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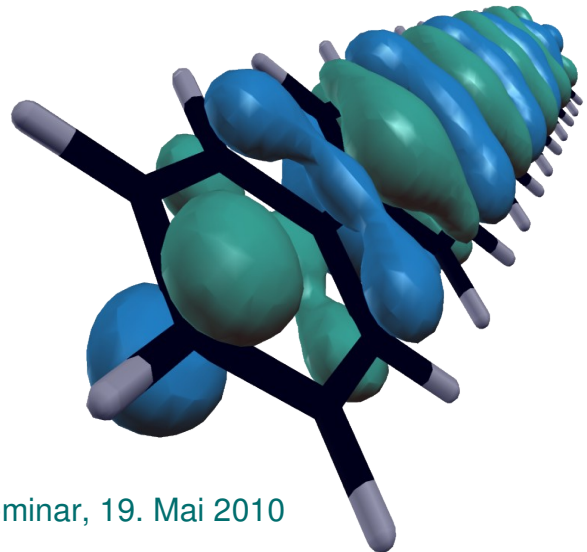
The electronic structure of organic molecular layers: DFT compared to ARPES



Collaborations and Funding

Lehrstuhl für Atomistic Modelling and Design of Materials – MU Leoben
- Peter Puschnig
- Claudia Ambrosch-Draxl

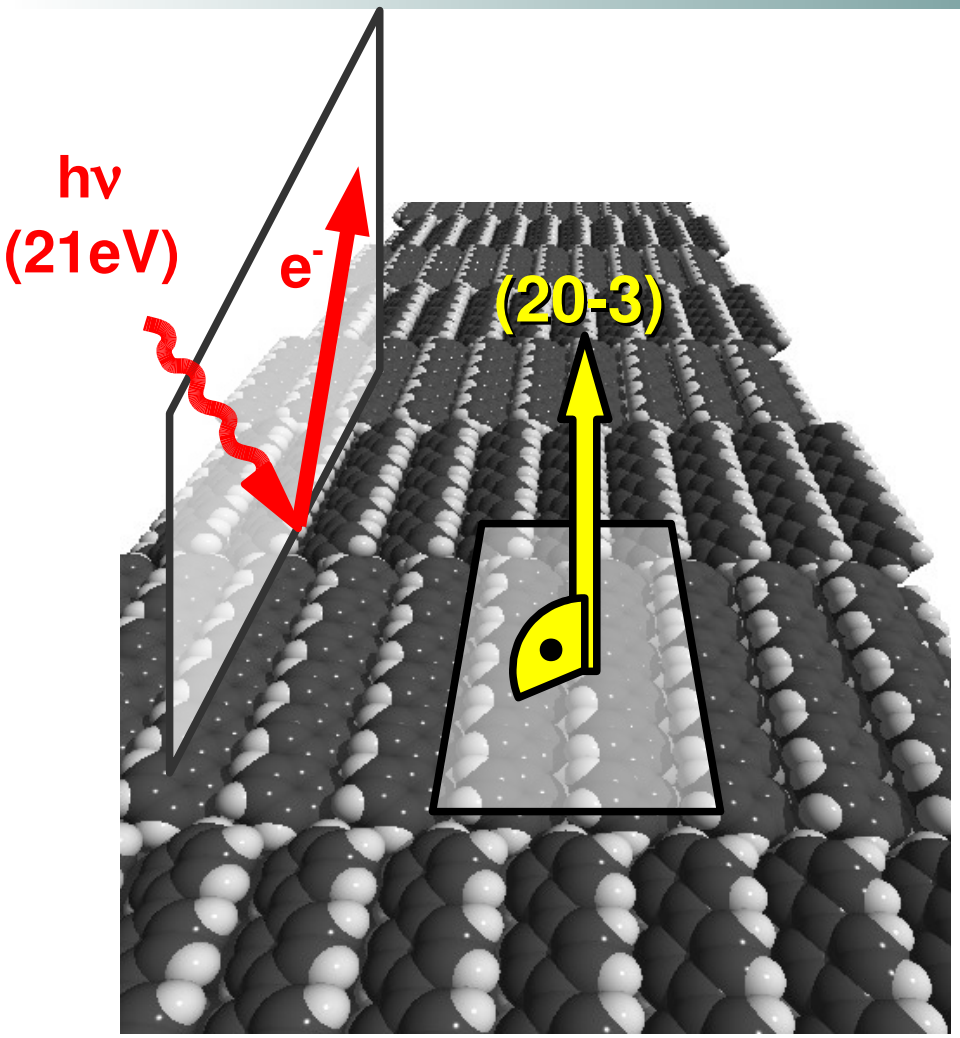
Experimental Surface Science Group – University Graz, Austria
- Stephen Berkebile
- Alexander Fleming
- Georg Koller
- Mike Ramsey

Lehrstuhl für Technische Physik – University Erlangen-Nürnberg
- Thomas Seyller
- Konstantin Emtsev

Experimentelle Physik VII – Universität Würzburg, Germany
Johannes Ziroff, Frank Forster,
Achim Schöll, Friedrich Reinert

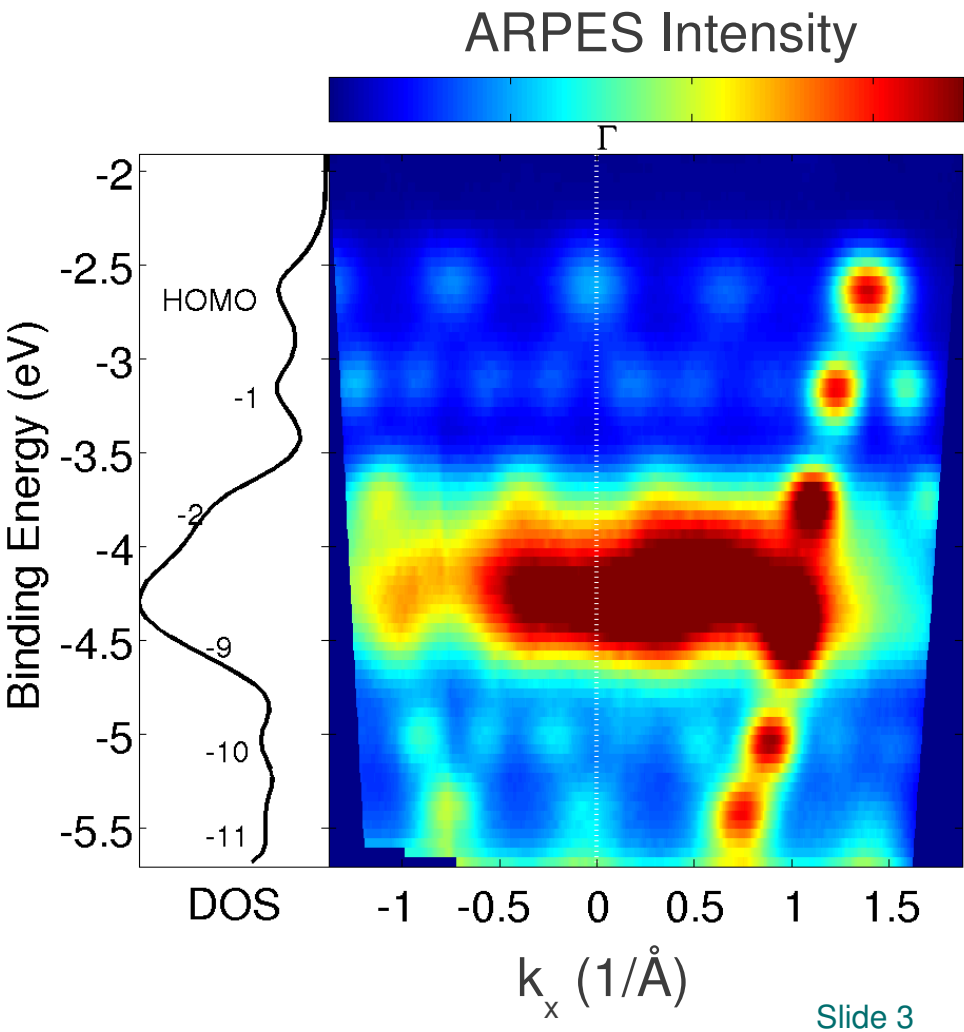
The work is part of the National Research Network
„Interface controlled and functionalized organic films“

Uniaxially Aligned Sexiphenyl

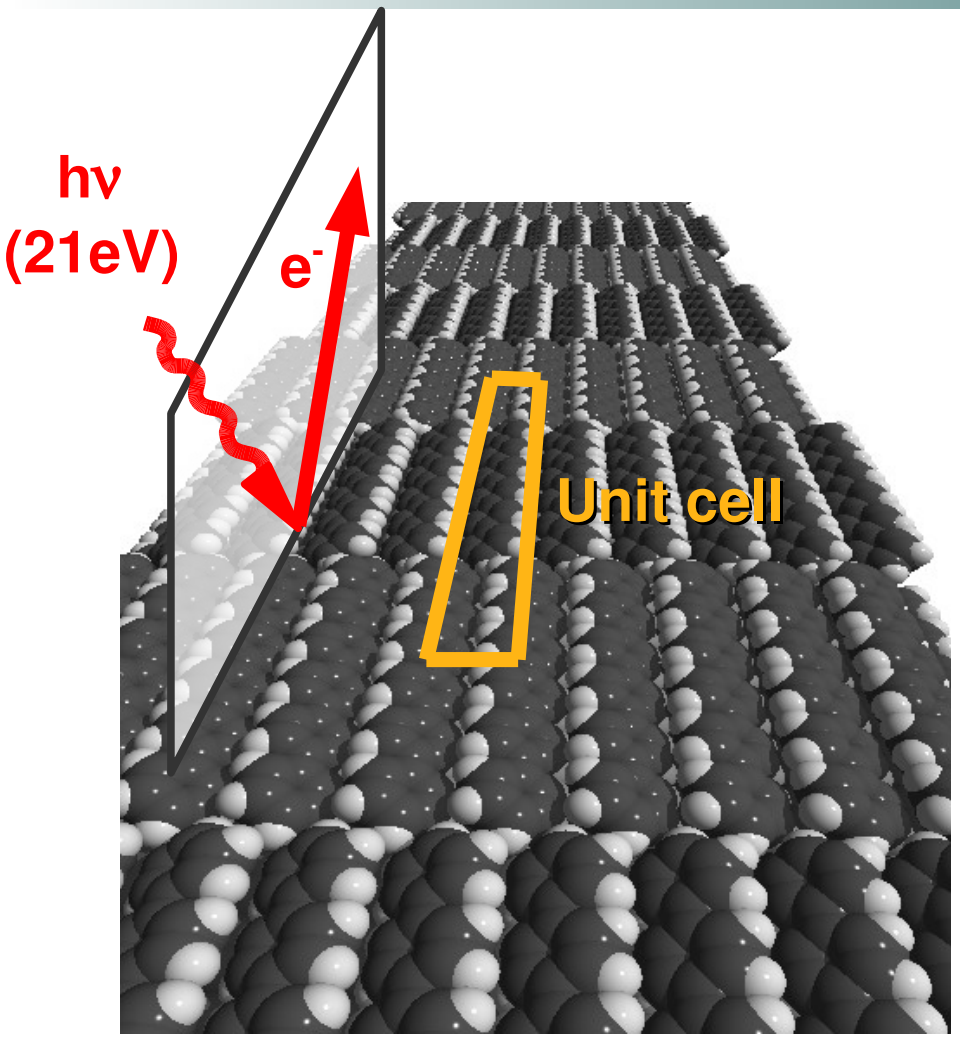


Uniaxially ordered para-sexiphenyl film
on Cu(110)_(2x1)O

ARPES data from Stephen Berkebile

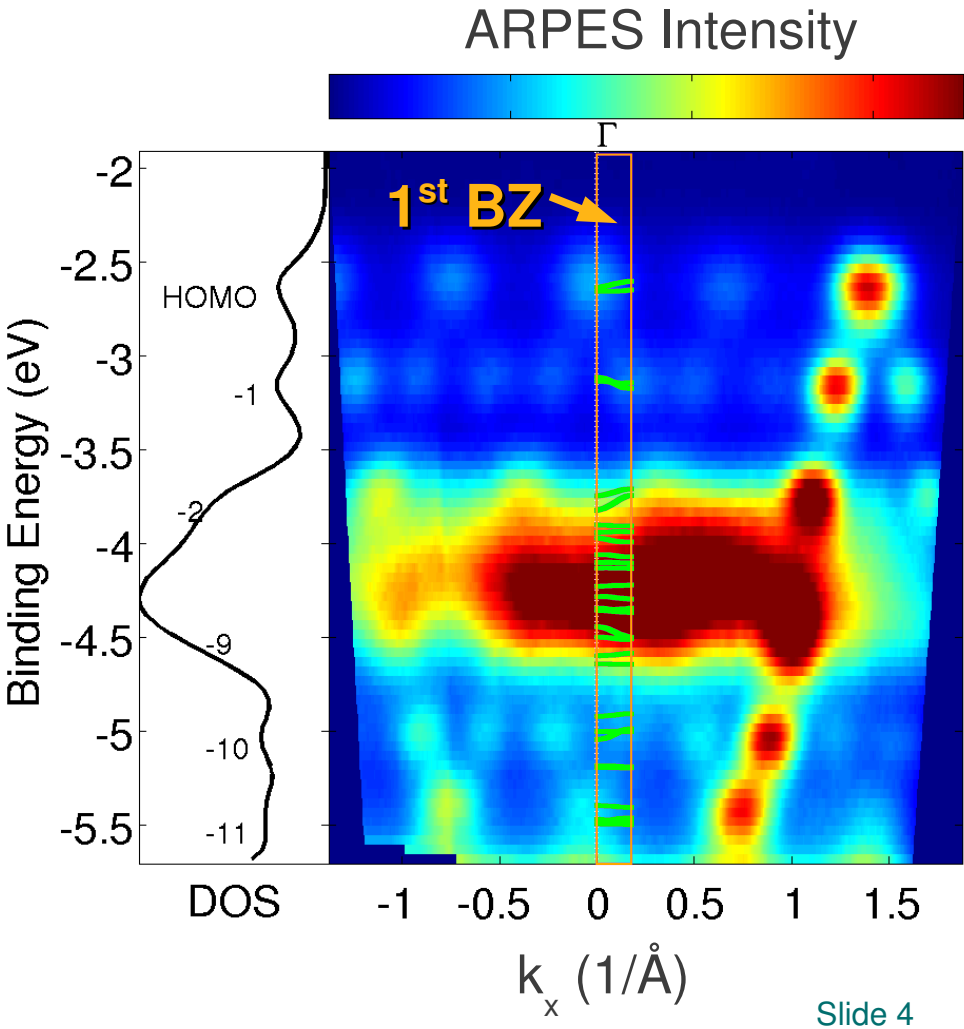


Uniaxially Aligned Sexiphenyl

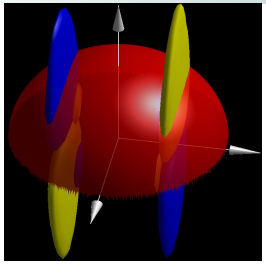


Uniaxially ordered para-sexiphenyl film
on Cu(110)_(2x1)O

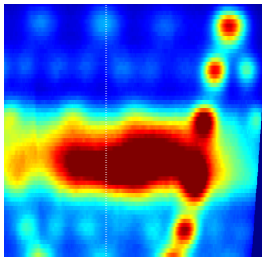
Band structure from:
Puschnig et al., *PRB* **60**, 7891 (1999).



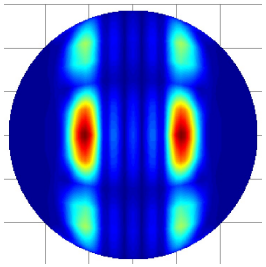
Overview



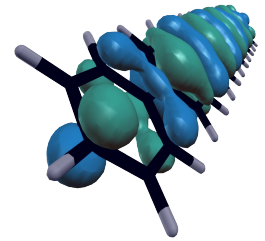
Photoemission Intensity



Intra- and Intermolecular Dispersion

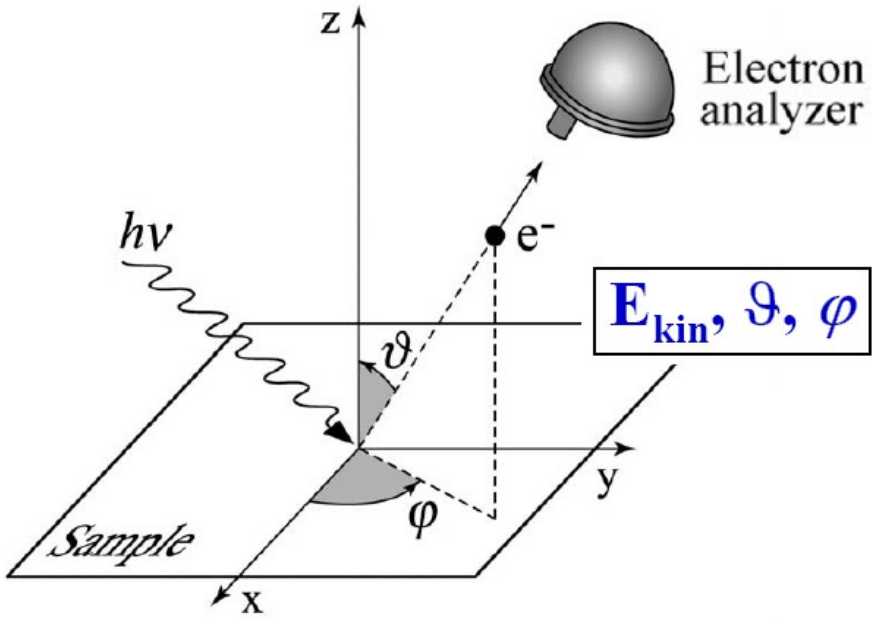


From reciprocal to real space



Conclusion and Outlook

Photoemission Spectroscopy



$$\mathbf{K} = \mathbf{p}/\hbar = \sqrt{2m\boldsymbol{E_{kin}}}/\hbar$$

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

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

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

Vacuum

$\boldsymbol{E_{kin}}$

$\mathbf{K}$

Conservation laws

$$E_f - E_i = h\nu$$

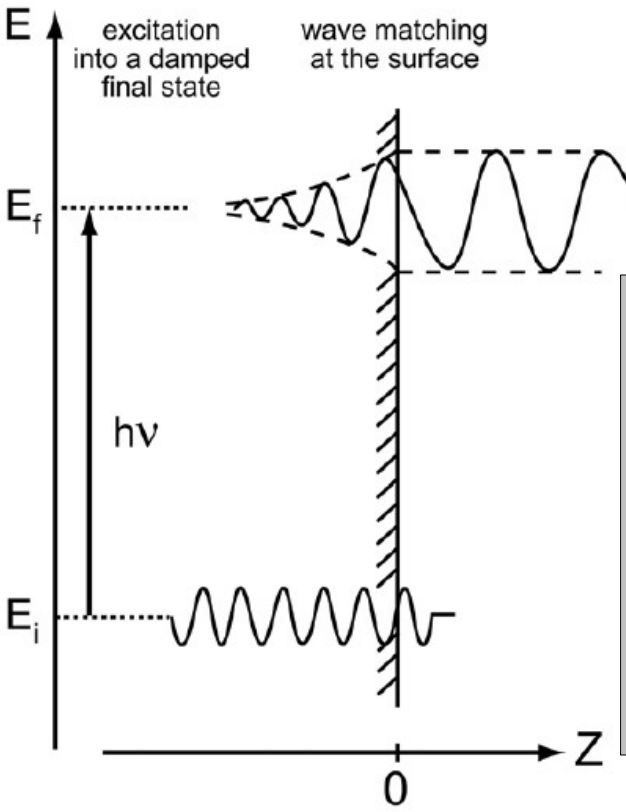
$$\mathbf{k}_f - \mathbf{k}_i = \cancel{\mathbf{k}_{h\nu}}$$

Solid

$\boldsymbol{E_B}$

$\mathbf{k}$

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)

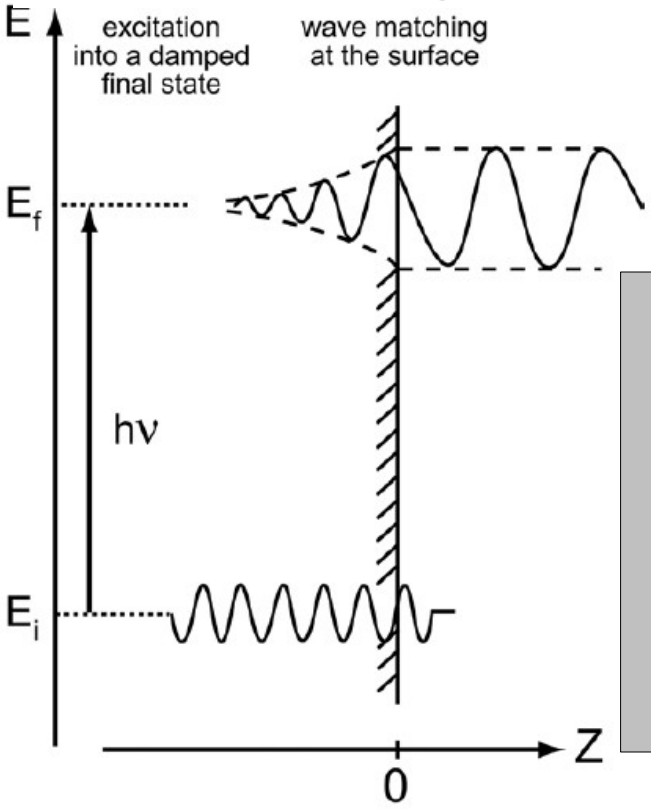
Spectral Function
(energy renormalzation and life time due to many-body effects)

[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

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

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

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

Photoemission Intensity

One Step Model

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

Photoemission Intensity

One Step Model

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

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

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

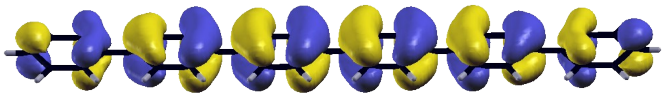
Interaction with the photon field treated as perturbation

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

Photoemission Intensity

One Step Model

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

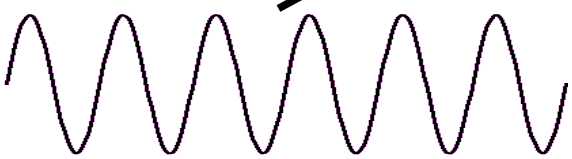


molecular orbital

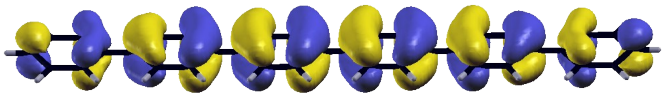
Photoemission Intensity

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 $e^{i\,k\,r}$



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).]

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

- Widely used for molecules adsorbed at surfaces
- Goes beyond plane wave final state approximtion
- Describes the PE intensity as independent, but coherent sum from individual atomic centers.

Plane Wave Final State

The **I**ndependent **A**tomic **C**entre approximation (IAC)

[W. D. Grobman, Phys. Rev. B **17**, 4573 (1978).]

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

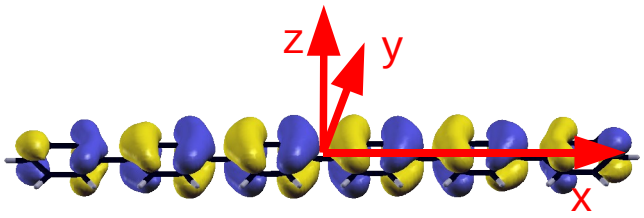
Reduces to the PW final state result, if

- All contributing atomic orbitals are of the same type (e.g. 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

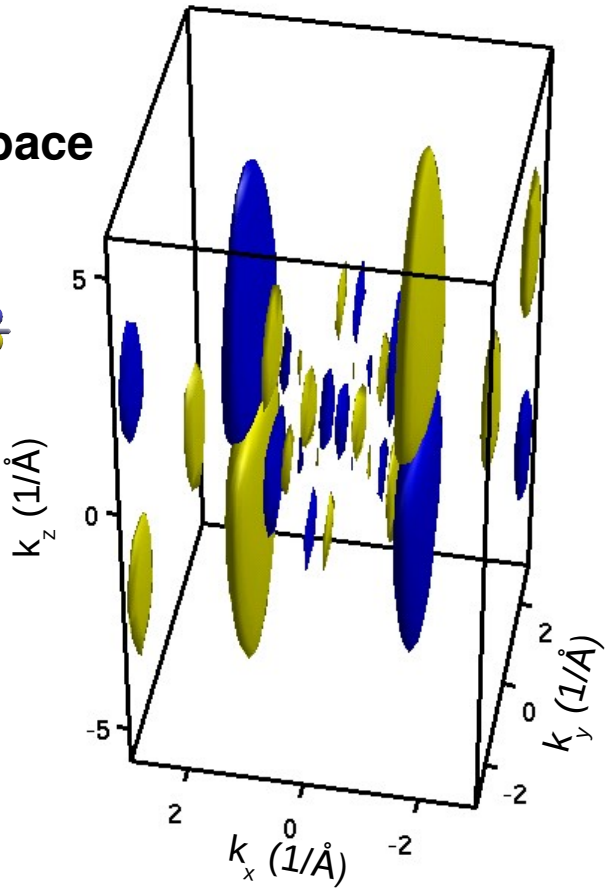
[Goldberg et al, Solid State Commun. **28**, 459-463 (1978),
Puschnig et al., supporting online material to Science **326**, 702 (2009)]

Comparison with DFT

Molecular Orbital in Real Space

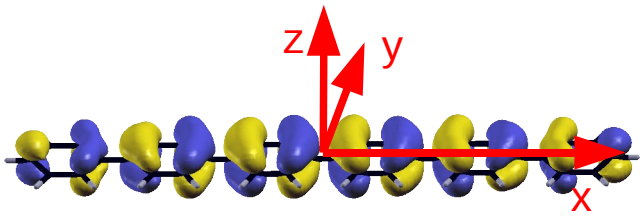


Calculation of the Fourier Transform

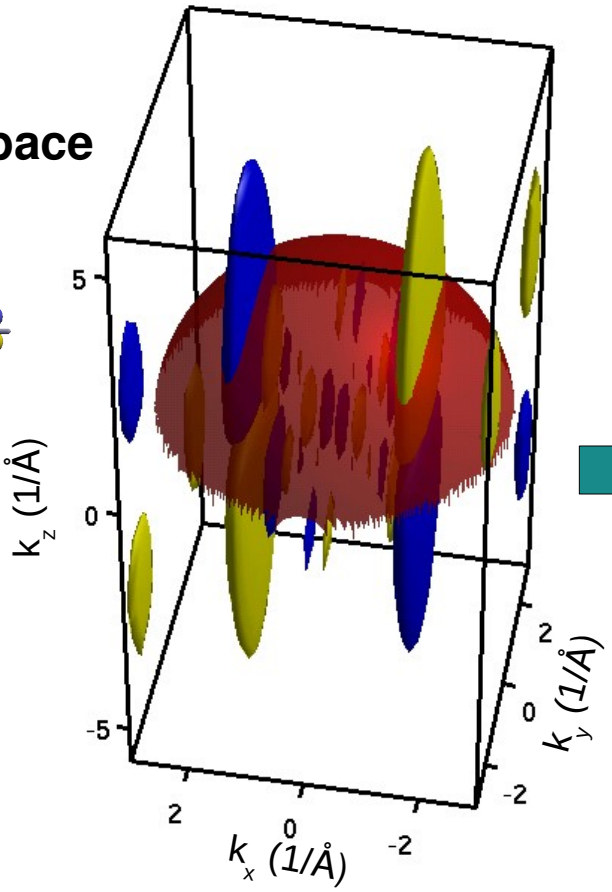


Comparison with DFT

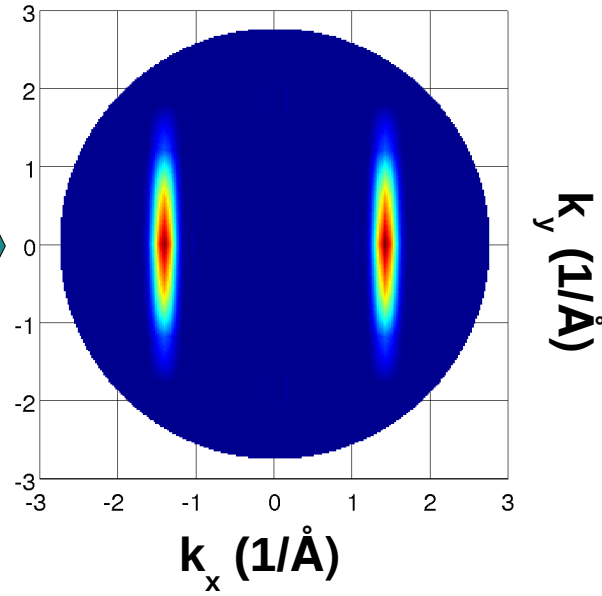
Molecular Orbital in Real Space



Calculation of the Fourier Transform

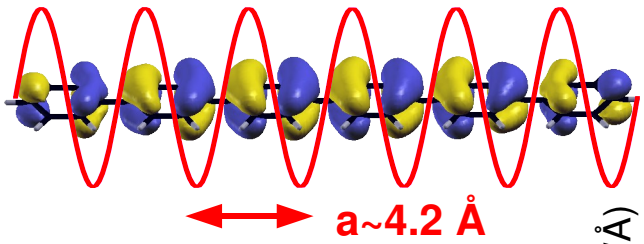


Hemispherical Cut Through 3D Fourier Transform

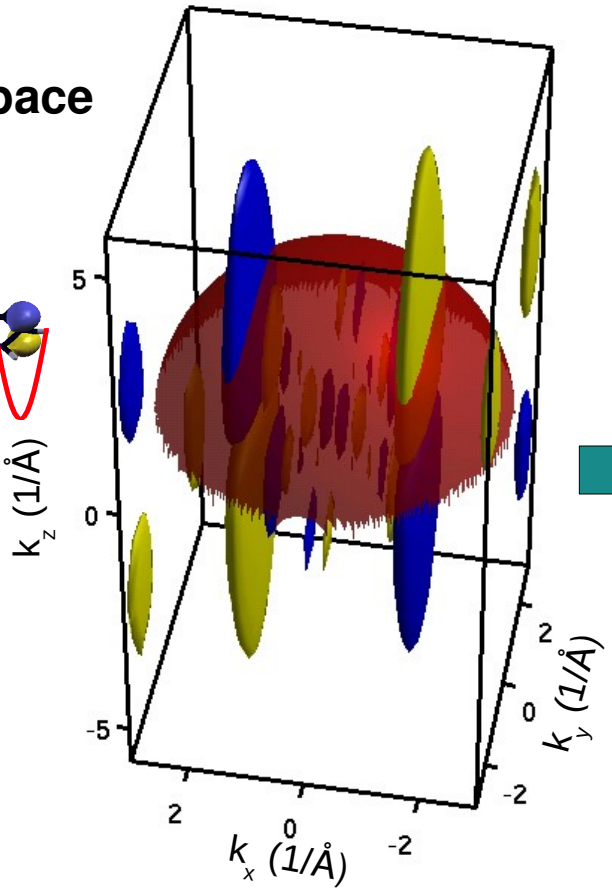


Comparison with DFT

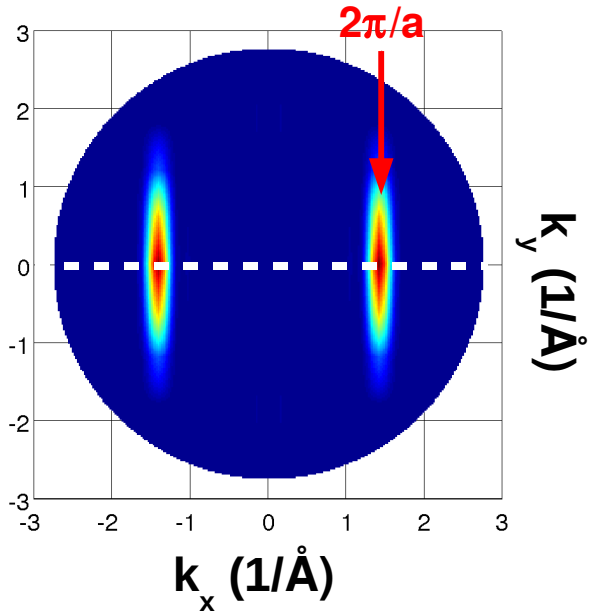
Molecular Orbital in Real Space



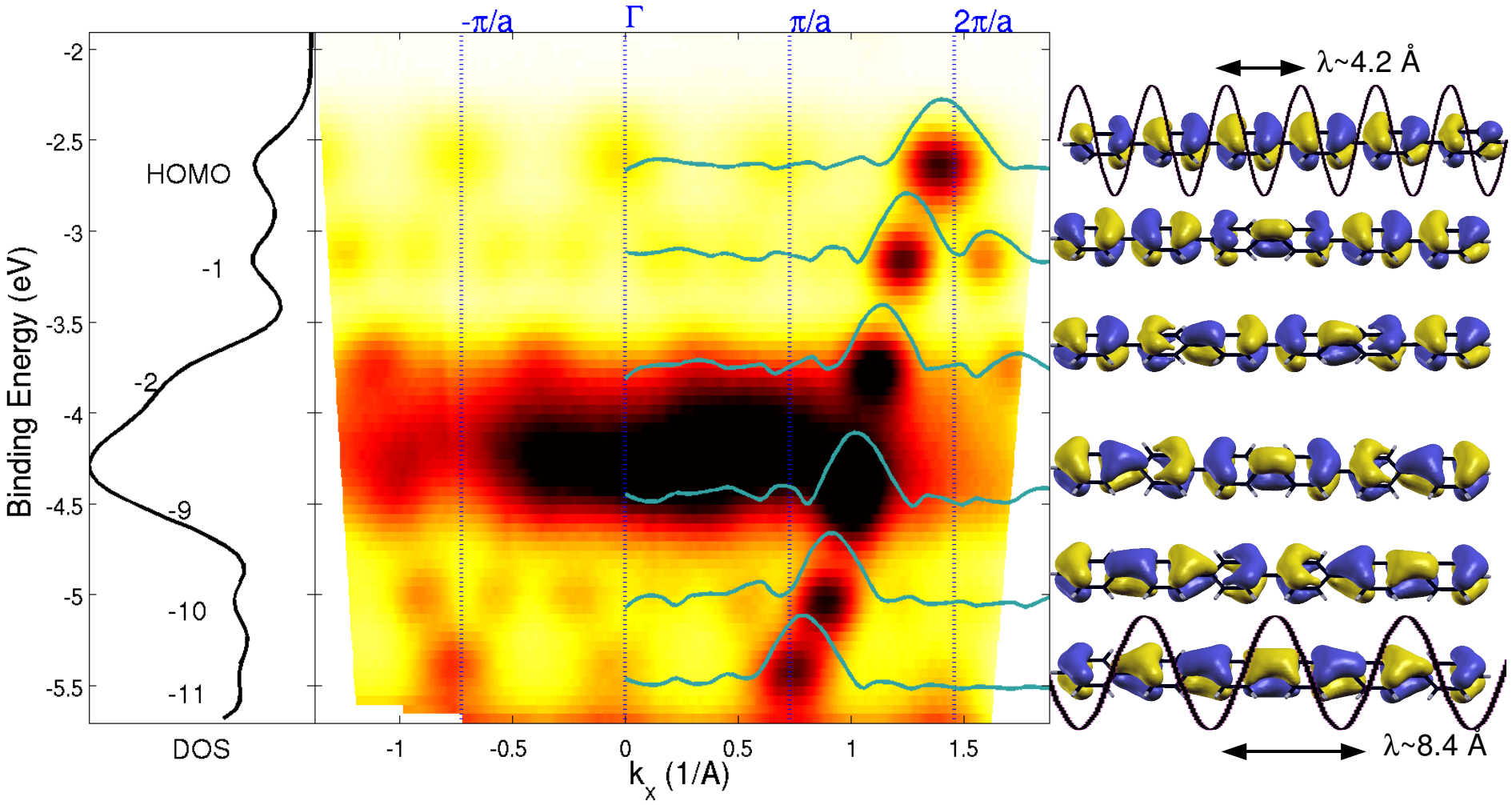
Calculation of the Fourier Transform



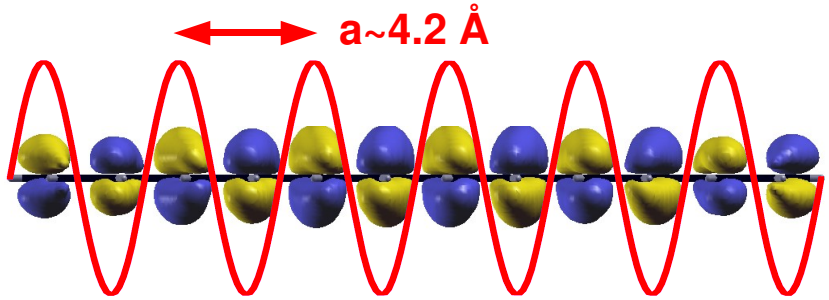
Hemispherical Cut Through 3D Fourier Transform

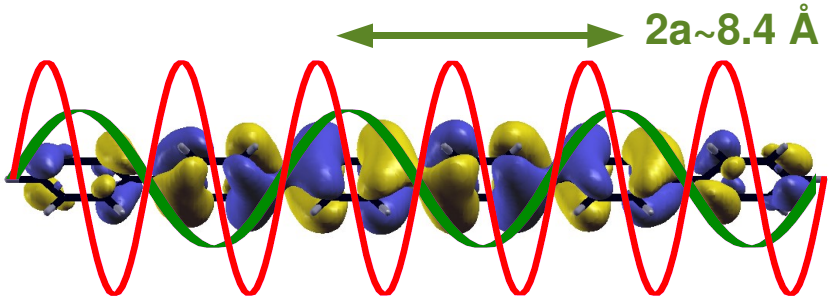


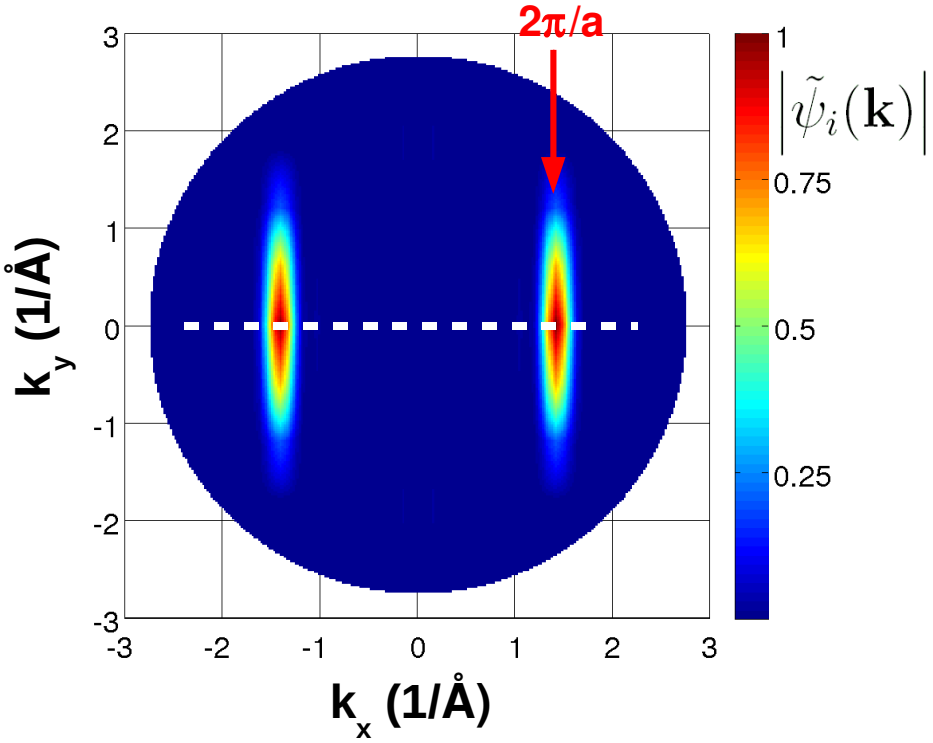
*Intra*molecular Band Structure

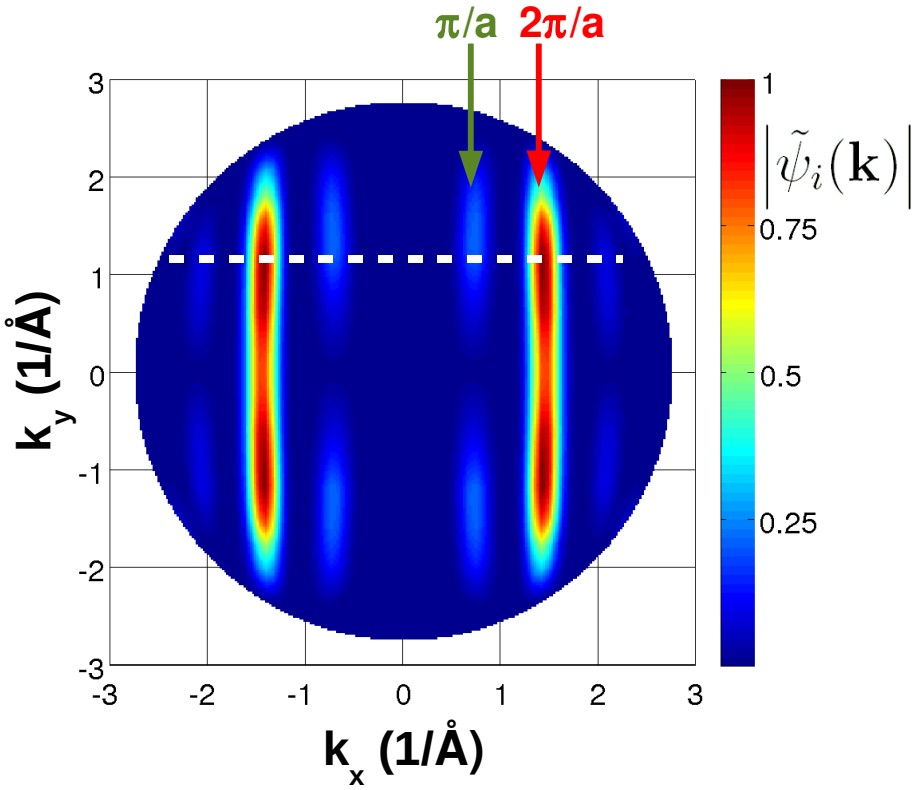


Planar vs. Twisted

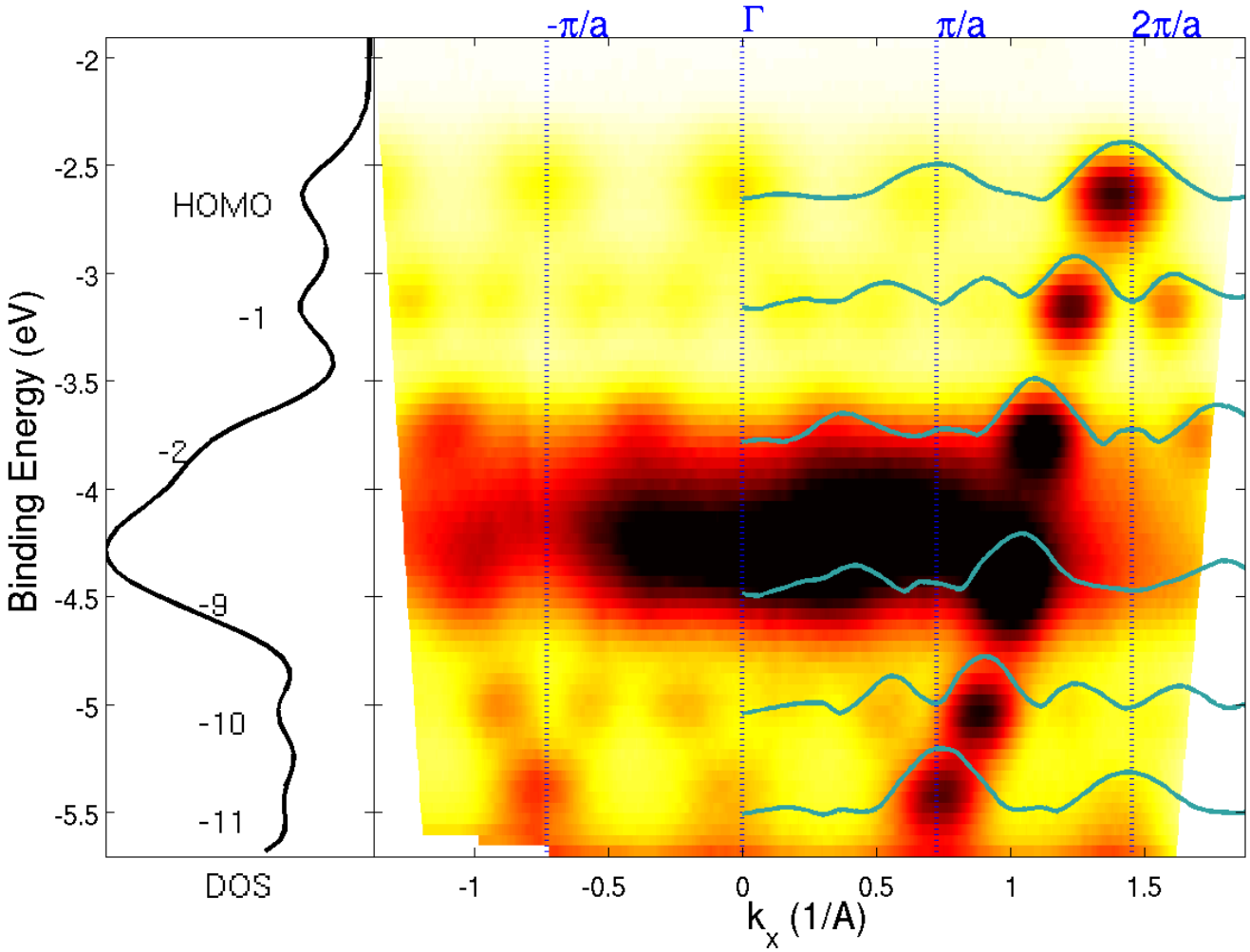


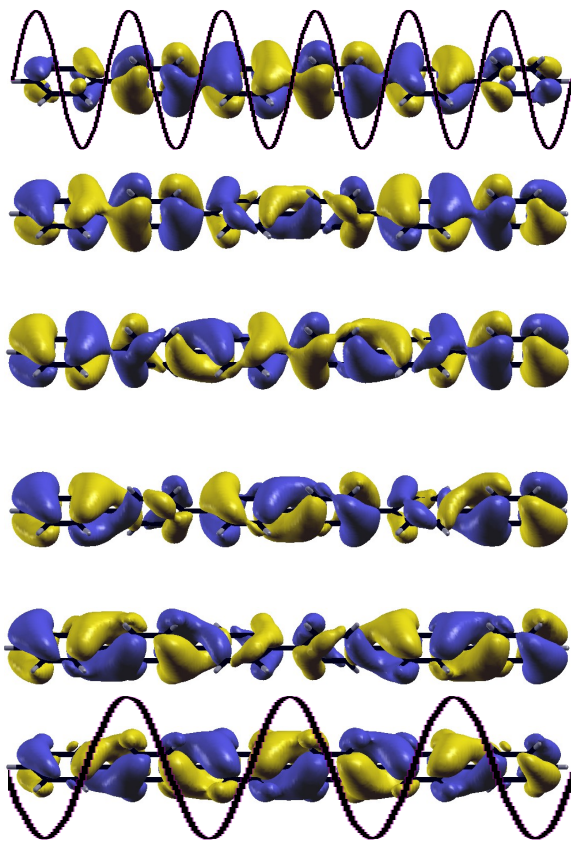






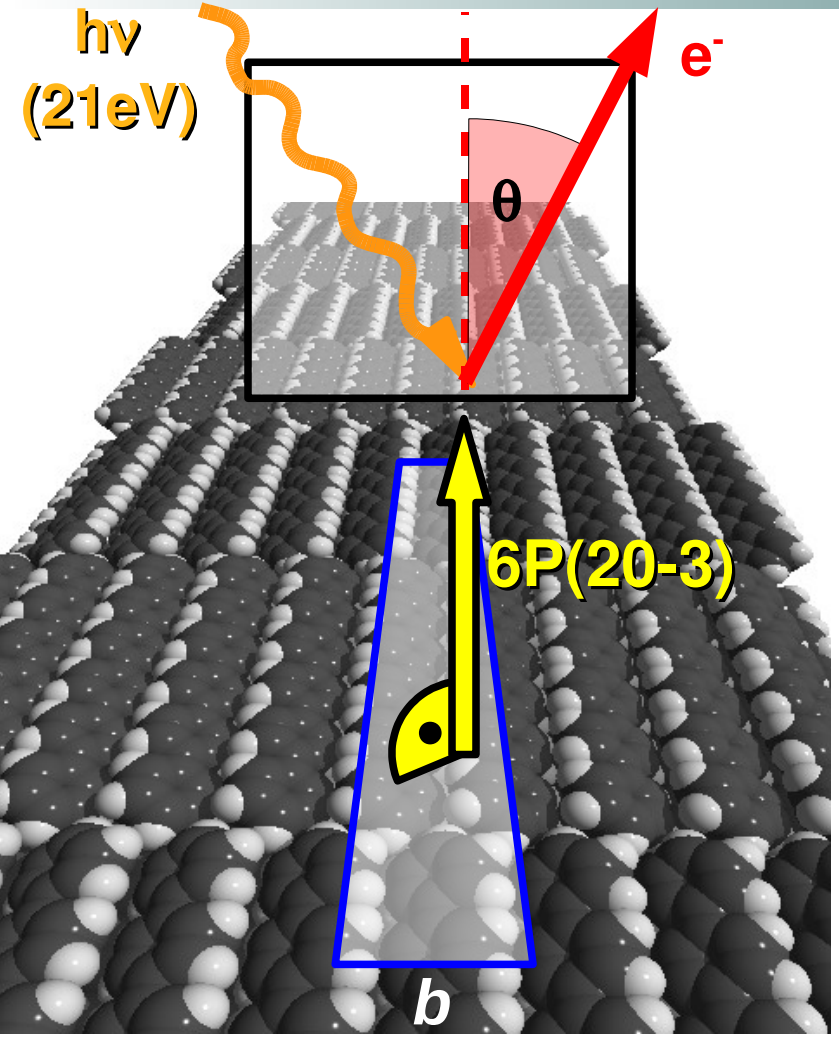
Twisted Sexiphenyl



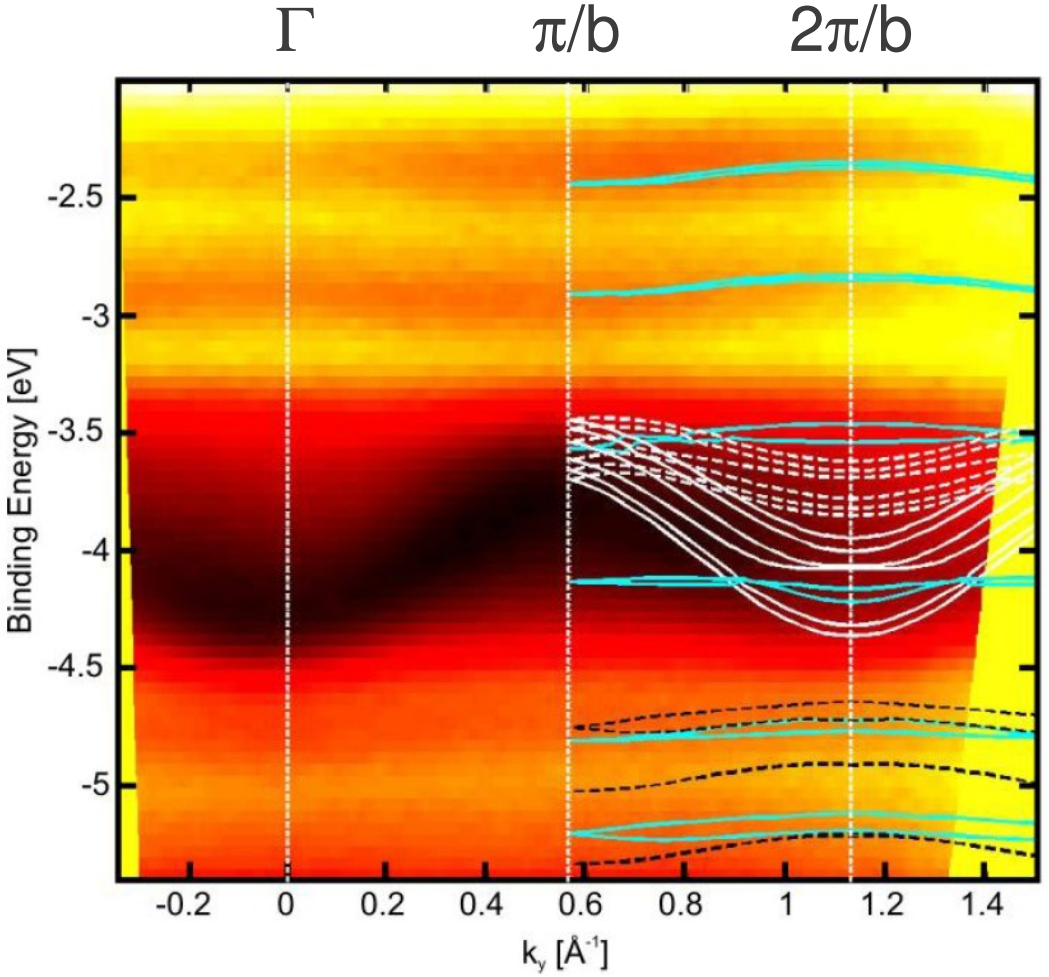


G. Koller et al., *Science* ***317****, 351 (2007).*

Intermolecular Dispersion



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



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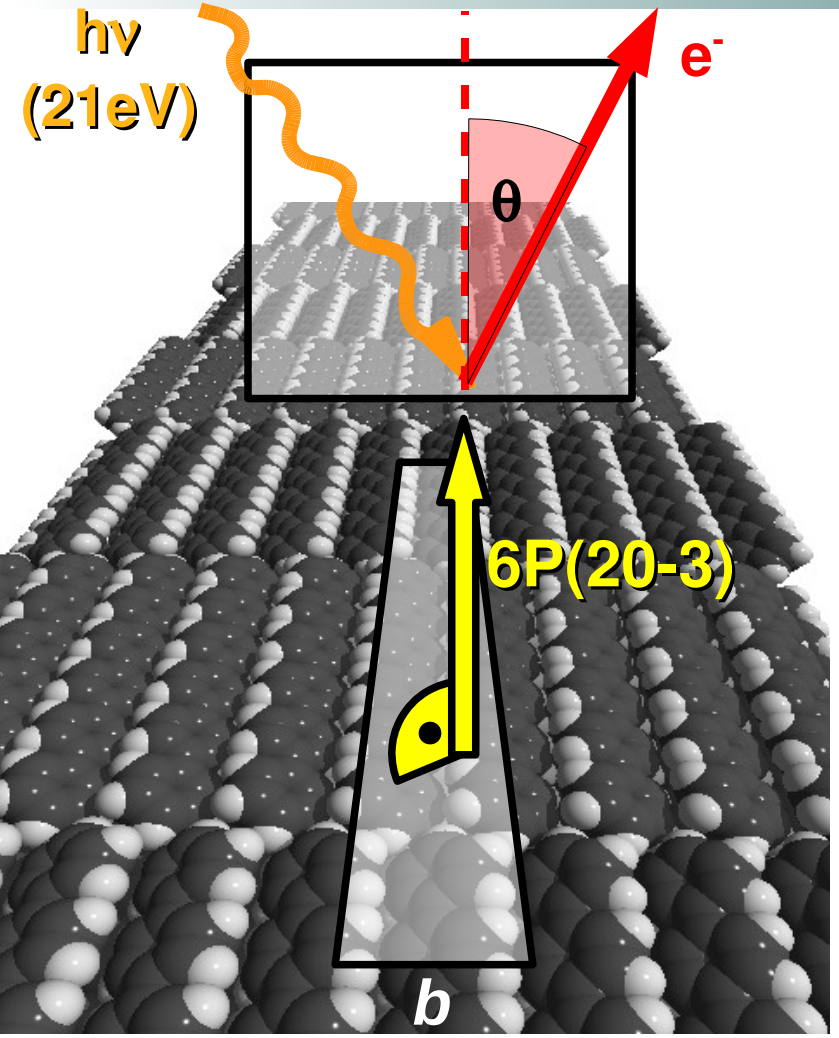
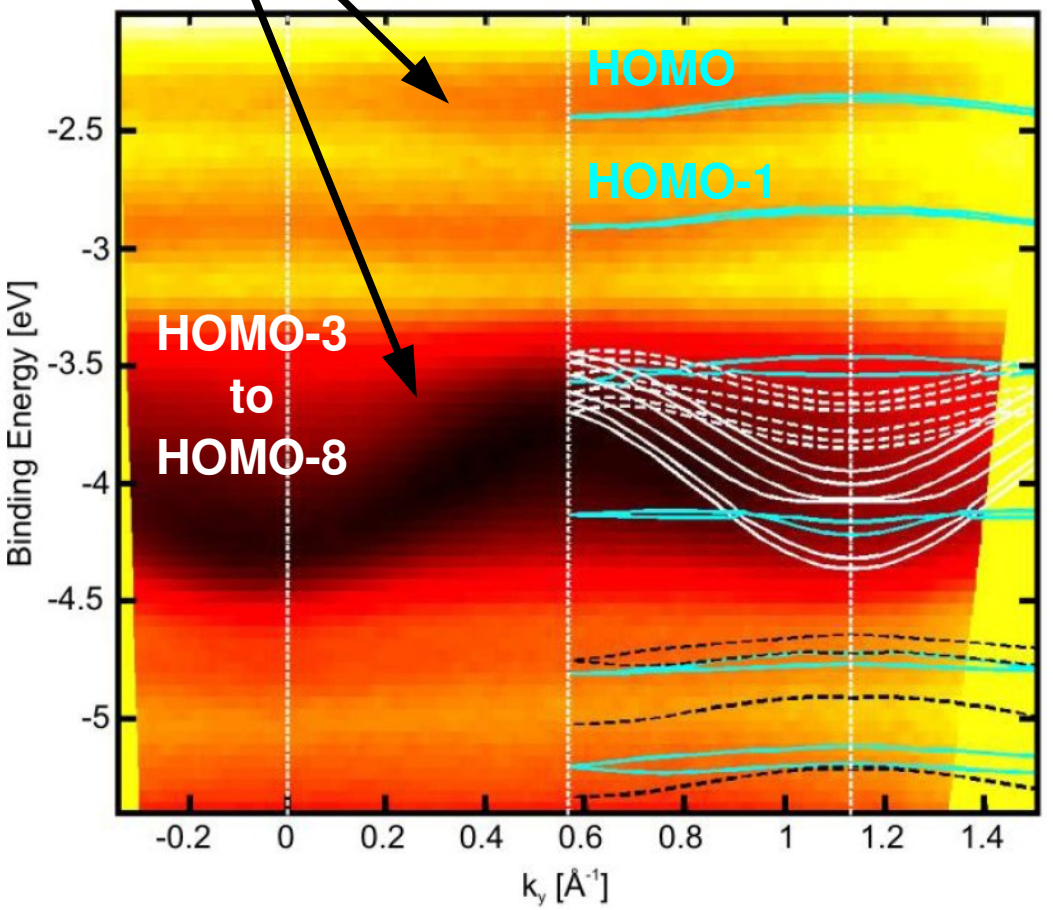
Intermolecular Dispersion



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

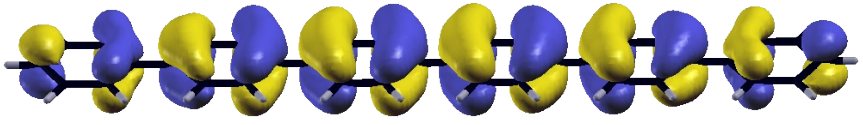
1. Why is the dispersion so different?
2. Why is the PE intensity so different?



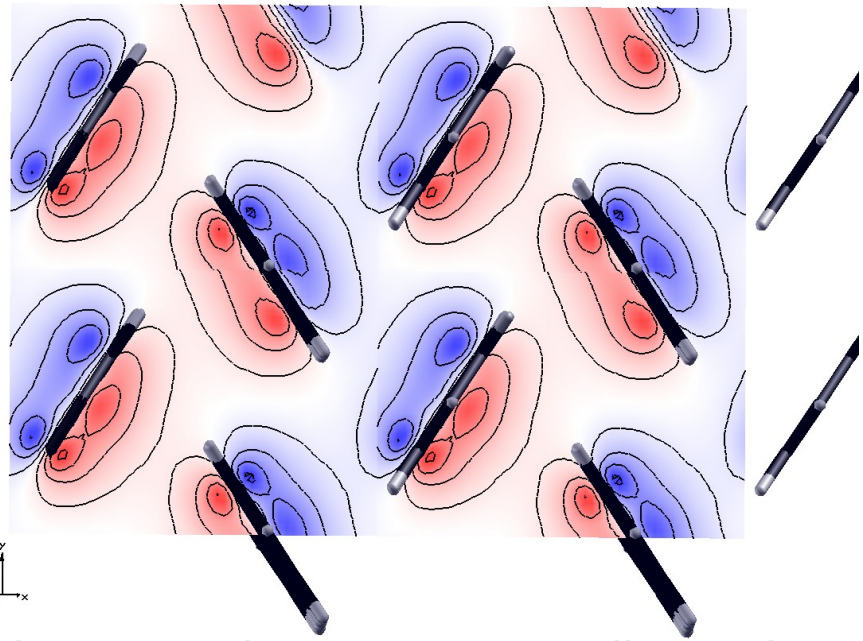
G. Koller et al., *Science* ***317****, 351 (2007).*

1. Dispersion

HOMO

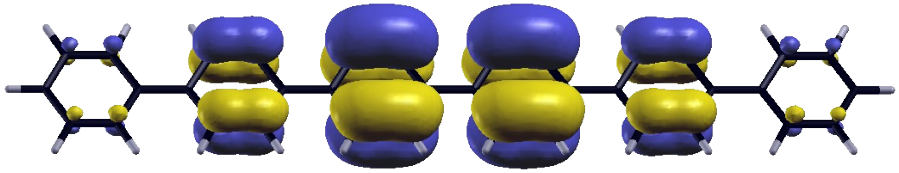


de-localized over a molecule

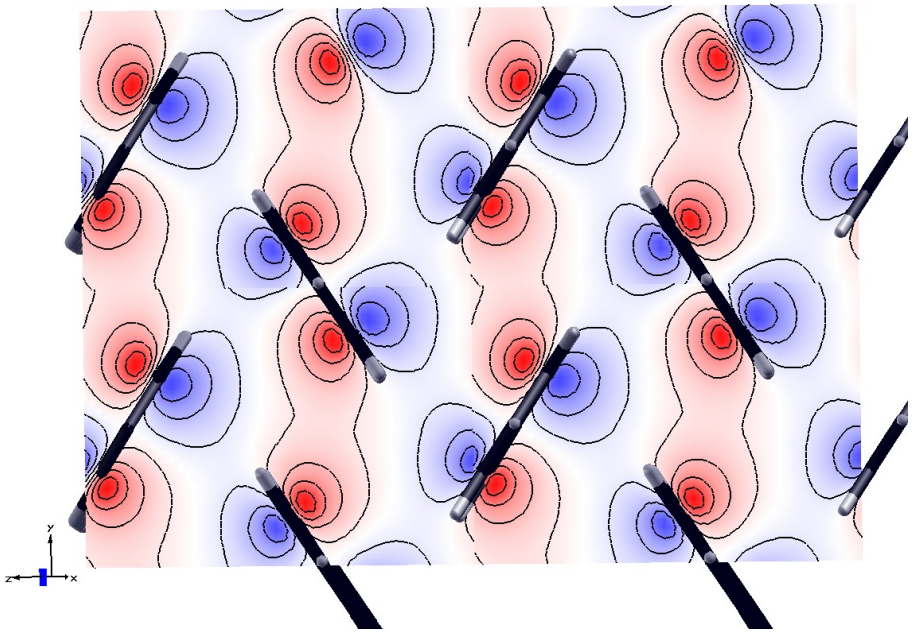


... but small intermolecular dispersion

HOMO-8

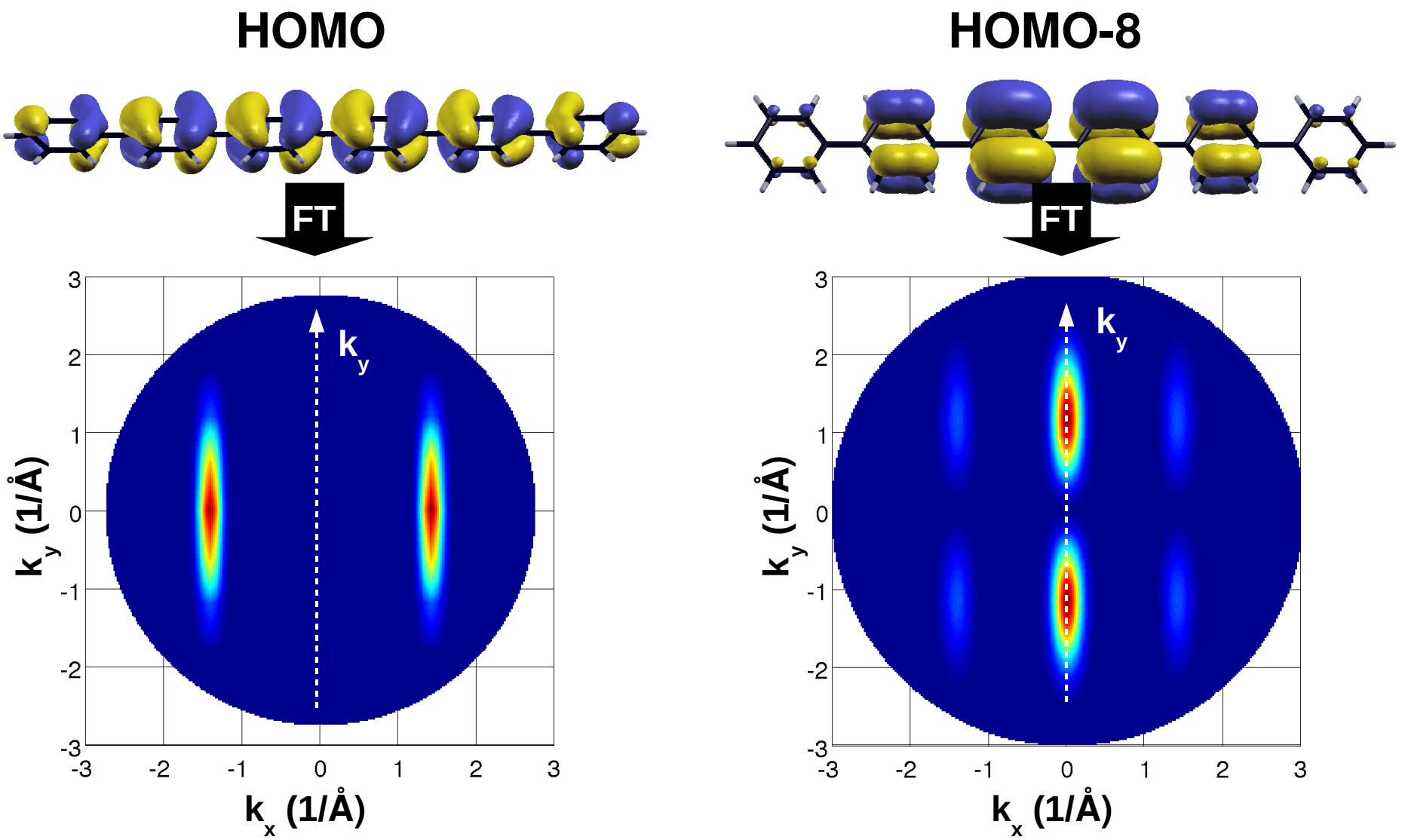


localized on rings

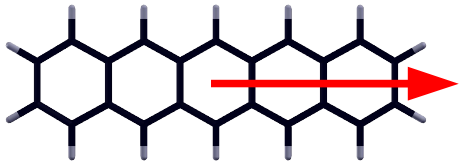


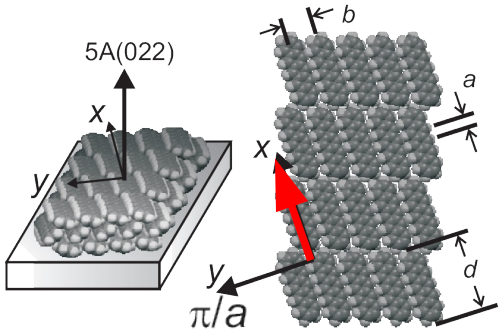
... and sizeable intermolecular dispersion

2. Photoemission Intensity

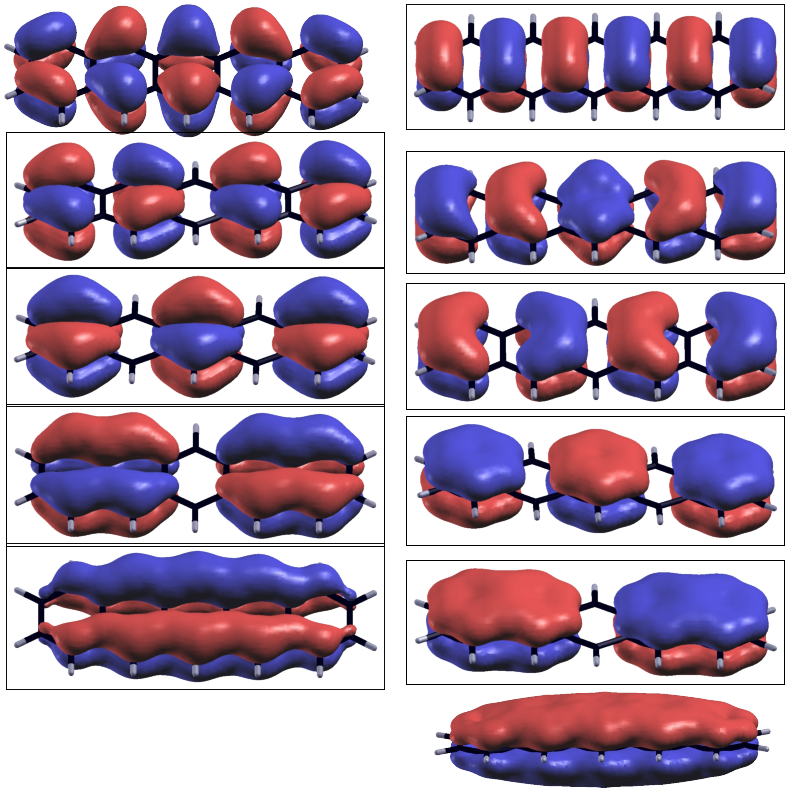


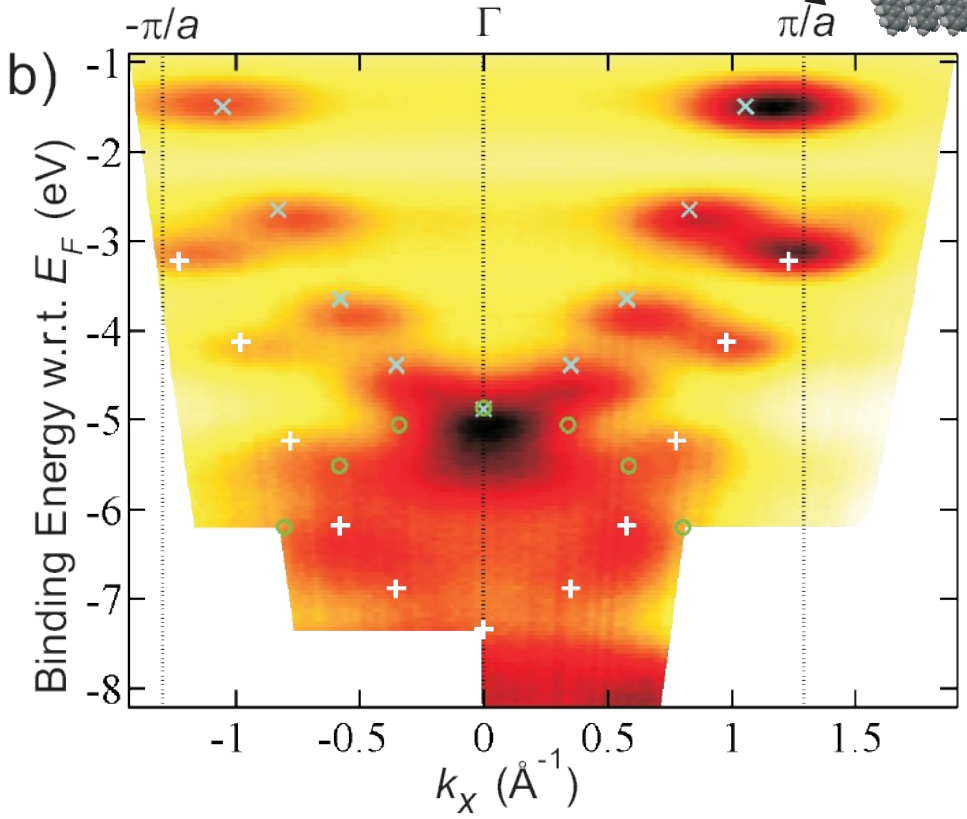
ARPES of Oriented Pentacene





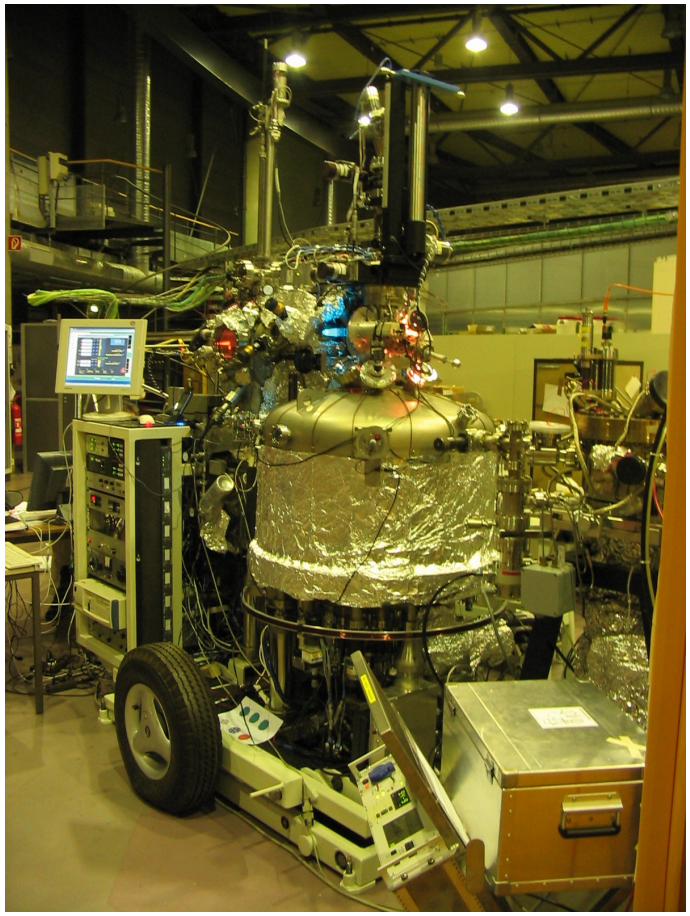
22 Carbons lead to
11 occupied π orbitals



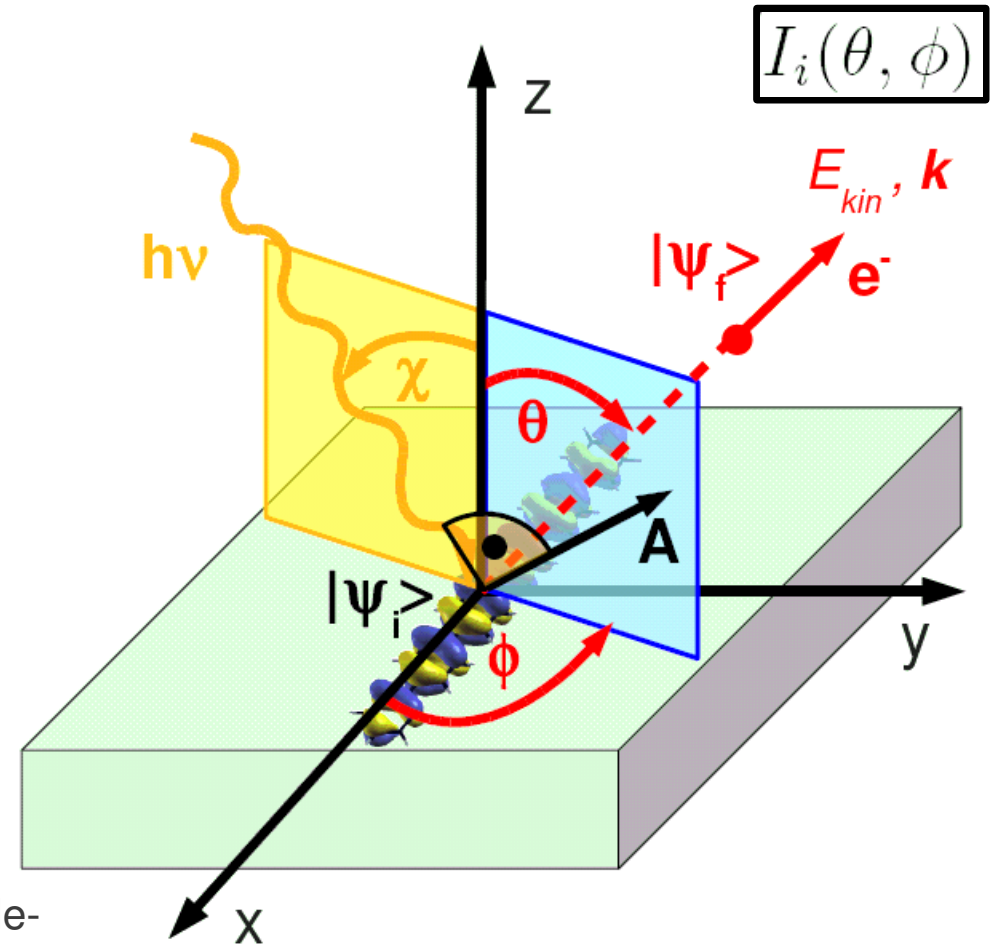


S. Berkebile et al., *Phys. Rev. B* **77**, 115312 (2008)

Orbital Tomography

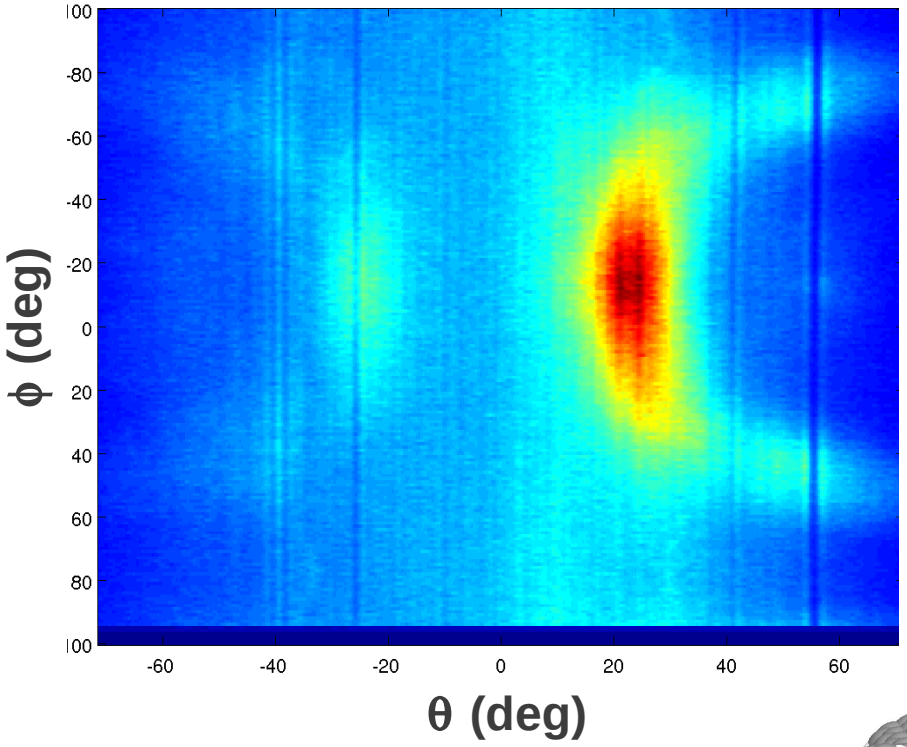


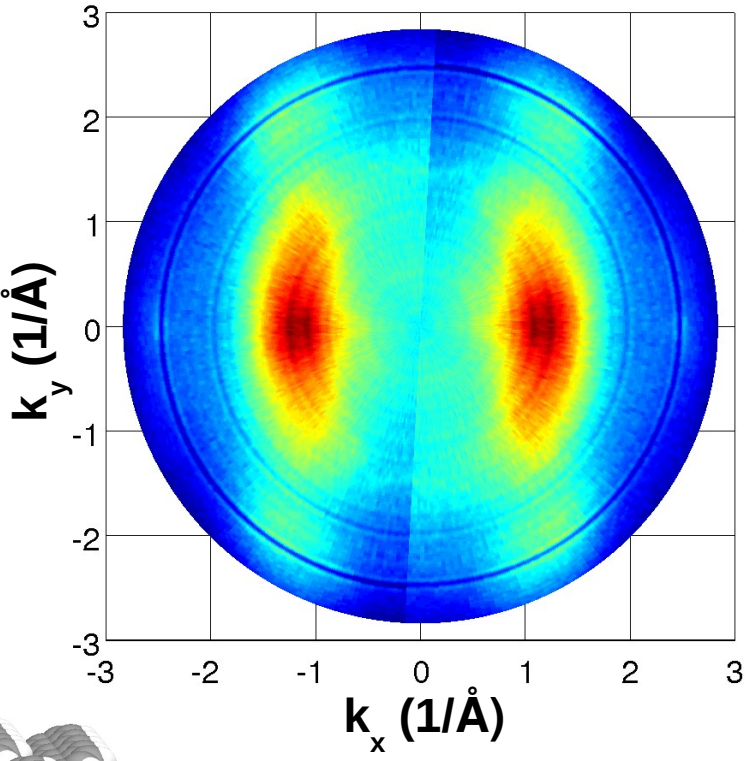
The Toroidal Electron Spectrometer for Angle-Resolved Photoelectron Spectroscopy with Synchrotron Radiation at BESSY II



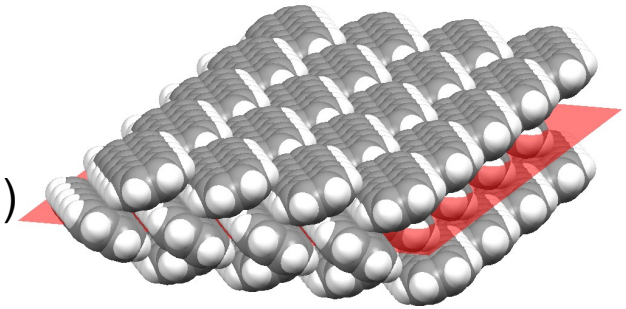
Pentacene HOMO

Azimuthal Scans at constant photon energy and constant kinetic energy





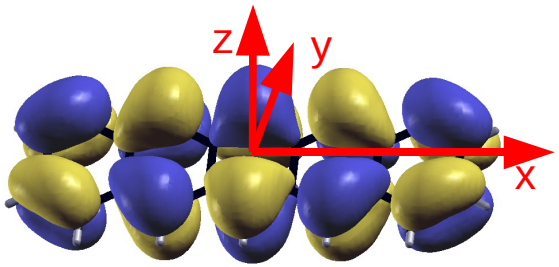
Azimuthal scan from a multilayer of **Pentacene**/Cu(110)_(2x1) at the **HOMO** energy



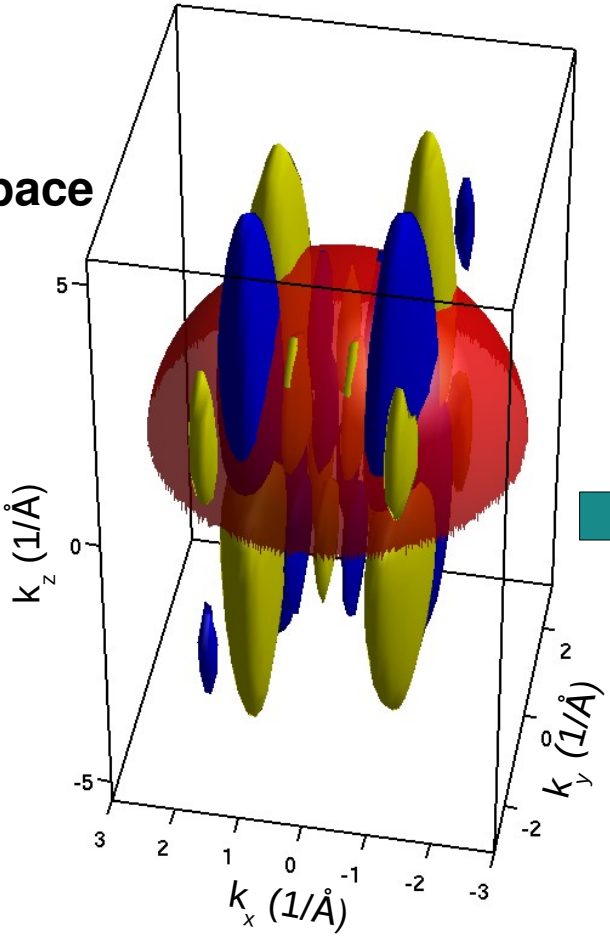
$$k_{\parallel} = \sqrt{\frac{2m}{\hbar^2} E_{\mathrm{kin}}} \sin\theta$$

Pentacene HOMO

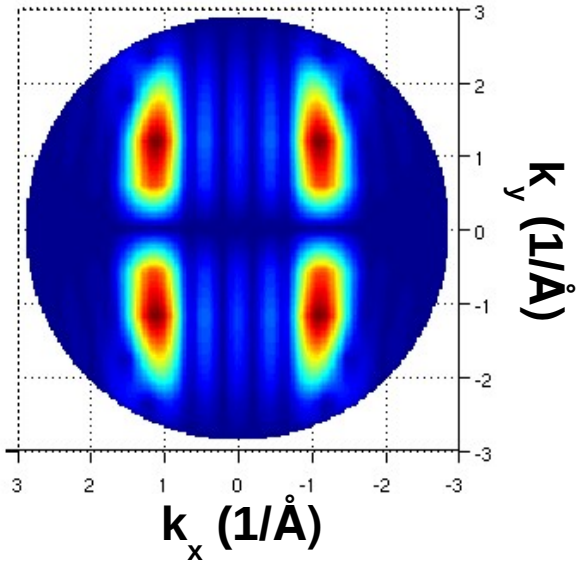
Molecular Orbital in Real Space



Calculation of the Fourier Transform

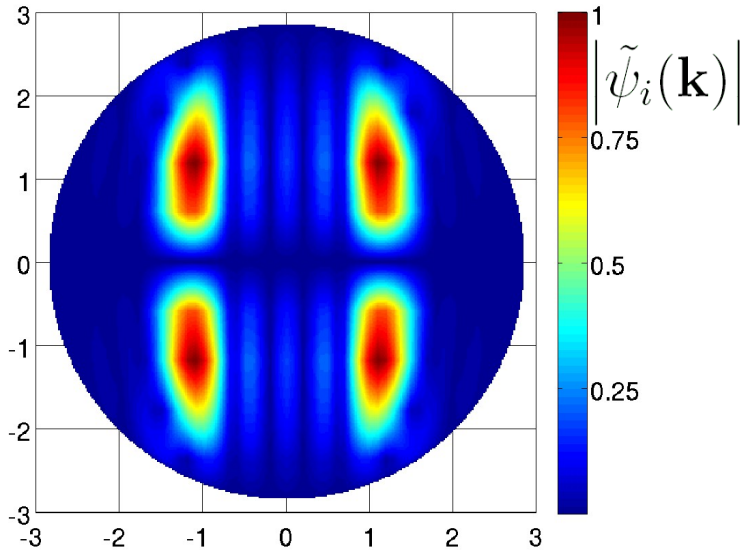


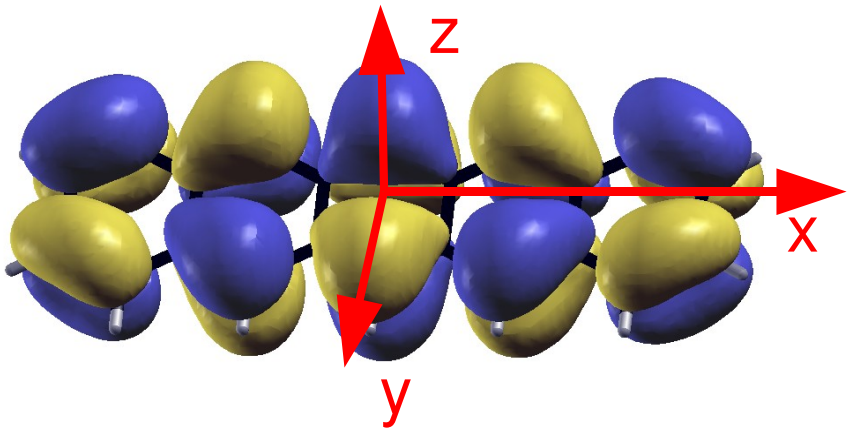
Hemispherical Cut Through 3D Fourier Transform



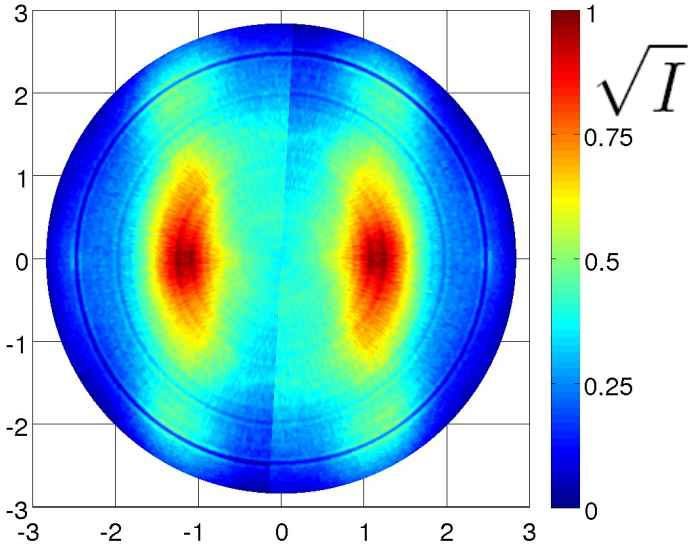
Pentacene HOMO

Theory





ARPES



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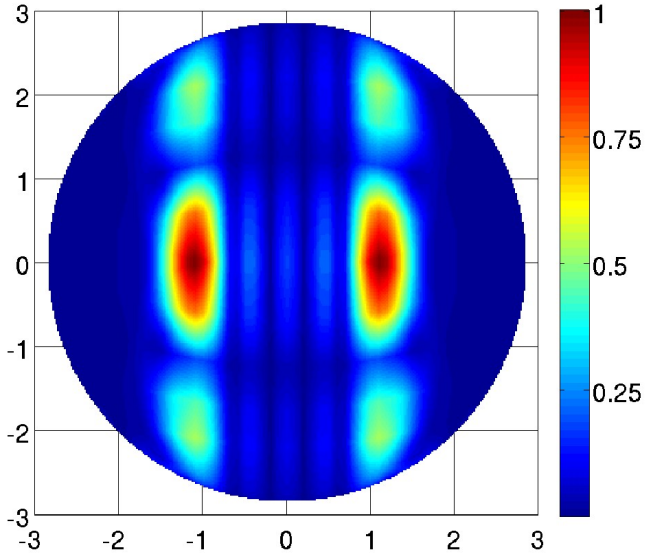
Pentacene HOMO

Theory



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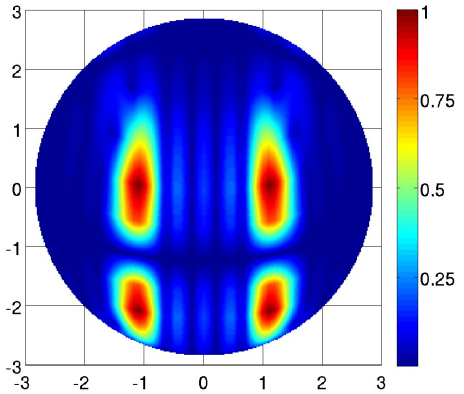
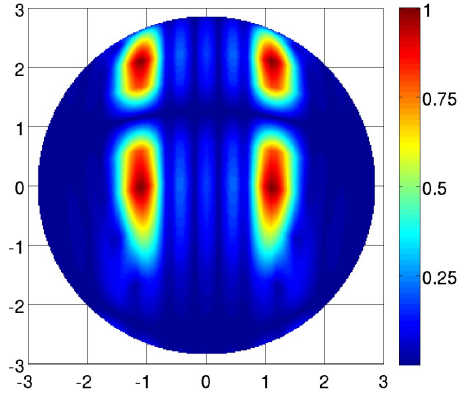


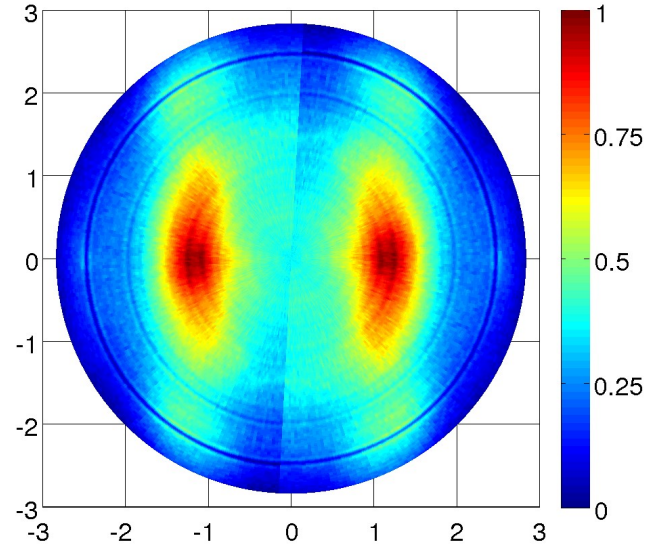
+26 deg tilt

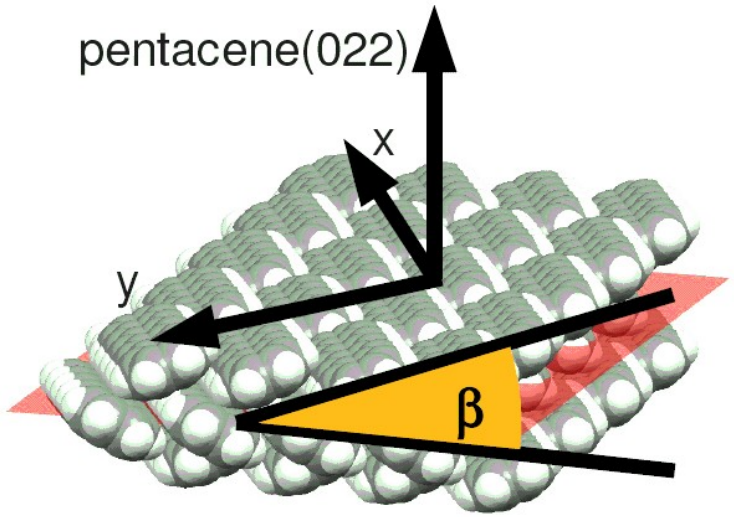
+



–26 deg tilt

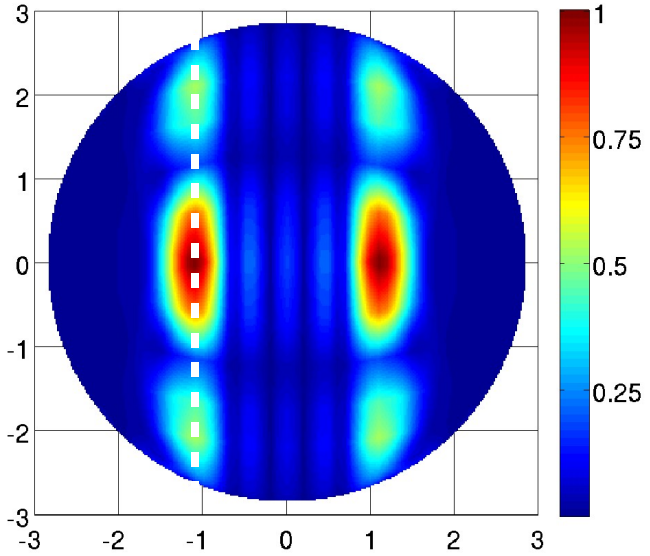
ARPES



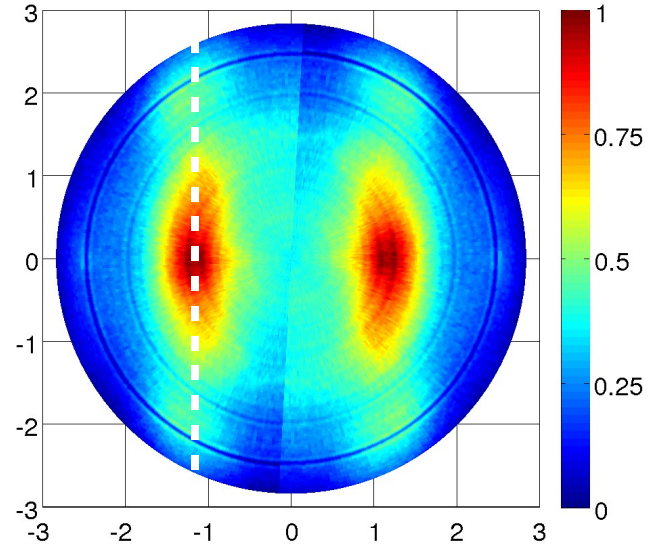


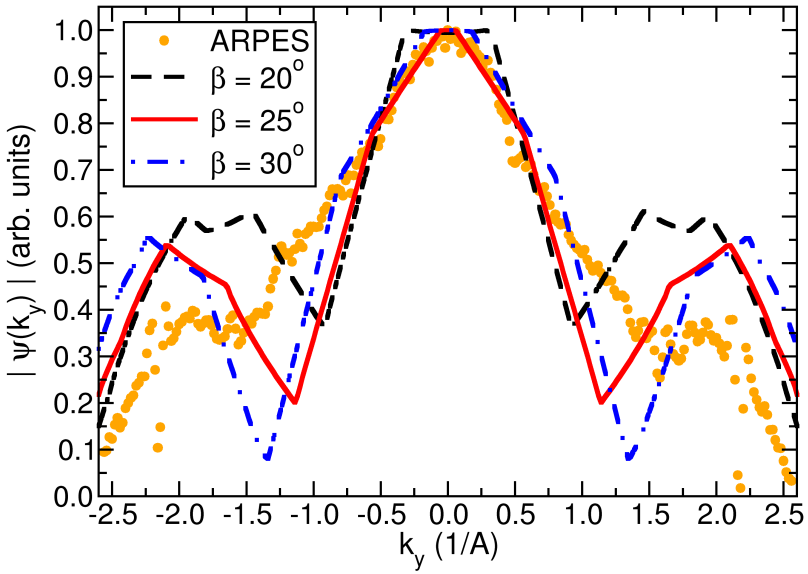
Pentacene HOMO

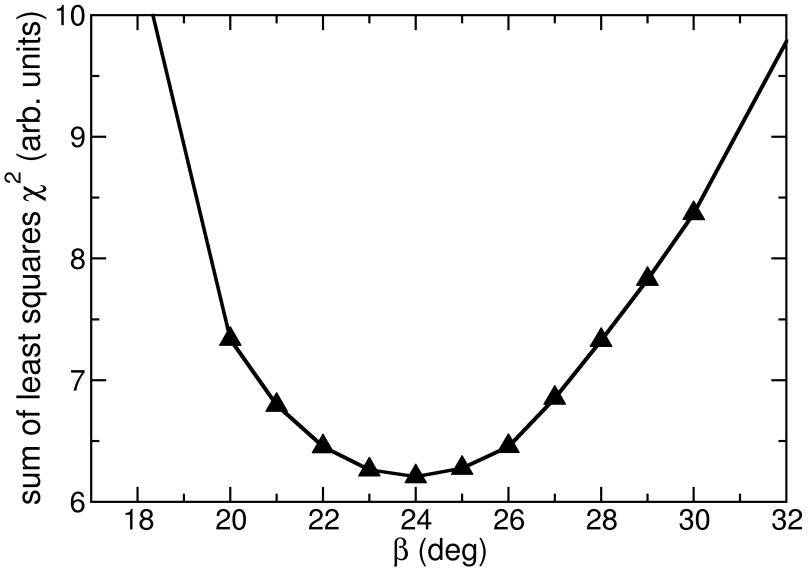
Theory



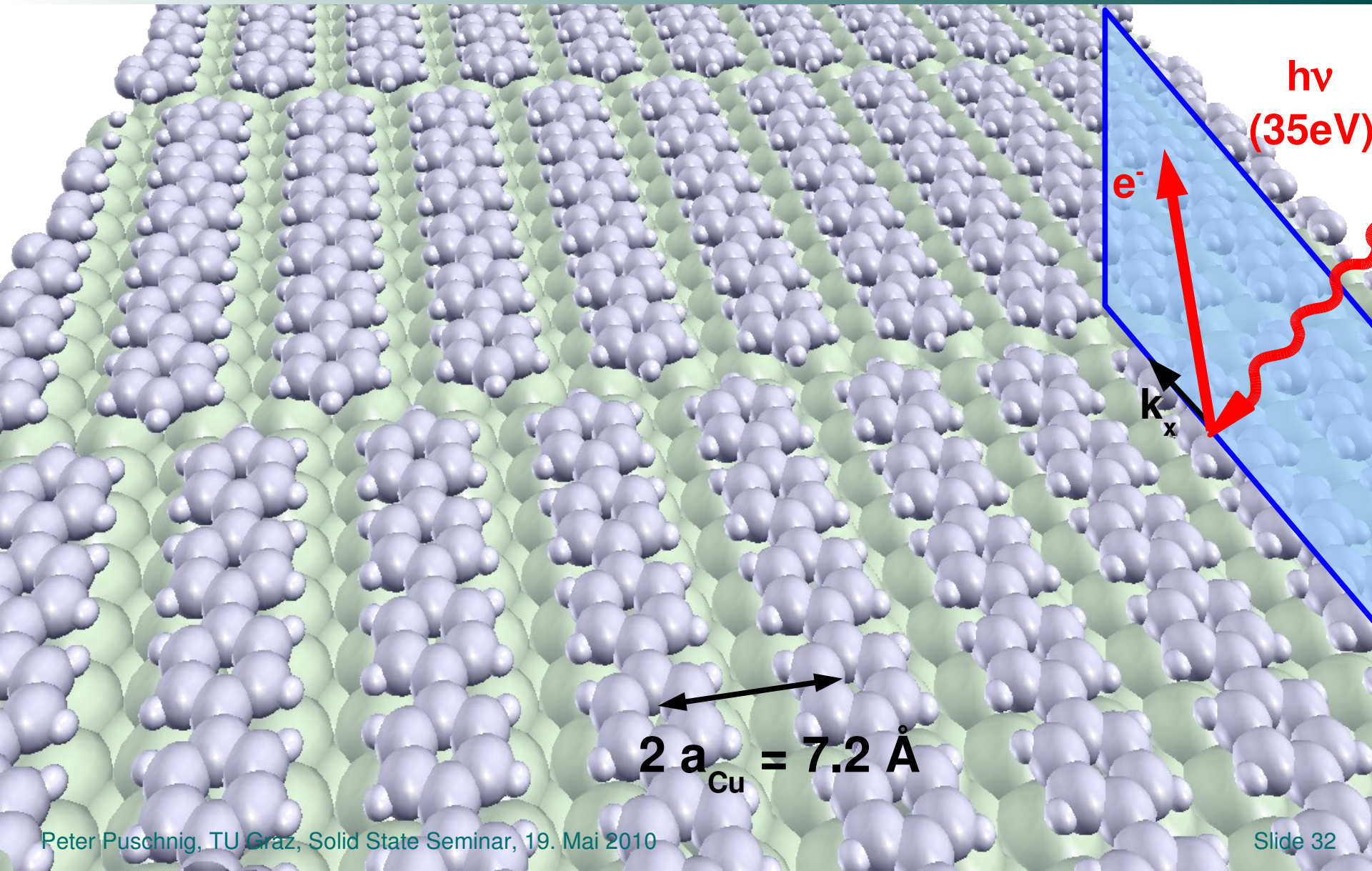
ARPES



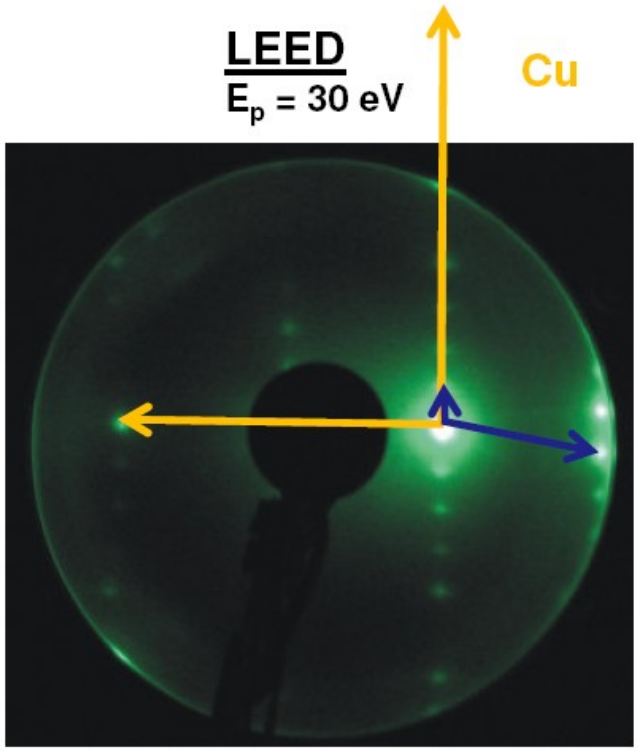


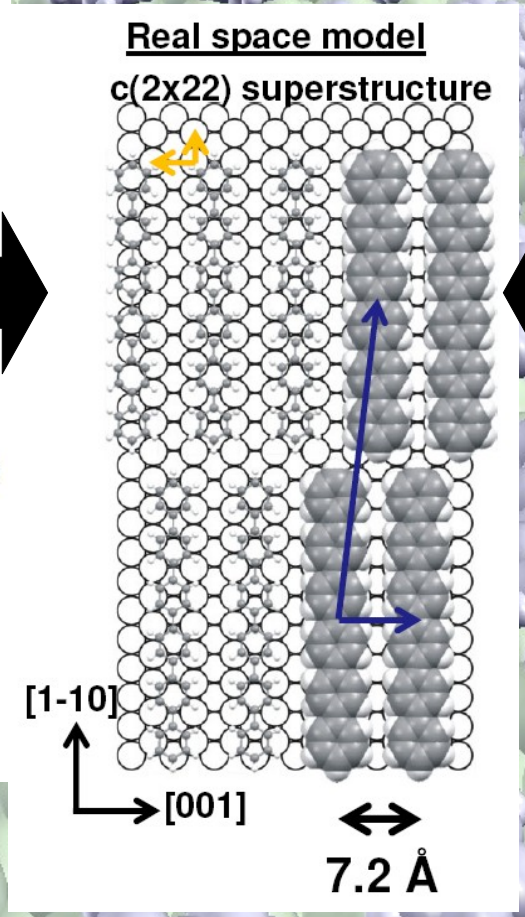


Sexiphenyl Monolayer on Cu(110)

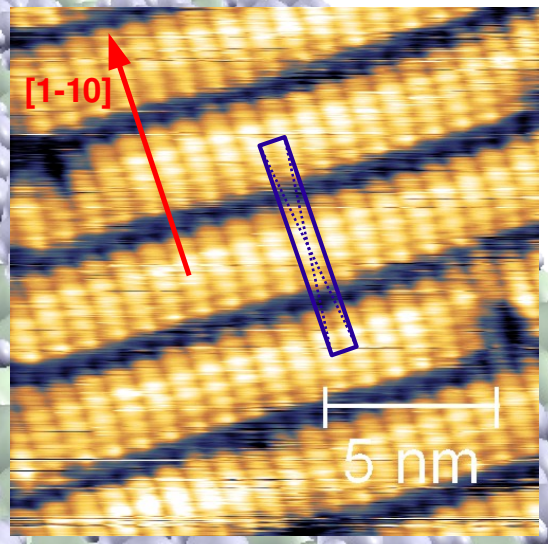


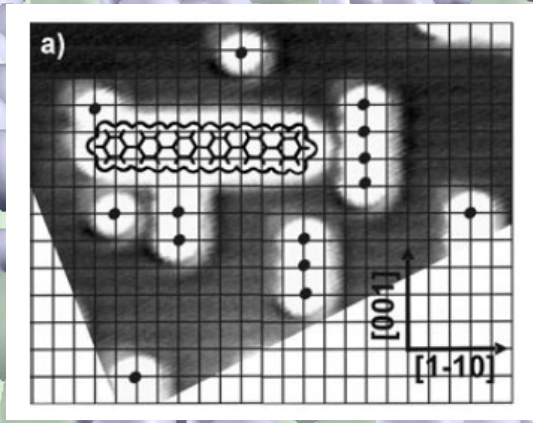
Sexiphenyl Monolayer on Cu(110)





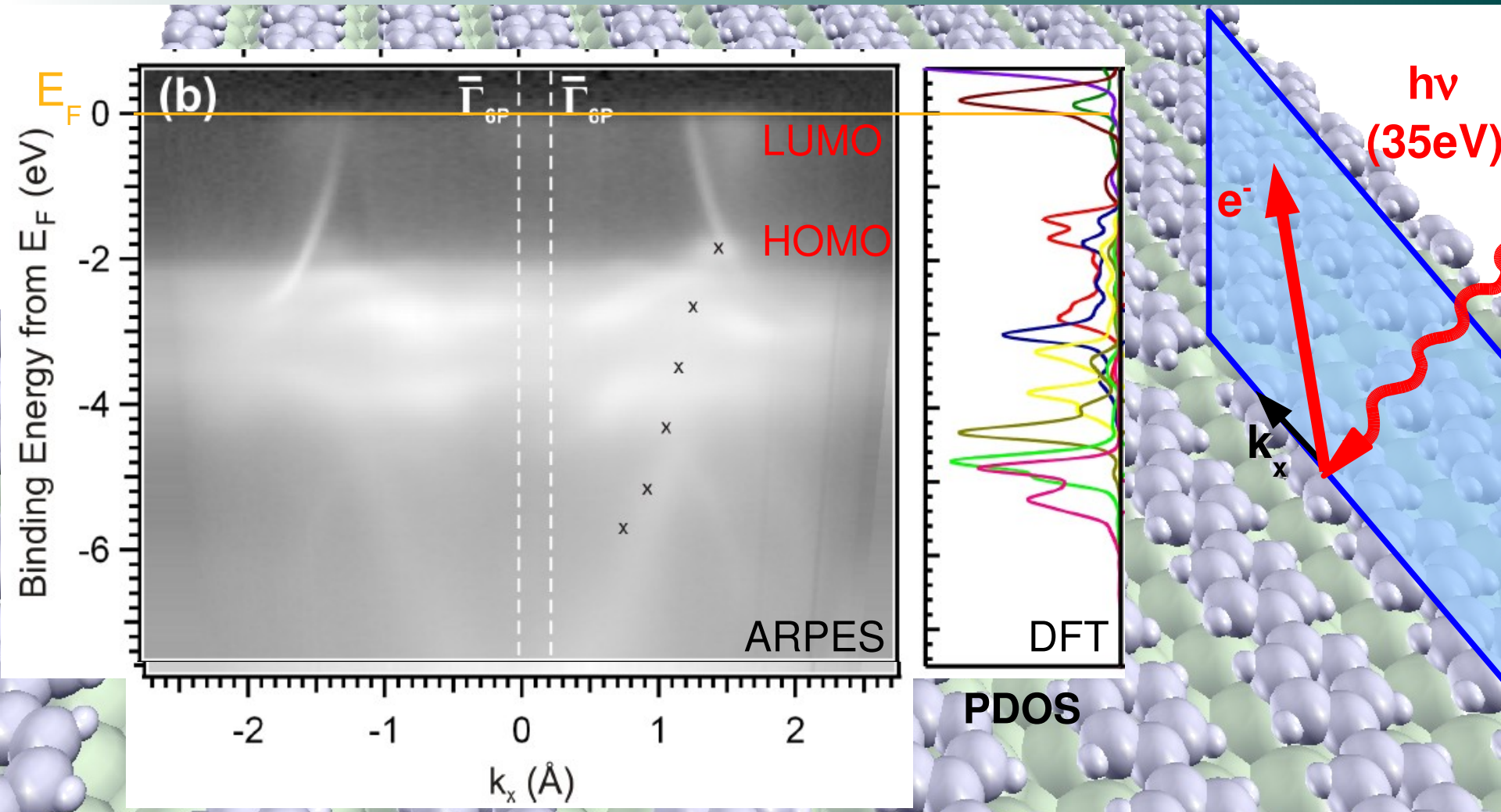
STM





M. Oehzelt et al., ChemPhysChem 8, 1707 – 1712 (2007).

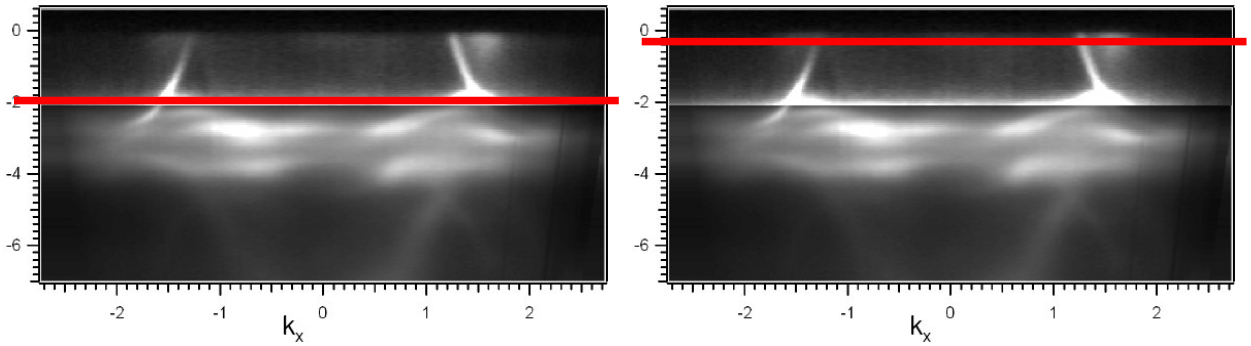
Sexiphenyl Monolayer on Cu(110)



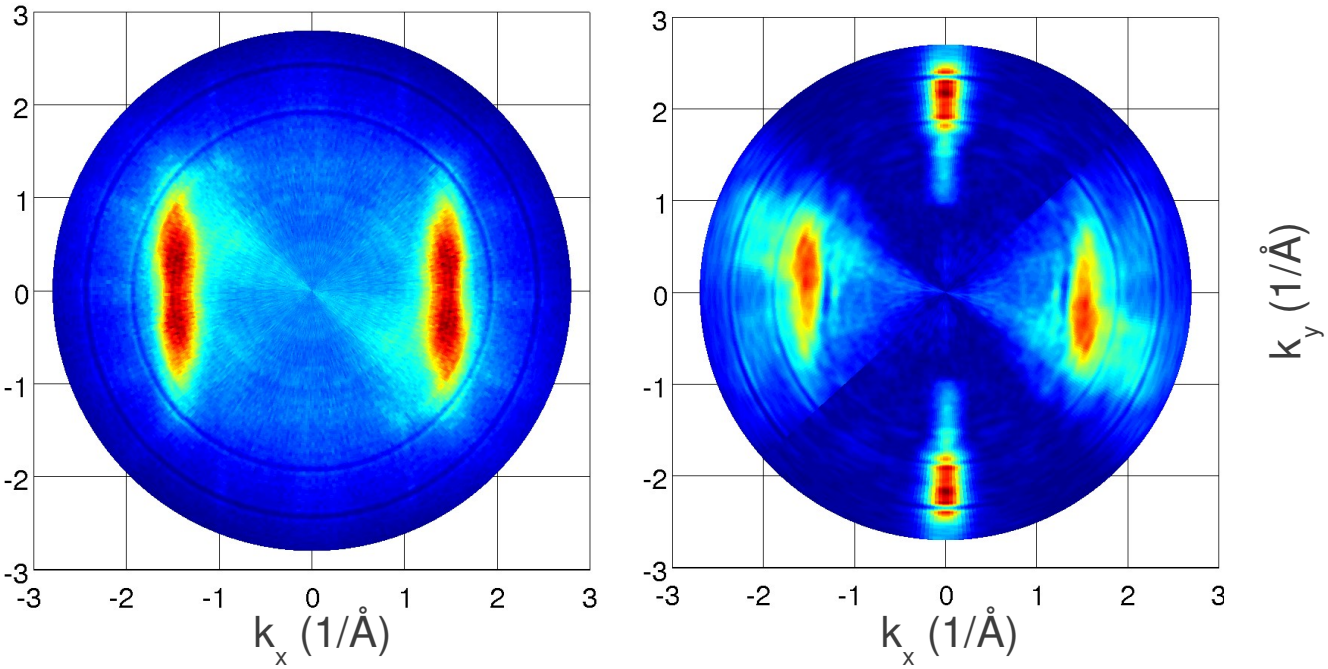
Berkebile et al. (submitted to PNAS)

2D-Momentum Maps

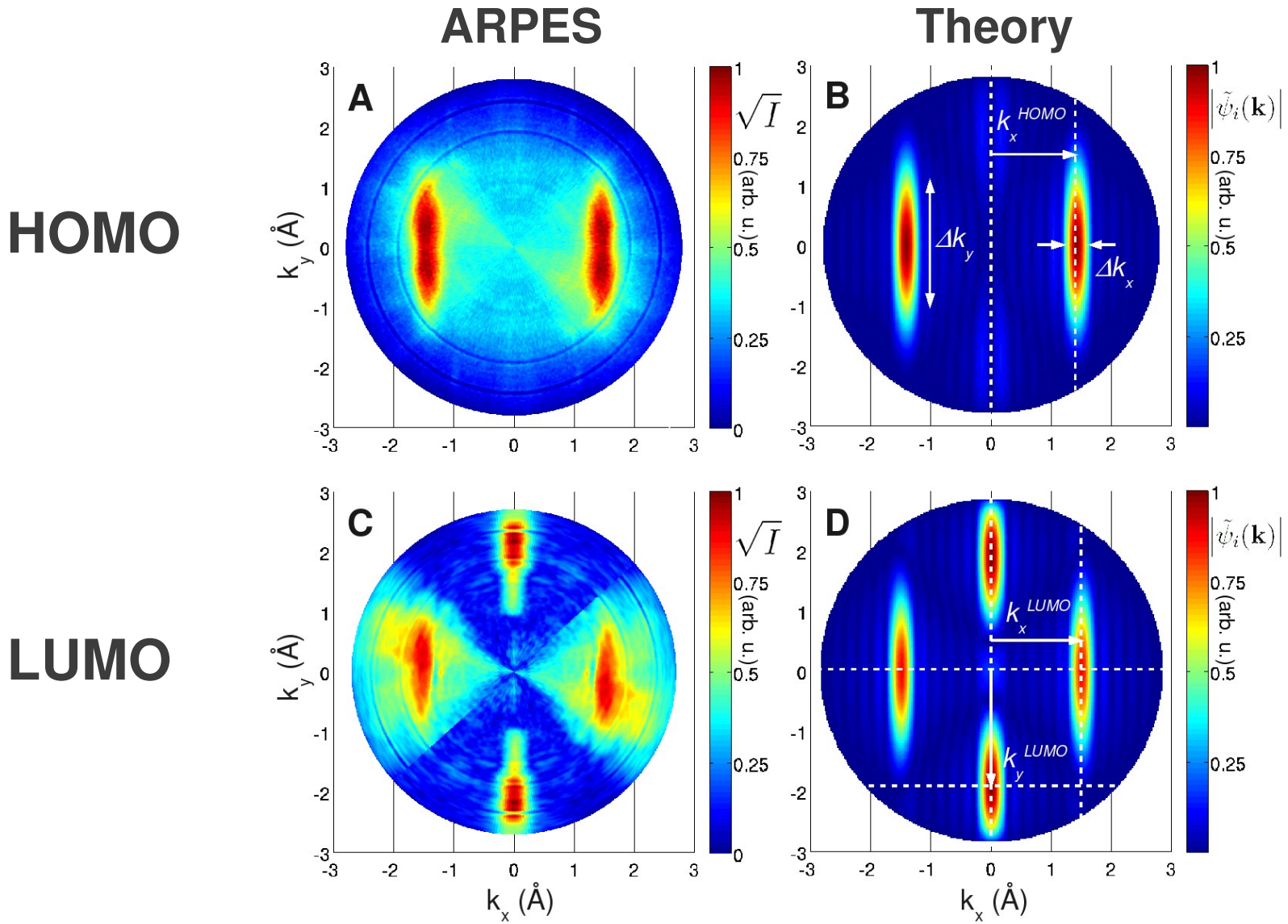
ARPES data for a monolayer of 6P / Cu(110)



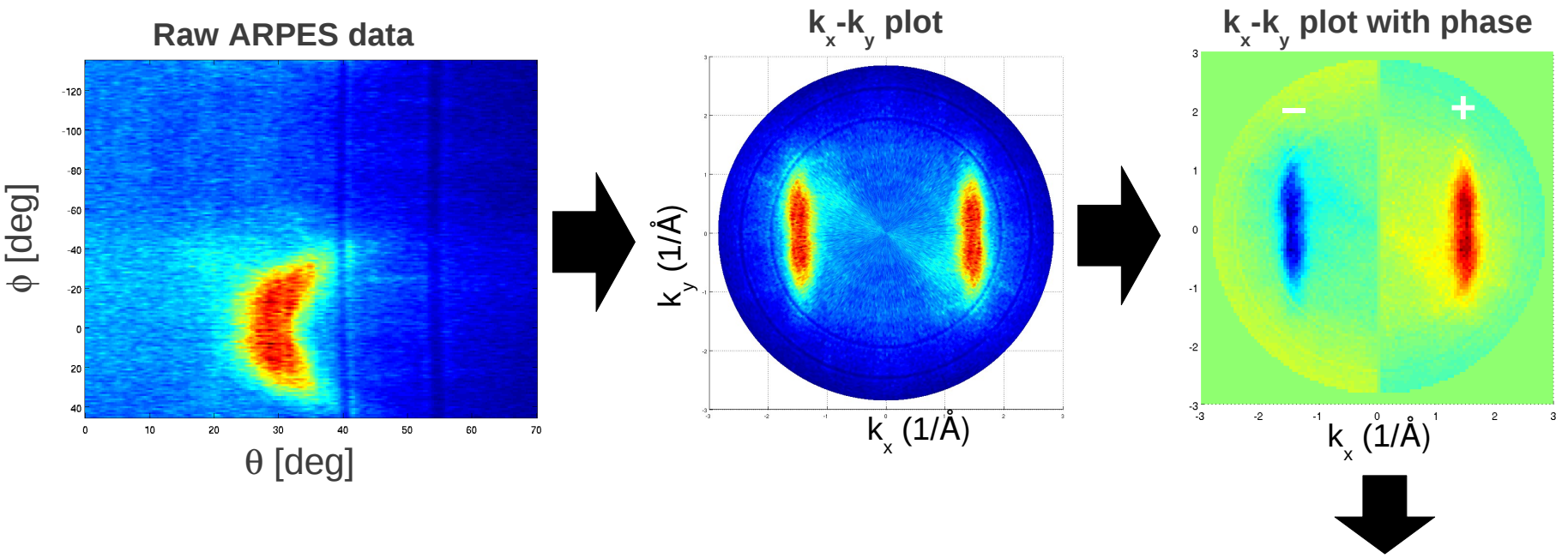
HOMO **filled LUMO**



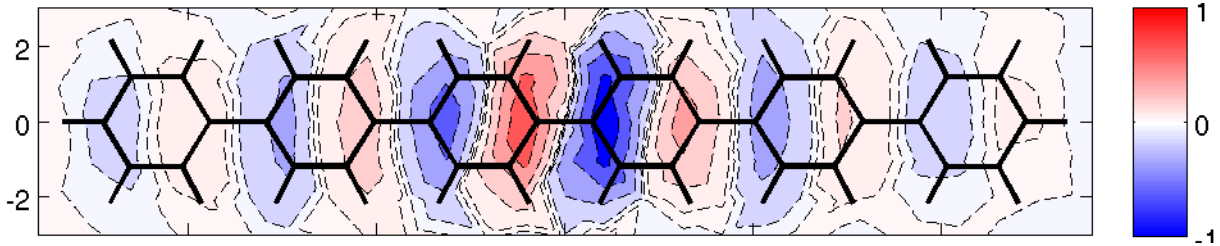
2D-Momentum Maps



Reconstruction of Orbitals



6P HOMO from ARPES

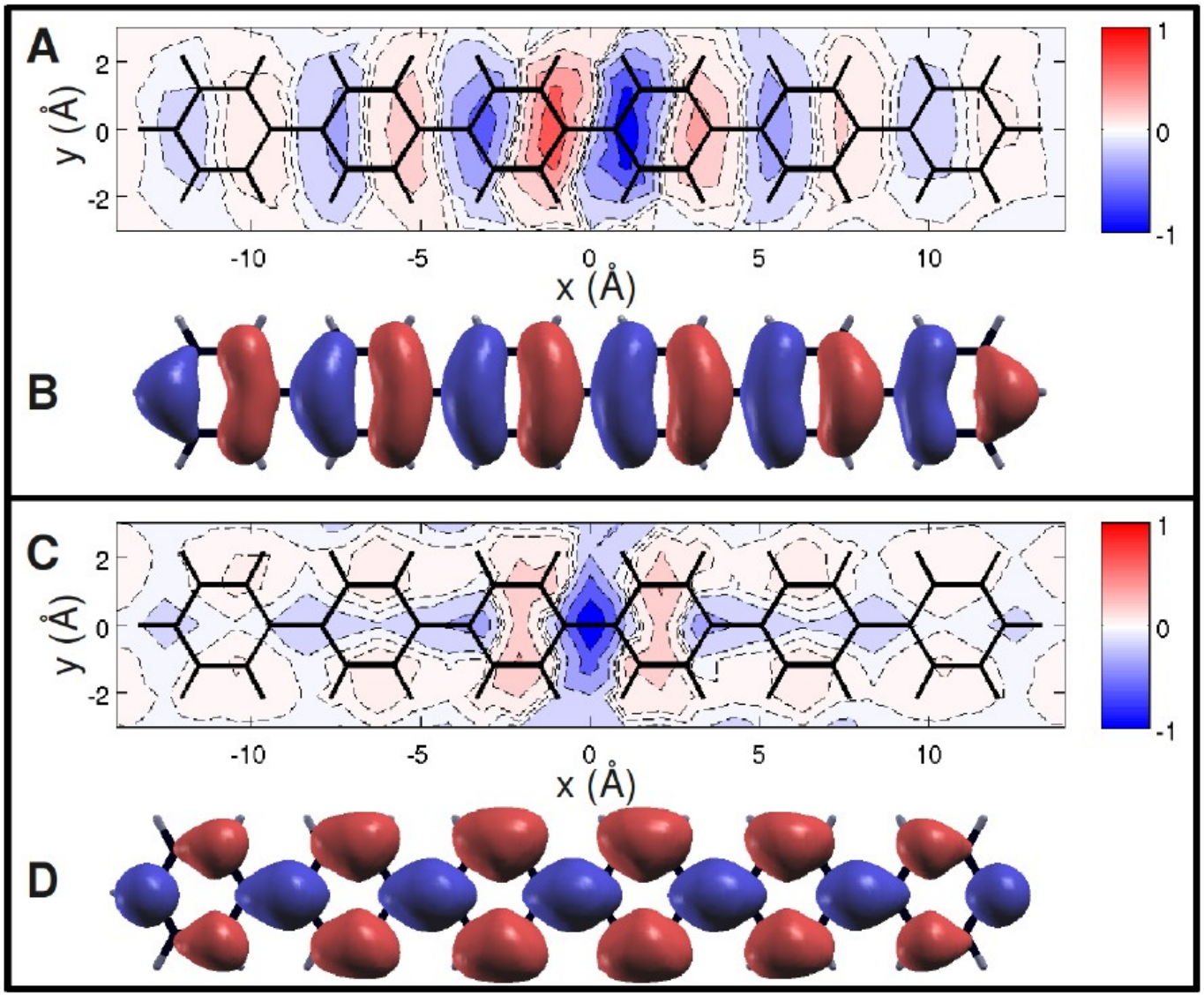


Puschnig et al., *Science* **326**, 702 (2009).

Reconstruction of Orbitals

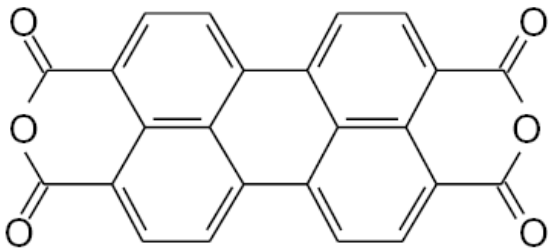
HOMO

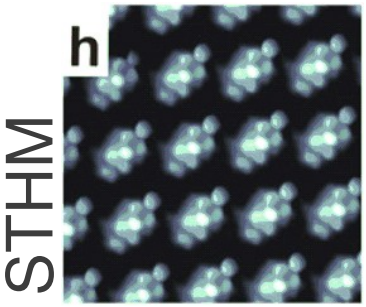
Filled LUMO



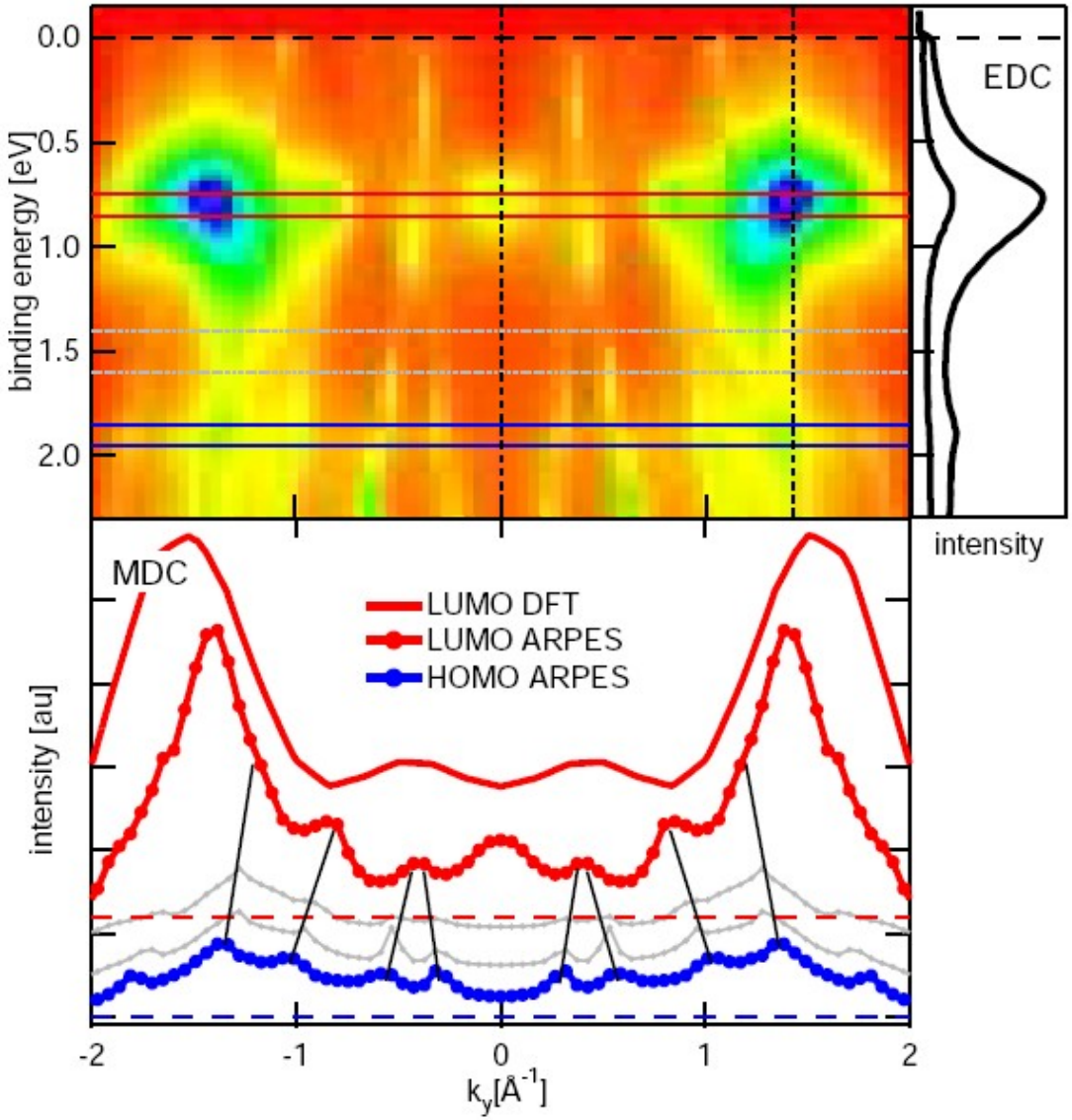
Monolayer PTCDA / Ag(110)

PTCDA
perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride



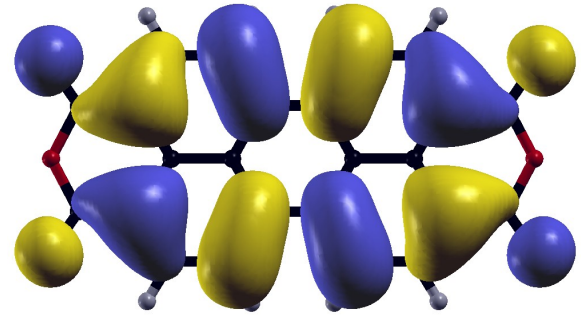


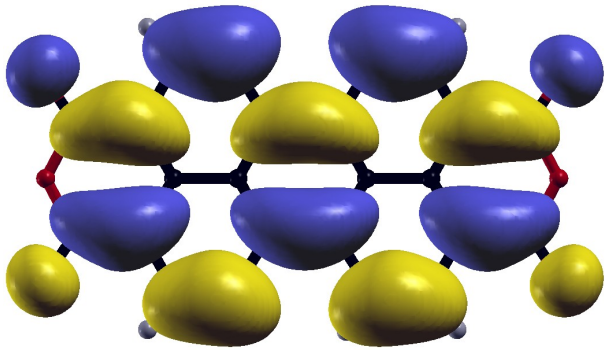
Uniaxially aligned PTCDA/Ag(110)
Temirov et al., New J. Phys. 10, 053012 (2008)

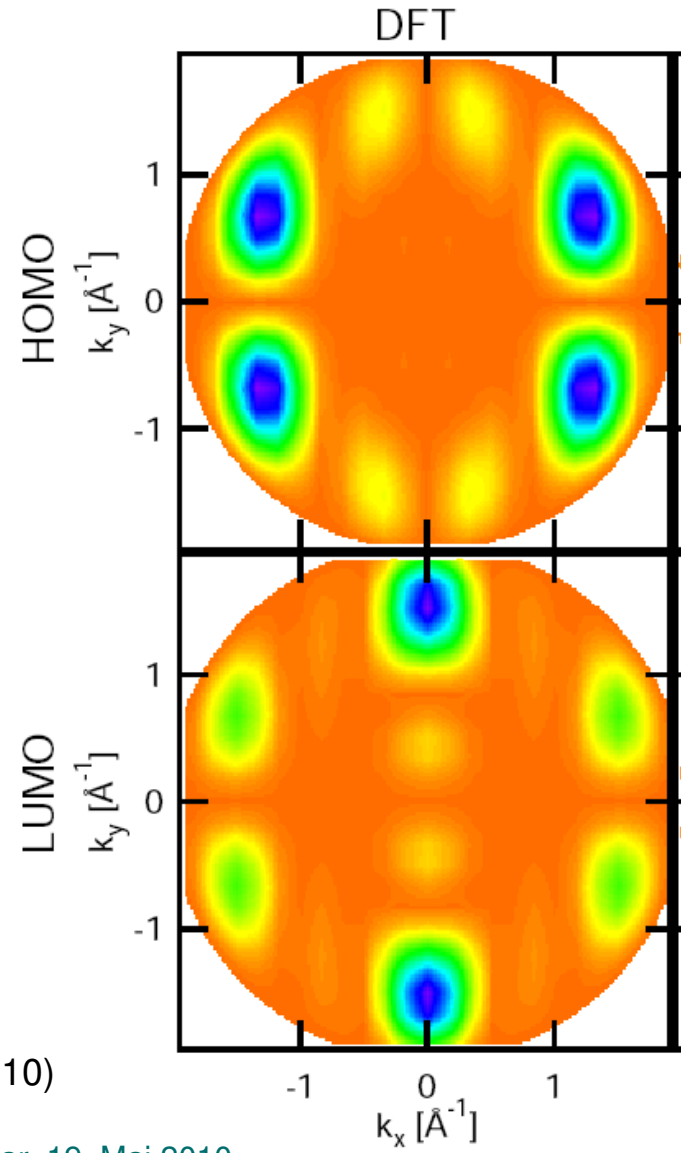


Ziroff et al., *Phys. Rev. Lett.* (June, 2010)

Monolayer PTCDA / Ag(110)

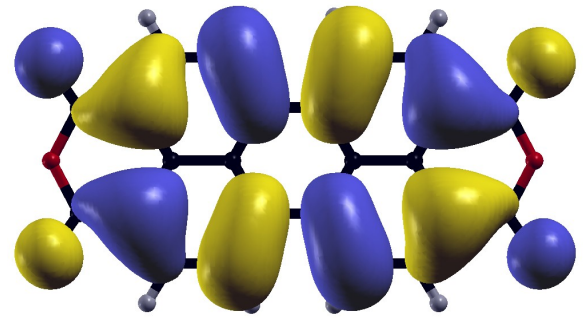


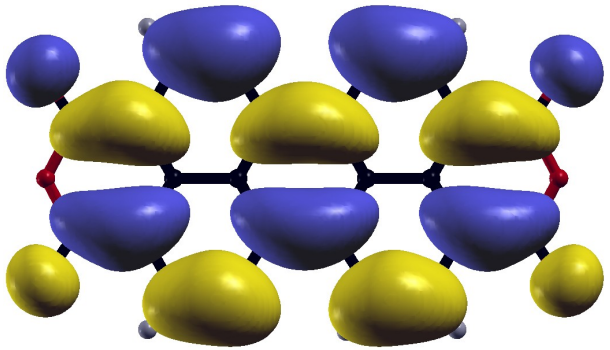


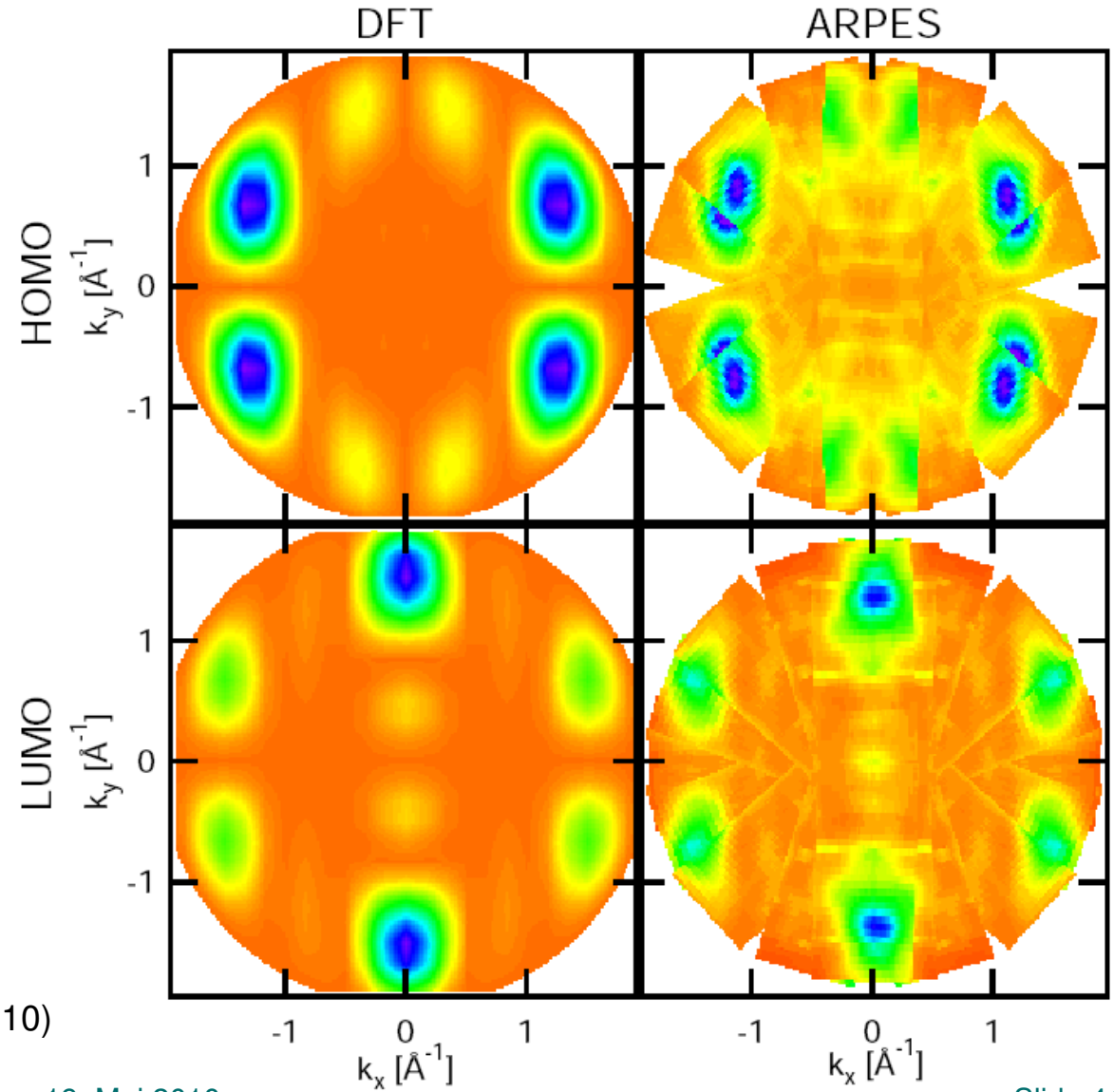


Ziroff et al., *Phys. Rev. Lett.* (June, 2010)

Monolayer PTCDA / Ag(110)

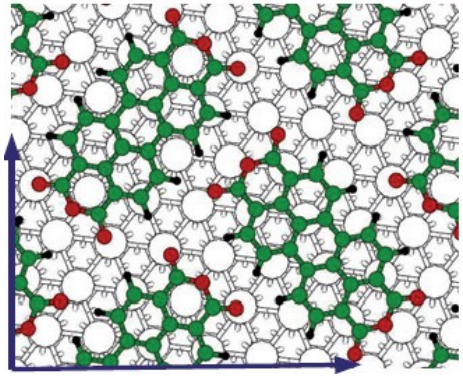






Ziroff et al., *Phys. Rev. Lett.* (June, 2010)

Monolayer PTCDA / Ag(111)

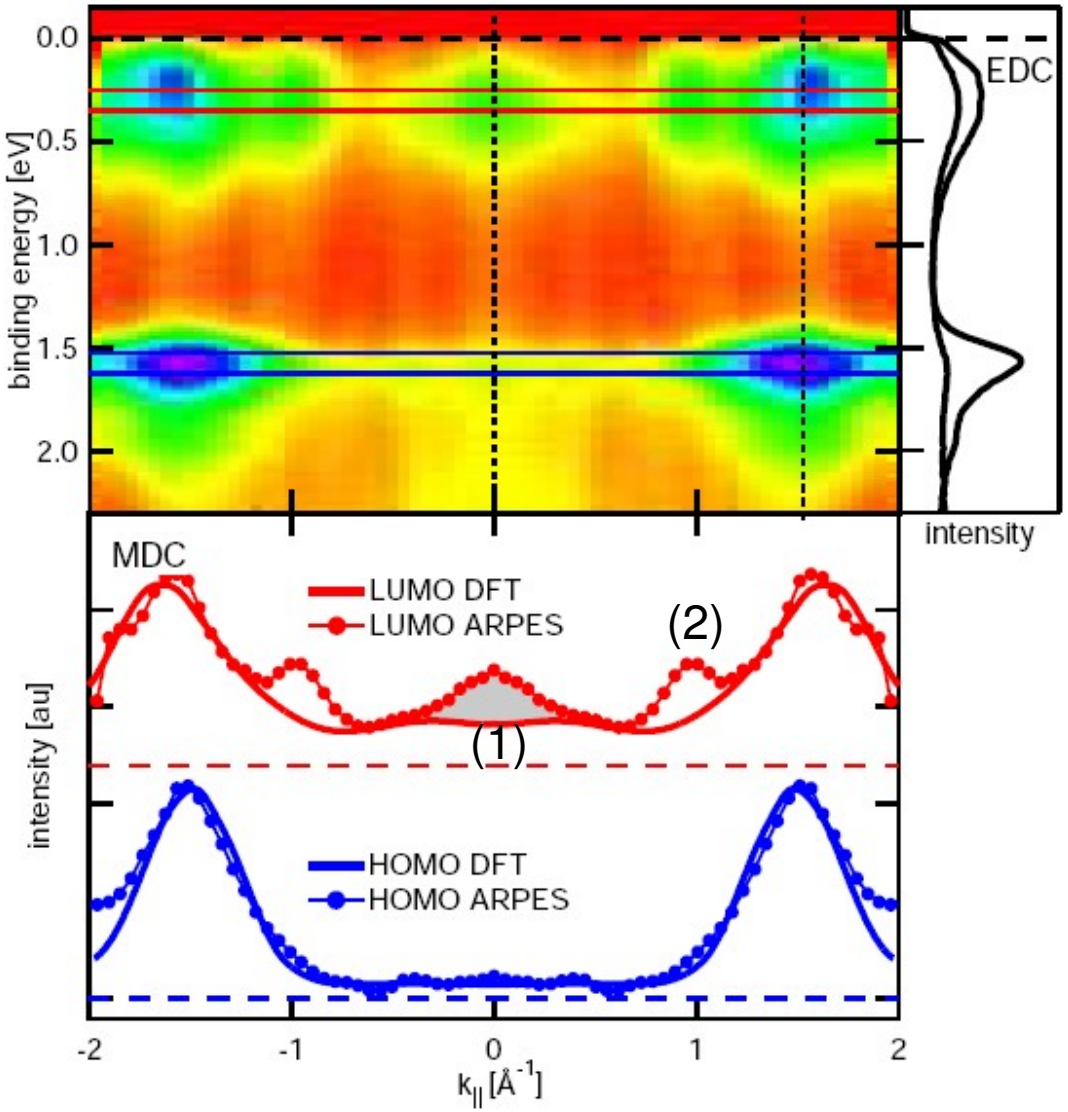


2 molecular orientations +
6 symmetrically equivalent domains

LUMO shows signature of hybridization with Ag:

(1) Node-free charge accumulation around the central carbon ring
(2) Maybe due to intermolecular interactions

HOMO remains undistorted upon adsorption on Ag(111)



Ziroff et al., *Phys. Rev. Lett.* (June, 2010)

Conclusion and Outlook

Angle-resolved photoemission: From reciprocal space to real space

F.J. Himpsel, J. Electron Spectrosc. Relat. Phenom. (2010), doi:10.1016/j.elspec.2010.03.007

Conclusion and Outlook

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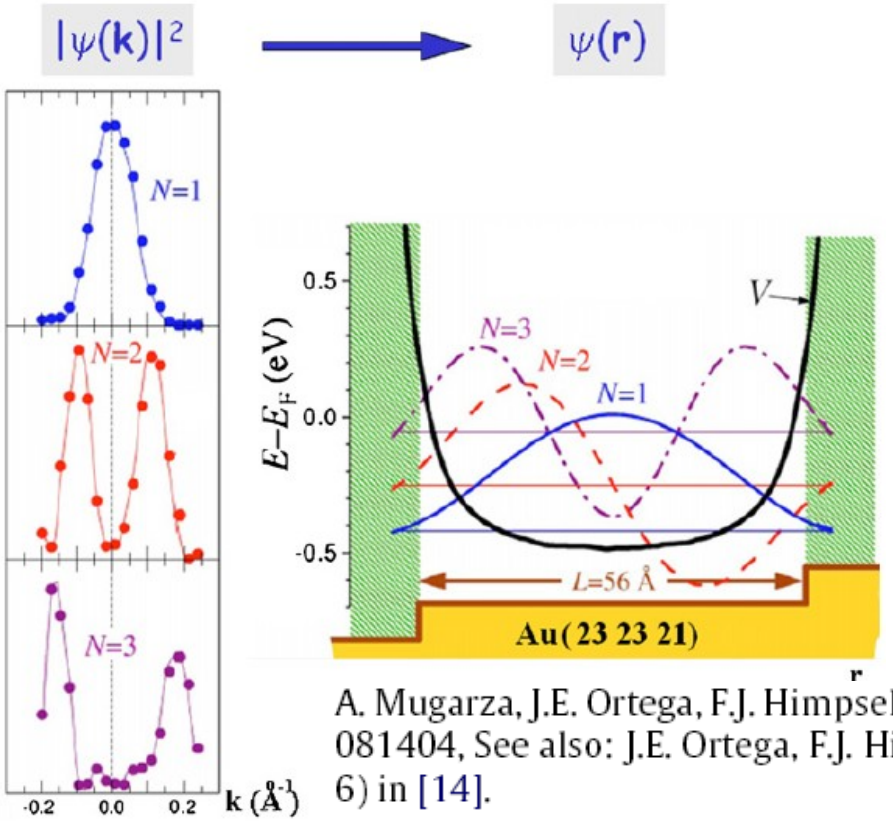
- **1D and 2D wave function imaging demonstrated**



A. Mugarza, J.E. Ortega, F.J. Himpsel, F.J. García de Abajo, Phys. Rev. B 67 (2003) 081404, See also: J.E. Ortega, F.J. Himpsel, Atomic chains at surfaces, (Chapter 6) in [14].

Conclusion and Outlook

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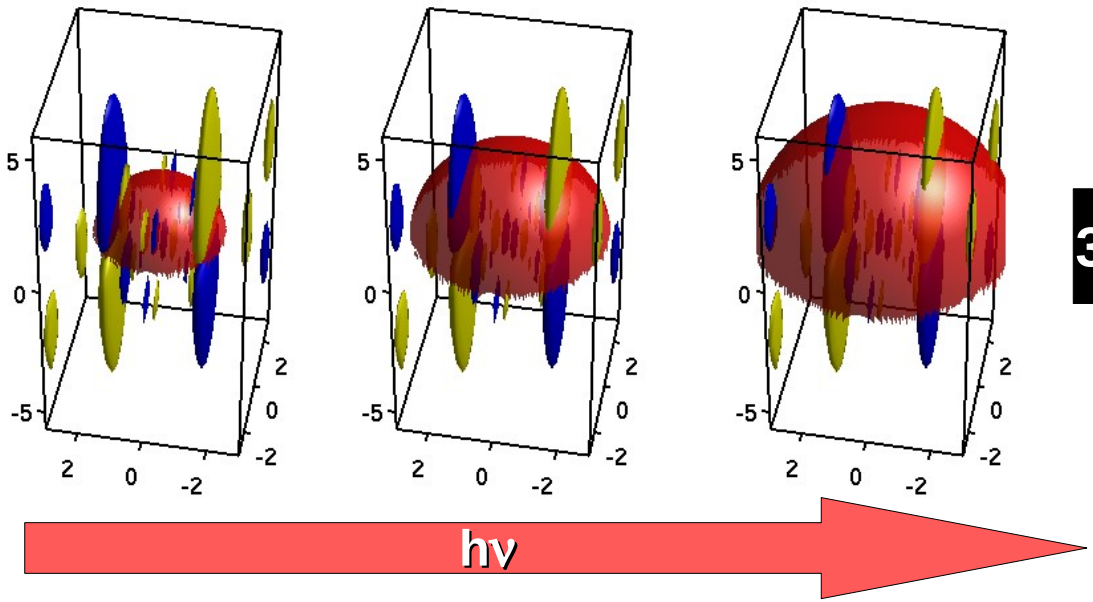
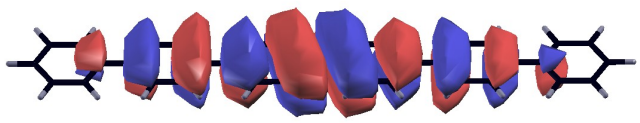
- 1D and 2D wave function imaging demonstrated
- **Prospect of 3D imaging through scans of the photon energy**





Conclusion and Outlook

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- 1D and 2D wave function imaging demonstrated
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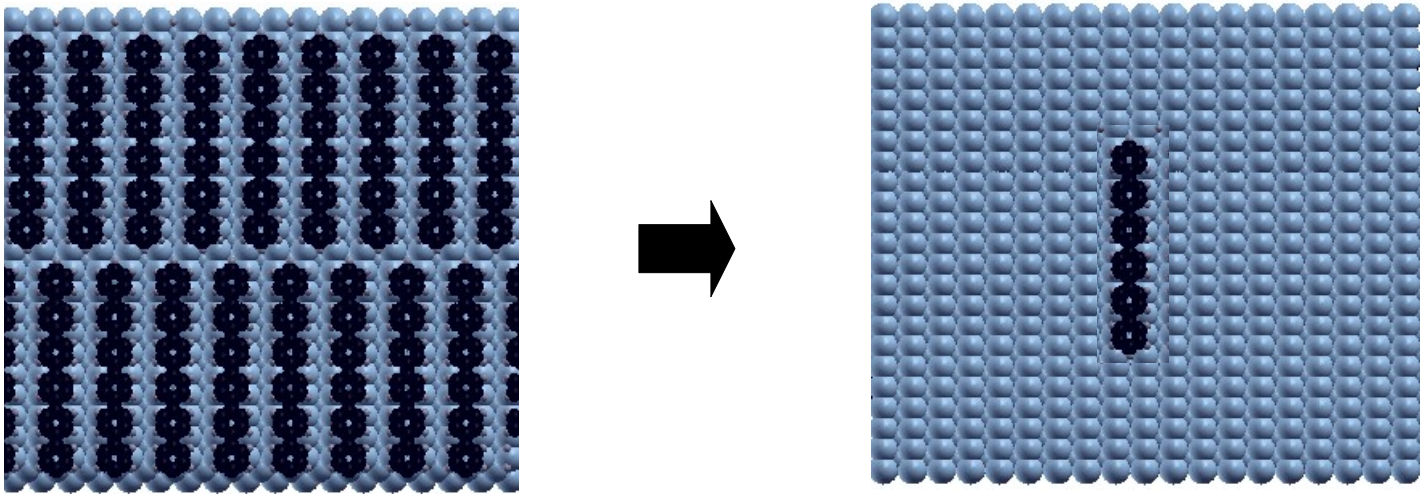
- **Desireable to do PE experiments on individual nano-objects**

  (goal is to reach the focussing limit of soft x-rays 25 nm)



Conclusion and Outlook

Angle-resolved photoemission: From reciprocal space to real space

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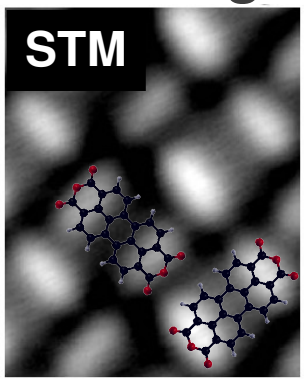
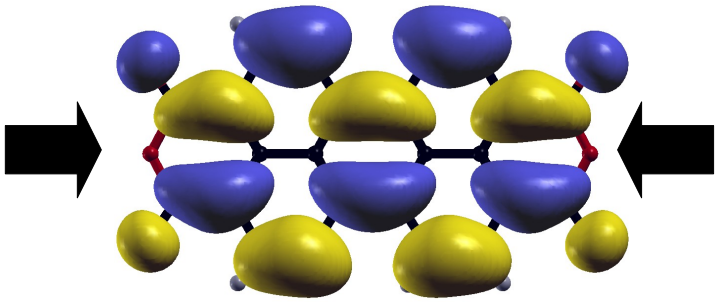
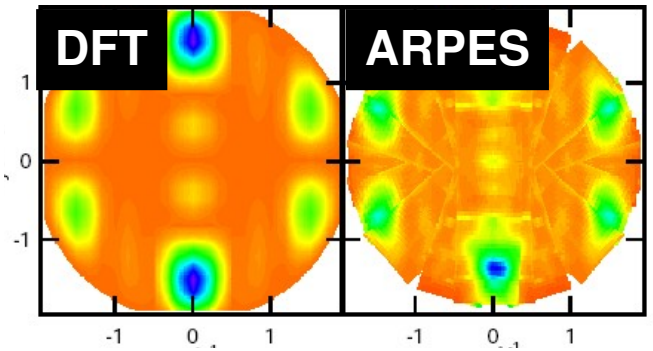
- 1D and 2D wave function imaging demonstrated
- Prospect of 3D imaging through scans of the photon energy
- Desireable to do PE experiments on individual nano-objects (goal is to reach the focussing limit of soft x-rays 25 nm)
- **Scanning tunneling microscopy and PE complement each other**







Rohlfing et al. PRB 76 (2007)

Ziroff et al. PRL (2010)

Improvements in Theory

- **Electronic structure**
  - Band structure: go beyond DFT
  - Accurate band energies and band alignments from GW
  - Van der Waals Interactions
- **Description of the Photoemission Intensity**
  - Take into account Molecule / Substrate Interactions
  - More accurate description of final state

Thank You for Your Attention!