected onto the surface BZ is shown as a solid ellipse. The scattering on the 6P overlayer periodicity of the states surrounding this gap are shown as dashed ellipses in Fig. 2b at the positions in which they are visible in the LUMO photoemission signal in Fig. 4d.

3.3 Valence band

Photoemission intensity plots $E(k_x)$ of valence band emission in a plane containing the surface normal and the 6P long axis (the Cu[110] azimuth) are shown in Fig. 3 for (a) clean Cu(110), (b) the dense 6P ML and (c) a 200 Å thick bulk 6P film. To the right of the photoemission plots, DFT calculations of the projected density of states (pDOS) onto the molecular π orbitals and onto Cu d states are shown. In the clean Cu(110) valence band plot in Fig. 3a, emissions from s- and p-state derived bands are dominant from $E_F$ to binding energies $E_b$ around $-2$ eV. From $E_b = -2$ to $-5$ eV, emissions from d bands are the most prominent feature. The pDOS of the d states of the Cu surface layer is shown with and without the 6P overlayer. The 6P overlayer modifies these states slightly, but the general shape is maintained.
The same photoemission region after adsorption of the 6P ML is shown in Fig. 3b. For a comparison to the ML data, a photoemission intensity map from the crystalline 6P film that grows on the ML is presented in Fig. 3c. Note that these crystallites oriented with the (1/0 2/2) plane parallel to the Cu(110) substrate surface have their molecules parallel to those of the underlying ML. In a previous publication,18 we showed that the photoemission behavior of the $\pi$ orbitals in the direction of the long molecular axis is determined by the intramolecular band structure. In particular, each molecular orbital can be observed as a discrete emission centered at a characteristic $E(k)$ value defined by the quasiperiodic structure of the molecule. In the photoemission plot of the bulk film in (c), two sets of six orbitals, each of which can be referred to as six member bands arising from the quasiperiodicity of the six phenyl rings of the molecule, can be clearly identified. One band, marked with the symbol ‘$\times$’, consists of orbitals with a large overlap between member rings and, hence, has a large band spread. This band (HOMO to HOMO-2 and HOMO-9 to -11) will be referred to as the delocalized $\pi$ band. The other band has little interring overlap and appears as a broad stripe of unresolved orbitals from $E_B = -4$ to $-5.5$ eV. It consists of HOMO-3 to -8 and will be referred to as the localized $\pi$ band.

As the molecules of the 6P ML have the same orientation, the molecular emission features (Fig. 3b) can be directly related to those of the crystalline film that grows upon it. The HOMO emission is found at the intersection of the s,p and d bands, at an energy value of $E_B = -1.9$ eV and momentum value of $k_x = 1.3$ Å$^{-1}$, the same momentum value as found for the multilayer 6P film. On close inspection, other orbitals of the delocalized $\pi$ band within the energy region of the complex d band can also be distinguished. Although significantly broadened and less distinct than those of the bulk crystalline 6P film, they can be found near the corresponding multilayer $k_x$ values from the HOMO to the HOMO-11 which lies at $E_B = -5.5$ eV and $k_x = 0.85$ Å$^{-1}$. To aid the reader, the

![Fig. 2](image-url)  
(a) LEED image of 6P ML on Cu(110) at a primary electron beam energy of 30 eV. The reciprocal space unit cell vectors have been drawn. (b) The Brillouin zone boundaries of the 6P overlayer structure are compared to those of the Cu(110) surface. (The scattering on the 6P overlayer periodicity of the states surrounding this gap are shown as dashed ellipses at the positions in which they are visible in the LUMO photoemission signal in Fig. 4d.) (c) The real space structure and coordination, assuming the absorption site observed in ref. 32. The real space vectors are $a_1 = 2.55$ Å, $a_2 = 3.6$ Å, $b_1 = 7.2$ Å and $b_2 = 28.05$ Å, resulting in a c(2 × 22) overlayer structure.

![Fig. 3](image-url)  
On the left, the $E(k_x)$ valence band maps (Cu[110], Γ to X) showing (a) clean Cu(110), (b) Cu(110) with a ML of 6P and (c) a 200 Å thick 6P film. The photon energy is $hv = 35$ eV, and photon incidence angle is $\alpha = 40^\circ$. The intensity grayscale is logarithmic. Black is lowest and white is highest intensity. On the right, the projected density of states from DFT calculations of (a) the d states of the topmost Cu layer with and without the 6P overlayer, (b) the delocalized $\pi$ orbitals of the 6P overlayer with (left) and without (right) the Cu substrate and (c) the delocalized $\pi$ orbitals of the bulk 6P.
The delocalized band has been marked using the symbol '×' with the same \( k \)-values as for the bulk crystalline film. The energy span from the HOMO to HOMO-11 is around 3.9 eV in the ML, which is 1.2 eV greater than that of the bulk film of 2.7 eV observed in Fig. 3c.

On the basis of calculations, the large energy spread of the ML \( \pi \) band will be argued to arise from planarization and interactions with the Cu substrate. To the right of the photoemission plots, the calculated pDOS of the delocalized \( \pi \) band is shown for the 6P overlayer with and without the Cu substrate (Fig. 3b) and for the bulk 6P crystal assuming an inter-ring torsional angle of 20° (Fig. 3c). The freestanding overlayer and bulk calculations have been aligned in energy to the center of mass of the observed \( \pi \) band. The intramolecular \( \pi \) band spread from the HOMO to the HOMO-11 of the bulk calculation is 2.46 eV, while that of the unsupported 6P overlayer is 2.8 eV. Both calculations display almost no intermolecular dispersion of the individual orbitals, as evidenced by the sharp peaks obtained (artificially broadened by 0.1 eV for comparison to experiment). Once the Cu substrate is introduced to the calculation, the \( \pi \) orbitals of the 6P overlayer are drastically modified. They are all broadened in energy and display small energetic splittings. The total delocalized \( \pi \) band width increases to 3.8 eV as a consequence thereof. In contrast to the case of Fig. 3a, emissions in the Cu d band region have changed considerably.

Significantly, new emissions originating from the presence of the 6P ML appear at \( k_x = 1.5 \sim 1 \) and extend from \( E_F \) to over 1 eV below \( E_F \), as seen in Fig. 3b just to the right of the s,p band. This new intensity can be viewed as an extension of the delocalized \( \pi \) band. The \( k_x \) position is that predicted by a FT of the LUMO orbital of a free molecule, identifying this emission as a LUMO-derived state. This identification is supported by the calculations on the right of Fig. 3b where it can be seen that the LUMO (and LUMO +1, +2) are pulled down in energy towards the HOMO. The LUMO, in particular, displays a significant population below 0 eV, indicating a partial filling.

### 3.4 The LUMO in detail

In Fig. 4, an \( E(k_y) \) photoemission plot near \( E_F \) (a) is displayed together with a constant energy photoelectron momentum \((k_x,k_y)\) map (b) for the clean Cu(110) substrate. The same two regions are displayed for the complete 6P ML in (c) and (d), respectively. Note that the \( y \) direction is perpendicular to the molecular axis. The Cu surface and 6P overlayer BZ boundaries are indicated on the images. In Fig. 4e, the Fourier transform (FT) of an isolated molecule LUMO for the same \((k_x,k_y)\) region is shown for comparison. The strongest features of the clean Cu(110) are the s,p band around \( k_x = 0.6 \sim 1 \) and the surface state seen as a parabola in the \( E(k_y) \) representation of (a) or as a ring round the first \( Y_{Cu} \) point in the momentum map in (b). Once the 6P ML has been deposited, the surface state disappears, as also seen in Fig. 1, and the intensity increases between \( k_y = 0.9 \) to 2.7 \( \sim 1 \). A comparison to the FT of the LUMO in Fig. 4e reveals that this increase is due to the angular dependent photoemission intensity of the LUMO state. Both the increase in intensity and absence of the Shockley surface state allow the gap in the bulk projected density of states to be clearly observed at the \( Y_{Cu} \) points in both the \((k_x,k_y)\) and the \( E(k_y) \) representations. A roughly parabolic feature with a similar form to the gap can be seen to appear at the \( \Gamma_{6P} \) and \( \Gamma_{Cu} \) points at \( k_y = 1.74 \sim 1 \). In the \((k_x,k_y)\) plot of Fig. 4d, it can be seen that the parabola observed in (c) actually consists of two intersecting elliptical paraboloids centered at \( k_y = 1.74 \sim 1 \) and \( k_x = \pm 0.11 \sim 1 \) (\( X_{6P} \)) on either side of the \( \Gamma_{6P} \) point within the LUMO-derived photoemission feature.

![Fig. 4](image-url)
4. Discussion

4.1 Occupied π band and d band

The extent of interaction of the occupied molecular orbitals with the Cu electronic states is revealed both in the photoemission data and in the DFT calculations. Relative to the multilayer film, the delocalized π band of the 6P ML displays a large increase in energy spread of the orbitals. Although these states appear less distinct in energy in comparison to a thick 6P film, the π orbital emissions can be identified due to their $k_x$ values.

As was shown in the comparison of the ML valence band with the bulk valence band (see Fig. 3b and c), the energy width of the π band in the ML is 1.2 eV greater than that of the bulk crystallites. The difference in π band spread can be understood as a consequence of the bonding on the surface in two respects: the broadening and splitting of the molecular levels, and a conformational change through planarization. In the gas phase, neighboring phenyl rings alternate in their angle to the average plane due to steric hindrance, which has also been demonstrated for the surfaces of 6P crystallites. A conformational change in which neighboring phenyl rings are forced into a common plane would induce a greater π band energy spread through greater overlap of the electron densities on neighboring rings. Indeed, near-edge X-ray absorption fine structure (NEXAFS) measurements show the phenyl rings of the molecule to have an inclination of around 0° to the surface (see ESI†). The planarization certainly suggests a significant bond to the surface, as the steric energies that must be overcome are around 125 meV per molecule.**

Although the planarization of the molecule alone increases the π band width (by about 12% in a calculation between torsional angles of 25° and 0°, see ESI†), a greater contribution arises directly from mixing of molecular states with metal states. As shown in the calculation of Fig. 3b, all molecular orbitals of the delocalized π band (as well as those of the localized π band, see ESI†) broaden in energy due to their interactions with the Cu states, indicating that both the π bands, localized and delocalized on the molecule, are involved in bonding interactions with the substrate. In the calculations, the broadening of the molecular levels is clearly seen, as expected for interactions with delocalized s,p bands, and some energetic splitting is observed in a number of orbitals with two or more strong peaks in the adsorbed system. However, the splitting is not necessarily a sign of interaction with the d band. It should be noted that there appears to be a degree of rehybridization among the molecular orbitals due to a loss of molecular symmetry upon interaction with the surface which could account for this splitting.

The effects of adsorption on the Cu d band in the photoemission data are strong but changes observed between the clean and adsorbed systems are difficult to separate from emissions expected from the localized π orbitals in this energy range. In the $k_y$ direction, the six localized orbitals (HOMO-3 to -8) have a nodal plane and, from simple symmetry arguments, would not be expected to be observed in the ML. (Note, this is not the case for the bulk film as the aromatic plane is not parallel to the substrate.) The overlayer scattering vector is relatively small (1/11 of that of the clean Cu surface, 0.22 Å⁻¹) which, in part could account for the general smearing observed on adsorption in Fig. 3b.

4.2 LUMO hybridization

The partial filling of the LUMO near $E_F$ can be clearly identified in the photoemission data due to an intensity distribution resembling that of the FT of the real-space orbital (cf. Fig. 4 and ref. 19). The paraboloid features within this distribution reveal that the orbital is modified by the Cu surface. These parabolic features are not due to intermolecular LUMO overlap in the dense ML as calculations of a free standing 6P layer reveal a dispersion of only 0.1 eV (see ESI†). Calculations of the overlayer-substrate system display an energy spread of the LUMO comparable to the experimental observation of ≈1 eV. However, with states of LUMO character smeared over $k$ and no suggestion of the parabolic structure observed (see ESI†), we must consider the overlayer periodicity to understand the origin of the paraboloid features and reach a comprehensive picture of the LUMO-substrate interaction.

We suggest that the paraboloid structure arises from a hybridization of the available substrate s,p states with the LUMO of the 6P molecule, in essence, a folding of the Cu bands on the overlayer lattice. The momentum distribution of the LUMO extends over more than an entire overlayer BZ (as seen in Fig. 4), thereby allowing hybridization for all $k$ values. The BZ of the 2D overlayer structure in Fig. 4d reveals that the two intersecting paraboloids within the LUMO $k$ distribution lie at the $X_{6P}$ points at $k_y = 1.74$ Å⁻¹. The substrate gap at the $Y_{Cu}$ point coincides with the $X_{6P}$ point at $k_y = 0.87$ Å⁻¹. The paraboloids, therefore, arise from the Cu states surrounding the Cu gap scattering into a $k$ region of high electron emission intensity from states of LUMO character. The absence of Cu states in the gap allows hybridization of the LUMO only with the Cu states closest in energy, *i.e.* those which surround the gap. This mixing leads to a greater density of the interface states at the $E(k)$ values around the gap which are made clearly visible in the photoemission data. These hybridized states reveal their metallic character by their maintenance of the Cu $E(k)$ distribution and reveal their molecular character by their scattering to a position in $k$-space with high photoemission cross section for the LUMO. It is this combination of a defined overlayer scattering vector and LUMO momentum distribution that makes the hybridization observable. At first it might seem surprising that there is also a high intensity within the paraboloids at $k_y = 1.74$ Å⁻¹. However, Cu states that can mix with molecular states do exist here (around the $I_{Cu}$ point). Thus, an increased intensity with respect to clean Cu is observed within the high intensity paraboloids.

A pertinent question is how would simple charge transfer to the LUMO appear different to the case of hybridization. In the case of simple charge transfer, the photoemission intensity due to the LUMO would have the smoothly varying appearance of the calculation in Fig. 4 overlayed with possible intensity from the Cu surface state through an Umklapp process due to the surface periodicity. The clearly lower intensity within the LUMO surrounding the $X_{6P}$ points in Fig. 3d (also seen in
the $E(k_z)$ representation of Fig. 4 at $\Gamma_{6p}$ shows that simple charge transfer is not the case here.

The scattering by a reciprocal lattice vector of the overlayer structure can also be observed for the dilute 0.5 ML coverage. At room temperature the molecules are poorly ordered (Fig. 1b), leading to the absence of a defined scattering vector at the surface. As a result, only a rather structureless increase in the photoemission intensity near $E_F$ is observed, whose $k$ distribution closely reflects that which could be expected from an unperturbed/isolated molecule with partial filling of the LUMO. When this dilute layer is cooled to 100 K (see ESI†), thermal disorder is suppressed and clear periodicity emerges in which the molecules have a spacing of three Cu rows in the [001] direction (rather than the two Cu row spacing of the full ML coverage). Once the periodicity has emerged, the hybridization of molecular and metal states around the Cu bulk gap becomes apparent (see ESI†). The position of the parabolas are different to the dense ML and display a band folding characteristic of the three Cu-row spacing, i.e. a reduction of the BZ width by 1/3. This effect proves that the overlayer periodicity can scatter the Cu bands surrounding the gap into the LUMO momentum distribution and modify the $E(k_z)$ appearance of the hybrid electronic structure.

5. Conclusions

The comparison of photoemission data to predictions obtained by the FT of the molecular orbitals reveals several insights into the nature of the organic-metal interface bond. We have shown that all molecular $\pi$ orbitals are involved in the bond with the Cu, as revealed by their energetic broadening. This bonding does not greatly disturb the symmetry/topology of the molecular orbitals, which allows their molecular character to be largely maintained despite strong mixing between Cu and molecular states, as illustrated by the momentum distribution of the orbitals in the photoemission data. When adsorbates are quasi-periodic systems, such as $\pi$-conjugated oligomers, their orbitals will have well-defined momentum distributions, whose relation to the momentum distribution of the substrate states must be considered in the bond. The convolution observed here of the adsorbate LUMO and the states around the gap in the bulk DOS of Cu emphasizes that, for hybridization to occur, states must overlap in momentum, in addition to space and energy. The 6p/Cu(110) system is a particularly illustrative example of momentum-resolved bonding, as it makes this hybridization process clearly visible due to the scattering vector of the highly ordered overlayer.

References