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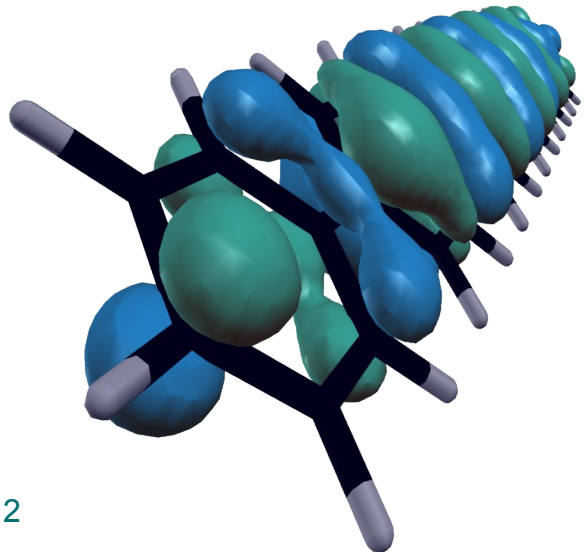
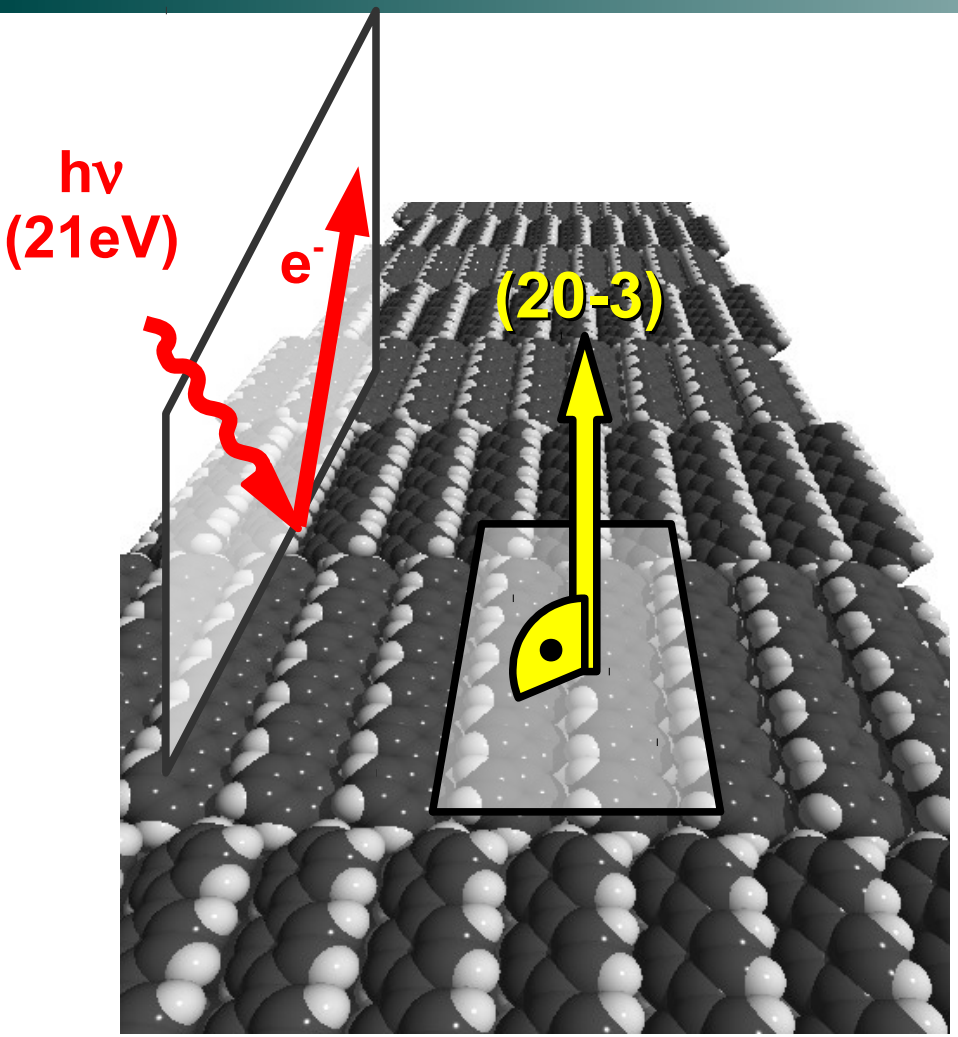
Orbital Tomography:
A Method to Obtain the Orbital-Projected DOS from ARPES



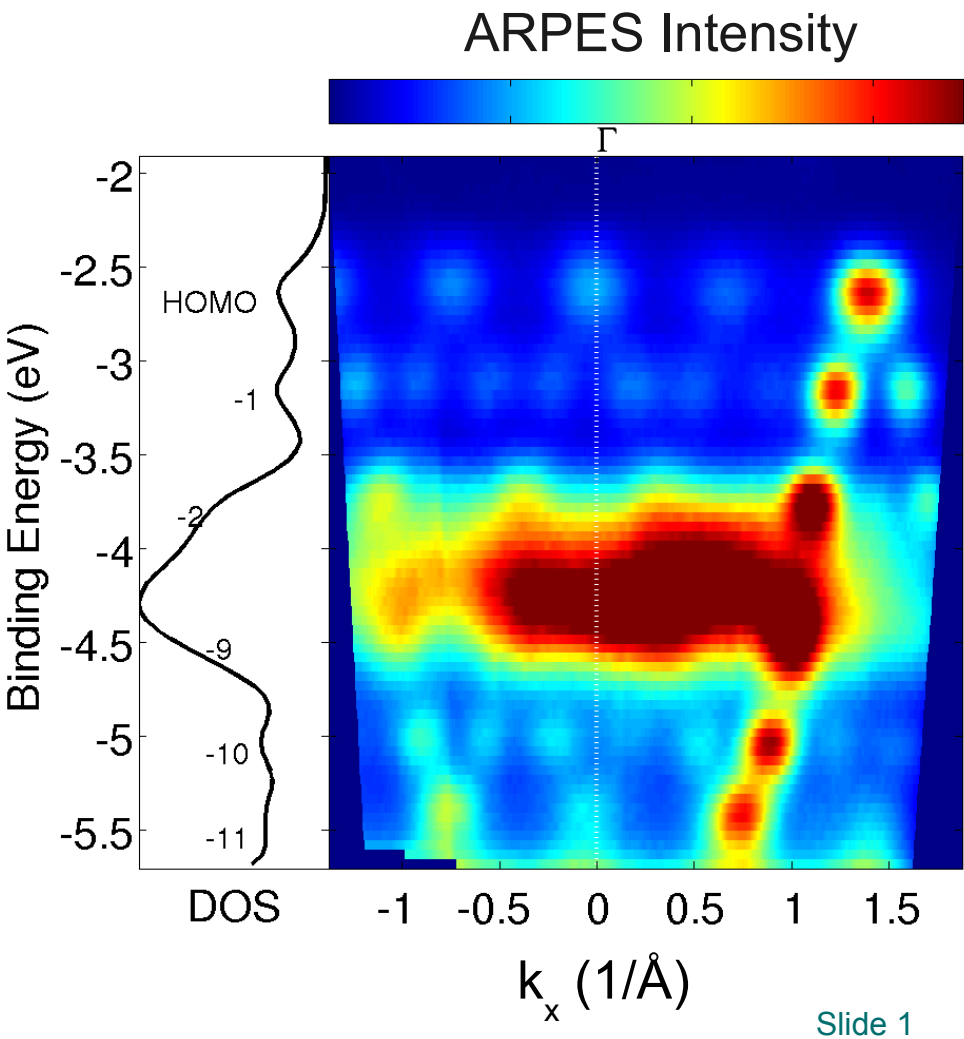
Peter Puschnig, Bayreuth, Sep. 10th 2012

Motivation

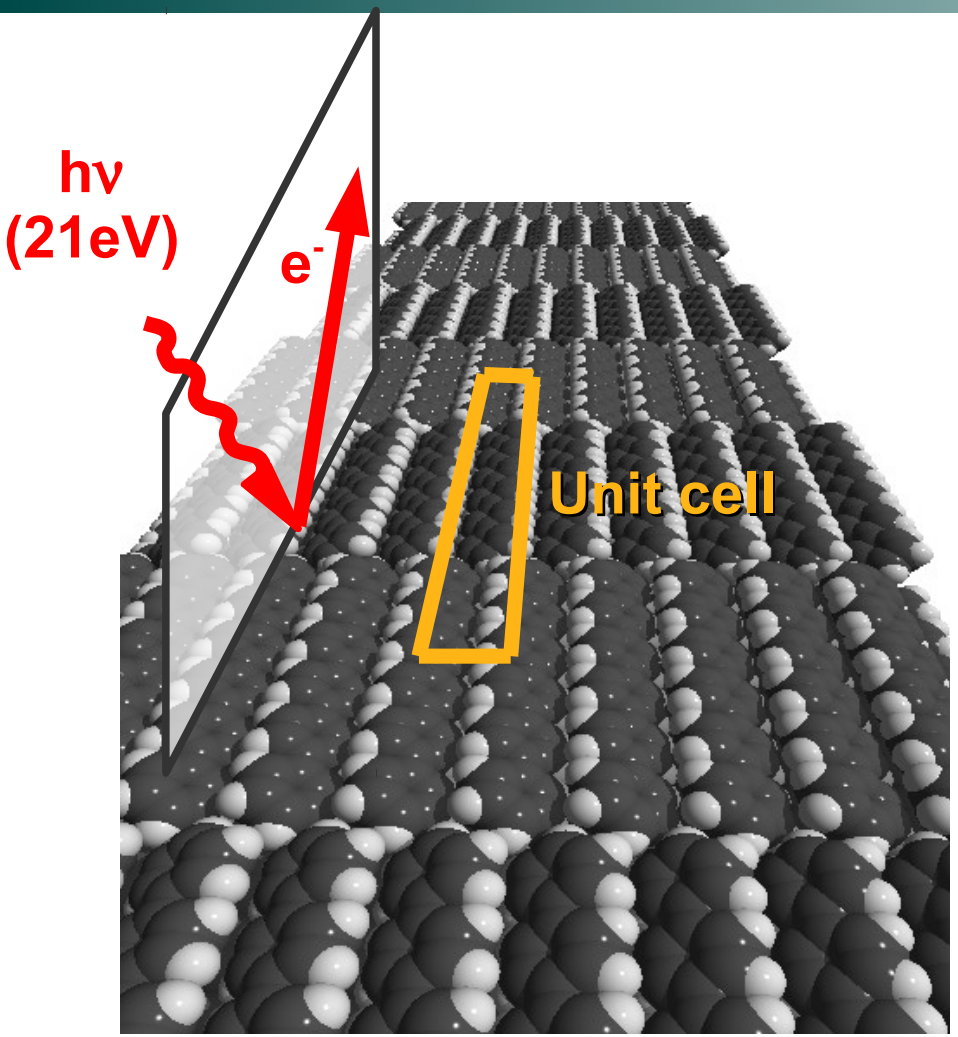


Uniaxially aligned para-sexiphenyl film
on Cu(110)_(2x1)O

ARPES data from
Stephen Berkebile et al. (2007)



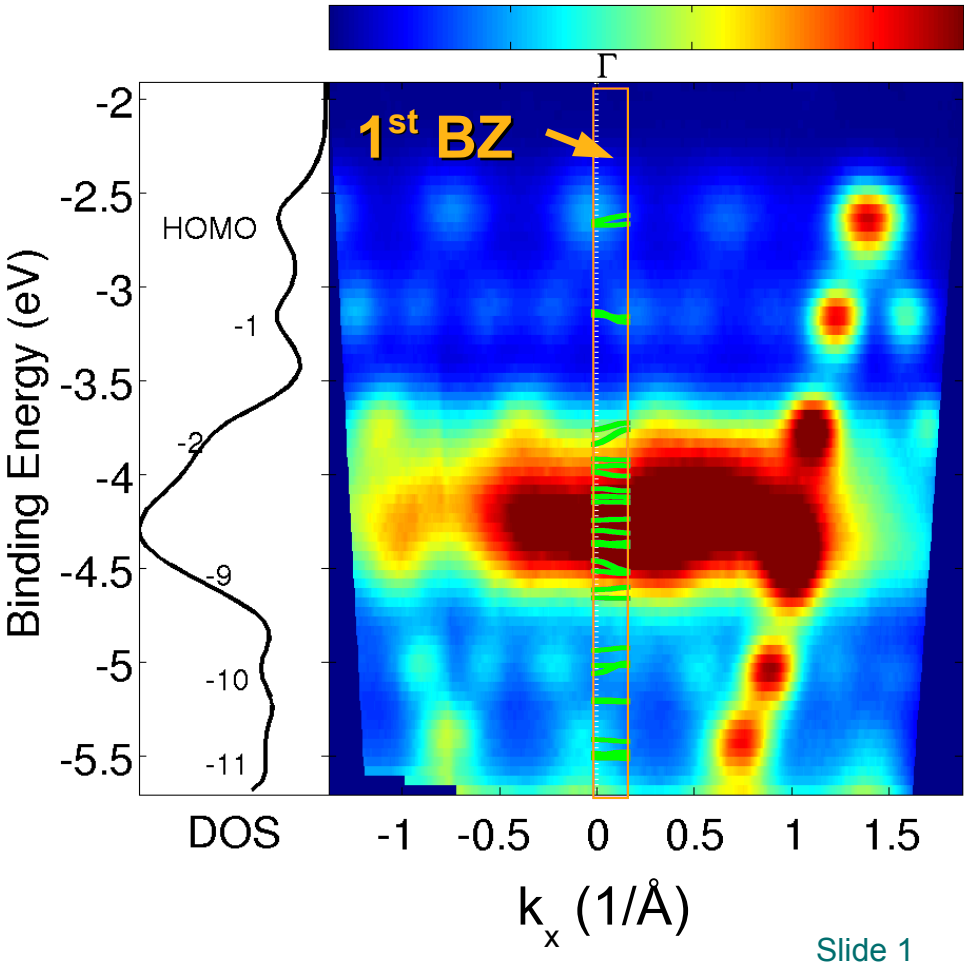
Motivation



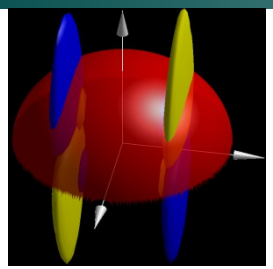
Uniaxially aligned para-sexiphenyl film
on Cu(110)_(2x1)O

Band structure from:
Puschnig et al., *PRB* **60**, 7891 (1999).

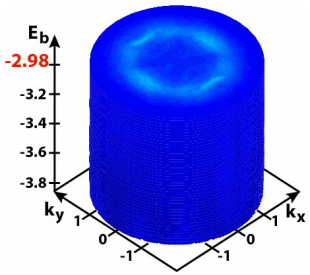
ARPES Intensity ?



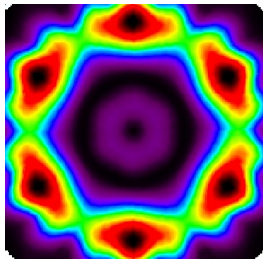
Overview



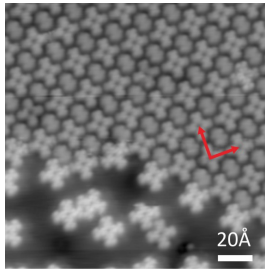
Angle-Resolved Photoemission



PTCDA / Ag(110)

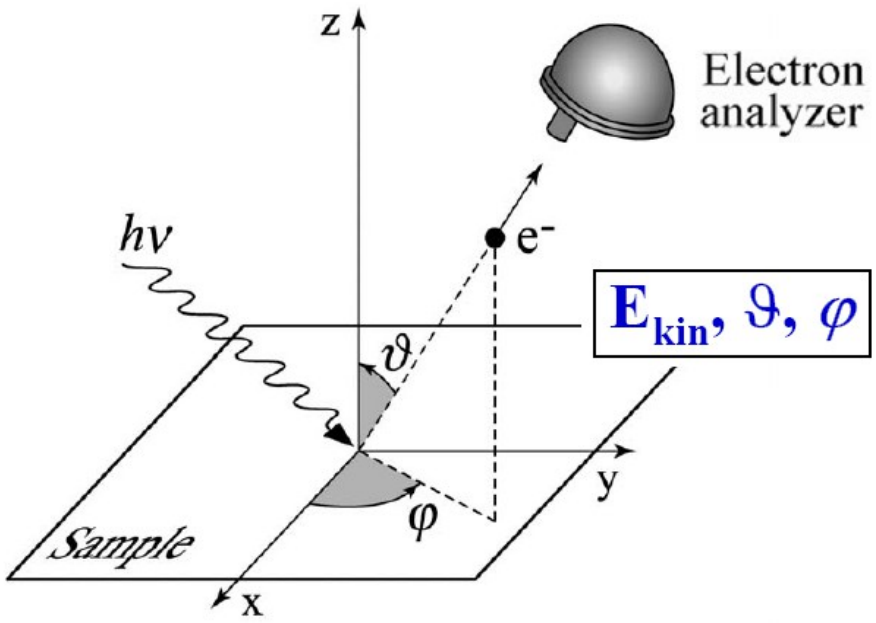


PTCDA / Ag(111)



CuPc + PTCDA / Ag(111)

Photoemission Spectroscopy



$$\mathbf{K} = \mathbf{p}/\hbar = \sqrt{2mE_{kin}}/\hbar$$

$$K_x = \frac{1}{\hbar}\sqrt{2mE_{kin}}\sin\vartheta\cos\varphi$$

$$K_y = \frac{1}{\hbar}\sqrt{2mE_{kin}}\sin\vartheta\sin\varphi$$

$$K_z = \frac{1}{\hbar}\sqrt{2mE_{kin}}\cos\vartheta$$

Vacuum

E_{kin}

$\mathbf{K}$

Conservation laws

$$E_f - E_i = h\nu$$

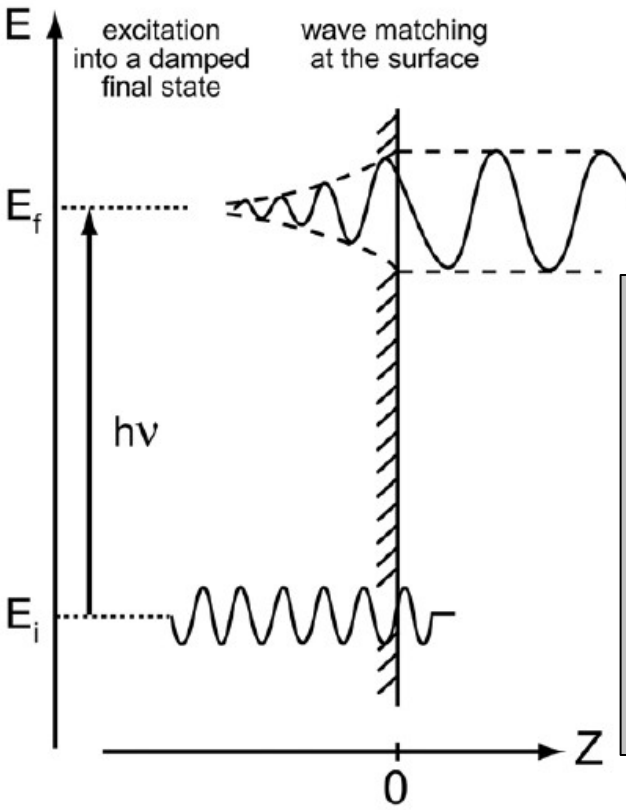
$$\mathbf{k}_f - \mathbf{k}_i = \cancel{\mathbf{k}_{h\nu}}$$

Solid

E_B

$\mathbf{k}$

Photoemission Intensity



$$I(\boldsymbol{k}, \omega) = I_0(\boldsymbol{k}, \nu, \boldsymbol{A}) f(\omega) A(\boldsymbol{k}, \omega)$$

"Matrix-Element-Effects"
(depends on energy and polarization of photon, and on the electron momentum)

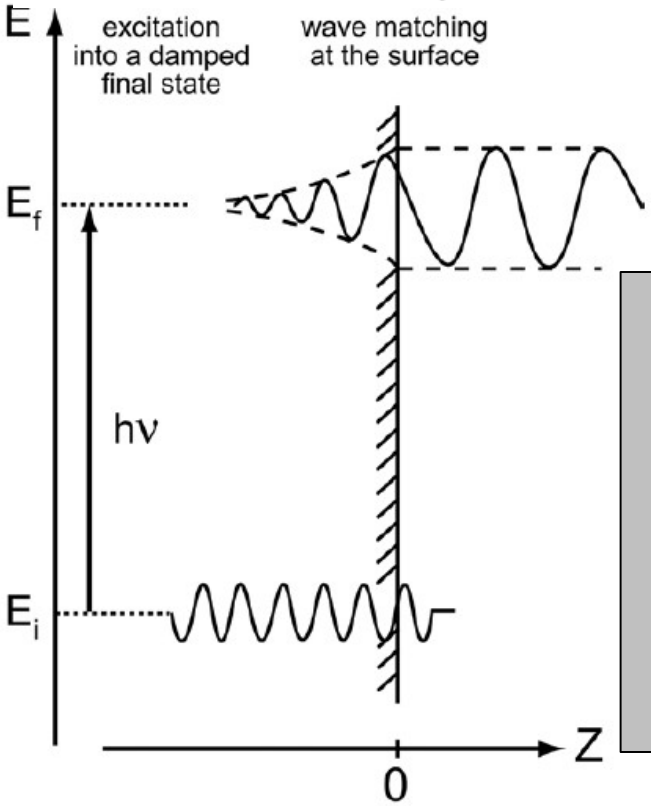
Spectral Function
(energy renormalzation and life time due to many-body effects)

[Hüfner, ''Photoelectron Spectroscopy,'' (Springer, 1995), Damascelli, Phys. Scr., **T109**, 61-74 (2004).

Photoemission Intensity

One Step Model

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



- Independent-Particle Picture
- Sudden Approximation

$$I(\boldsymbol{k}, \omega) = I_0(\boldsymbol{k}, \nu, \boldsymbol{A}) f(\omega) A(\boldsymbol{k}, \omega)$$

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[Hüfner, ''Photoelectron Spectroscopy,'' (Springer, 1995). Damascelli, Phys. Scr., **T109**, 61-74 (2004).

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Photoemission Intensity

One Step Model

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

$$H_{int} = \frac{e}{2mc}(\boldsymbol{A}\cdot\boldsymbol{p} + \boldsymbol{p}\cdot\boldsymbol{A}) = \frac{e}{mc}\boldsymbol{A}\cdot\boldsymbol{p}$$

$$[\boldsymbol{p}, \boldsymbol{A}] = -\mathrm{i}\hbar\nabla\cdot\boldsymbol{A} = 0$$

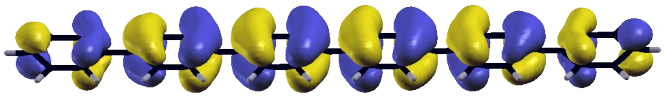
Interaction with the photon field treated as perturbation

Electric dipole approximation
(electric field is constant over atomic dimensions, which holds for the ultra-violet regime)

Photoemission Intensity

One Step Model

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

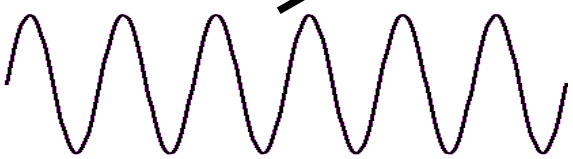


molecular orbital

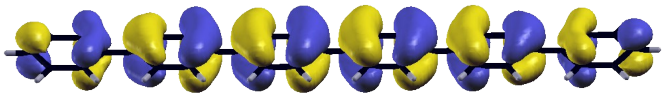
Photoemission Intensity

One Step Model

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



plane wave $e^{i\,\mathbf{k}\,\mathbf{r}}$



molecular orbital

Approximation: final state = plane wave

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

Fourier Transform of Initial State Orbital

[Feibelman and Eastman, *Phys. Rev. B* **10**, 4932 (1974).]

Plane Wave Final State

The **I**ndependent **A**tomic **C**entre approximation (IAC)
[W. D. Grobman, Phys. Rev. B **17**, 4573 (1978).]

$$A(\mathbf{R}, E_{\mathrm{kin}}) = \sum_{\alpha} \sum_{nlm} C_{\alpha,nlm} e^{i\mathbf{k}\mathbf{R}_{\alpha}} \sum_{LM} M^{LM}_{\alpha,nlm}(E_{\mathrm{kin}}) Y_{LM}(\hat{R})$$

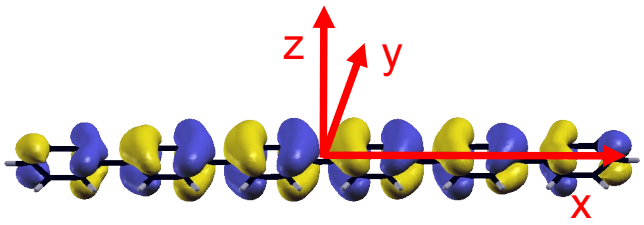
Reduces to the PW final state result, if

- All contributing atomic orbitals are of the same type (e.g. p_z as in π-orbitals)
- The emission direction is close to the polarization vector of the incoming photon
- The molecule consists of only light atoms (C, N, O) with small scattering cross sections

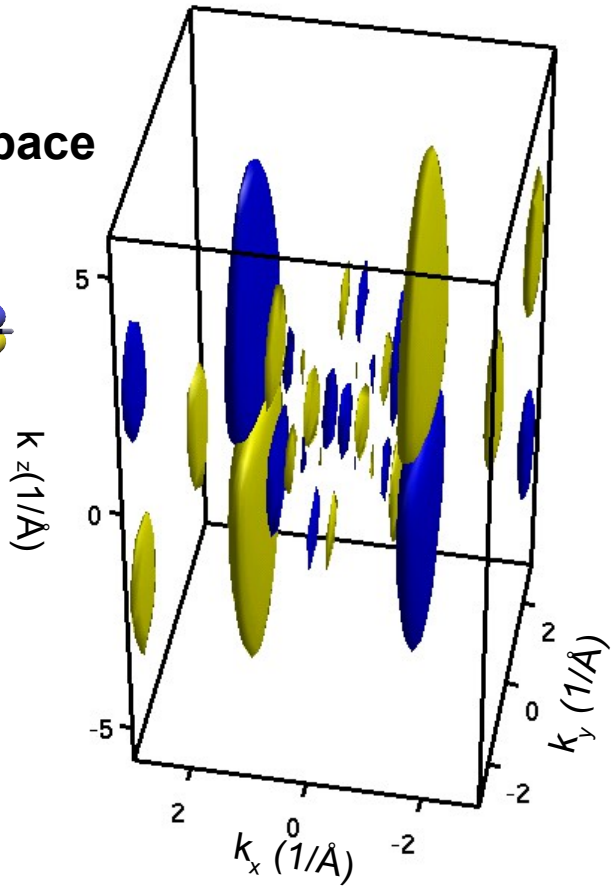
[Goldberg et al, Solid State Commun. **28**, 459-463 (1978),
Puschnig et al., supporting online material to Science **326**, 702 (2009)]

Fourier Transform of an Orbital

Molecular Orbital in Real Space

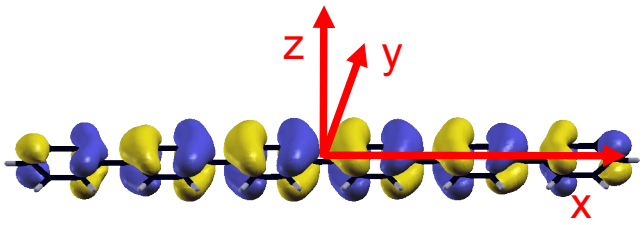


Calculation of the Fourier Transform

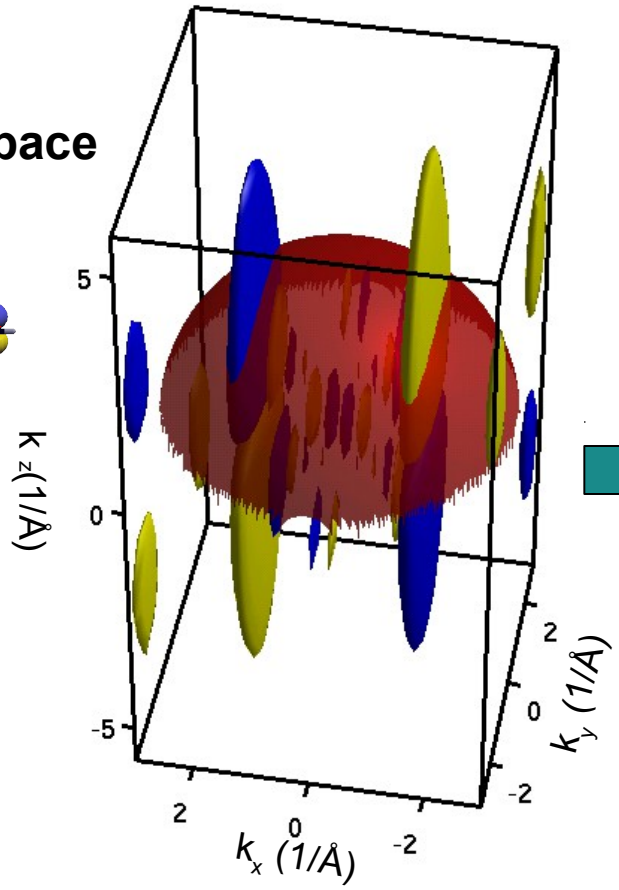


Fourier Transform of an Orbital

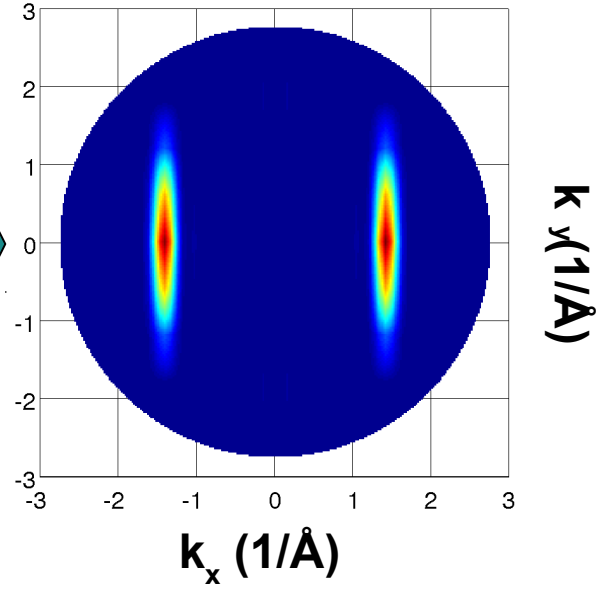
Molecular Orbital in Real Space



Calculation of the Fourier Transform

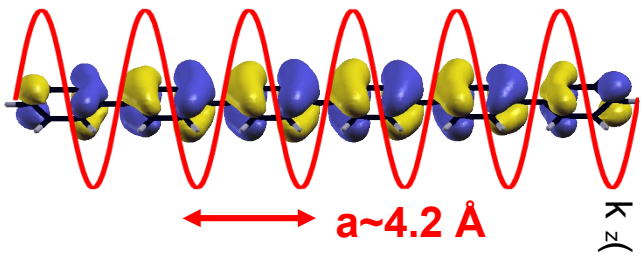


Hemispherical Cut Through 3D Fourier Transform

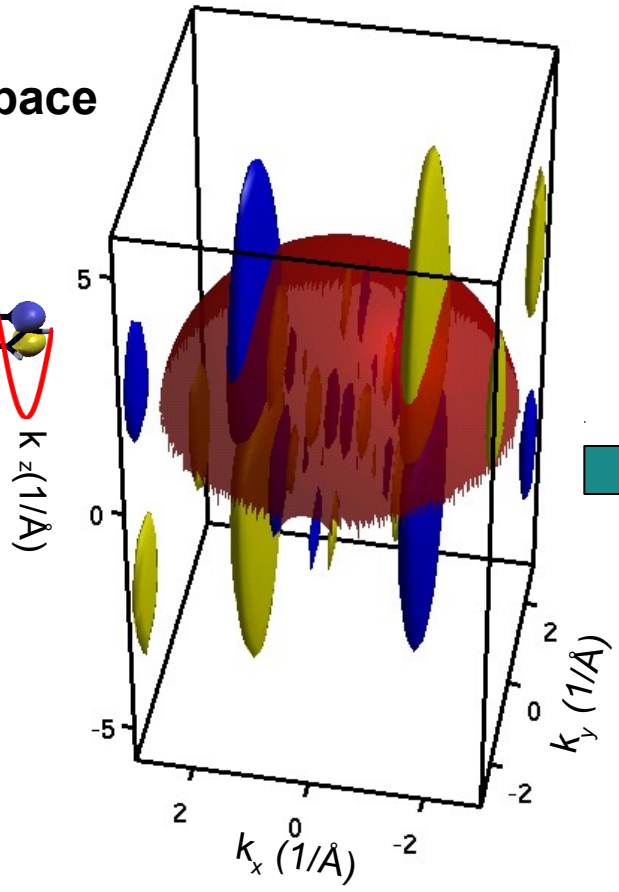


Fourier Transform of an Orbital

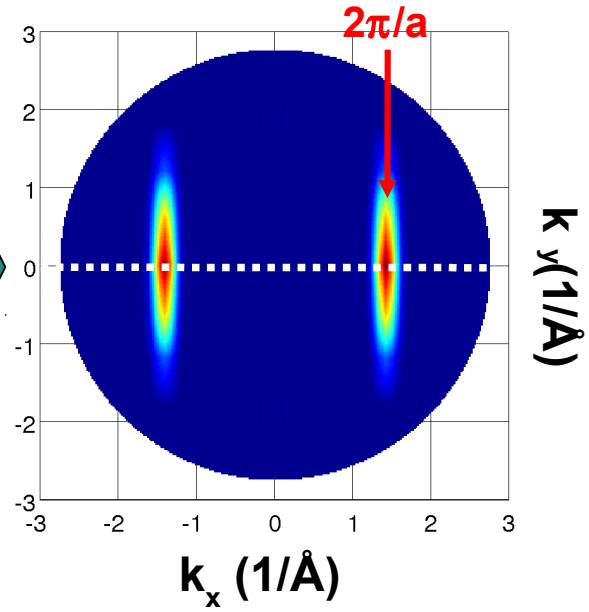
Molecular Orbital in Real Space



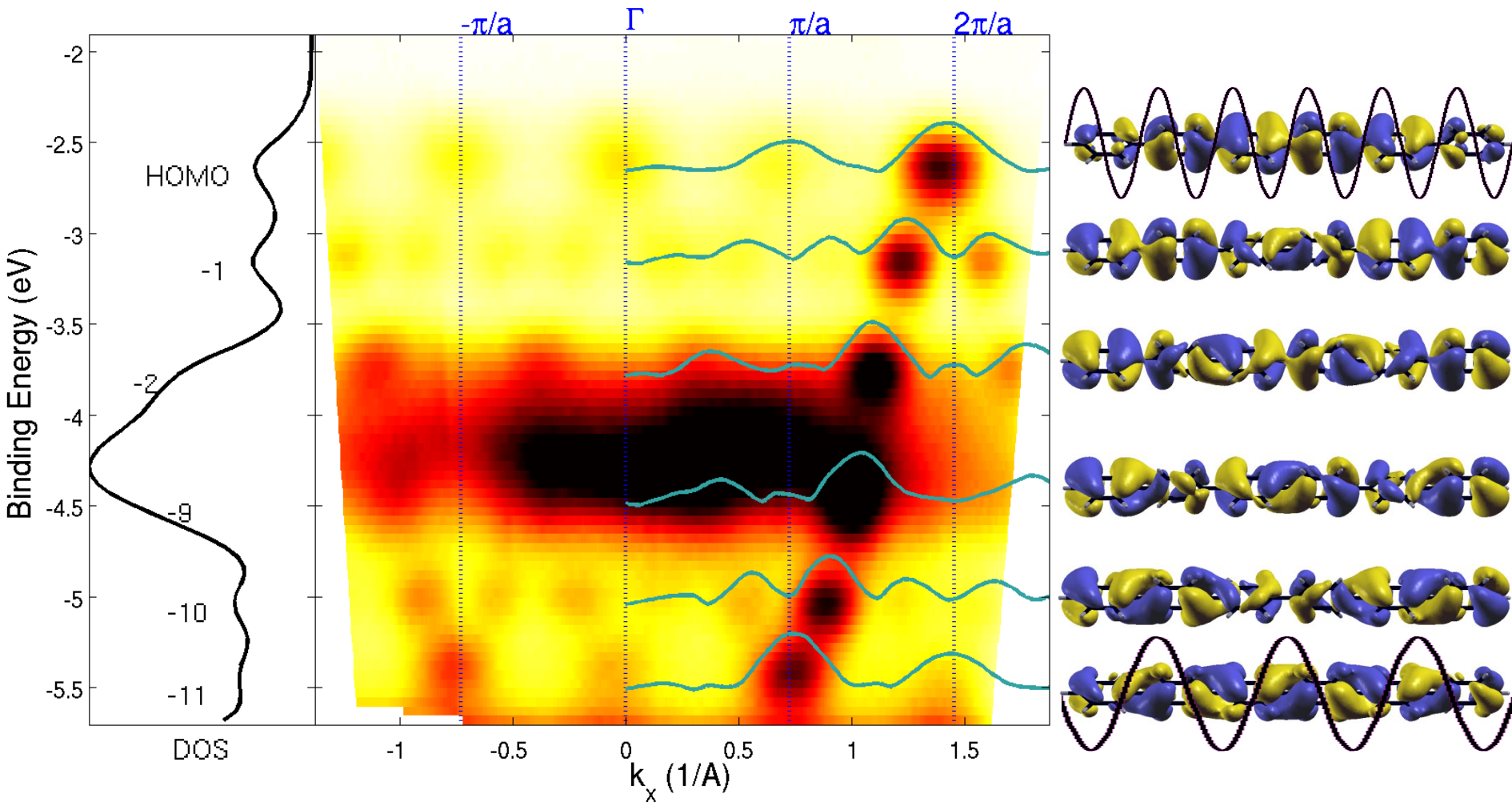
Calculation of the Fourier Transform



Hemispherical Cut Through 3D Fourier Transform

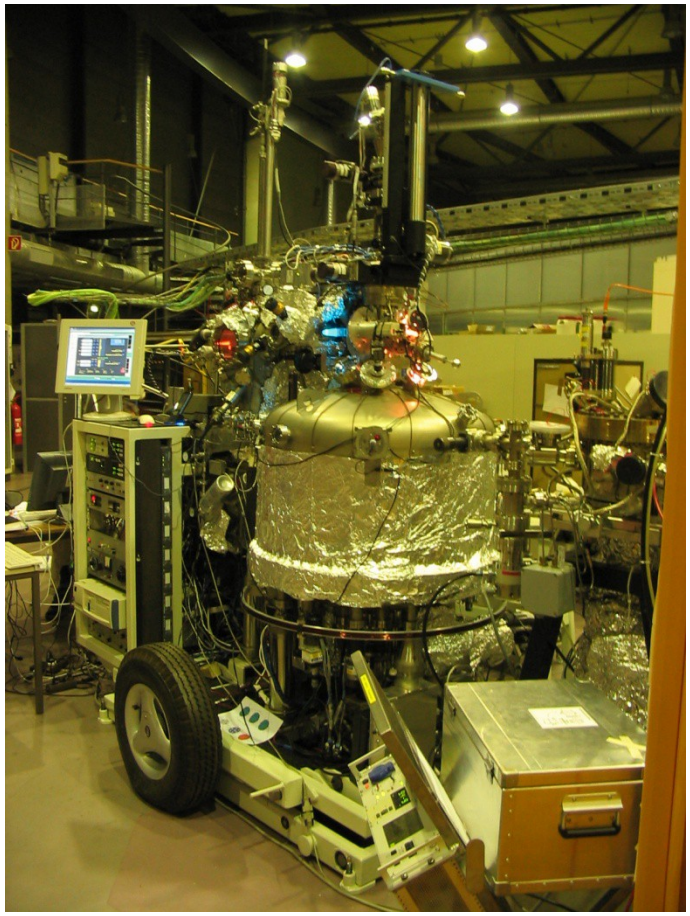


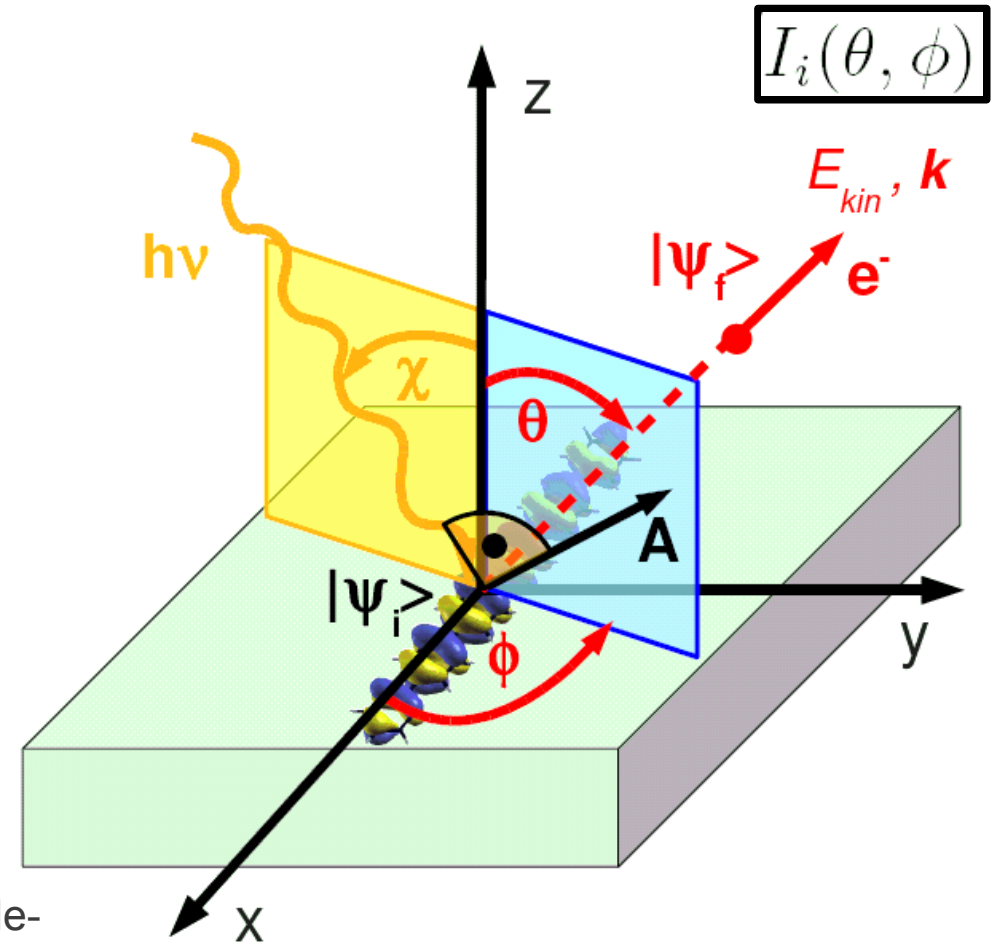
ARPES of *p*-Sexiphenyl



G. Koller et al., *Science* ***317****, 351 (2007).*

Toroidal Electron Energy Analyzer

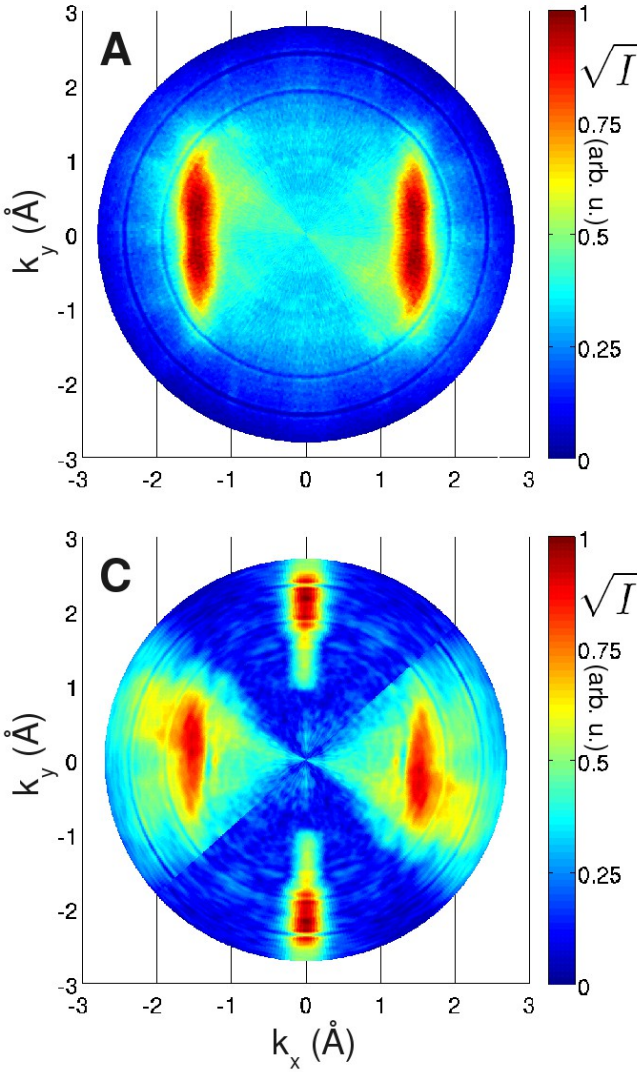


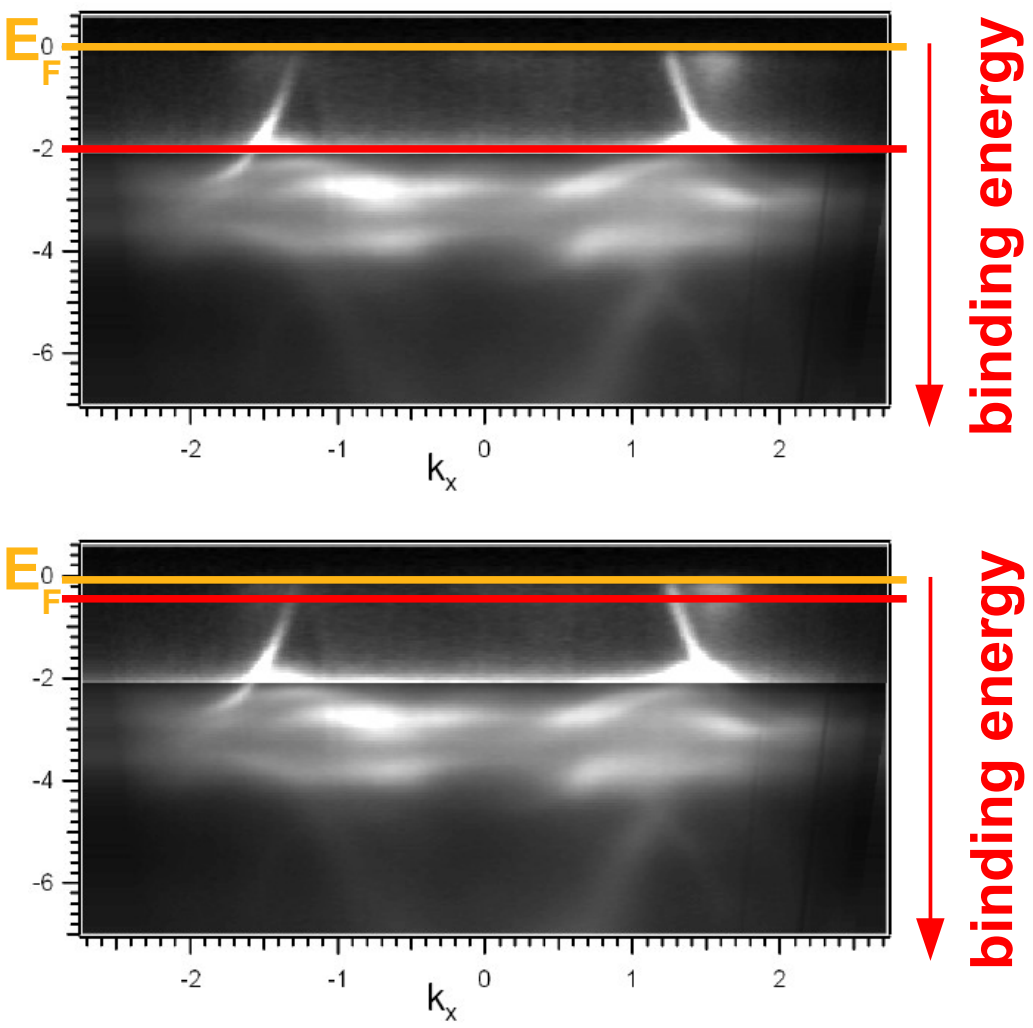


The Toroidal Electron Spectrometer for Angle-Resolved Photoelectron Spectroscopy with Synchrotron Radiation at BESSY II

Sexiphenyl Monolayer on Cu(110)

2D-Momentum Maps

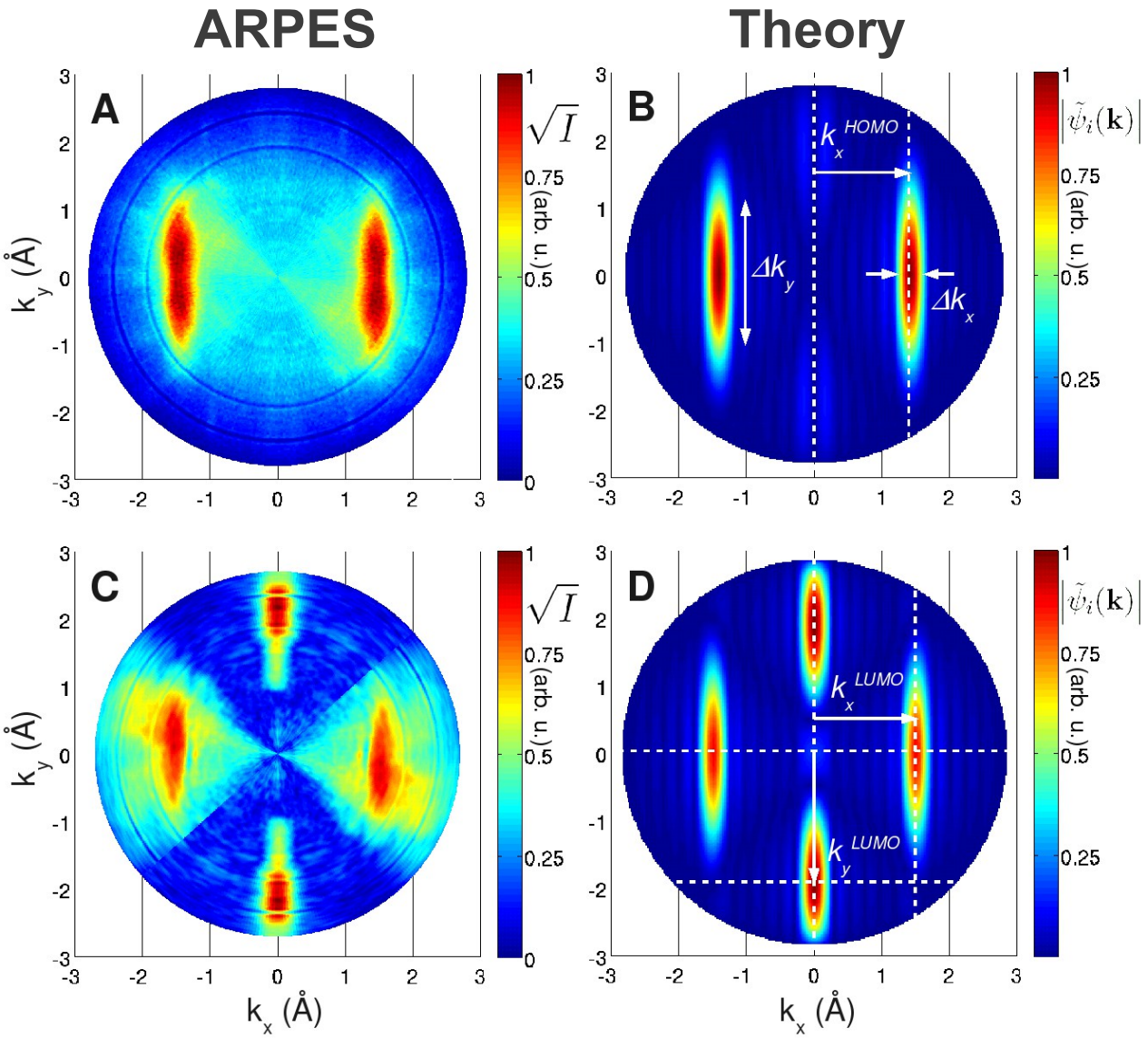




2D-Momentum Maps

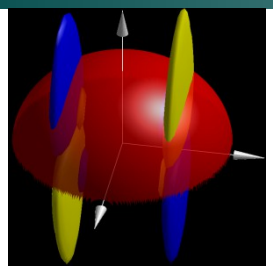
HOMO

Filled LUMO

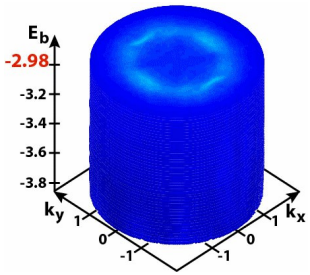


Puschnig et al.,
Science **326**, 702 (2009).

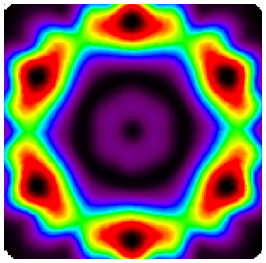
Overview



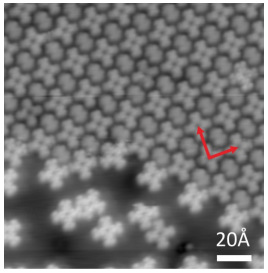
Angle-Resolved Photoemission



PTCDA / Ag(110)

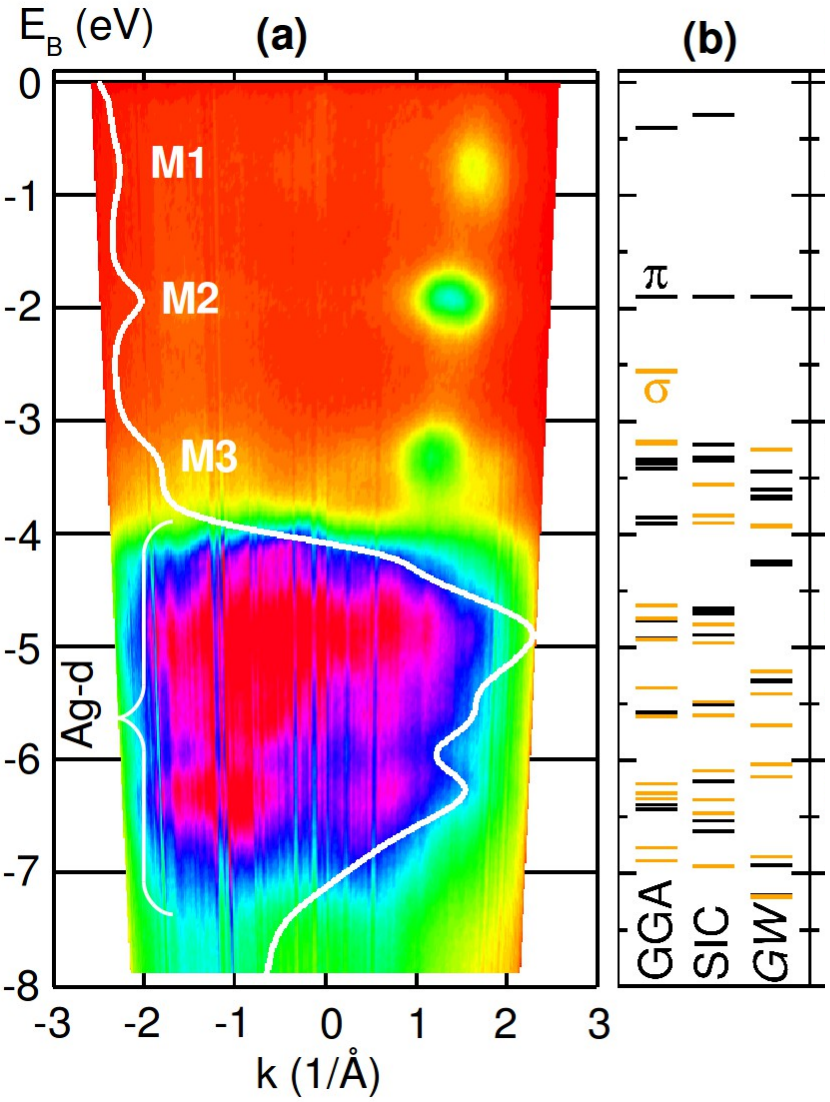


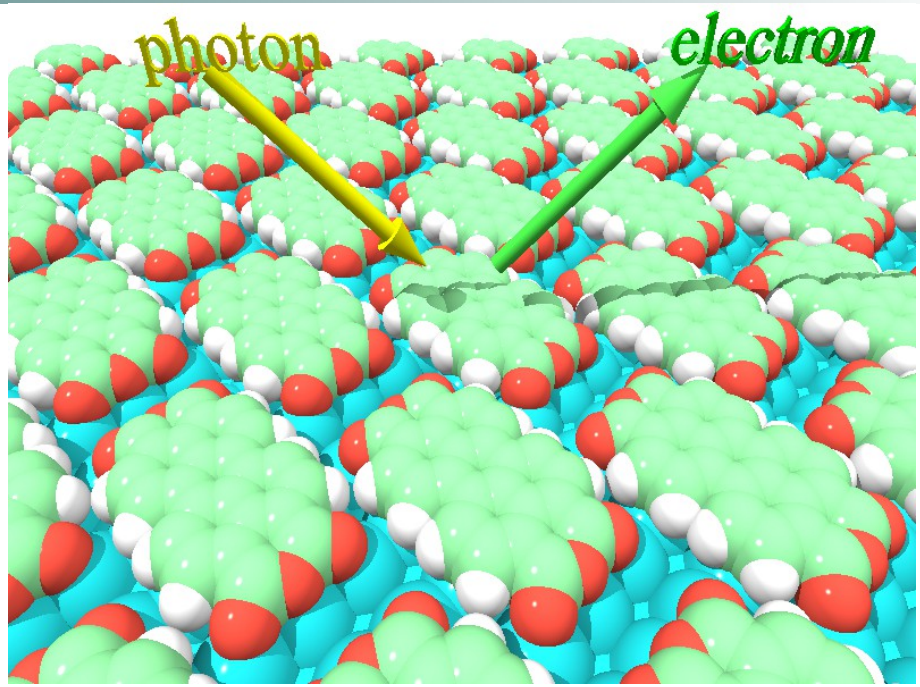
PTCDA / Ag(111)

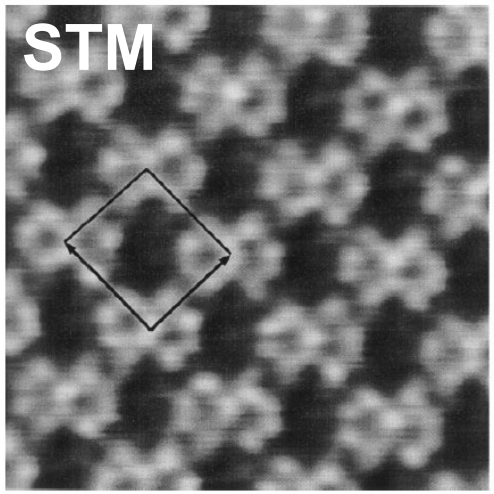


CuPc + PTCDA / Ag(111)

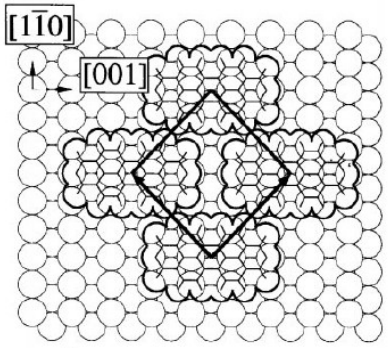
ARPES of PTCDA / Ag(110)







Glöckler et al,
Surf. Sci. **405**, 1-20 (1998).

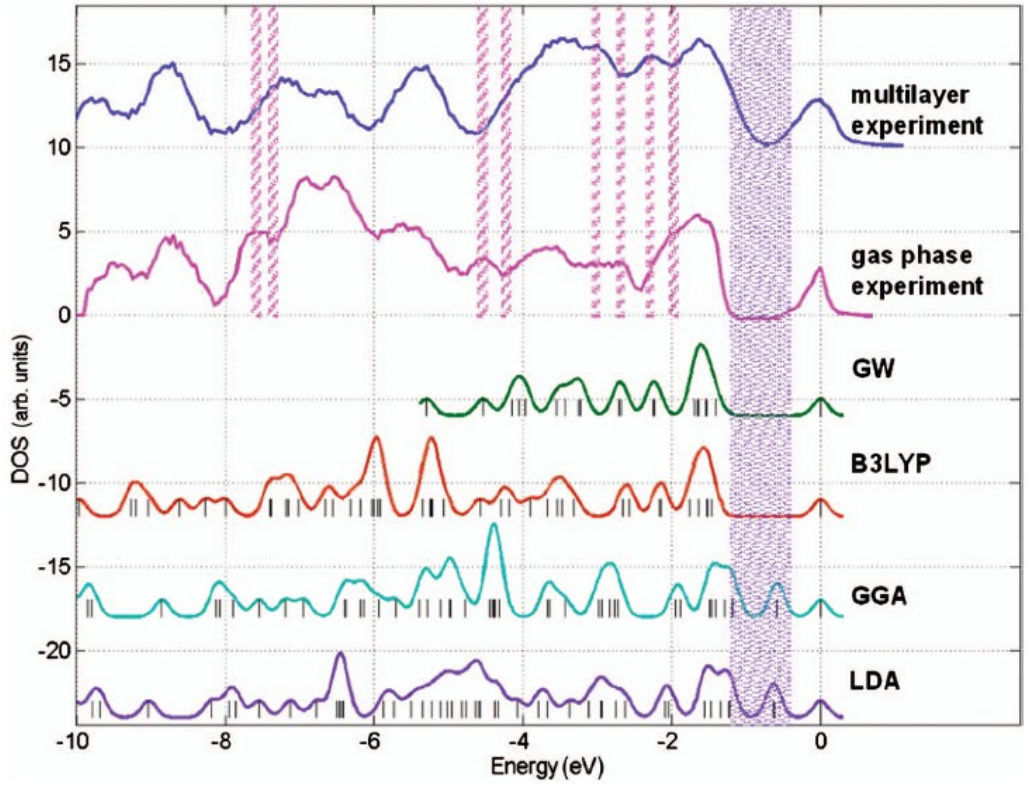


Identifying Orbitals

PHYSICAL REVIEW B 73, 195208 (2006)

Valence electronic structure of gas-phase 3,4,9,10-perylene tetracarboxylic acid dianhydride: Experiment and theory

Navit Dori,[1,*] Mahesh Menon,[1,*] Lennart Kilian,[2] Moritz Sokolowski,[2,3] Leeor Kronik,[1,†] and Eberhard Umbach[2]

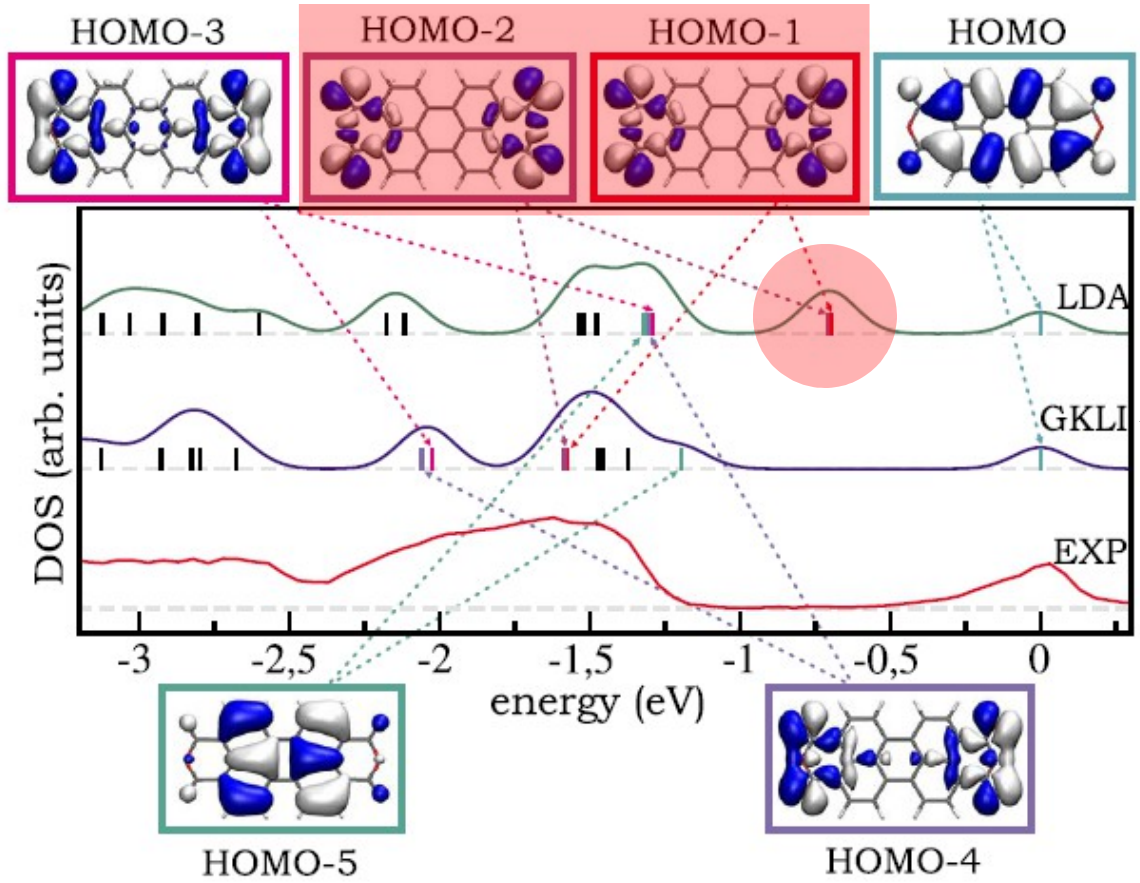


Identifying Orbitals

PHYSICAL REVIEW B **79**, 201205(R) (2009)

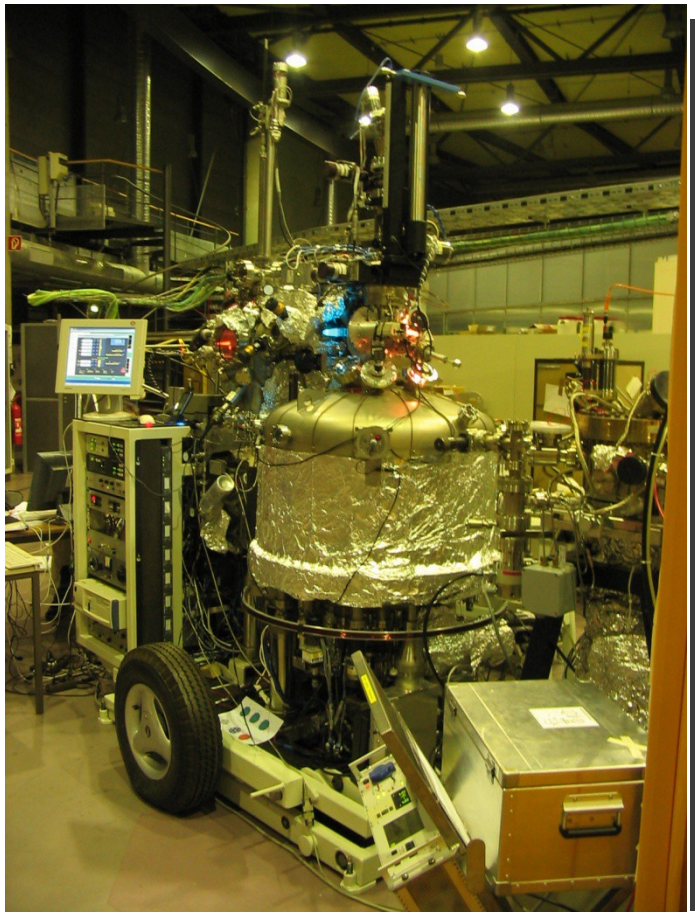
When to trust photoelectron spectra from Kohn-Sham eigenvalues: The case of organic semiconductors

T. Körzdörfer and S. Kümmel N. Marom and L. Kronik



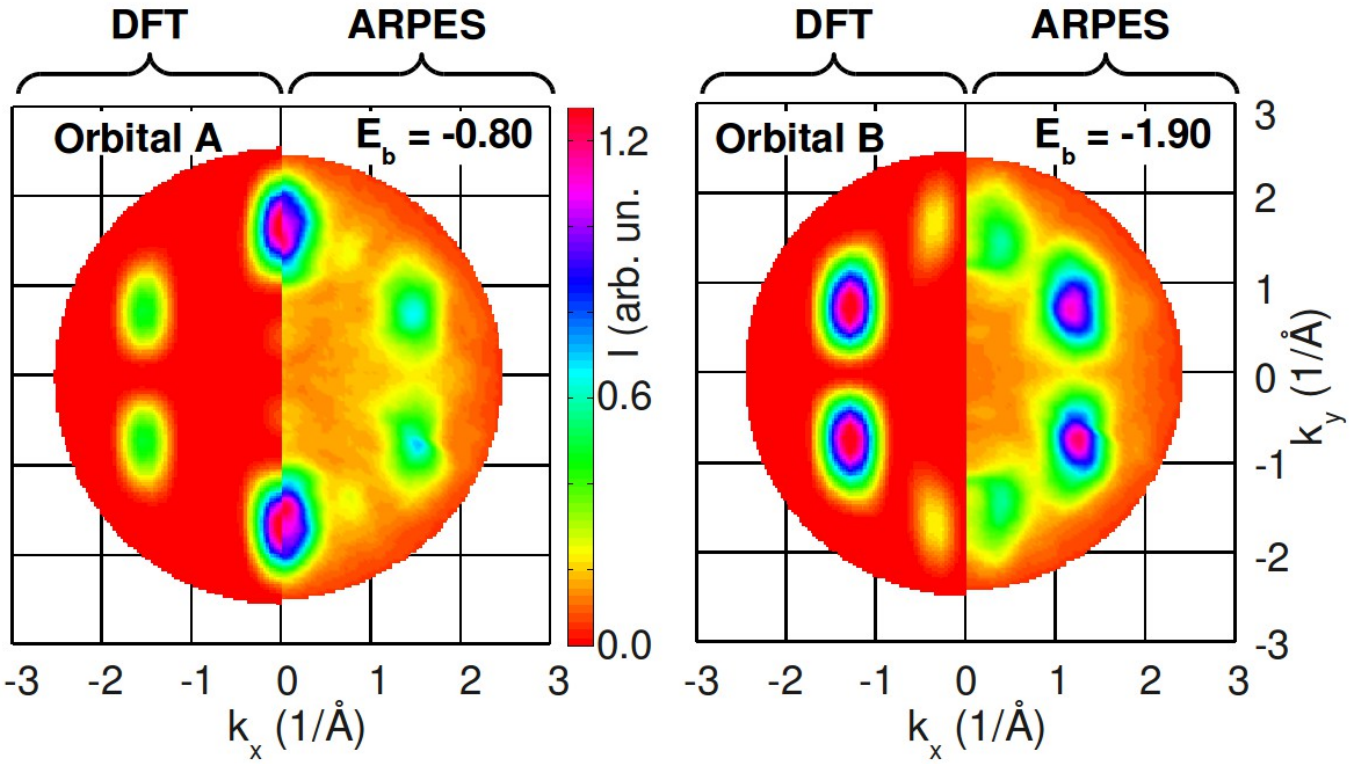
Self-interaction corrected functional

Toroidal Electron Energy Analyzer



The Toroidal Electron Spectrometer for Angle-Resolved Photoelectron Spectroscopy with Synchrotron Radiation at BESSY II

HOMO and Filled LUMO



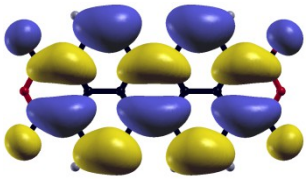
M1= FLUMO

M2= HOMO

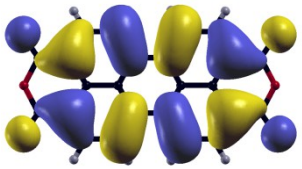
Puschnig et al. PRB **84**, 235427 (2011), Ziroff et al., PRL **104**, 233004 (2010).

What is the nature of M3?

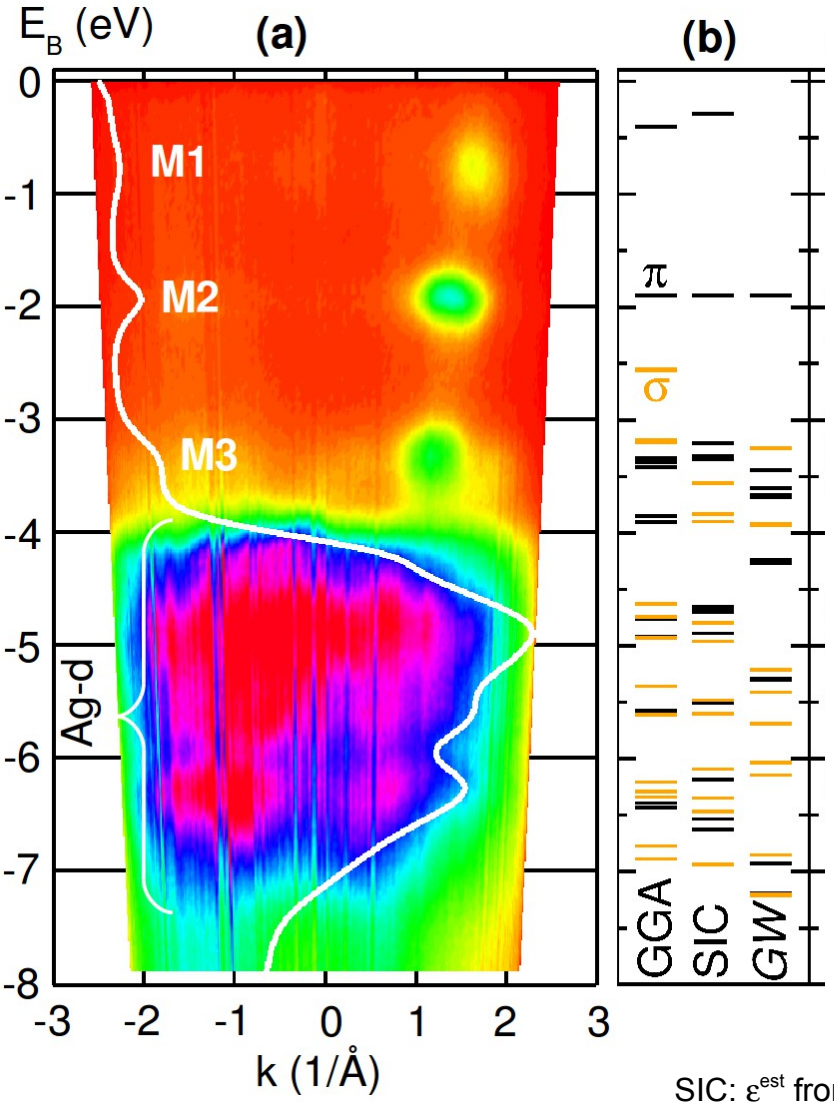
M1= FLUMO



M2= HOMO



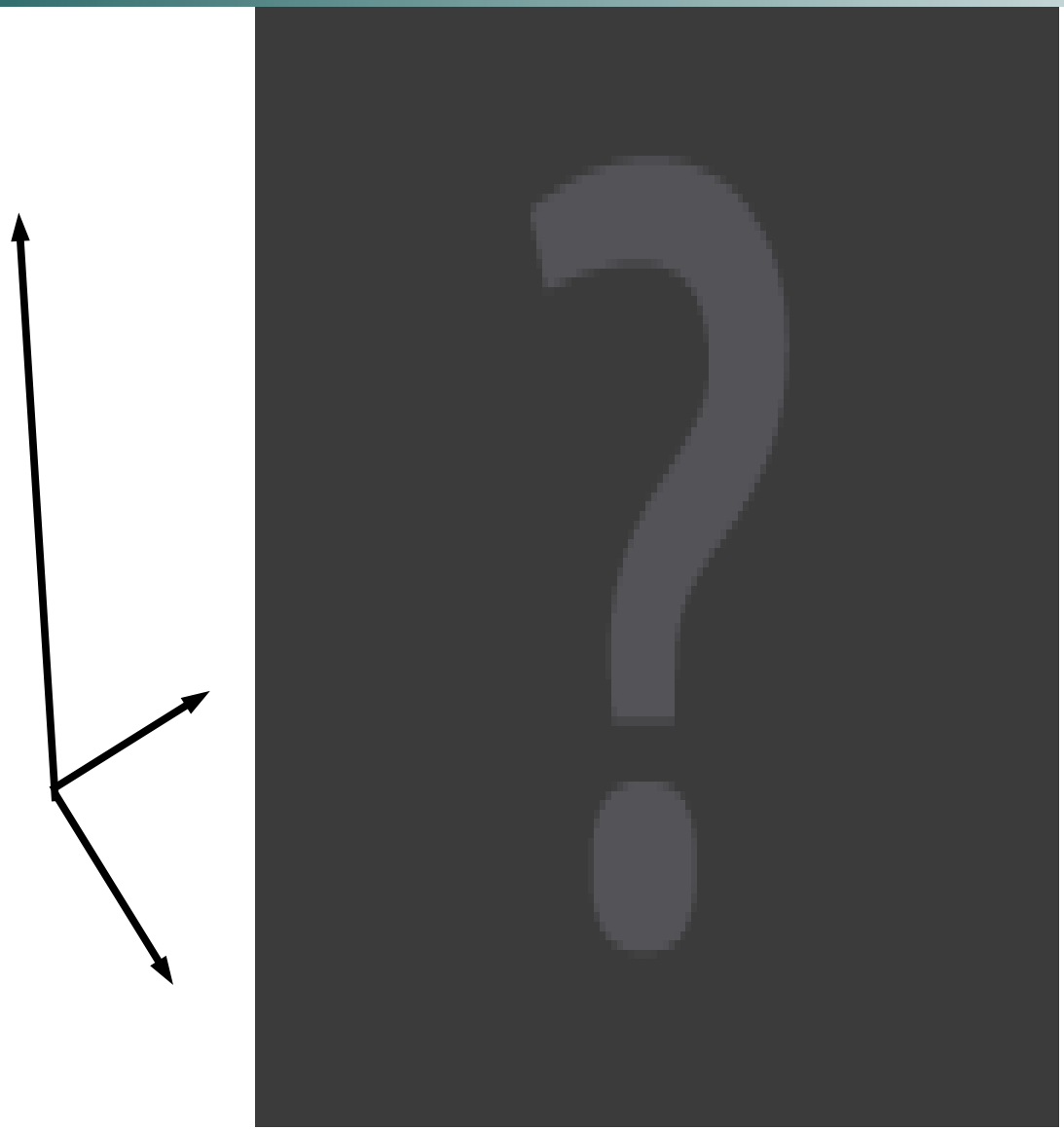
?



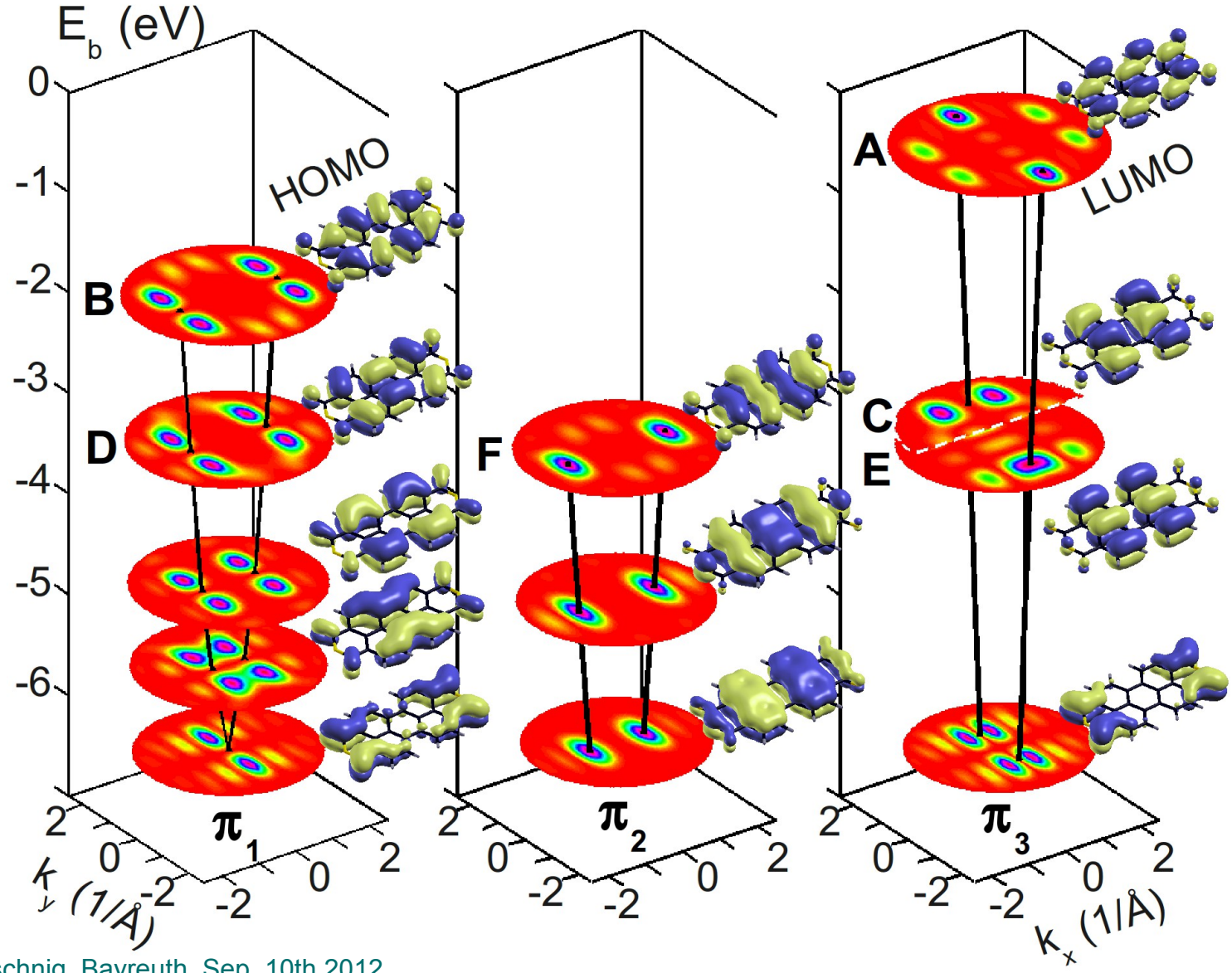
HOMO aligned with experiment

SIC: ε^{est} from Eq. (2) PRB 79, 201205 (R)
GW: G_0W_0@GGA

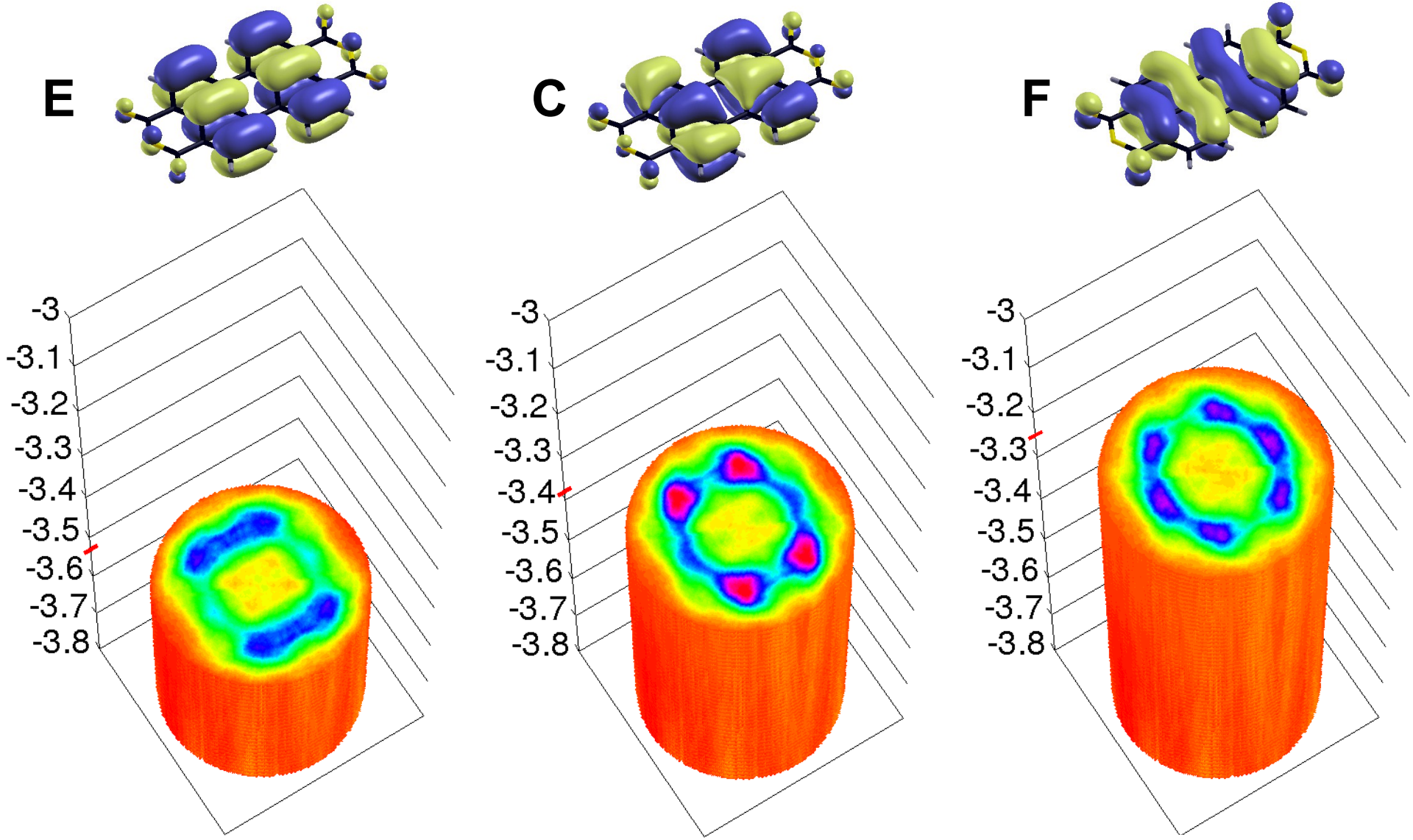
ARPES Data-Cube



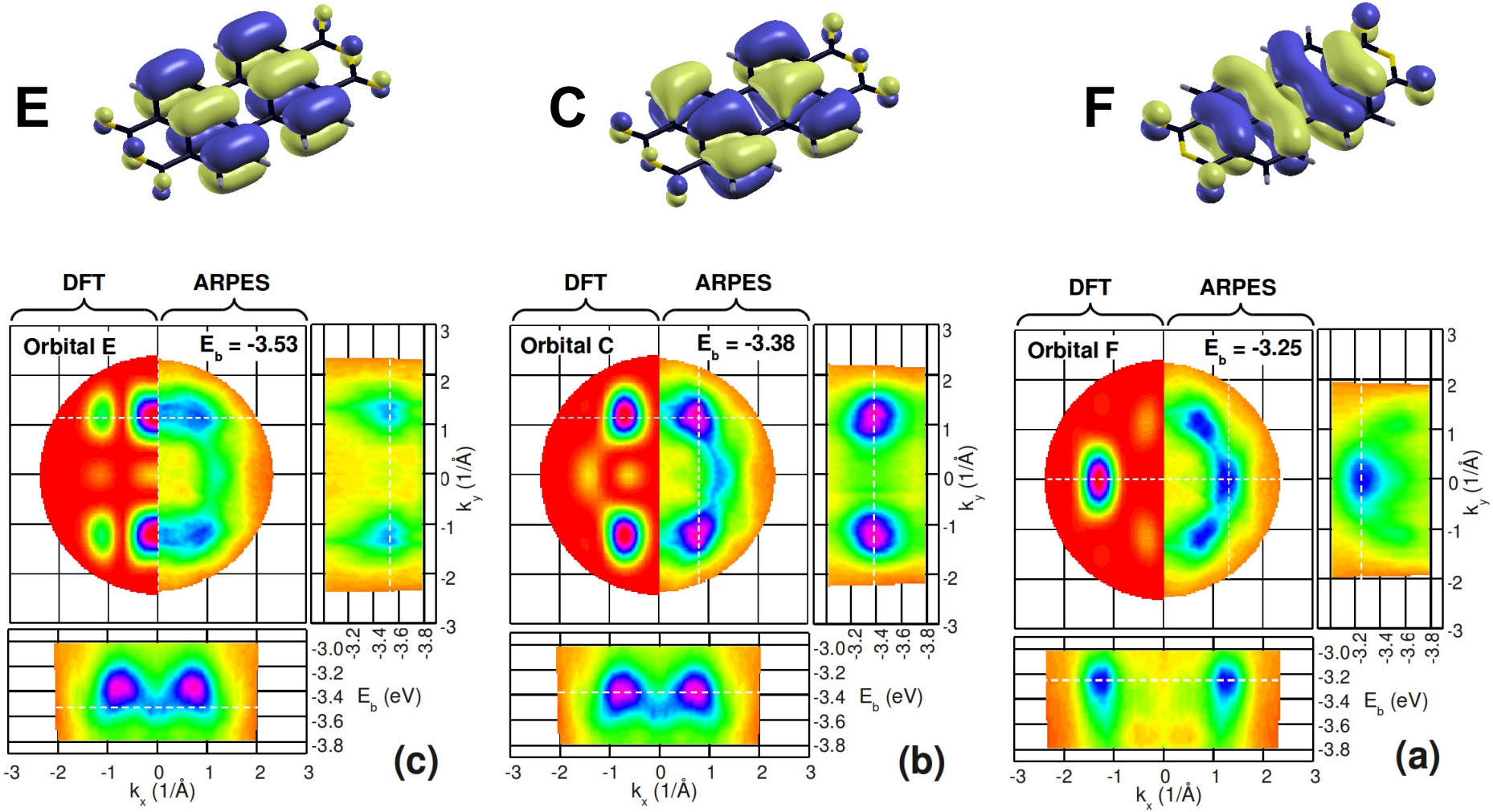
Pi-„bands“ of PTCDA



What is the Origin of M3?

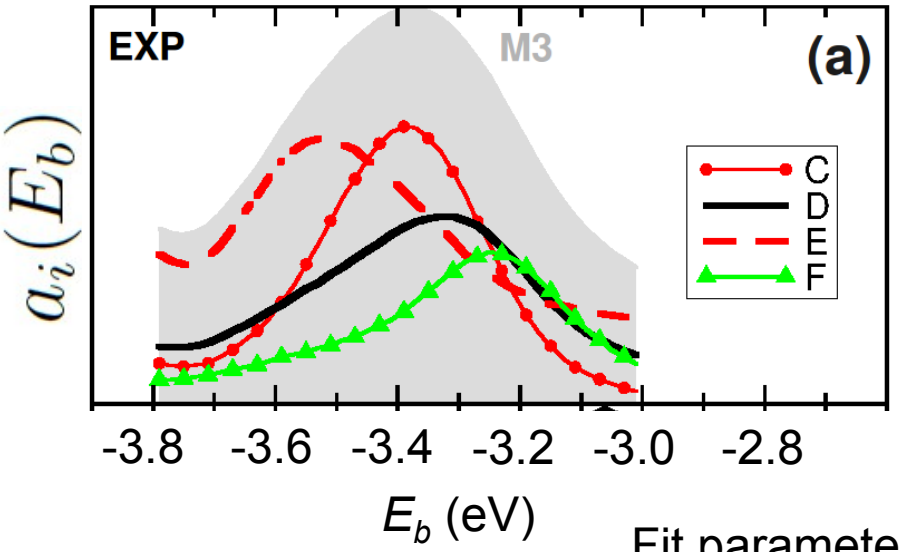


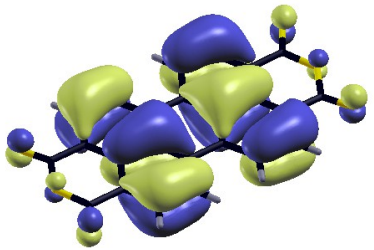
What is the Origin of M3?

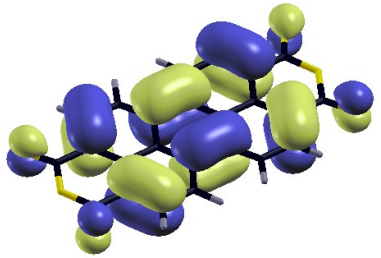


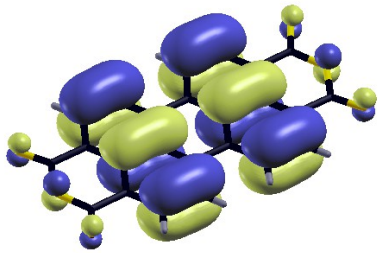
Puschnig et al. PRB **84**, 235427 (2011), see also: Dauth et al., PRL **107**, 193002 (2011).

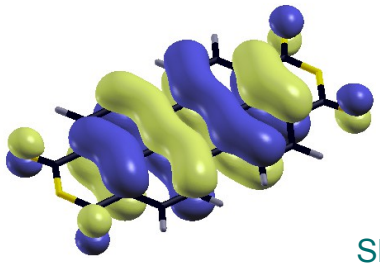
Projected DOS from ARPES!











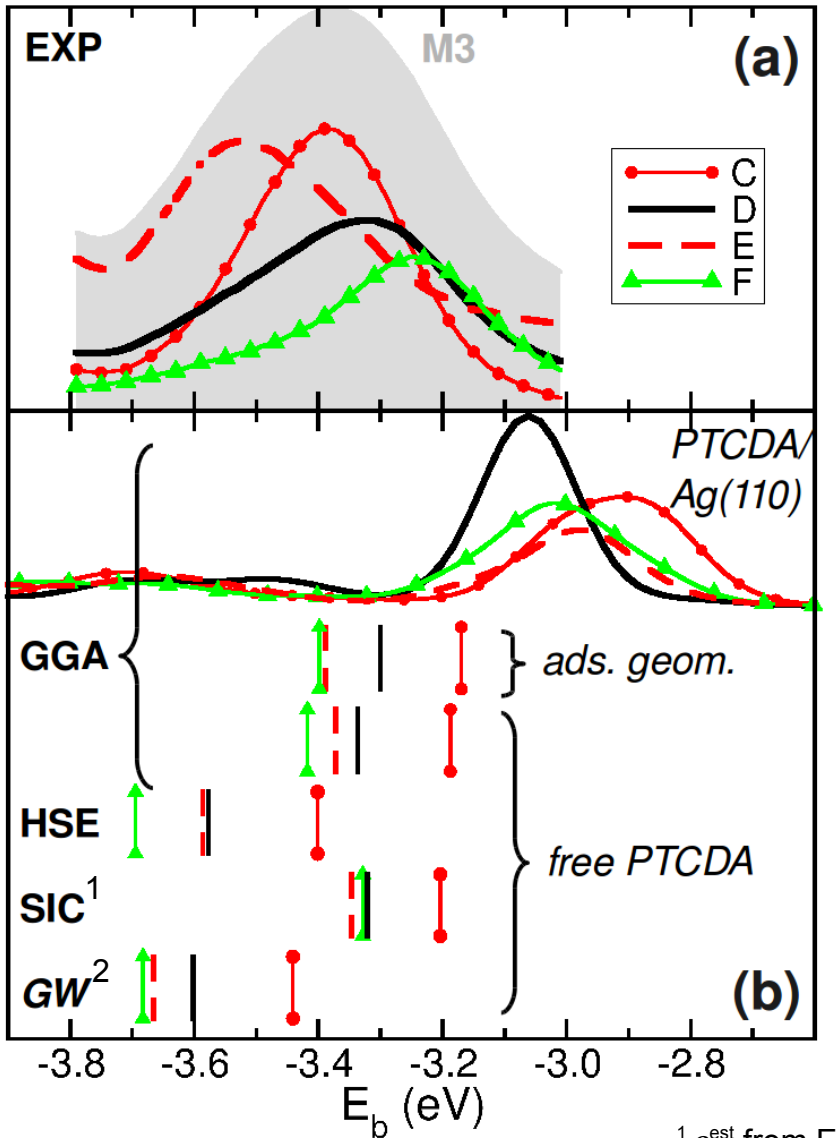
Fit parameters = PDOS

calculated orbitals

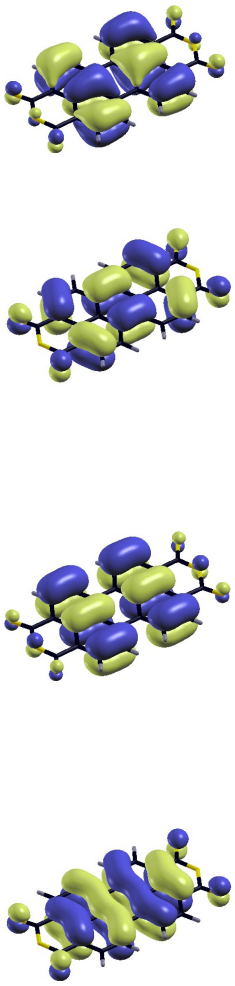
$$\chi^2 = \int dk_x dk_y \left[I(E_b, k_x, k_y) - \sum_i a_i(E_b)\phi_i(k_x, k_y) \right]^2$$

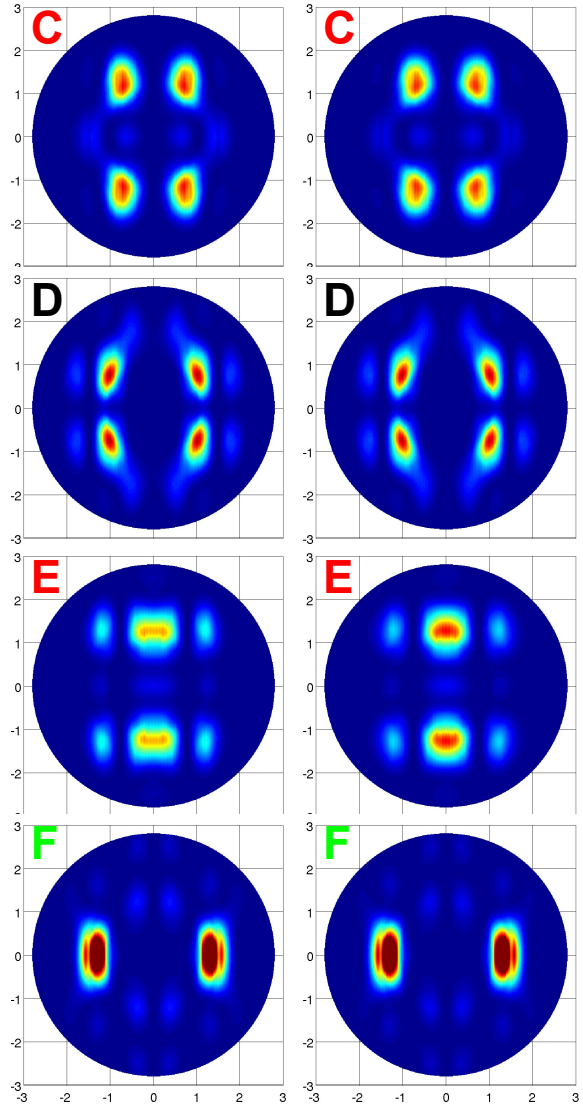
measured photemission data cube

Projected DOS from ARPES!



orbital energies / projected DOS (arb. units)

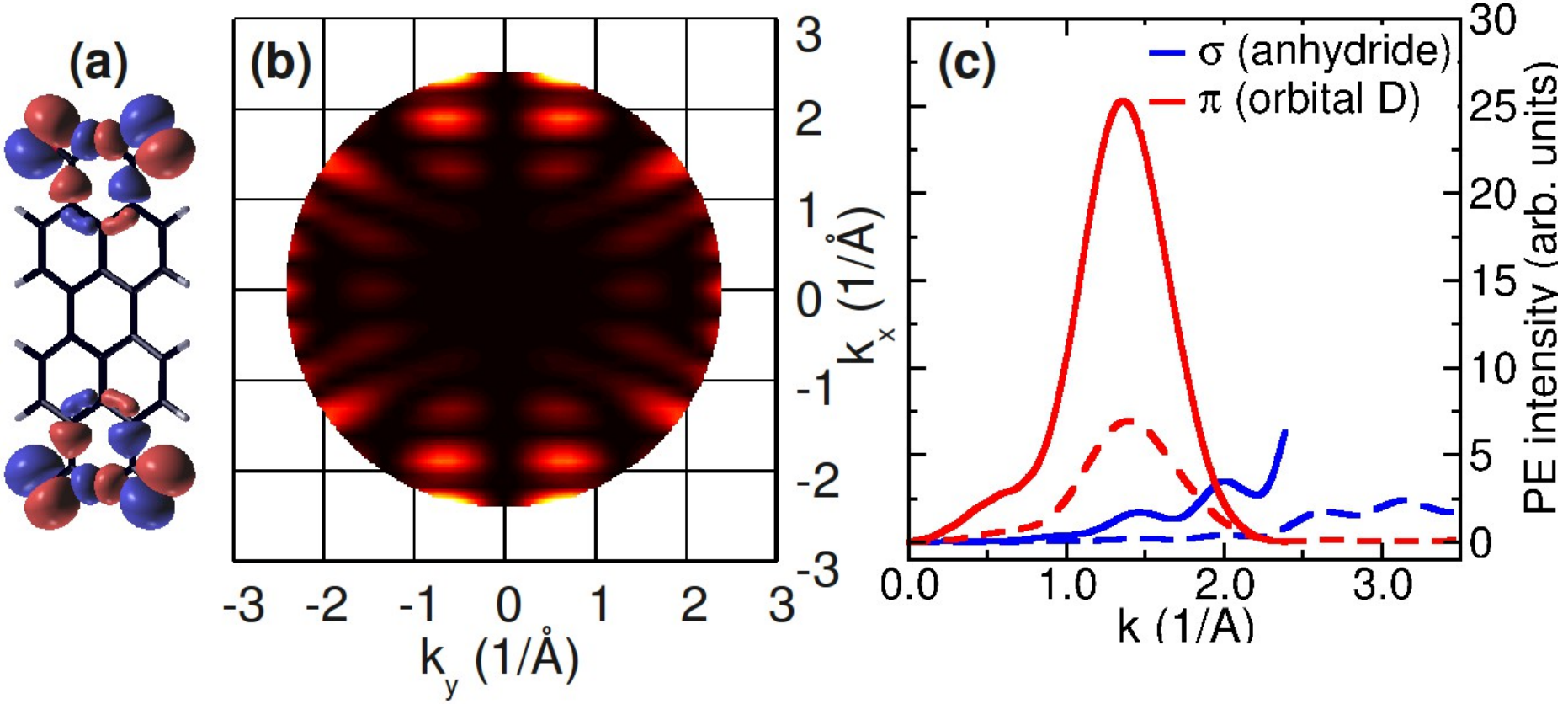




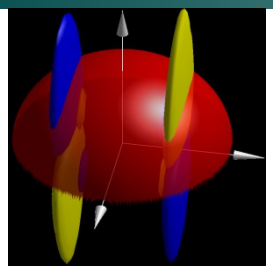
GGA HSE

[1] ε^{est} from Eq. (2) PRB 79, 201205 (R)
[2] G_0W_0@GGA

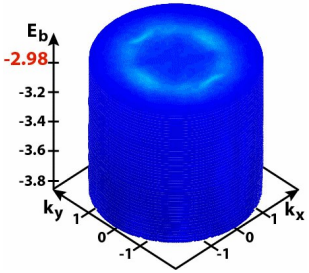
What about Sigma Orbitals?



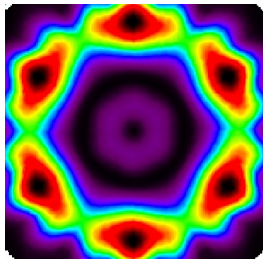
Overview



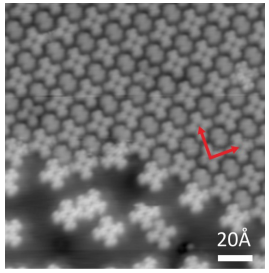
Angle-Resolved Photoemission



PTCDA / Ag(110)



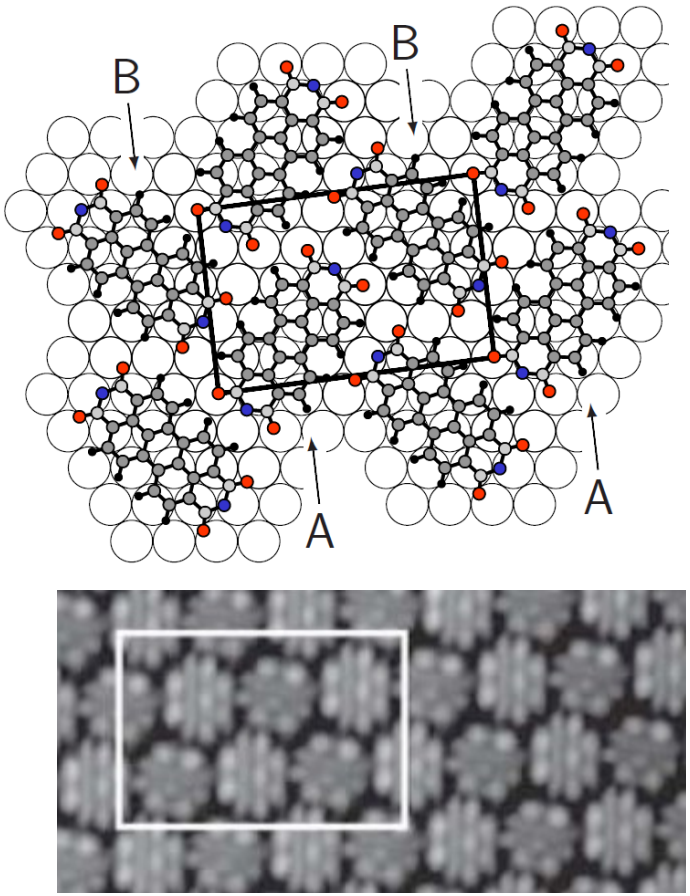
PTCDA / Ag(111)



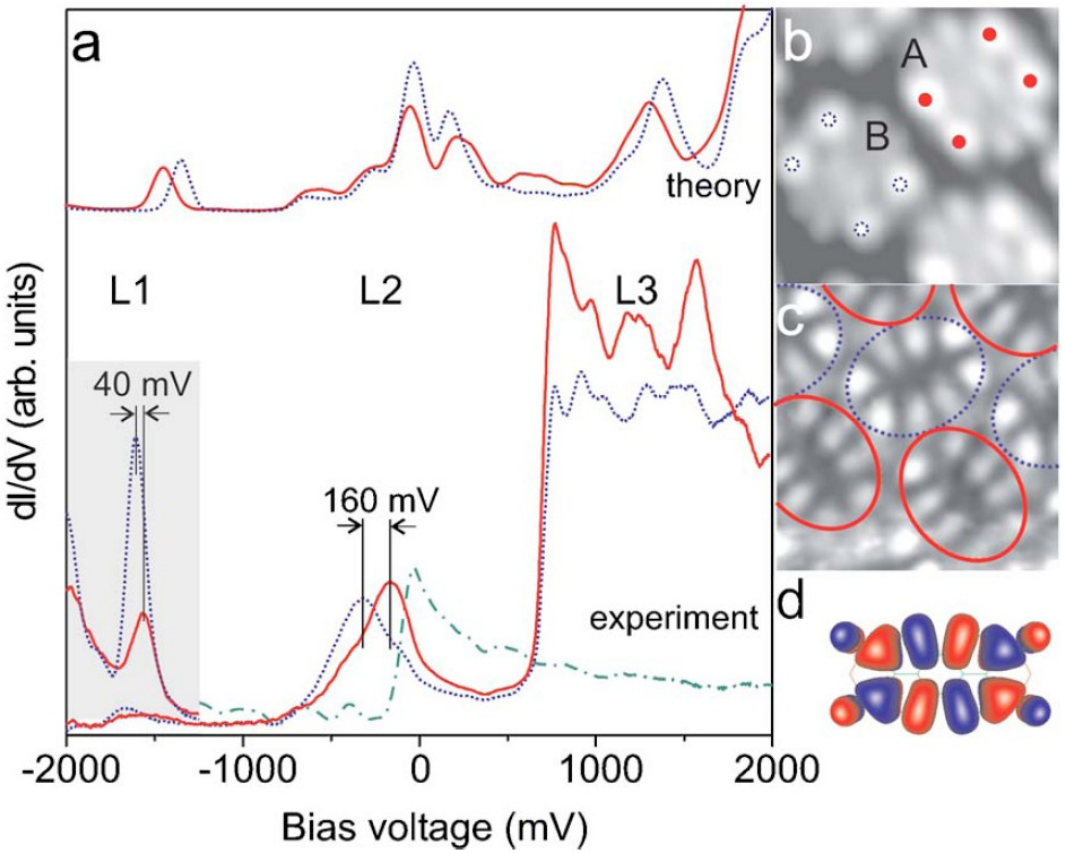
CuPc + PTCDA / Ag(111)

PTCDA/Ag(111)

Structure: 2 molecules / cell



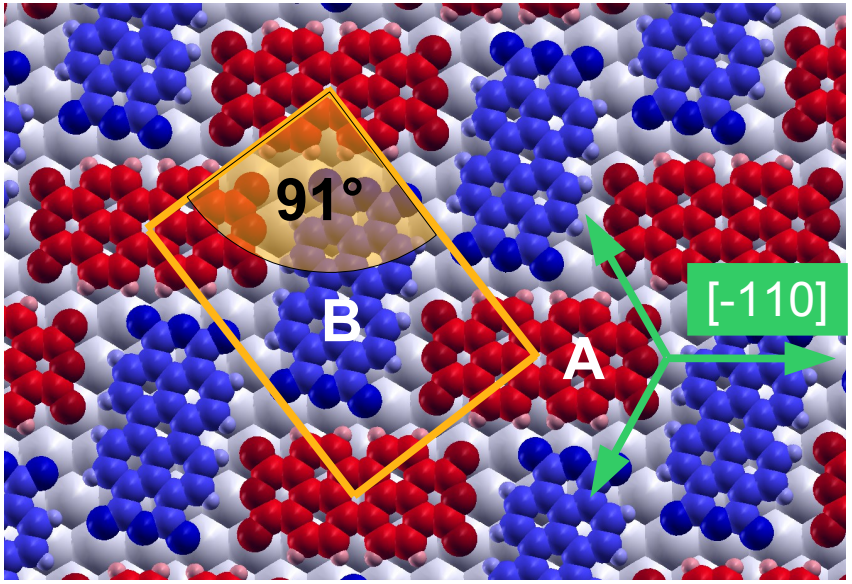
Local Spectroscopy: STS

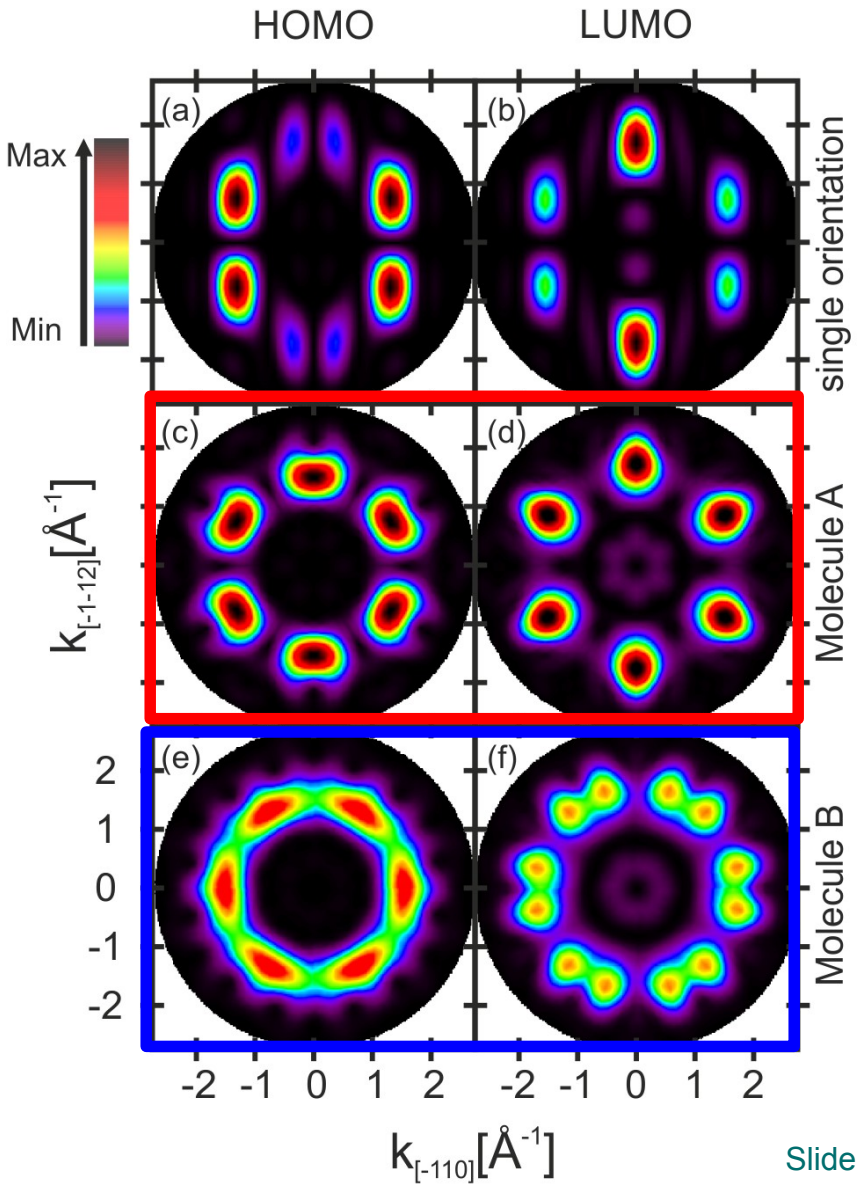


Kraft et al, PRB **74**, 041402(R) (2006); Rohlfing, Temirov, Tautz, PRB **76**, 115421 (2007)

Rotational and Mirror Domains

ARPES spatially averages over a large Sample area
→ 3-fold symmetry of (111) surface
→ Molecule A has 3 orientations
→ Molecule B has 3 x 2 orientations





Theory vs. Experiment

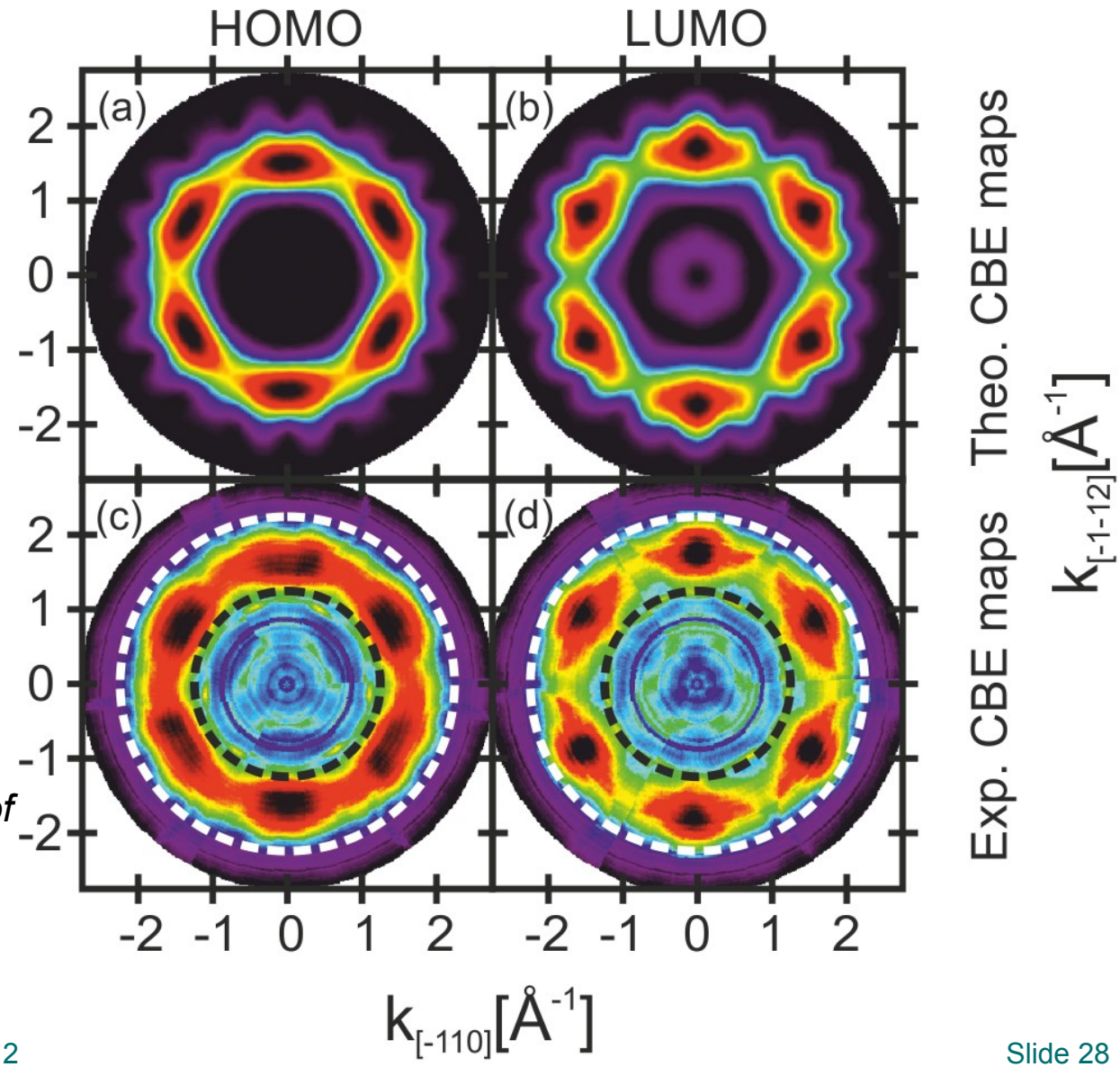
Theory:

Molecule A + Molecule B

Experiment:

Monolayer PTCDA/Ag(111)

Experimental data by courtesy of Benjamin Stadtmüller (Jülich) Submitted to Eur. Phys. Lett.



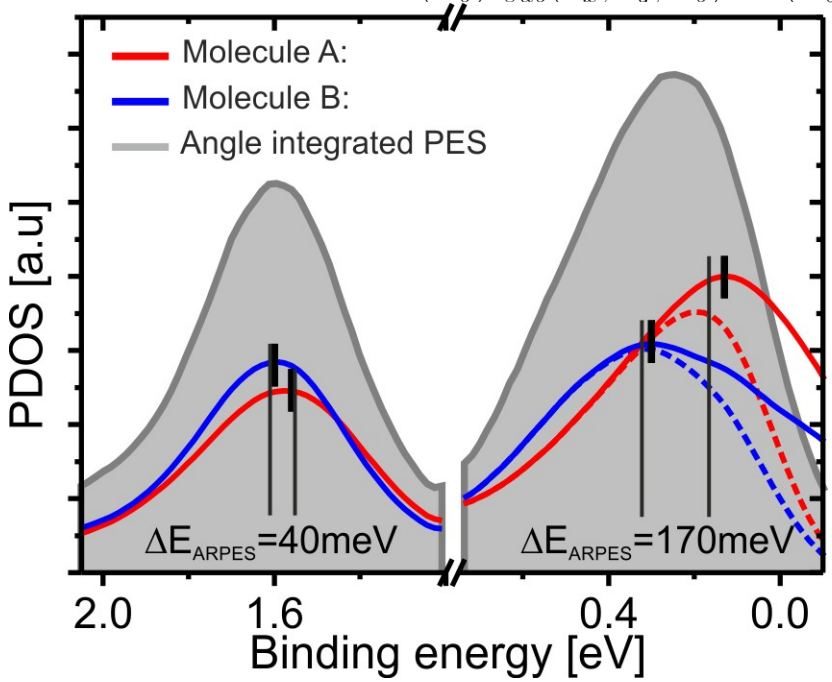
Photoemission vs. Scanning Probe

ARPES Tomography

Least-squares fit: $S = \sum_{k=1}^{M} w_k \left[I(k, E_b) - F(k, E_b) \right]^2$

$$F(k_x, k_y, E_b) = \sum_i a_i(E_b)\Phi_i(k_x, k_y) + b(E_b) I_{sub}(k_x, k_u, E_b) + c(E_b)$$

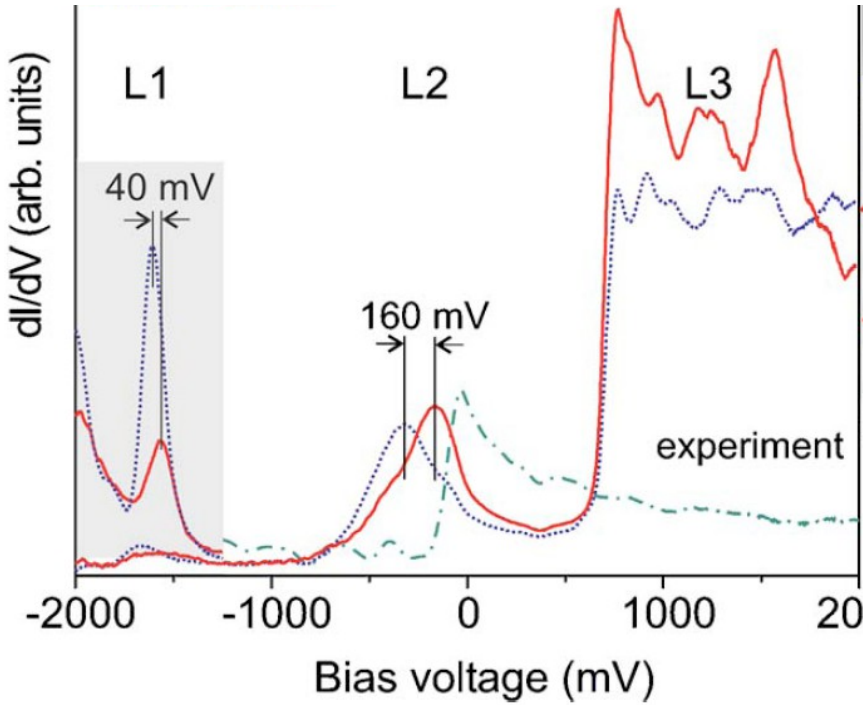
Mol. A / B



B. Stadtmüller, submitted to European Physics Letters

Scanning Tunneling Spectroscopy (STS)

Kraft et al, PRB **74**, 041402(R) (2006)



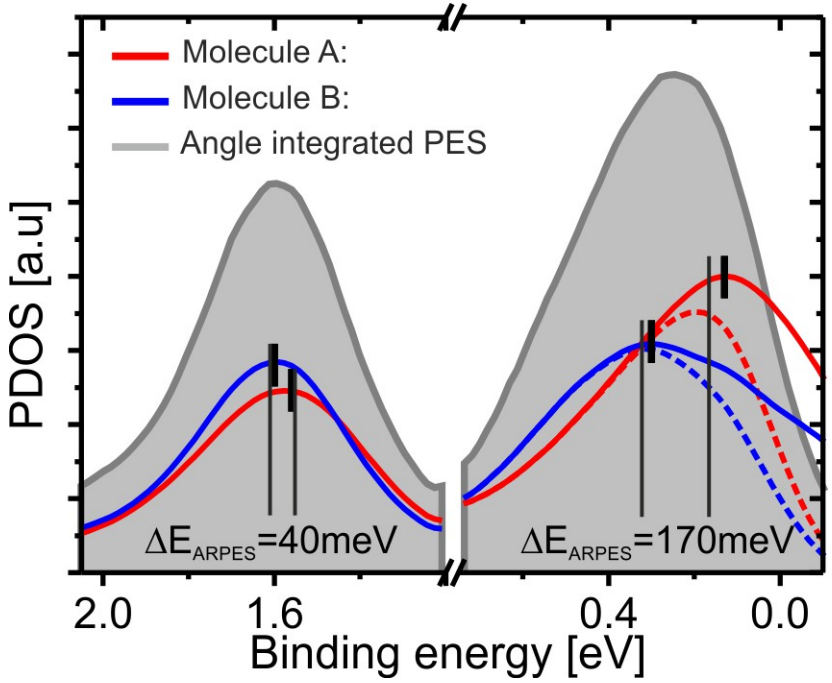
Origin of A / B Inequivalence

ARPES Tomography

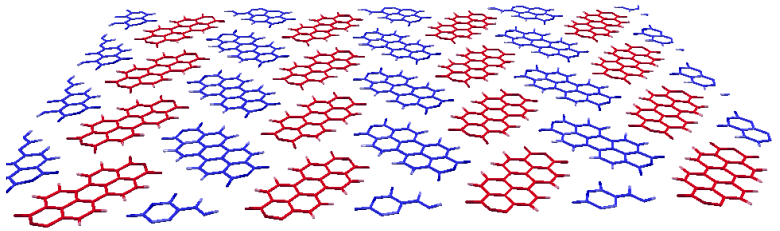
Least-squares fit: $S = \sum_{k=1}^{M} w_k \left[I(k, E_b) - F(k, E_b) \right]^2$

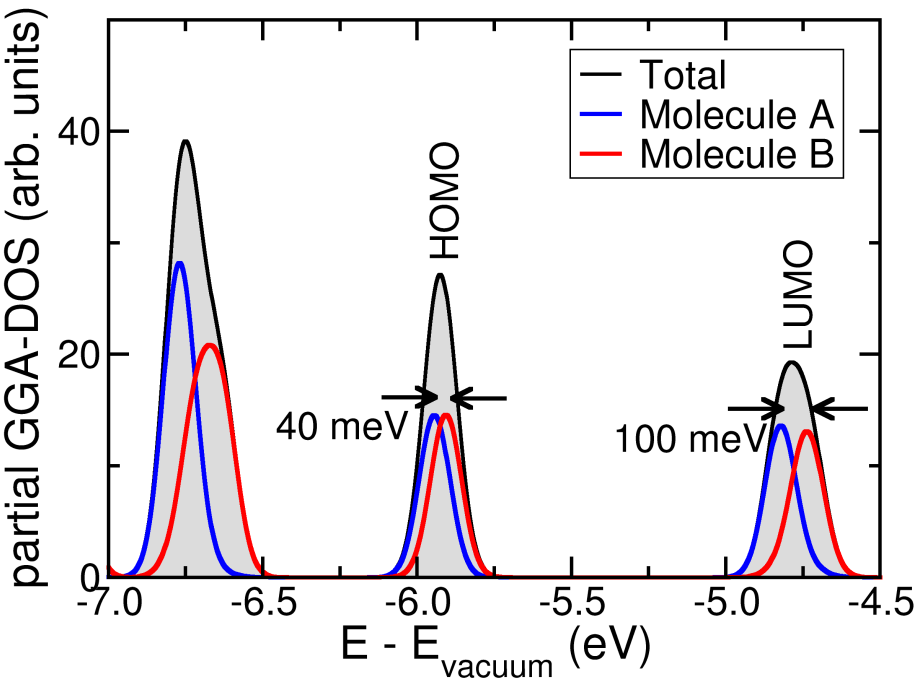
$$F(k_x, k_y, E_b) = \sum_i a_i(E_b) \Phi_i(k_x, k_y) + b(E_b) I_{sub}(k_x, k_y, E_b) + c(E_b)$$

Mol. A / B

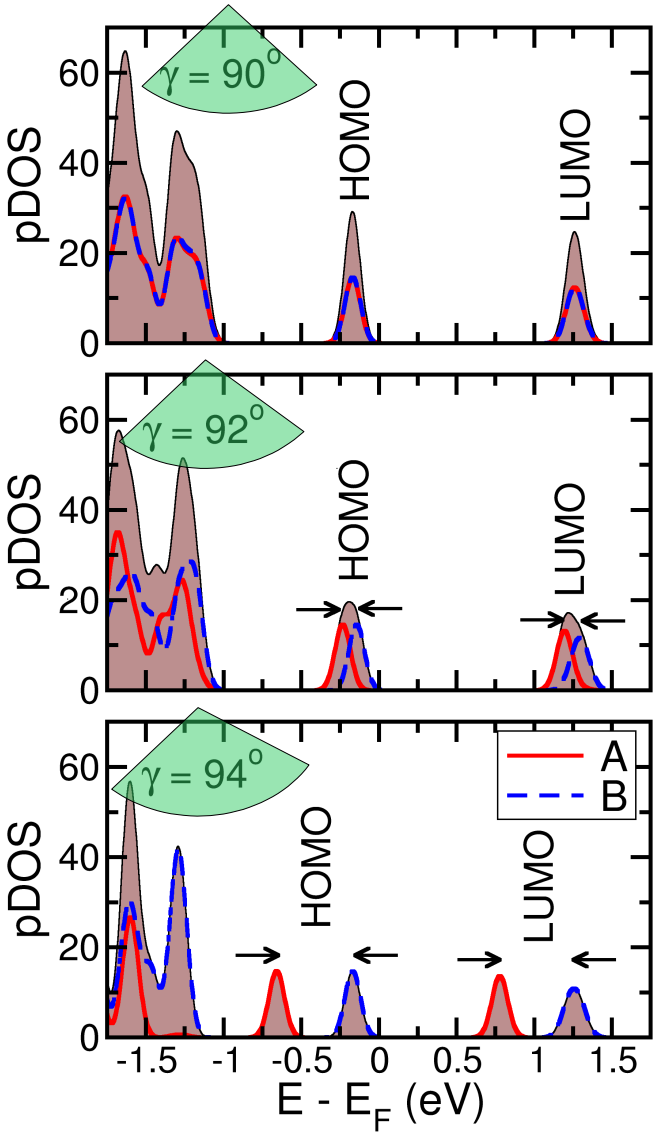


GGA-DFT: Freestanding Layer

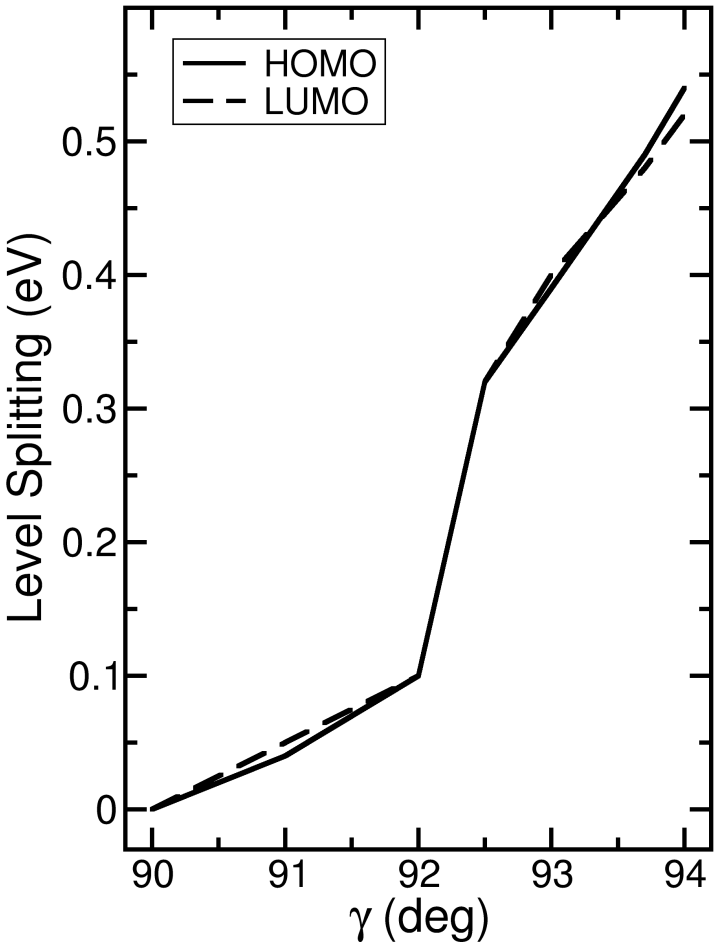




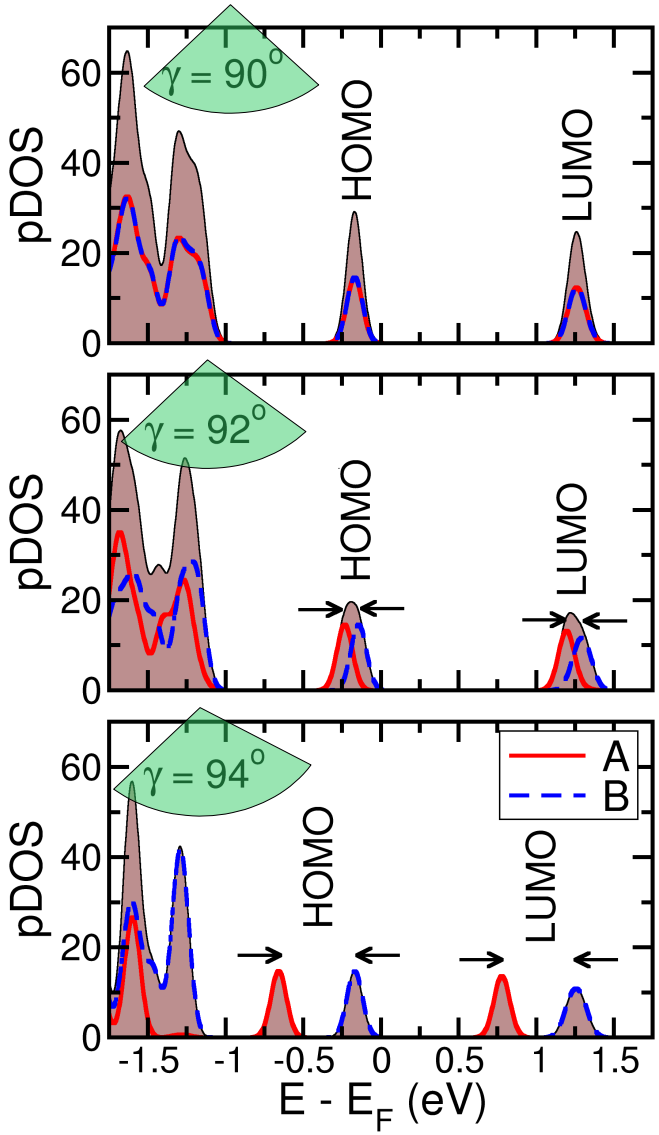
Small Changes / Big Effects

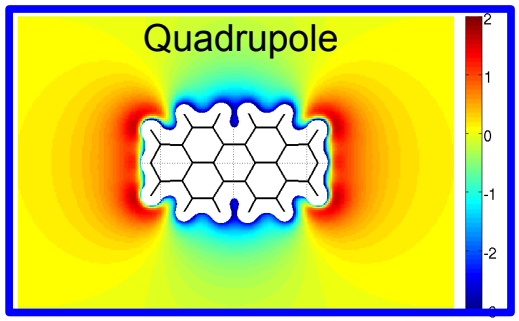


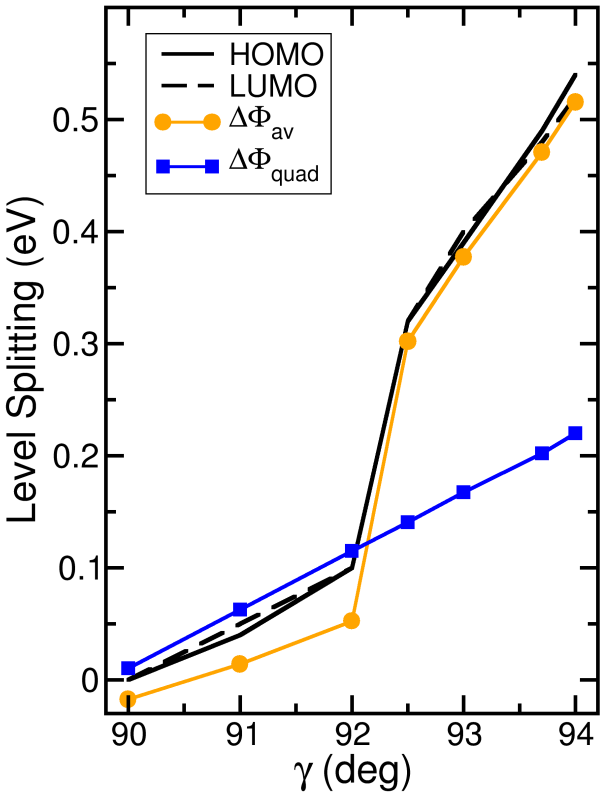
Herring-Bone Structure on Ag(110): dependence on monoclinic angle γ

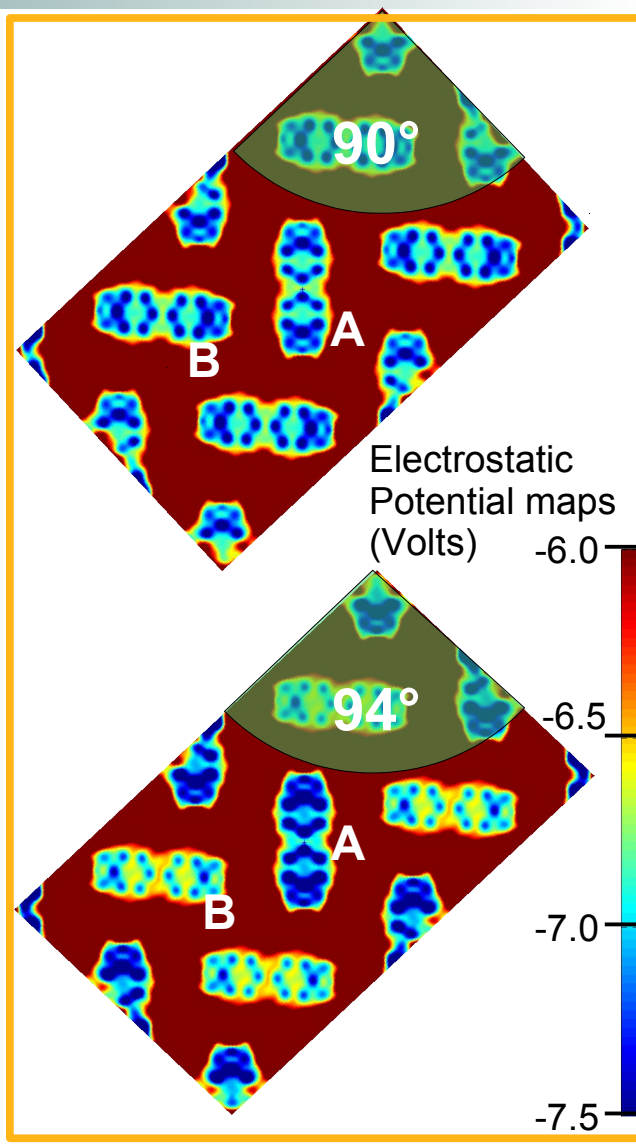


Quadrupoles Field



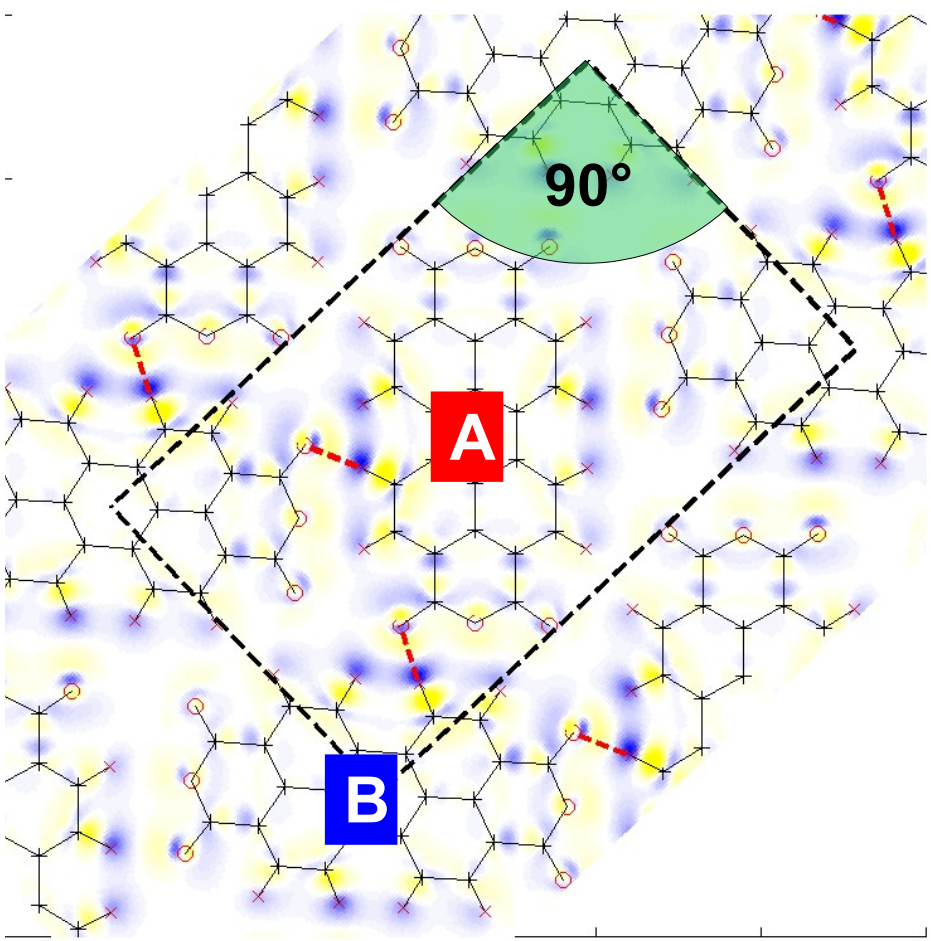


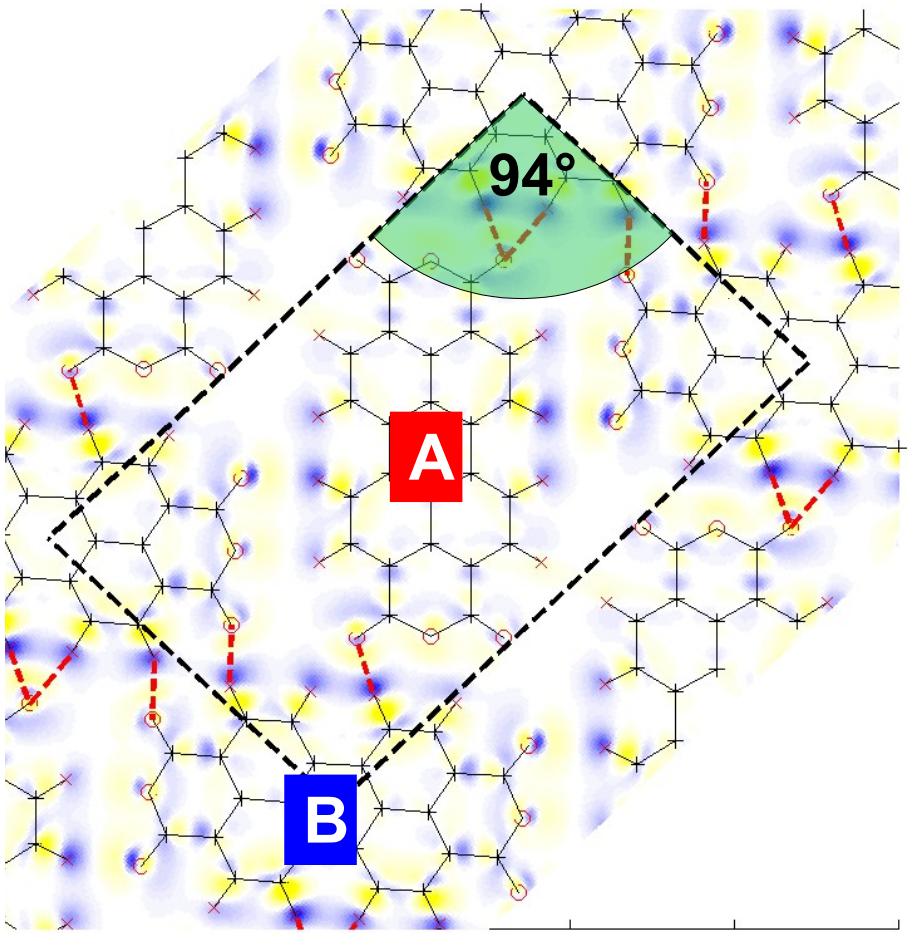


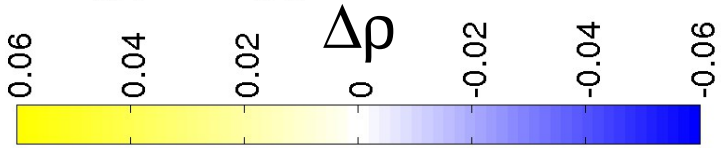


Hydrogen Bonds

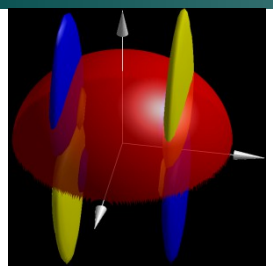
Herring-Bone Structure on Ag(110): dependence on monoclinic angle γ



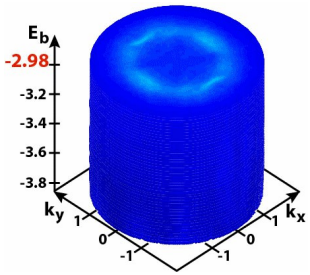




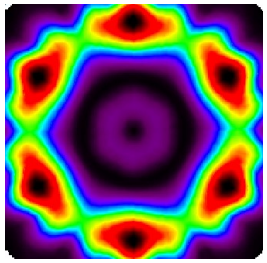
Overview



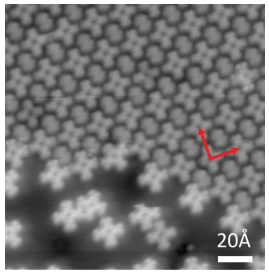
Angle-Resolved Photoemission



PTCDA / Ag(110)



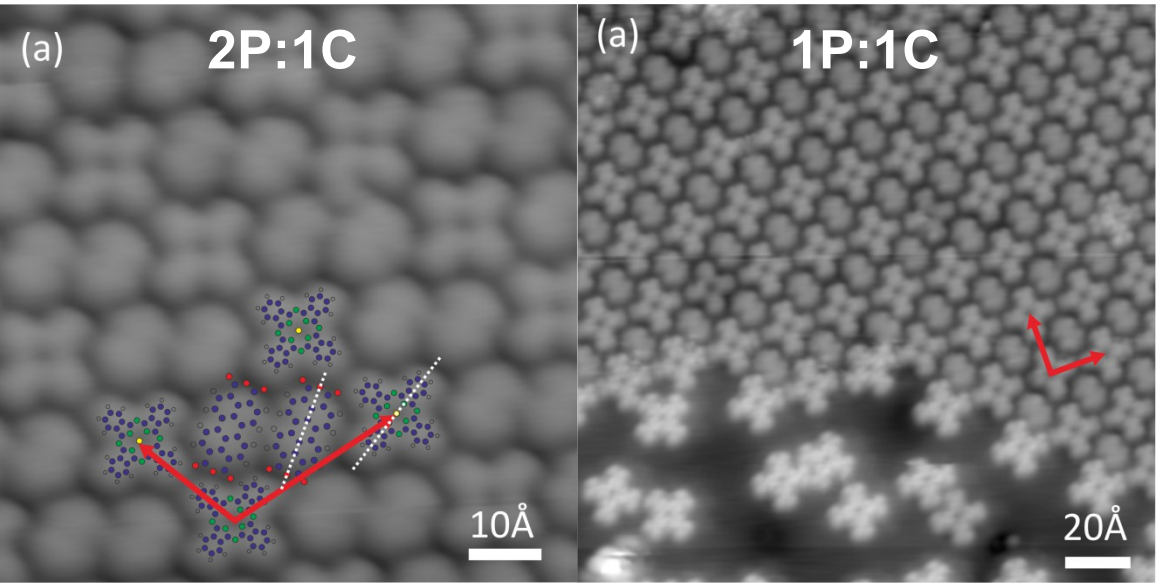
PTCDA / Ag(111)



CuPc + PTCDA / Ag(111)

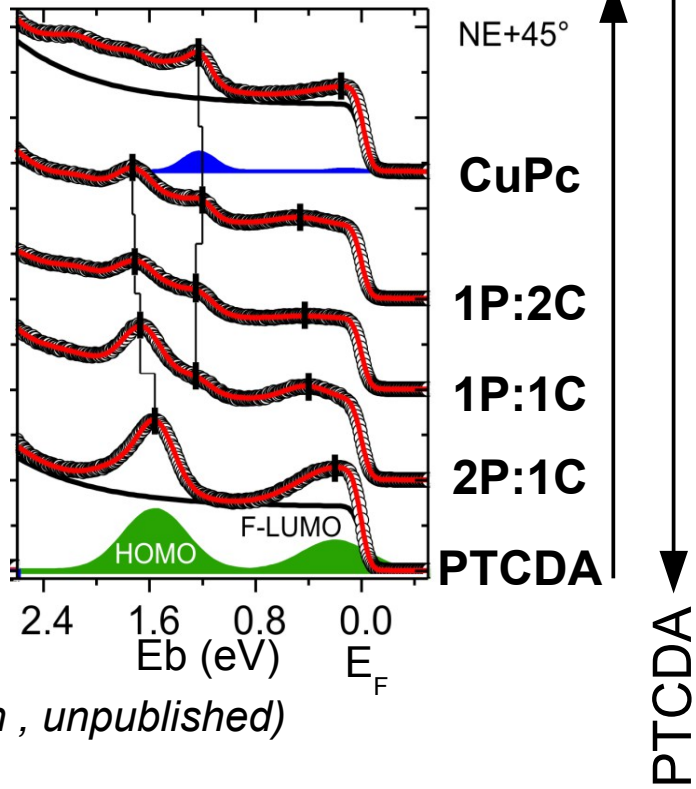
PTCDA+CuPc / Ag(111)

STM: mixed monolayer 2:1



STM: mixed monolayer 1:1

UPS: variation of PTCDA / CuPc ratio



Experimental data by courtesy of Benjamin Stadtmüller (Jülich , unpublished)

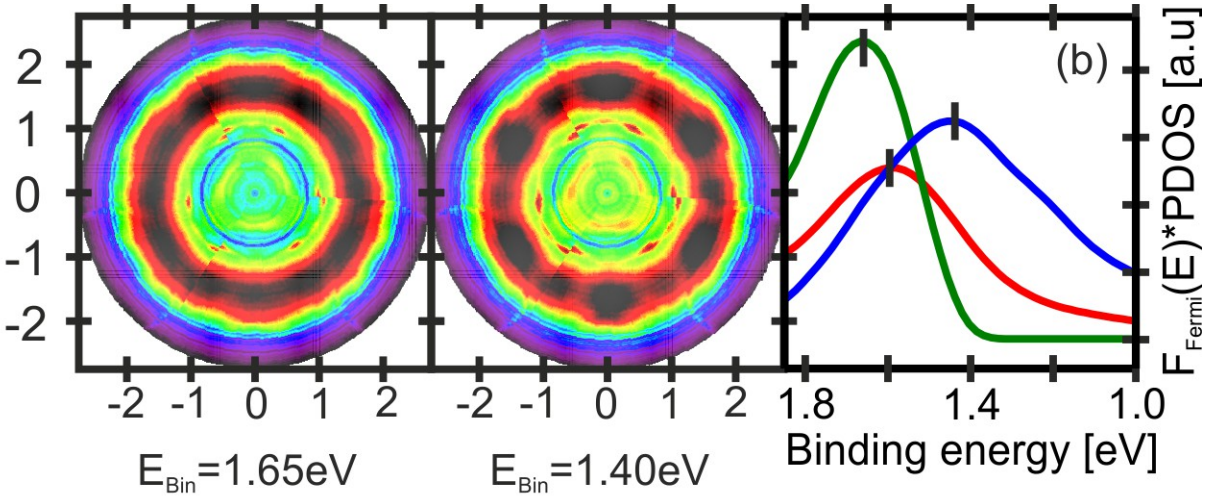
Can we use ARPES tomography to disentangle contributions from PTCDA / CuPc?

Does DFT yield the correct HOMO / fLUMO energies of PTCDA and CuPc?

HOMO(s) of PTCDA : CuPc = 2:1

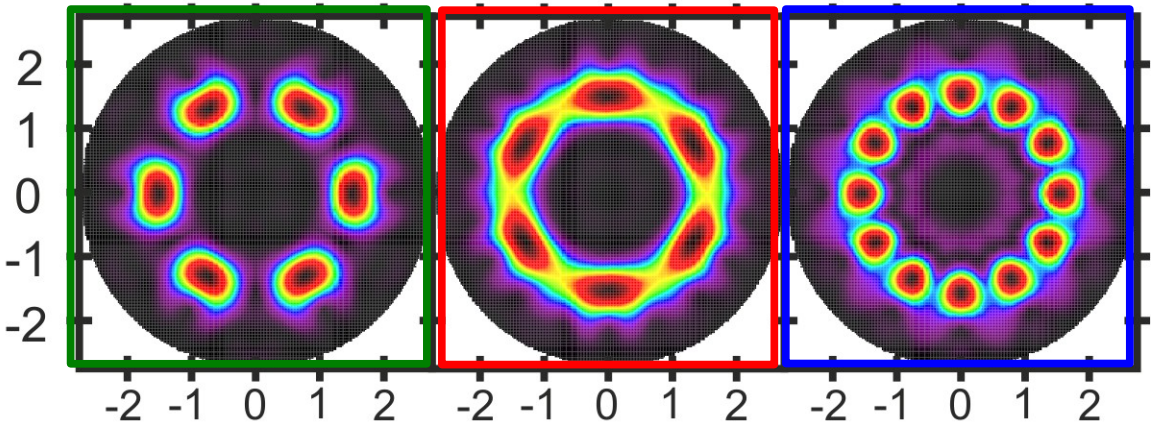
Experiment:

Mixed Monolayer
2 PTCDA + 1CuPc / Ag(111)
+
HB-Phase of PTCDA



Theoretical Maps:

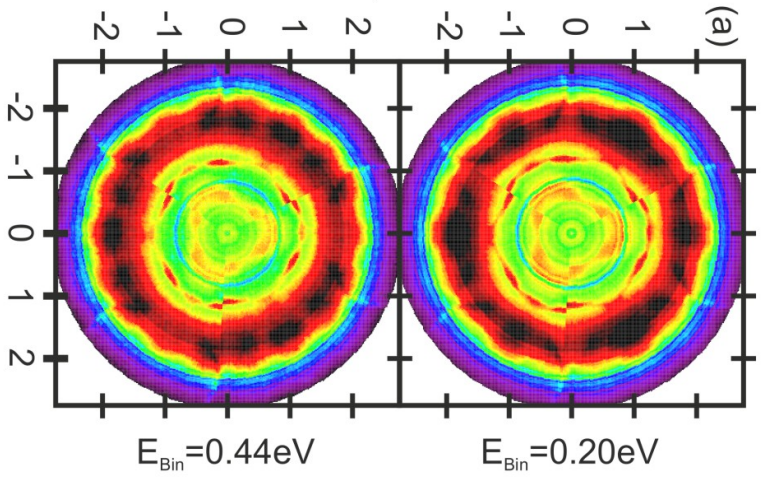
(1) PTCDA in 2P:1C
(2) PTCDA in HB-phase
(3) CuPc in 2P:1C

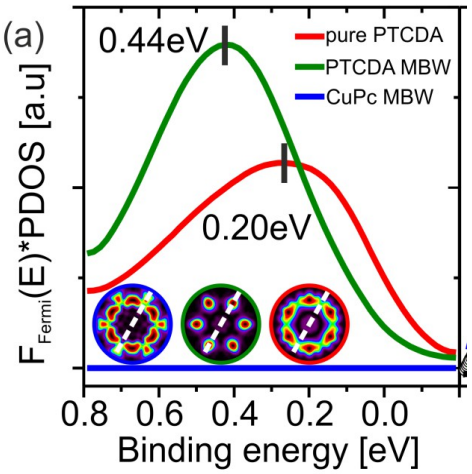


LUMO(s) of PTCDA : CuPc = 2:1

Experiment:

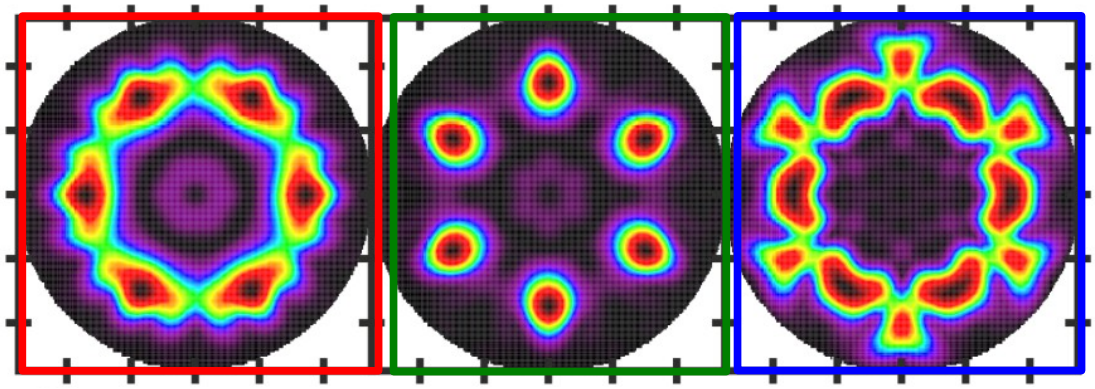
Mixed Monolayer
2 PTCDA + 1CuPc / Ag(111)
+
HB-Phase of PTCDA





Theoretical Maps:

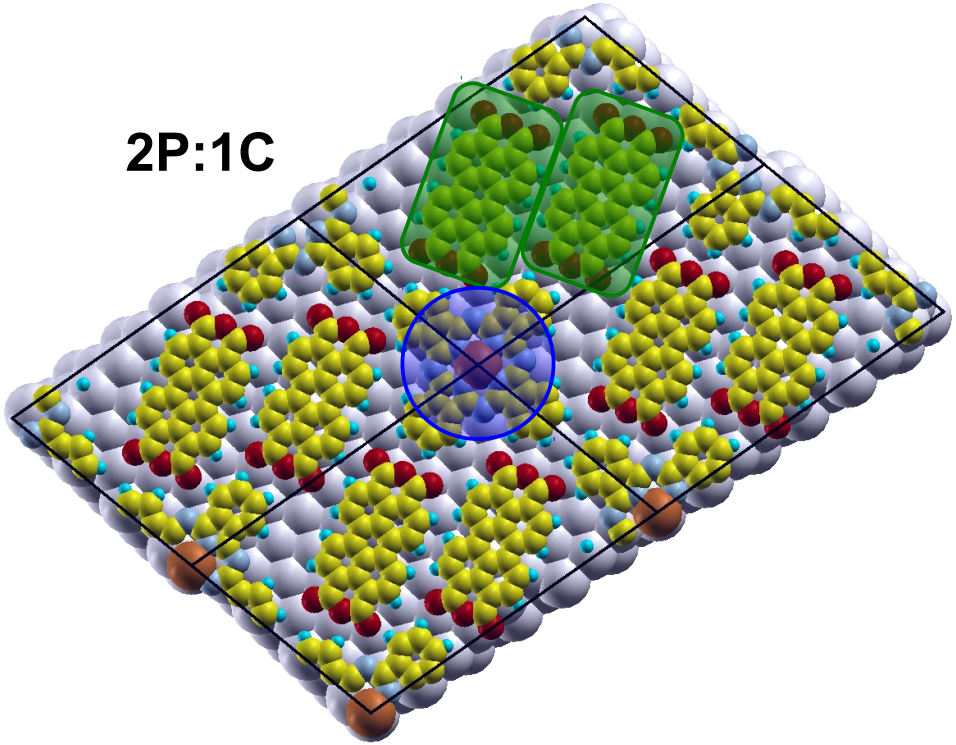
(1) PTCDA in 2P:1C
(2) PTCDA in HB-phase
(3) CuPc in 2P:1C



PTCDA HB-phase PTCDA in 2P:1C CuPc in 2P:1C

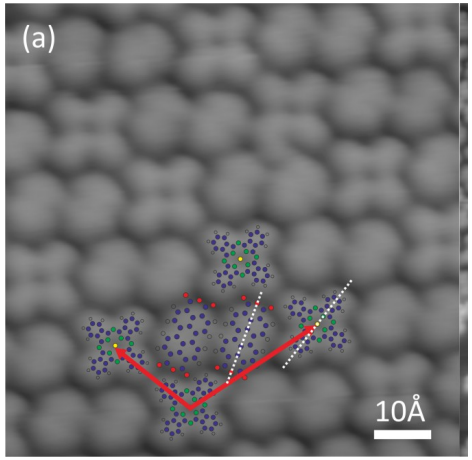
Preliminary GGA-DFT Results

2P:1C cell used for DFT calculations:
based on exp. STM, LEED, XSW data

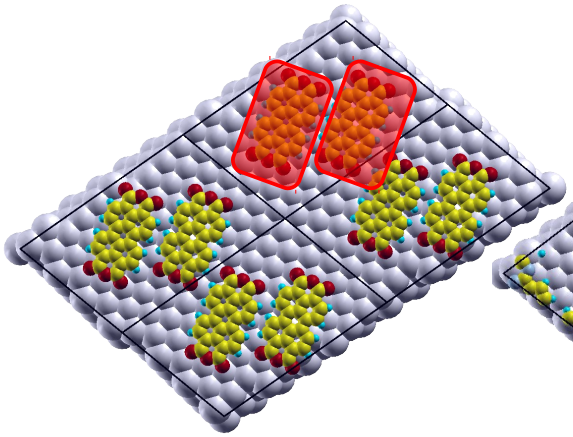


VASP-PAW GGA calculations
Slab geometry with 5 layers of Ag
443 atoms, 3885 electrons
non-spinpolarized

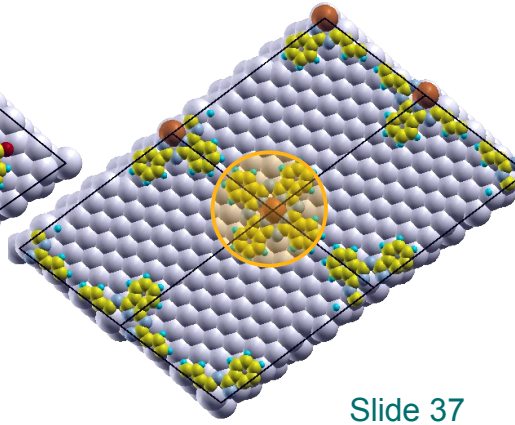
STM:
mixed monolayer 2P:1C



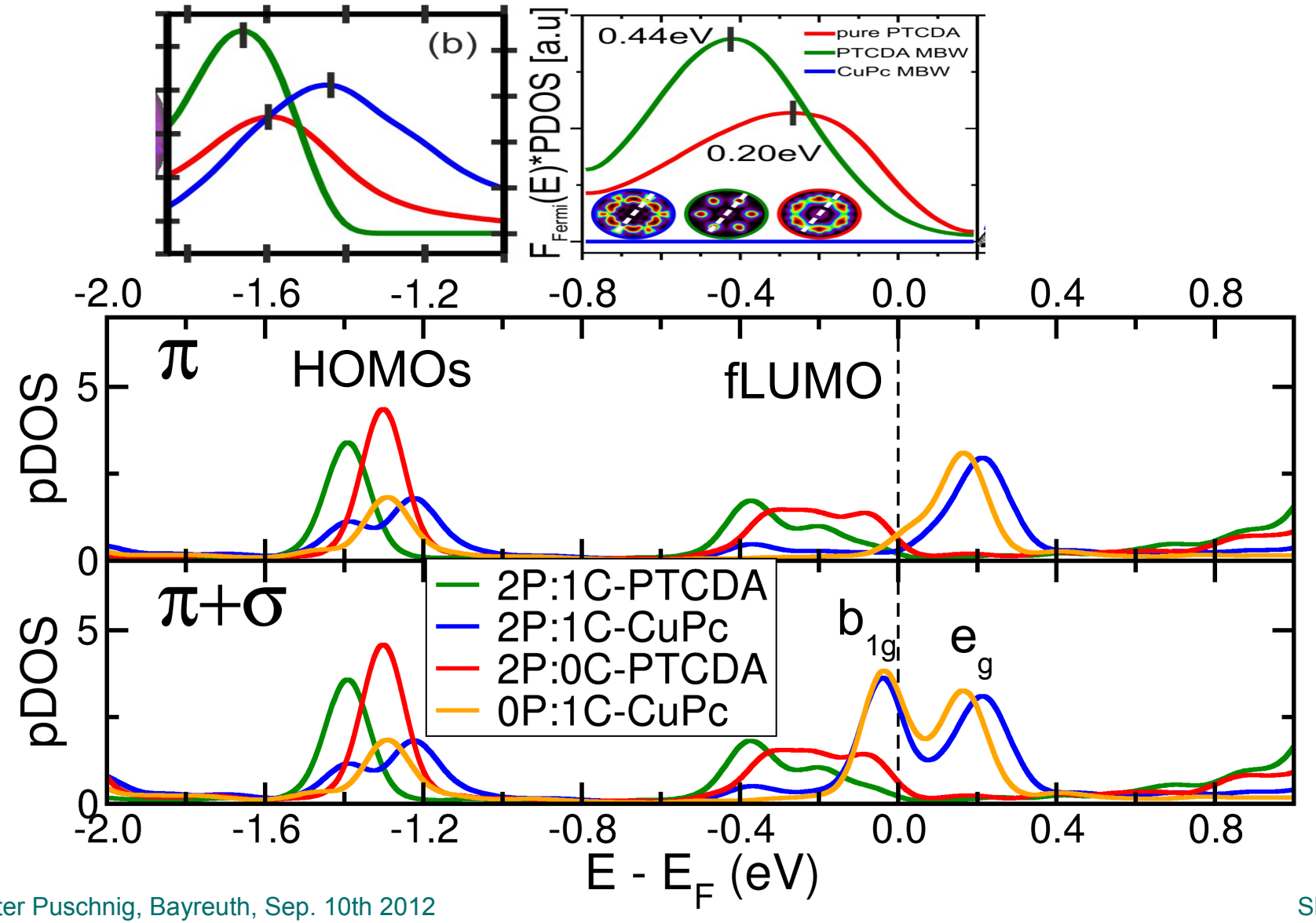
2P:0C



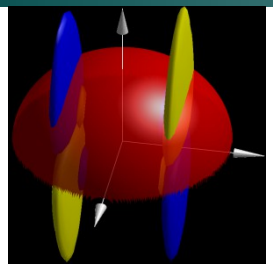
0P:1C

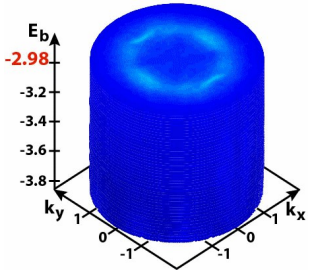


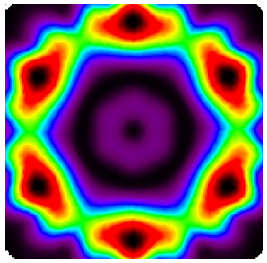
Preliminary GGA-DFT Results

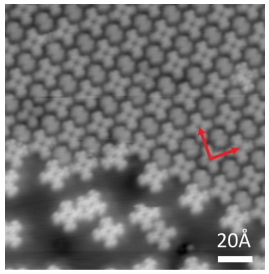


Summary









- **ARPES intensity proportional to FT of molecular orbital**
- Plane wave final state approximation works for …
  - pi-orbitals of organic molecules
  - No heavy atoms
  - Electron emission direction close to electric field vector of incoming photon

- **Orbital Tomography**
  - Identification of molecular orbitals
  - Experimentally determined DOS projected onto MOs
  - Comprehensive experimental data to benchmark ab-initio calculations
  - PTCDA / Ag(110): PRB **84**, 235427 (2011).
  - pentacene / Ag(110), pentacene / Cu(110) *in preparation* → **Daniel Lüftner**
  - Determination of site-specific orbital energies: PTCDA/Ag(111)
  - Disentangling moelcular states in mixed monolayers: 2PTCDA+1CuPc/Ag(111)

- **Other Applications**
  - Azimuthal orientation of CuPc / Au(110): in preparation → **Matus Milko**
  - Azimuthal orientation of tetraphenyl-porphyrine / Cu(110): in preparation
  - Cs-doped sexiphenyl / Cu(110) : in preparation
  - Real space images of p-6P HOMO and LUMO: *Science* **326**, 702 (2009).
  - Analysis of 6P / Cu(110) hybridization: *PCCP* **13**, 3604 (2011)
  - PTCDA / Ag(110): *PRL* **104**, 233004 (2010).
  - Coronene / Hexa-benzo-coronene („graphene quantum well states“), *submitted to New Journal of Physics*

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Thank You for Your Attention!