Supporting Online Material for

Reconstruction of Molecular Orbital Densities from Photoemission Data


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Correction: An acknowledgments section has been added following the SOM Text.
Reconstruction of Molecular Orbital Densities from Photoemission Data

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S1 Experimental details

S1.1 Sample preparation

Pentacene(022) films are grown and measured in situ in ultrahigh vacuum (UHV) on the p(2x1) oxygen reconstructed Cu(110) substrate template surface [S1]. The Cu(110)-p(2x1)O substrate surface is prepared by cleaning the copper crystal by repeated cycles of Ar+ ion bombardment (1 keV) and annealing at 800 K, followed by exposure to 40 L (1 L = 1 × 10−6 torr s) oxygen at 600 K. Pentacene (Fluka) is deposited in situ using a nominal growth rate of 4 Å min⁻¹, as monitored by a quartz microbalance assuming a density of 1.33 g cm⁻³. After a deposition of 200 Å pentacene on the Cu(110)-p(2x1)O surface at 200 K, the film is brought to 300 K for measurement. This procedure is used to control the morphology in order to avoid a superposition of
the multilayer features with substrate and monolayer features, which are difficult to suppress in films grown at room temperature due to the propensity of pentacene to island. Near-edge x-ray absorption spectroscopy (NEXAFS) and x-ray diffraction (XRD) show that the long axis of the molecules in such films are parallel to the [001] substrate direction, with the pentacene(022) crystallite orientation [S2] of the structure reported in Mattheus et al. [S3].

Submonolayer and monolayer sexiphenyl (sexiphenyl) films are grown and measured in-situ in UHV. The Cu(110) substrate surface is prepared by cleaning the copper crystal by repeated cycles of Ar$^+$ ion bombardment (1 keV) and annealing at 800 K. Sexiphenyl (Tokyo Chemical Industry Co., Ltd.) is deposited in-situ from a thoroughly degassed evaporator such that the pressure in the system remained in the $10^{-10}$ mbar range during film growth. A nominal growth rate of 2 Å min$^{-1}$, as monitored by a quartz microbalance assuming a density of 1.3 g cm$^{-3}$, is used. For coverages up to the first monolayer ($< 3$ Å), NEXAFS shows that the phenyl rings are flat on the surface to within the limits of the technique ($\pm 10^\circ$). Scanning tunneling microscopy (STM) and angle-resolved photoelectron spectroscopy (ARPES) show that the molecules are oriented with their long molecular axes parallel to the Cu atomic rows (the [1-10] Cu azimuth).

**S1.2 Experimental setup**

Presently, there are a number of display-type analyzers that are capable of obtaining angular-dependent photoemission intensity maps suitable for our approach [S4]. Our ARPES experiments are performed at room temperature using a toroidal electron energy analyzer described elsewhere [S5] attached to the TGM-4 beamline at the synchrotron radiation facility BESSY II. This toroidal electron analyzer allows simultaneous collection of photoelectrons in a kinetic energy window of 0.8 eV over a polar angle $\theta$ range of 180° in the specular plane. Azimuthal scans are then made by rotating the sample around the surface normal in 1° steps for $> 180^\circ$ of azimuthal angle $\phi$ (see Fig. S5). The angular emission data is then converted to momentum $k_\parallel$.
using the formula $k_{||} = \sqrt{2m_e E_{\text{kin}}/\hbar^2 \sin \theta \, [\text{Å}^{-1}]}$ to create the momentum maps. The photon incidence angle is $\alpha = 40^\circ$, and the polarization direction is always in the specular plane. A photon energy of $h\nu = 35$ eV is used throughout.

**S2 Theory**

**S2.1 Photoemission intensity**

As outlined in the main text, throughout this work we calculate the photoemission intensity by assuming a plane wave final state which leads to the simple result that the PE intensity $I_i$ from a given initial state $i$ is proportional to the Fourier transform of the initial state wave function $\tilde{\psi}(k)$. More precisely, one finds (compare main text)

$$I_i(\theta, \phi) \propto (\mathbf{A} \cdot \mathbf{k})^2 |\tilde{\psi}_i(k)|^2,$$

where $\mathbf{k}$ and $\mathbf{A}$ are the wave vector of the emitted electron and the vector potential of the incident photon, respectively. Indeed such an approach has been proposed already more than 30 years ago by Gadzuk [S6] and Goldberg et al. [S7]. However, it was realized rather soon that the plane wave final state approximation had problems in describing the observed photoemission intensity of some large polyatomic molecules and/or certain experimental geometries [S8,S9], which led to the conclusion that the plane wave final state approximation should not be used and nourished the development of the independent-atomic-center (IAC) approximation [S10]. Nevertheless, all experimental data presented herein are found to be in excellent agreement with the simple plane wave (PW) final state assumption. Hence, the goal of this section is to shed light on the relation between the IAC and the simpler PW approach and to hint towards possible limitations of the latter.

In the IAC approximation the transition matrix element between the initial and final state is decomposed into a sum over individual matrix elements between atomic eigenfunctions, which build up the initial molecular orbitals, and the solution of the Schrödinger equation in an atomic
potential at the final state energy $E_k = \frac{\hbar^2}{2m} k^2$. The IAC expression for the photoelectron wave function $A$ with kinetic energy $E_{\text{kin}}$ at the detector position $\mathbf{R}$ can be written in the following form [S10]

$$A(\mathbf{R}, E_{\text{kin}}) = \sum_{\alpha} \sum_{nlm} C_{\alpha,nlm} e^{i \mathbf{kR}_\alpha} \sum_{LM} M^{LM}_{\alpha,nlm}(E_{\text{kin}}) Y_{LM}(\hat{R}).$$  \tag{2}$$

Here, the initial orbital $\psi_1(\mathbf{r})$ is expressed as a linear combination of atomic orbitals $\phi_{\alpha,nlm}$ centered at the position $\mathbf{R}_\alpha$, where $nlm$ represent the principal and angular-momentum quantum numbers of the orbital and $\alpha$ the atomic center on which it resides:

$$\psi(\mathbf{r}) = \sum_{\alpha} \sum_{nlm} C_{\alpha,nlm} \phi_{\alpha,nlm}(\mathbf{r} - \mathbf{R}_\alpha).$$  \tag{3}$$

The matrix elements $M^{LM}_{\alpha,nlm}$ in Eq. (2) are dipole matrix elements between the atomic wave functions $\phi_{\alpha,nlm}$ and solutions of the Schrödinger equation in an atomic potential at the energy $E_{\text{kin}}$ and angular momentum $LM$. It was already noted by Grobman that expression (2) can be considerably simplified if the initial molecular orbital is comprised of atomic orbitals of the same chemical and orbital character. A specific example of such a situation is given by a $\pi$ molecular orbital of a planar polyatomic molecule. Then the coefficients $C_{\alpha,nlm}$ are only non-zero for atomic $p_z$ orbitals and only one term remains of the sum over $nlm$:

$$A(\mathbf{R}, E_{\text{kin}}) = \sum_{\alpha} C_{\alpha,2p_z} e^{i \mathbf{kR}_\alpha} \sum_{LM} M^{LM}_{2p_z}(E_{\text{kin}}) Y_{LM}(\hat{R}).$$  \tag{4}$$

In the above expression we have also omitted the atomic index $\alpha$ in the transition matrix elements since they do not depend on the position of the atom but only on the type of atomic orbital which is assumed to be $2p_z$ for all contributing atoms. Thus, the sum over the final state angular-momentum quantum numbers $LM$, the atomic factor, which we abbreviate as

$$N_{2p_z}(E_{\text{kin}}, \hat{R}) = \sum_{LM} M^{LM}_{2p_z}(E_{\text{kin}}) Y_{LM}(\hat{R}).$$  \tag{5}$$

can be put in front of the summation over atoms $\alpha$ and we are left with the simplified expression
for the photoemission amplitude at the detector:

\[ A(R, E_{\text{kin}}) = N_{2p_z}(E_{\text{kin}}, \hat{R}) \sum_{\alpha} C_{\alpha, 2p_z} e^{i k R_\alpha} \quad (6) \]

As has been noted by Grobman [S10] the term \( N_{2p_z}(E_{\text{kin}}, \hat{R}) \) acts only as a weakly varying envelope function while the main angular dependence of the photoemission intensity is dominated by the last term in Eq. (6), which is closely related to the Fourier transform of the initial molecular orbital. By taking the Fourier transform (FT) on both sides of Eq. (3) we see that the FT of the initial molecular orbital \( \tilde{\psi}(k) \) can be written as

\[ \tilde{\psi}(k) = \tilde{\phi}_{2p_z}(k) \sum_{\alpha} C_{\alpha, 2p_z} e^{i k R_\alpha}, \quad (7) \]

Here, we have introduced the FT of a \( p_z \) orbital, \( \tilde{\phi}_{2p_z}(k) \), whose angular part is simply given by the spherical harmonic, \( Y_{10}(\theta, \phi) \propto \cos \theta \) [S6]. Thus for large \( \pi \) conjugated molecules, the main angular dependence will be determined by the last term in Eq. (6). By combining Eqs. (6) and (7) we see that the IAC produces a result which is in fact very similar to the PW final state assumption, compare Eq. (1), provided that the initial molecular orbital is composed of atomic orbitals of the same type as is the case for planar \( \pi \) conjugated molecules:

\[ A(R, E_{\text{kin}}) = \left( \frac{N_{2p_z}(E_{\text{kin}}, \hat{R})}{\tilde{\phi}_{2p_z}(k)} \right) \times \tilde{\psi}(k). \quad (8) \]

Last but not least we note that the prefactor, \( N_{2p_z}/\tilde{\psi}_{2p_z} \), can be shown to become completely independent of the emission direction \((\theta, \phi)\) for the special case where the polarization vector \( \mathbf{A} \) of the photon is exactly parallel to the emission direction \( \mathbf{k} \). For this particular geometry the photoemission intensity resulting from the IAC, which is the square of \( A(R, E_{\text{kin}}) \), reduces exactly to the intensity emerging from the plane wave final state assumption. This observation has already been made by Goldberg for the photoemission cross section from atoms [S7]. Moreover, due to the overall weak angular dependence of the envelope factor \( N_{2p_z}/\tilde{\psi}_{2p_z} \), the Fourier transform of the initial molecular orbital \( \tilde{\psi}(k) \) continues to provide a good description
of the angle-dependent PE intensity also when the direction of the polarization vector deviates from the emission direction. Hence it is expected that the difference between the PW result, Eq. (1), and the IAC expression, Eq. (7), only grows weakly with the deviation from the above mentioned condition.

S2.2 Comparison between IAC and PW final state calculations

Here, we compare our calculations resulting from the PW final state approximation with theoretical results based on the IAC approach and experimental data, both from the literature, for the 1,4,5,8-Naphthalene-tetracarboxylic-dianhydride molecule (NTCDA) [S11]. We have chosen this molecule here since (i) it is a typical planar \( \pi \) conjugated molecule and (ii) calculations within the IAC approximation – and also within the single-scattering (SS) extension of it – are available from the literature [S11]. The highest occupied molecular orbital of NTCDA is depicted in Fig. S1A exhibiting the \( \pi \) orbital character of this planar molecule. We show the Fourier transform of the HOMO in Fig. S1B which should be compared to the computation of Kera et al. in Fig. 4a of Ref. [S11]. There is an overall good agreement between the two methods. Note that in our figure we display the PE intensity as a function of \( k_x \) and \( k_y \) while Kera et al. have chosen a polar diagram, i.e. intensity versus polar and azimuthal angles \( \theta \) and \( \phi \), respectively. To further emphasize the numerical equivalence of the two approaches we also display two line scans of the PE intensity in our Figs. S1C and S1D corresponding to Fig. 5 in Kera et al. The polar angle dependence using a PW final state approximation is in very good agreement with the IAC calculation. Note that we have assumed an angle of incidence of \(-50^\circ\) for the incident photon in accordance with Kera at al. and Fig. S1C shows the absolute value squared of the initial state FT (blue line) as well as the full PW final state result including the polarization factor as defined in Eq. (1). Fig. S1D displays the azimuthal dependence of the PE intensity at a polar angle of \( \theta = 26^\circ \) for an average of two different molecular orientations
characterized by molecular azimuths $\phi_m$ of $40^\circ$ and $140^\circ$ in accordance with the simulation of Kera et al. in their Fig. 5b. Again the PW final state assumption and the IAC approximation lead to very similar results. Finally, we note that for NTCDA molecule the inclusion of single scattering events produces only minor changes to the IAC result as can be seen from Fig. 5 of Kera et al. [S11].

**S2.3 Computational details**

All calculations are performed within the framework of density functional theory (DFT) [S12,S13]. We utilize the ABINIT software package which is a plane-wave based implementation of density functional theory for periodic systems [S14]. Exchange and correlation effects are treated with the generalized gradient approximation (GGA) using the parametrization of Perdew, Burke, and Ernzerhof [S15]. The all-electron potentials are replaced by extended norm-conserving, highly transferable Troullier-Martins pseudo potentials [S16] using a plane wave cut-off of 30 Ryd. DFT calculations are performed for isolated pentacene and para-sexiphenyl by using a super cell approach with box sizes of $120 \times 30 \times 30$ Bohr$^3$ for pentacene and $160 \times 30 \times 30$ Bohr$^3$ for sexiphenyl, respectively, and $\Gamma$ point sampling of the Brillouin zone.

**S3 Additional results**

**S3.1 Pentacene multilayer**

In the main text we discuss momentum maps from the pentacene HOMO of a multilayer of pentacene grown on the (2x1) oxygen reconstructed Cu(110) surface. There, we point out that the apparent disparity between the results of the photoemission data and the theoretical Fourier transforms are in fact due to the tilt angle of the molecules found in the (022) surface termination as depicted in Fig. 1C. Here, we illustrate this fact further by showing the theoretical results for molecules tilted by $\beta = \pm 26^\circ$, in Fig. S2A and S2B, respectively. Since both tilt angles are present in the (022) crystallite orientation, an effective average of the two molecular
orientations, $+26^\circ$ and $-26^\circ$, is expected. Therefore, we also display the sum of the former two computations in Fig. S2C. Indeed, the comparison between the superposition (Fig. S2C) and the measurement (Fig. S2D) is very satisfying. In particular, the maxima at the $k_y = 0$ line are now clearly found to originate from the tilt angle of the molecules. (Note that Fig. S2C and Fig. S2D are identical to the Figs. 2D and 1D of the main text, respectively, and are repeated here to facilitate a convenient comparison.)

In order to emphasize the sensitivity of the PE intensity on the tilt angle we show a line scan along $k_y$ at constant $k_x = -1.1$ Å as indicated by the white dashed line in Fig. 2D. These plots are shown in Fig. 3A where we compare the experimental line scan (symbols) with our simulated PE intensity according to Eq. (1) for three different tilt angles $\beta$ of the pentacene molecule. Clearly, the simulation result for $\beta = 25^\circ$ is in better agreement with the measurement than the computations for $20^\circ$ and $30^\circ$, respectively. In particular the peak position of the maxima around $k_y \approx \pm 2$ Å$^{-1}$ are shifted to lower (higher) values by decreasing (increasing) the tilt angle. But also the shape of the main feature centered around $k_y = 0$ is reproduced better by the simulation for $\beta = 25^\circ$. To quantify the quality of the simulations for various tilt angles $\beta$ we also show the sum of the squared differences between the experimental line scans and the simulated ones in Fig. 3B. The curve shows a minimum at $\beta = 24^\circ$ which is very close to the value of $26^\circ$ obtained from x-ray pole figure measurements on these pentacene multilayer films [S2] and assuming the bulk structure from Mattheus et al. [S3].

S3.2 Adsorbed para-sexiphenyl

When deposited on the clean Cu(110) substrate, sexiphenyl molecules align with their long molecular axes parallel to the [1-10] azimuth of Cu(110) [S1], i.e., parallel to the copper rows and, upon saturation, form a well ordered monolayer. A structural motif of this adlayer together with the underlying Cu(110) substrate is displayed in Fig. S4A. Here we show the primitive
surface unit cell of the saturated adlayer indicated by the blue arrows. This structure has been deduced from both low energy electron diffraction and the STM in Fig. S4B. This typical room temperature STM image of a saturated monolayer of sexiphenyl on Cu(110) was obtained with a bias voltage 0.19 V. Note that the STM appearance of the molecule does not simply reflect a molecular orbital (the ex-LUMO at this bias). However, the higher intensity at the molecular center may reflect the increased weight seen in the orbitals reconstructed from the ARPES data (Fig. 4).

In Fig. S4C we show the angle-dependent photoemission of the sexiphenyl monolayer adsorbed on Cu(110) with the emission plane parallel to the long molecular axis. Comparison with equivalent photoemission data for the clean Cu(110) surface identifies the two features indicated by the red arrows as stemming from molecule. The state slightly below the Fermi level is attributed to the partially filled LUMO, while the newly appearing emission with a binding energy of 2 eV is due to the sexiphenyl HOMO. The fact that the peaks are at positions in $k_x$ direction which reflect the main spatial periodicity of the sexiphenyl HOMO and LUMO, respectively, is already the first indication for this assignment. A further proof will be given by the momentum maps at the respective energies as outlined below.

The PE momentum map for the sexiphenyl HOMO as presented in Fig. 3A of the main text is the average over an energy window of 200 meV centered at the energetic position indicated by the lower red arrow in Fig. S4c. Note that the sexiphenyl HOMO lies just above the Cu $d$ bands, and the Cu $sp$ band is in fact intersecting the sexiphenyl HOMO energy when viewing along the [1-10] direction of the substrate. The full momentum map is shown in Fig. 3A and compared to the Fourier transform of the isolated sexiphenyl molecule HOMO in Fig. 3B.

The peak originating from the sexiphenyl LUMO along the [1-10] direction (upper red arrow Fig. S4C), i.e., along the long molecular axis, appears at slightly larger $k_x$ value than that of the sexiphenyl HOMO. This is in accordance with the spatial structure of the sexiphenyl
LUMO which has one more nodal plane perpendicular to the molecular axis than the sexiphenyl HOMO. Note that the Cu $sp$ band is intersecting the Fermi level at a slightly lower $k_x$. In order to extract the sexiphenyl LUMO features in the momentum map shown in Fig. 3A of the main text, we have subtracted PE data from clean Cu(110) substrate. This procedure is illustrated in Fig. S5. Panel (A) shows the raw data averaged over a kinetic energy of 250 meV, while (B) displays the corresponding data for the clean Cu(110) substrate being an average over the same kinetic energy window. We subtract 30% of the normalized clean Cu(110) data from the normalized sexiphenyl monolayer data in order minimize the Cu features appearing in the sexiphenyl monolayer data. The result is presented in panel (C). The main difference between (A) and (C) is hence a suppression of the Cu $sp$ features which are present in the sexiphenyl monolayer data due to emission through the sexiphenyl monolayer. Finally, we subtract a smooth instrumental background yielding the processed data given in panel (D). There, we have also marked the polar (0 to 70°) and azimuthal (−70 to 110°) angle range by the yellow rectangle used for the conversion to the $(k_x, k_y)$ plot shown in Fig. 3C of the main text. Note that an azimuthal range of 180° has been extended to the full 360° by imposing the two-fold symmetry of the adlayer, as shown by the box in Fig. S5D.

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Electron Lasers - Grant Agreement 226716”.

References


Figure S1: Calculated photoemission intensity within the plane wave final state approach for the 1,4,5,8-Naphthalene-tetracarboxylic-dianhydride molecule (NTCDA). (A) Highest occupied molecular orbital of NTCDA as calculated from density functional theory. (B) Calculated Fourier transform of the NTCDA HOMO for a kinetic energy of 51.2 eV. (C) Polar angle dependence for an azimuthal angle $\phi = 30^\circ$ with and without the polarization factor $(A.k)^2$, respectively. (D) Azimuthal dependence of the PE intensity at a take-off angle of $\theta = 26^\circ$ averaged over two molecular orientations characterized by $\phi_m = 40^\circ$ and $\phi_m = 140^\circ$, respectively. Graphs (A)-(D) should be compared to the experimental data and calculations within IAC and SS theories from Kera et al. [S11].
Figure S2: Calculated Fourier transform of tilted pentacene molecules. (A) Calculated Fourier transform of an isolated pentacene molecule tilted by $\beta = +26^\circ$ about the long molecular axis. (B) Same as in (A) but for a tilt of $\beta = -26^\circ$. (C) The sum of the data shown in panels (A) and (B). Note that this corresponds to the experimental situation where both tilts will be present and should therefore be compared with the experimental data displayed in Fig. 1D of the main paper. (D) Experimental photoemission intensity from a momentum map at a constant binding energy corresponding to the pentacene HOMO from the multilayer of pentacene described in the text.
Figure S3: Experimental vs. theoretical line scans for the pentacene multilayer. (A) Experimental (symbols) vs. theoretical (lines) line scans $|\tilde{\psi}(k)|$ as a function of $k_y$ at $k_x = -1.1$ Å as indicated by the dashed line in Figs. S2C and S2D. Simulations for three different tilt angles $\beta$ are shown, 20° (black dashed), 25° (red full), 30° (blue dot-dashed). (B) Difference between experiment and simulation expressed as the sum of squared differences as a function of the pentacene tilt angle $\beta$. 
Figure S4: Photoemission from the monolayer of para-sexiphenyl on Cu(110). (A) Schematic representation of the para-sexiphenyl (sexiphenyl) monolayer on the Cu(110) surface. The long molecular axis is oriented parallel to the [1-10] direction of the Cu(110) surface. The surface unit cell of the clean Cu surface is indicated by the yellow arrows, the primitive surface unit cell of the ad-layer by the blue arrows. (B) STM image of the sexiphenyl monolayer on the Cu(110) surface. The substrate [1-10] direction is indicated by the red arrow, and the equivalent centered surface unit cell [c(2x2)] of the sexiphenyl adlayer is marked as the blue rectangle. (C) Angle-resolved photoemission intensity from the sexiphenyl monolayer on Cu(110) with an emission plane parallel to the long molecular axis as indicated by the red arrow in (A). The yellow line indicates the Fermi level and the red arrows point at the features that we identify as originating from the sexiphenyl HOMO and LUMO. Between 0 and -2 eV, the intensity scale has been magnified for clarity.
Figure S5: Extraction of the sexiphenyl LUMO data from the raw data. (A) Photoemission intensity from the monolayer of sexiphenyl on Cu(110) as a function of the polar angle \( \theta \) and the azimuthal angle \( \phi \). The data are averaged over 250 meV in a region slightly below the Fermi edge. The photon energy is 35 eV. (B) Photoemission intensity of the clean Cu(110) substrate averaged over the same kinetic energy window as in (A). (C) Subtraction of the clean Cu(110) data from the raw sexiphenyl monolayer data. (D) Data after subtraction of a smooth instrumental background from the data shown in (C). The yellow rectangle marks the polar (0 to 70°) and azimuthal (−70 to 110°) angle range that has been used for the conversion to the \( k_x - k_y \) plot shown in Fig. 3C of the main text. Note that the azimuthal range of 180° has been extended to the full 360° by imposing the two-fold symmetry of the adlayer.