Organic-metal interfaces investigated by photomission tomography
Collaborations and Funding

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Outline

Theory

Density Functional Theory (DFT) in a Nutshell

Photoemission Tomography: What ARPES tells us about molecular orbitals

Applications

Deconvoluting photoemission spectra into individual orbitals

Identifying on-surface reaction products
"[...] the physicists and chemists who use density functional theory so fruitfully have by and large shied away from attributing to [...] orbitals the reality that (we think) they deserve"

Photoemission Spectroscopy

\[ K = \frac{p}{\hbar} = \sqrt{\frac{2mE_{\text{kin}}}{\hbar}} \]

\[ K_x = \frac{1}{\hbar} \sqrt{2mE_{\text{kin}} \sin \theta \cos \varphi} \]
\[ K_y = \frac{1}{\hbar} \sqrt{2mE_{\text{kin}} \sin \theta \sin \varphi} \]
\[ K_z = \frac{1}{\hbar} \sqrt{2mE_{\text{kin}} \cos \theta} \]

Vacuum

\[ E_{\text{kin}} \]
\[ K \]

Conservation laws

\[ E_f - E_i = \hbar \nu \]
\[ k_f - k_i = \hbar \nu \]

Solid

\[ E_B \]
\[ k \]
Photoemission Intensity

One Step Model

\[ W_{\text{in} \rightarrow \text{f}} \propto \left| \left\langle \Psi_{f,l,k}^{N} \middle| A \cdot P \middle| \Psi_{\text{in},0}^{N} \right\rangle \right|^2 \delta \left( \hbar \omega + E_{\text{in},0} - E_l - E_{\text{kin}} \right) \]

**Initial State** = Ground state of N-electron system

**Final State** = Antisymmetrized product of emitted electron state and the I-th excitation of the (N-1) electron system

\[ \Psi_{f,l,k}^{N} = (x_1, ..., x_N) = \sum_{i=1}^{N} \frac{(-1)^{i+1}}{\sqrt{N}} \Psi_{i}^{N-1} \left( \{x \setminus i\} \right) \gamma_k(x_i) \]

Photoemission Intensity

One Step Model: Dyson orbitals

\[ \left| \langle \psi_{f,I,k}^N \left| A \cdot P \right| \psi_{in,0}^N \rangle \right| = \left| \int d^3x \: \gamma^*_k(x) \: A \cdot p(x) \: d_I(x) \right| \]

Initial State = Dyson orbital

\[ d_I(x_i) = \sqrt{N} \: \int d^3\{x\} \: \psi_{I}^{N-1*} \left( \{x\} \right) \psi_{in,0}^N \left( \{x\} \right) \]


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Photoemission Intensity

One Step Model

\[ I(\theta, \phi; E_{\text{kin}}) \propto \sum_i \left| \langle \psi_f^*(\theta, \phi; E_{\text{kin}}) | \mathbf{A} \cdot \mathbf{p} | \psi_i \rangle \right|^2 \times \delta (E_i + \Phi + E_{\text{kin}} - \hbar \omega) \]

Approximation: final state = plane wave

\[ I_i(\theta, \phi) \propto |(\mathbf{A} \cdot \mathbf{k})|^2 \times \left| \tilde{\psi}_i(\mathbf{k}) \right|^2 \]

Polarization Factor  Fourier Transform of Initial State Orbital

Fourier Transform of an Orbital

Molecular Orbital in Real Space:
(HOMO of para-sexiphenyl)

Calculation of the Fourier Transform

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Fourier Transform of an Orbital

Molecular Orbital in Real Space:
(HOMO of para-sexiphenyl)

Calculation of the Fourier Transform

Photoelectron Angular Distribution

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Calculation of the Fourier Transform

Molecular Orbital in Real Space:
(HOMO of para-sexiphenyl)

Hemispherical Cut Through 3D Fourier Transform

Fourier Transform of an Orbital

K_x (1/Å)

K_y (1/Å)

K_z (1/Å)

2π/a

a~4.2 Å

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6P/Cu(110): Experiment vs. Theory

Photoemission Tomography

Identification of Molecular Orbitals

*Science* **326**, 702 (2009),
*PRL* **104**, 233004 (2011),
*PRB* **84**, 235427 (2011),
*Nat. Comm.* **5**, 3685 (2014),
*Nat. Comm.* **8**, 335 (2017),

Reconstruction of Real Space Orbitals

*PNAS* **111**, 605-610 (2014),
*Nat. Comm.* **5**, 4156 (2014),

Molecular Orbitals in 3D


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Orbital Order in M3

M1 = fLUMO
M2 = HOMO
M3

Glöckler et al,

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Pi-"bands" of PTCDA
Projected DOS from ARPES!

Fit parameters = PDOS
calculated orbitals

measured photemission data cube

\[ \chi^2 = \int dk_x dk_y \left[ I(E_b, k_x, k_y) - \sum_i a_i(E_b) \phi_i(k_x, k_y) \right]^2 \]

Puschnig et al. PRB 84, 235427 (2011); Willenbockel et al., PCCP 17, 1530-1548 (2015).
Intrinsic M3 Order

Intrinsic M3 Order


(*) S. Refaely-Abramson et al., PRL 109, 226405 (2012)
Intrinsic M3 Order

1. Orbitals are robust

2. Static correlations beyond LDA/GGA are important for orbital order

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Reaction of DBBA on Cu(110)

DiBromo-BiAnthracene (DBBA, \( C_{28}H_{16}Br_2 \))

Annealing @335°C


Simonov et al: "Formation of zero-dimensional flat nanographenes with dehydrogenated zigzag edges bonded to Cu rows"

dehydrogenated molecular fragment \( (C_{28}H_8) \)

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Reaction of DBBA on Cu(110)

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DBBA/Cu(110)

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dehydrogenated molecular fragment (C_{28}H_{8})

hydrogenated BisAnthene (C_{28}H_{14})

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\( \text{C}_{28-n} \text{H}_n / \text{Cu}(110) \) – Band Maps

ARPES along [1-10]

ARPES along [001]

\( E_B \) (eV)

\( k[1-10] \) (1/Å)

\( k[001] \) (1/Å)
C_{28}H_{n}/Cu(110) – Band Maps

ARPES along [1-10]

 ARPES along [001]

Δk~1/L

E^B (eV)

k[1-10] (1/Å)

0

2

-2

-4

-6

-8

-10

-12

π-band

σ-band

Cu d-band

LUMO

E^B (eV)

k[001] (1/Å)

0

2

-2

-4

-6

-8

-10

-12

-14

π-band

σ-band

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$C_{28n}/\text{Cu}(110) - \text{Momentum Maps}$

ARPES

$E_B = -0.5 \text{ eV}$

$E_B = -1.1 \text{ eV}$

$E_B = -1.9 \text{ eV}$

ARPES along [001]

LUMO

$E_B = -1.9 \text{ eV}$
Bisanthene – Frontier Orbitals

**LUMO**

- $E_B = -0.5$ eV

**HOMO**

- $E_B = -1.1$ eV

**HOMO-1**

- $E_B = -1.9$ eV

**Simulation**

- ARPES along [001]

**ARPES**

- LUMO

- [001]
DFT-Calculations

fully hydrogenated bisanthene molecule $\text{C}_{28}\text{H}_{14}$

dehydrogenated molecular fragment $\text{C}_{28}\text{H}_{8}$

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Hydrogenated BisAnthene
($\text{C}_{28}\text{H}_{14}$)

Simulation BA/Cu(110)

Simulation gas phase

ARPES

[001]
ARPES-Simulation BA/Cu(110)

Hydrogenated BisAnthene (C$_{28}$H$_{14}$)

Simulation BA/Cu(110)
-0.3 eV
-0.8 eV
-1.3 eV

Simulation gas phase
-0.5 eV
-1.1 eV
-1.9 eV

ARPES
-0.5 eV
-1.1 eV
-1.9 eV

[001]

Binding Energy (eV)
-10
-9
-8
-7
-6
-5
-4
-3
-2
-1
0
1
2
3
4
5
6
7
8
9
10

Projected DOS
-10
-9
-8
-7
-6
-5
-4
-3
-2
-1
0
1
2

Total DOS (x 0.02)
Molecule
p states
LUMO
HOMO
HOMO-1

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**ARPES-Simulation for C28H8**

**De-hydrogenated (C$_{28}$H$_8$)**

Simulation C$_{28}$H$_8$/Cu(110)

-0.3 eV

-0.8 eV

-1.2 eV

**ARPES**

-0.5 eV

-1.1 eV

-1.9 eV

[001]

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Conclusions

"Photoemission tomography reveals the nature of the reaction product and its geometric and electronic structure."

Simonov et al.: "Formation of zero-dimensional flat nanographenes with dehydrogenated zigzag edges bonded to Cu rows”


dehydrogenated molecular fragment

hydrogenated BisAnthene

(\(\text{C}_{28}\text{H}_{14}\))

-0.5eV

-1.1eV

-1.9eV

-4.6eV

-5.3eV

-6.6eV
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Dibromo-Bianthracene (DBBA) → Cu(110)

1. Annealing @335°C

Bisanthene ($C_{28}H_{14}$)

2. Annealing @550°C

3. Annealing @750°C

Outlook

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partially de-hydrogenated \((\text{C}_{28}\text{H}_{12})\)

**Simulation BA/Cu(110)**

-0.3 eV

-0.8 eV

-1.2 eV

**Simulation gas phase**

-0.5 eV

-1.1 eV

-1.9 eV

**ARPES**

- [001]

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Evidence from STM

hydrogenated BisAnthene $(C_{28}H_{14})$

De-hydrogenated Molecular Fragment $(C_{28}H_8)$


Bisanthene LUMO

STM-simulations within Tersoff-Hamann approximation

Tunneling parameters: $(V_S / I_T): -0.1 \text{ V} / 500 \text{ pA}$