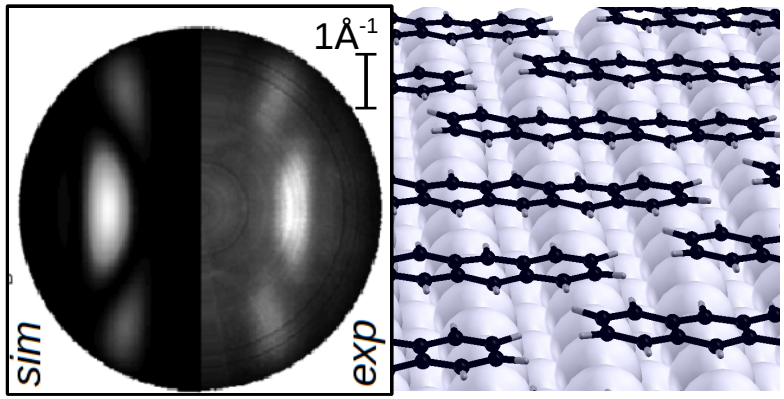
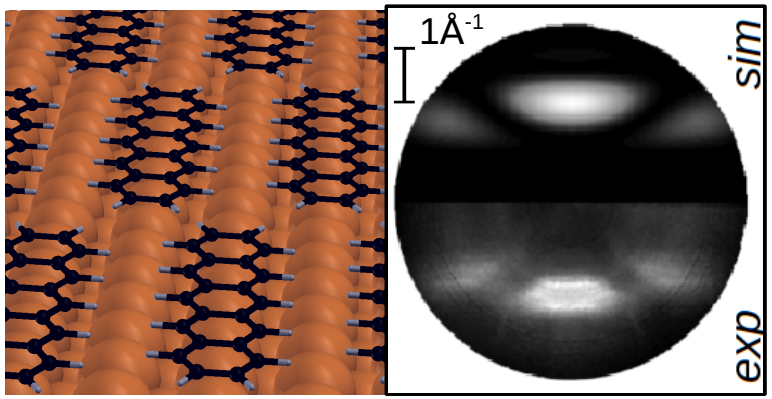
Substrate Induced Intermolecular Dispersion: Pentacene/Cu(110)



Pentacene/Ag(110)

vs.



Pentacene/Cu(110)

Kohn-Sham Equations

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

$$-\frac{Z}{r} \qquad \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}^3r' \qquad \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

Approximations: GGA, HSE

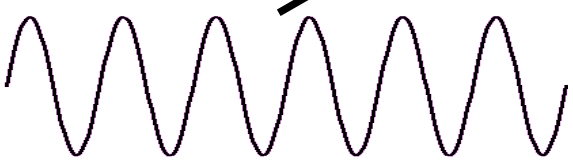
Self-consistency

$$n(\mathbf{r}) = \sum_{i}^{\text{occ}} |\psi_i(\mathbf{r})|^2$$

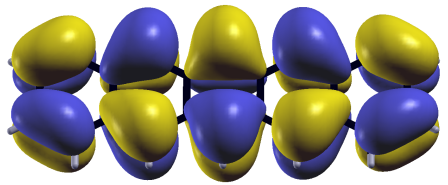
Photoemission Intensity

One Step Model

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



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



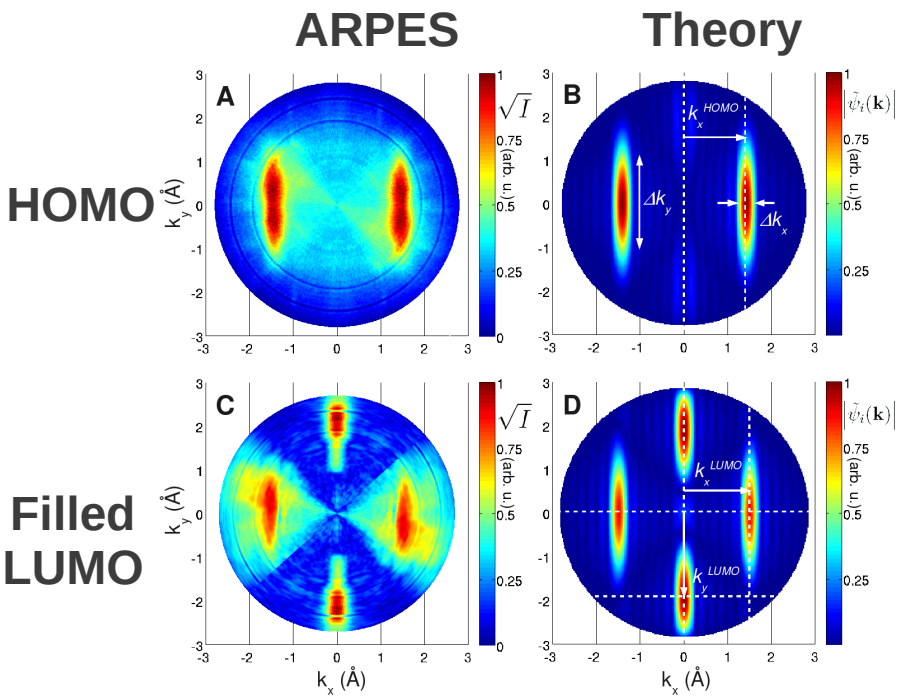
molecular orbital

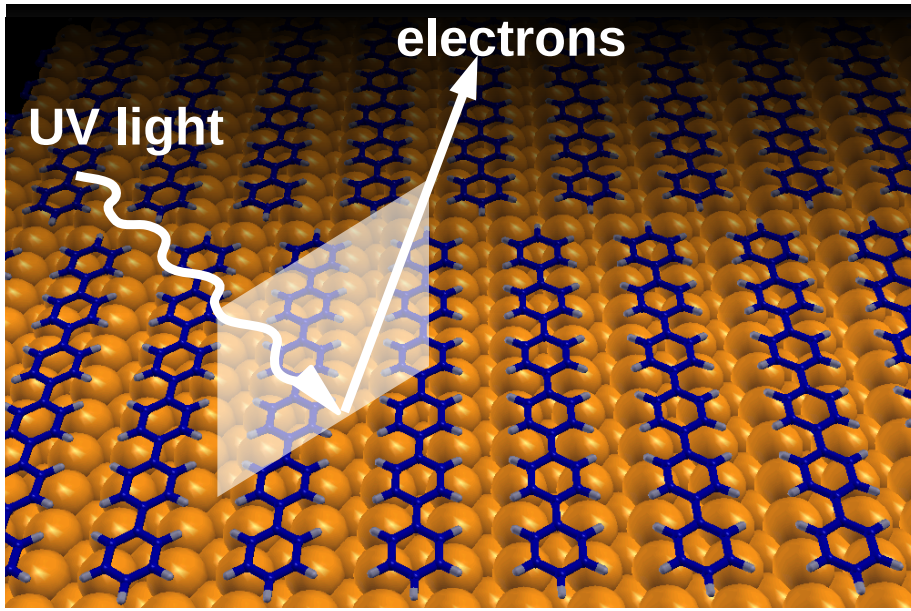
Approximation: final state = plane wave

$$I(k_x, k_y, E_{kin}; \omega, \mathbf{A}) \approx \sum_n^{\text{occ}} \sum_{\mathbf{q}}^{\text{BZ}} |\mathbf{A} \cdot \mathbf{k}|^2 \left| \langle e^{i\mathbf{kr}} | \psi_{n\mathbf{q}} \rangle \right|^2 \times \delta(\varepsilon_{n\mathbf{q}} + \Phi + E_{kin} - \omega). \qquad (2)$$

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

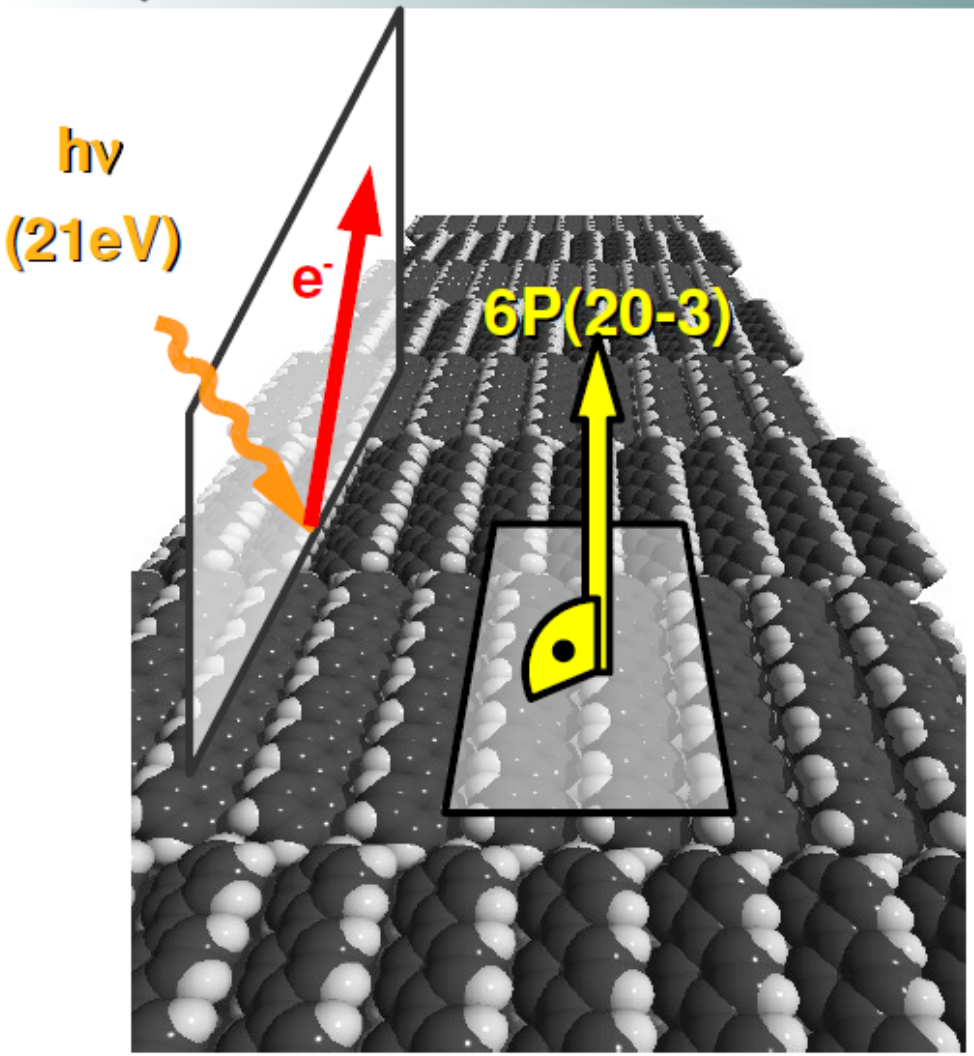
Orbital Tomography



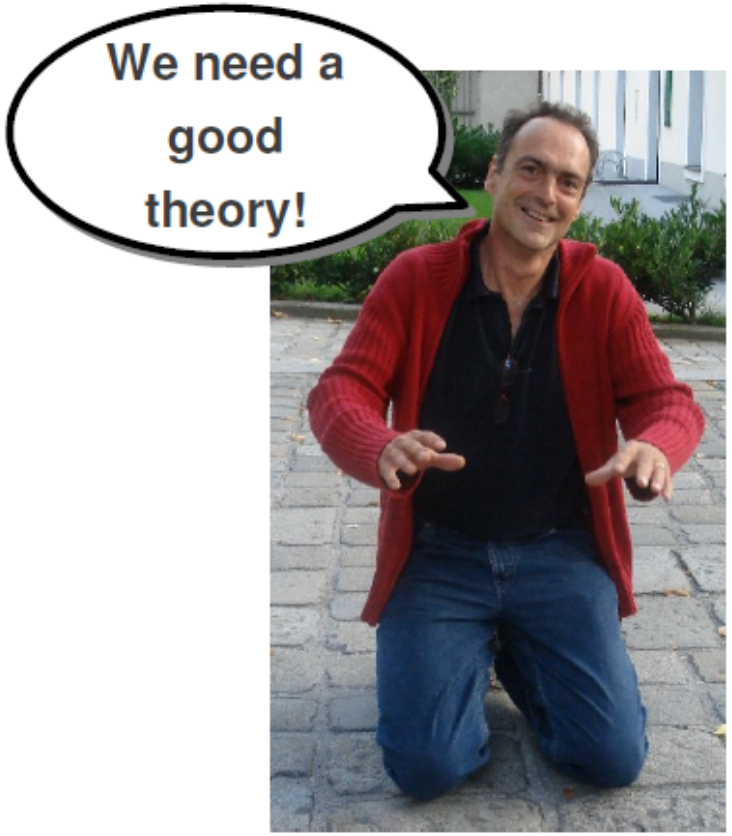


Sexiphenyl / Cu(110)
Puschnig et al.,
Science **326**, 702 (2009).

Uniaxially Aligned Molecules

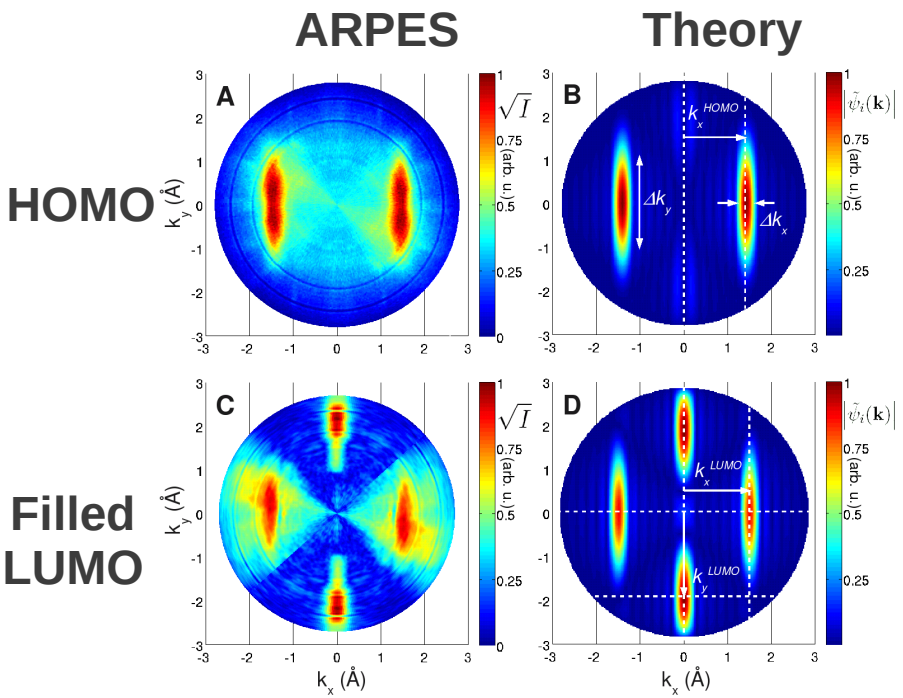


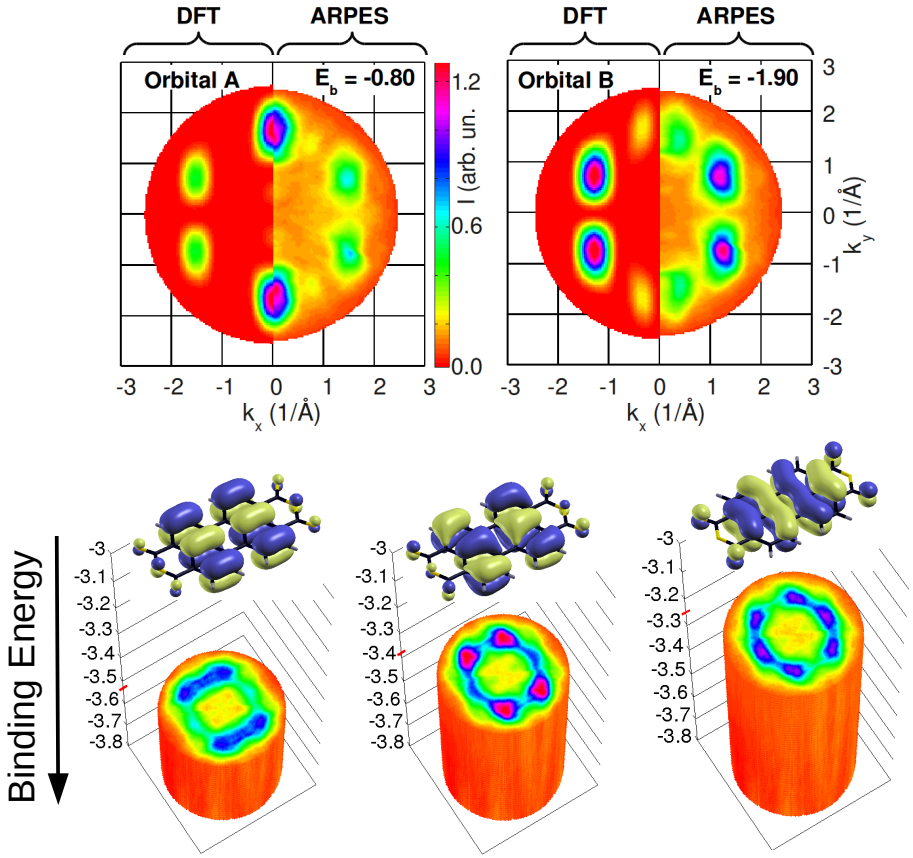
Uniaxially ordered para-sexiphenyl film



Mike Ramsey, Experimental Surface Scientist, University Graz
desperately longing for a good theory

Orbital Tomography

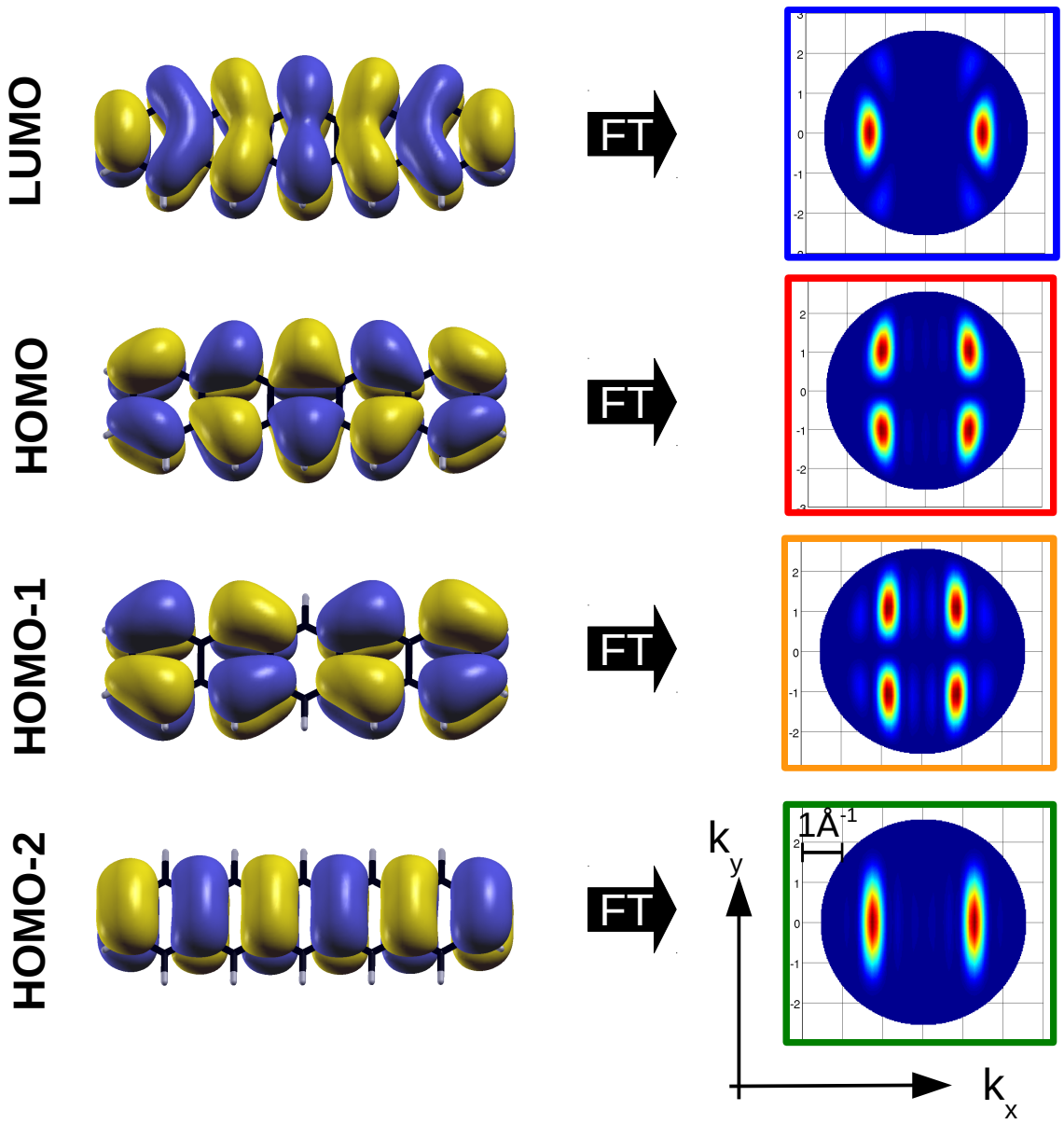




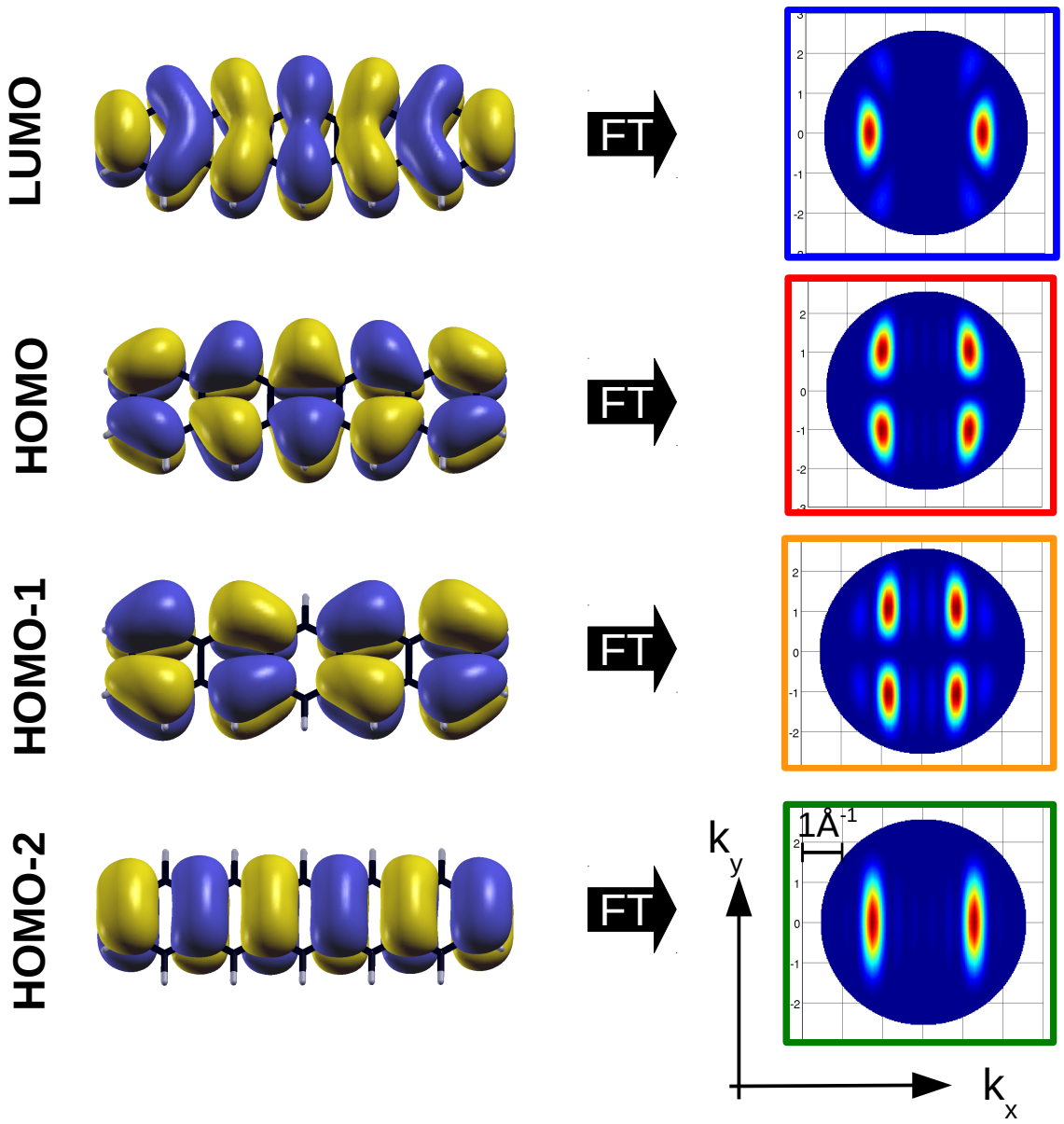
Sexiphenyl / Cu(110)
Puschnig et al.,
Science **326**, 702 (2009).

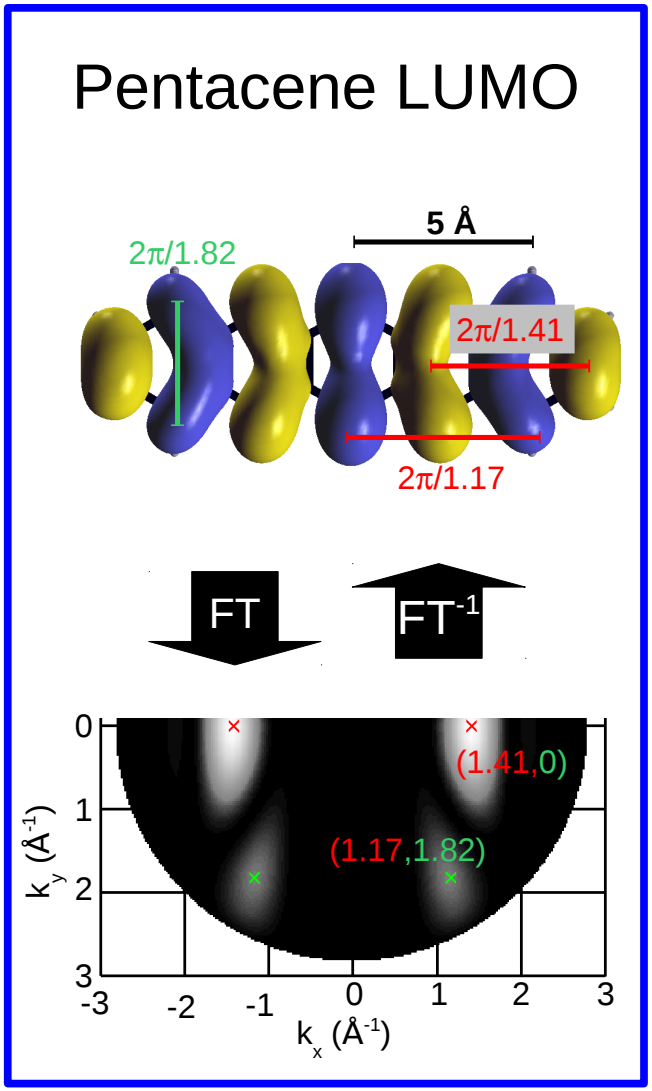
PTCDA / Ag(110)
Ziroff et al., *PRL* **104**, 233004 (2010)
Puschnig et al. *PRB* **84**, 235427 (2011)
Dauth et al., *PRL* **107**, 193002 (2011).
Lüftner et al., *PNAS* **111**, 605 (2014).

Frontier Orbitals of Pentacene



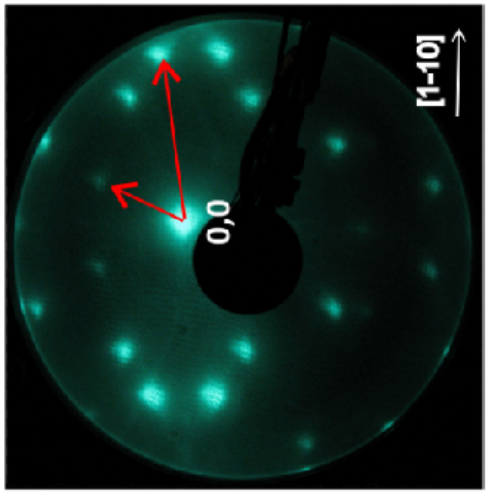
Frontier Orbitals of Pentacene



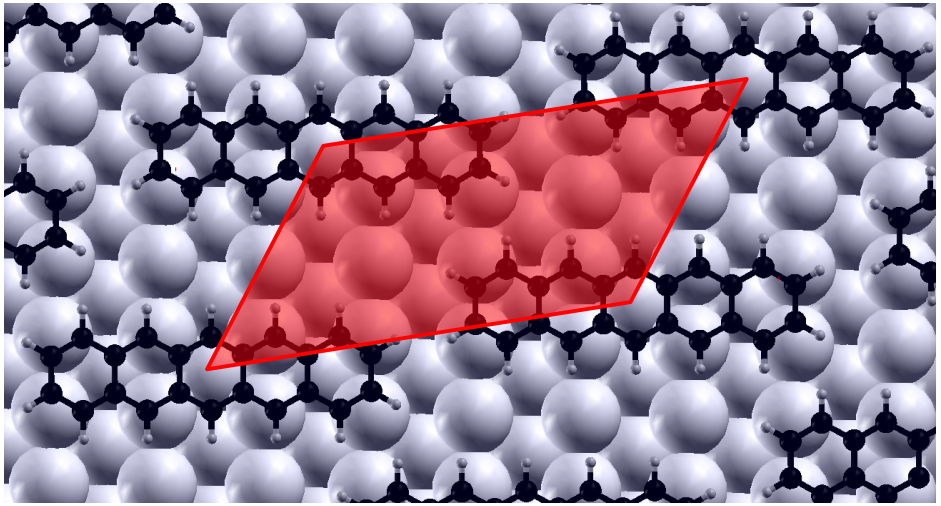


Pentacene/Ag(110)

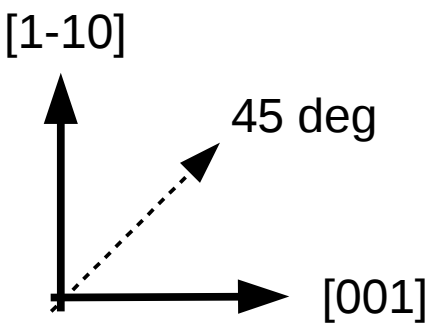
LEED

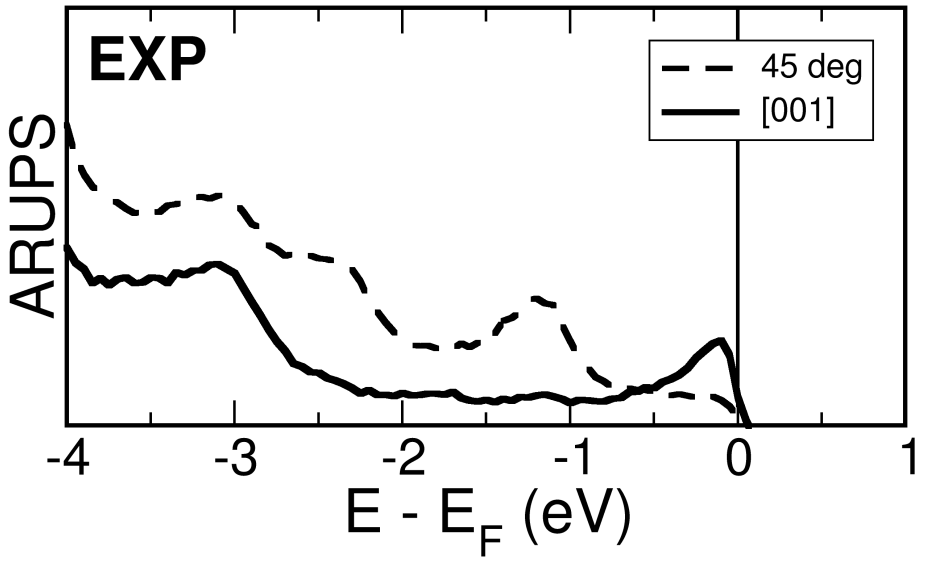


Commensurate Overlayer Structure

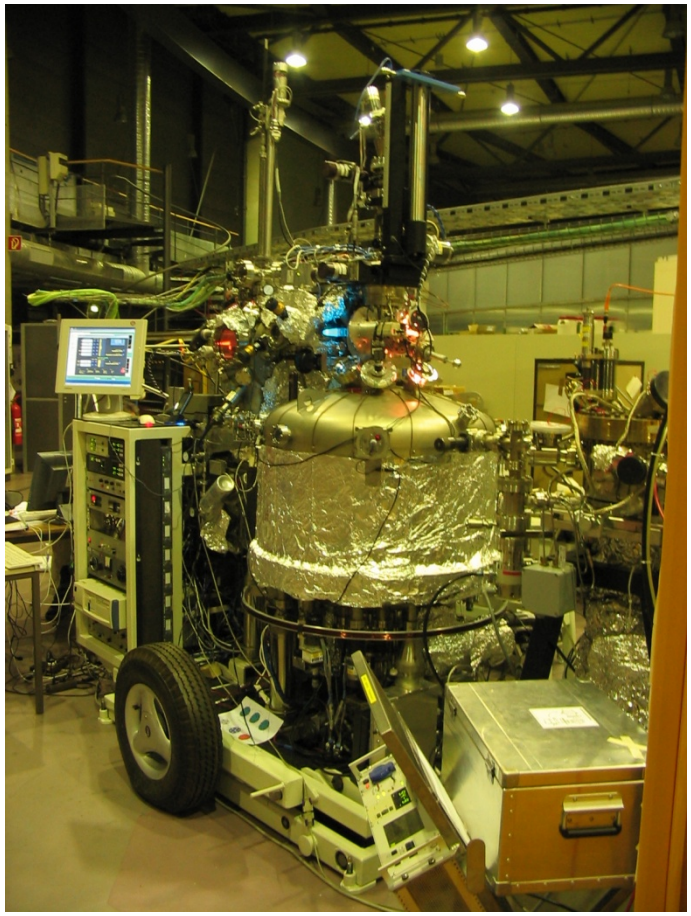


*Pentacene **across** the Ag-rows*

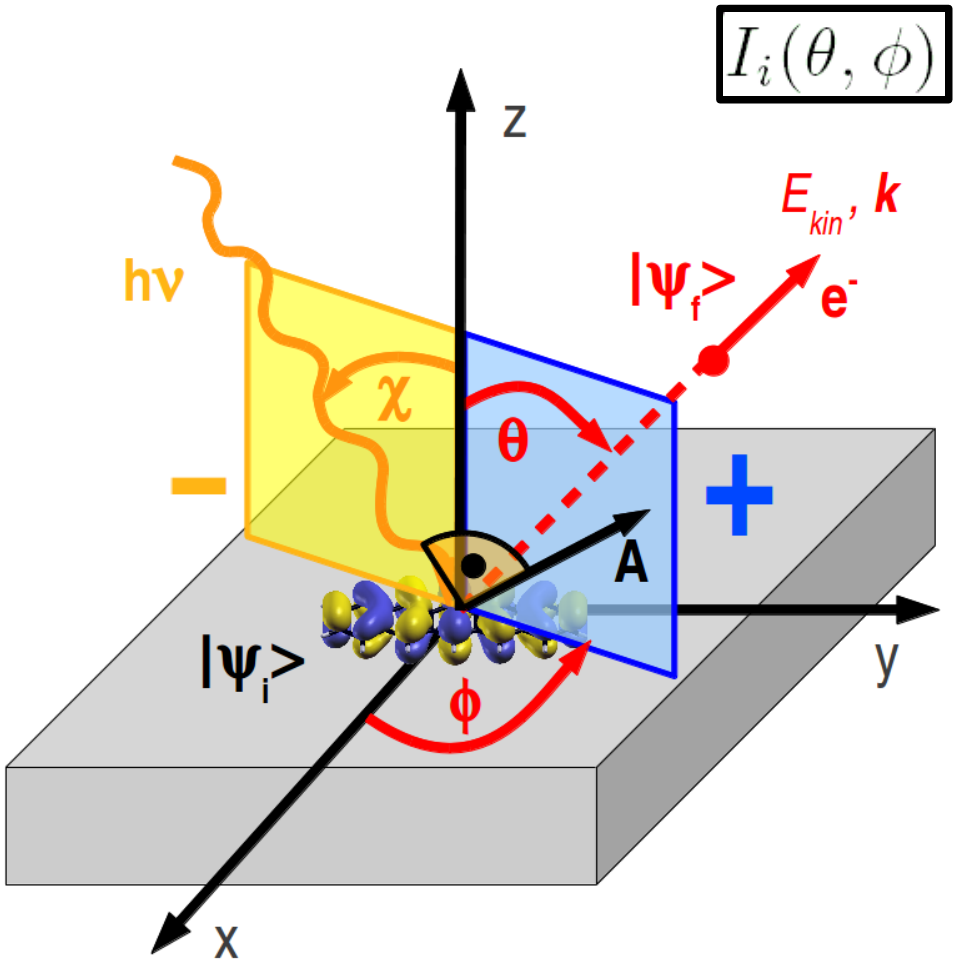




Toroidal Electron Energy Analyzer



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

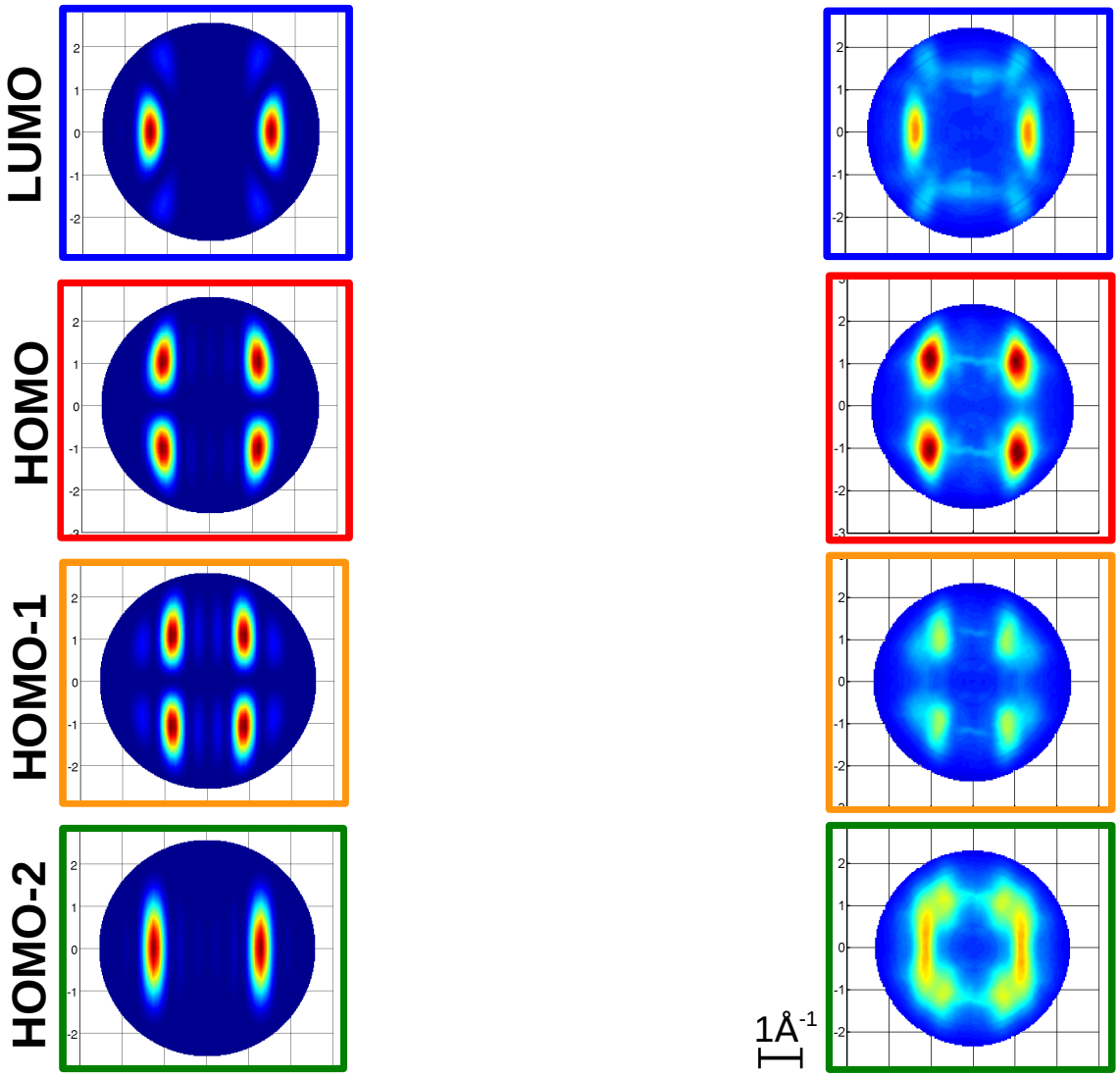


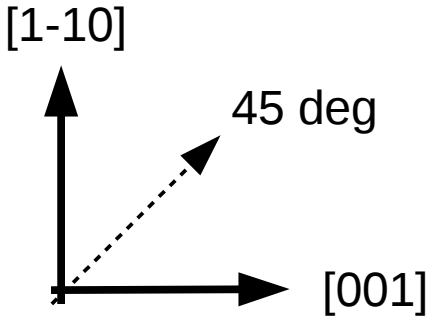
Pentacene/Ag(110)

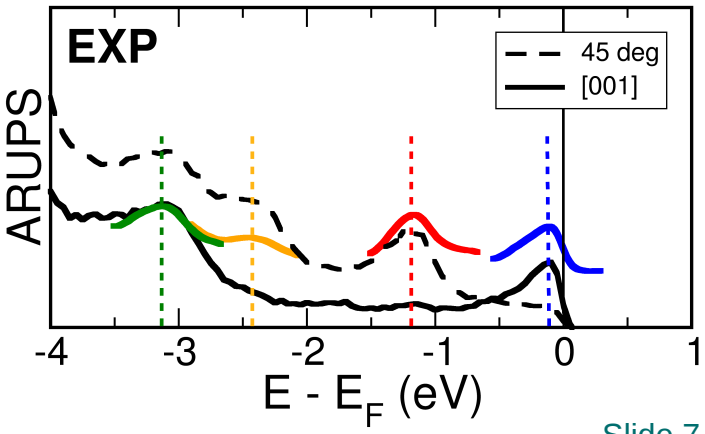
DFT

Isolated pentacene

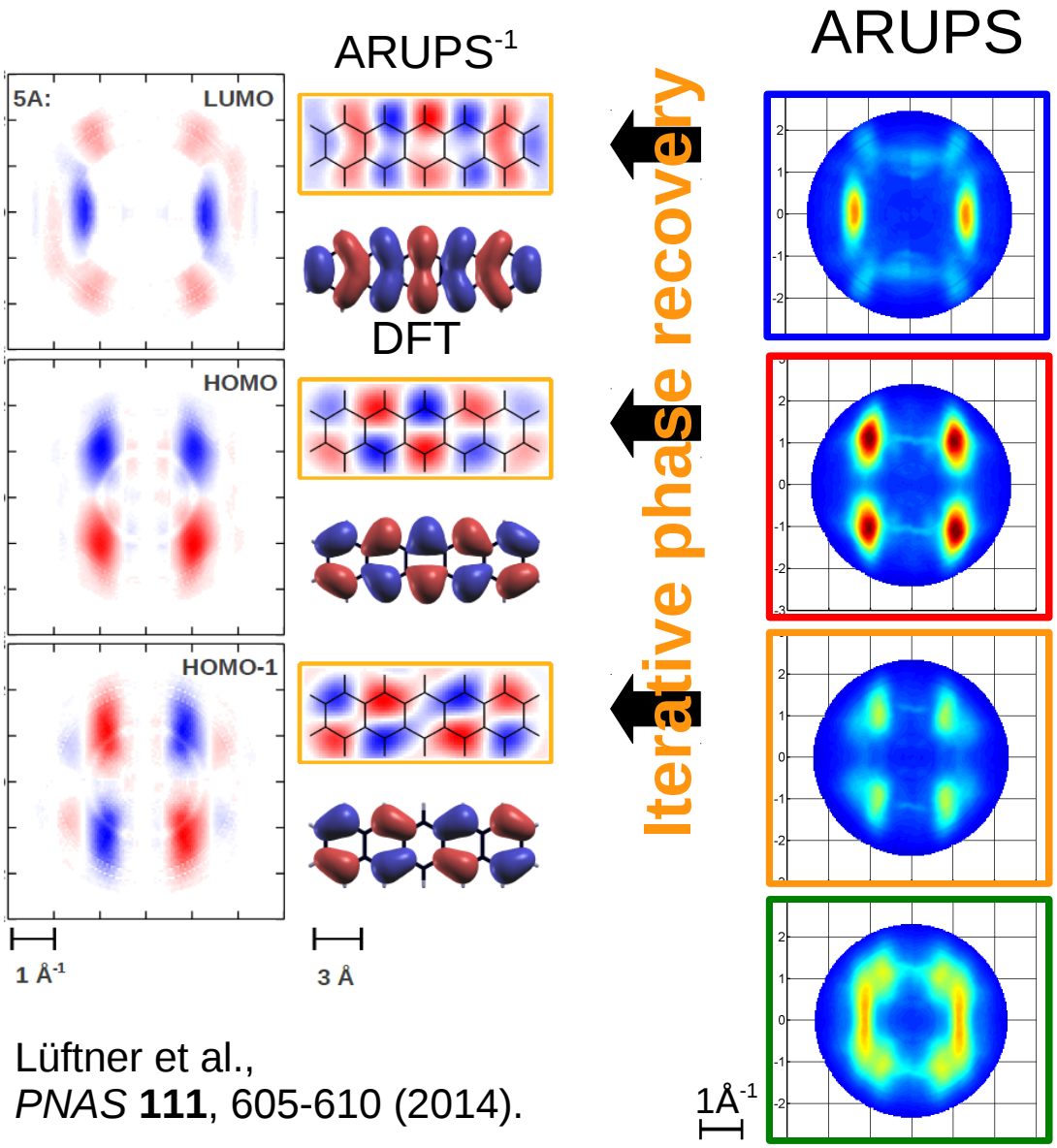
ARUPS

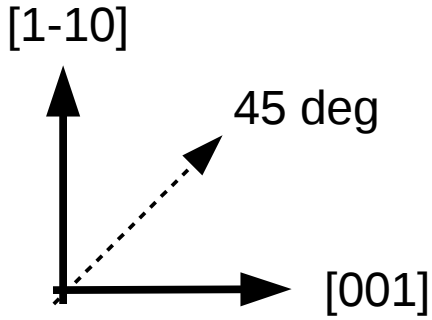


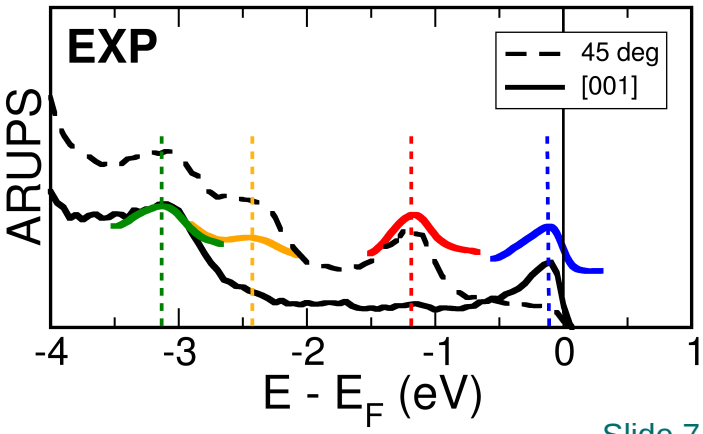




Pentacene/Ag(110)

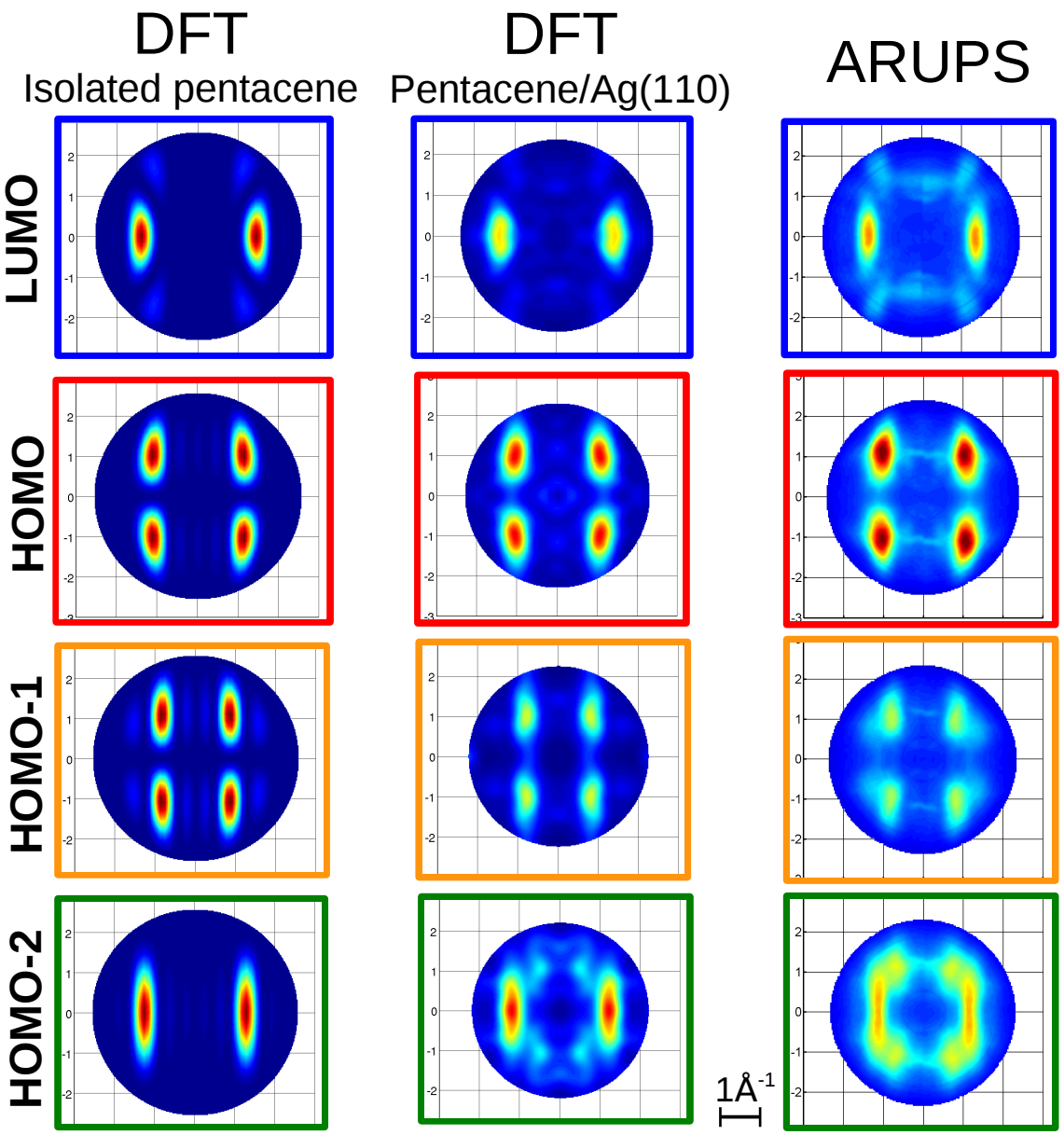


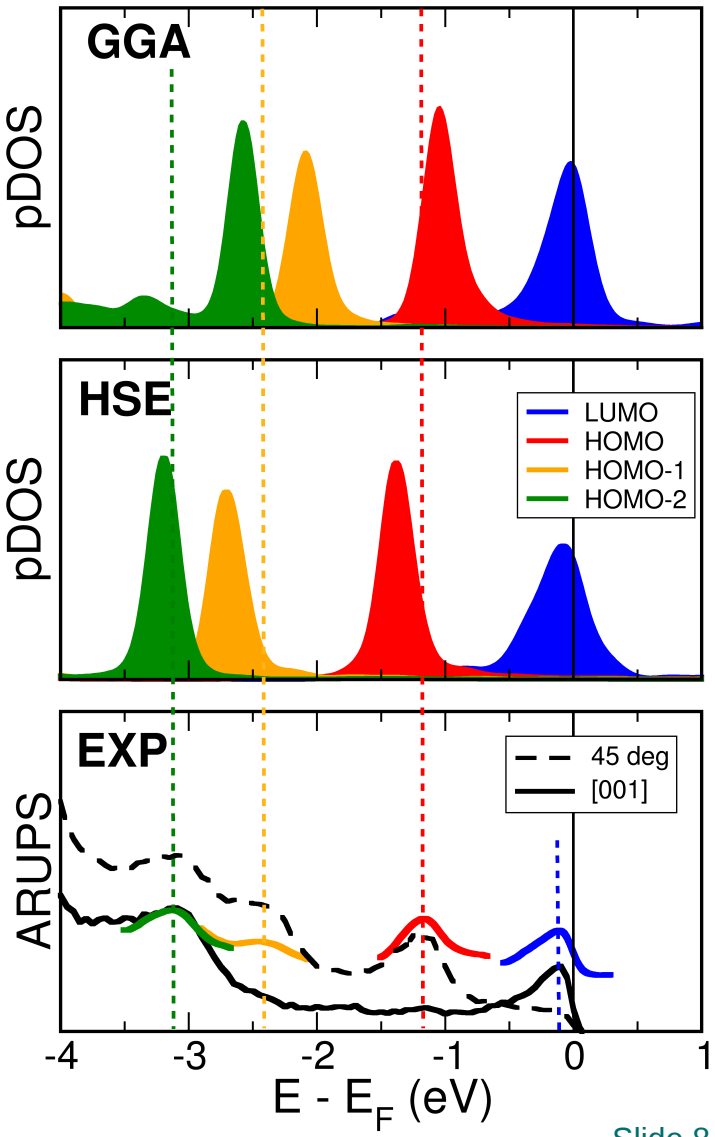




Lüftner et al.,
PNAS **111**, 605-610 (2014).

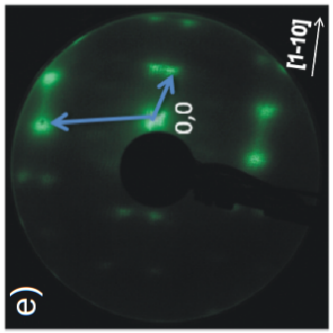
Pentacene/Ag(110)



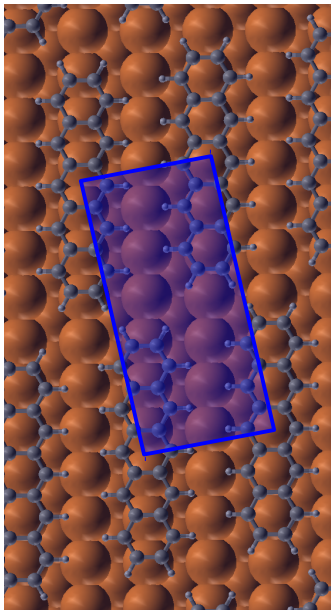


Pentacene/Cu(110)

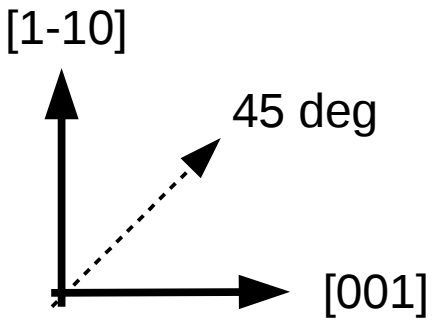
LEED

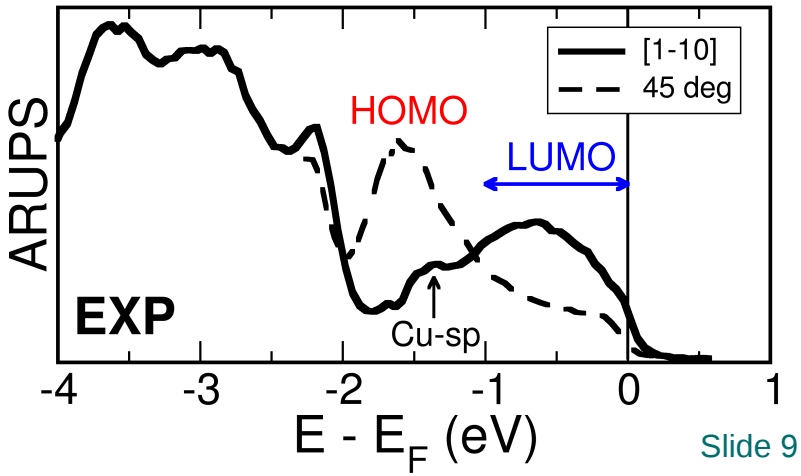


Non-Commensurate



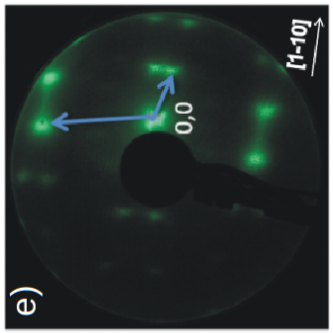
*Pentacene **along** the Cu-rows*



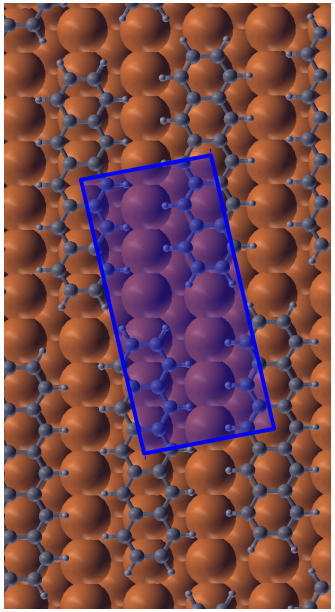


Pentacene/Cu(110)

LEED

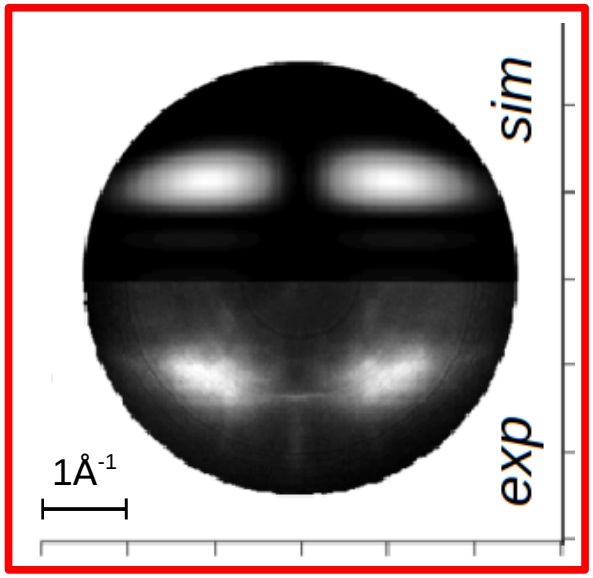


Non-Commensurate

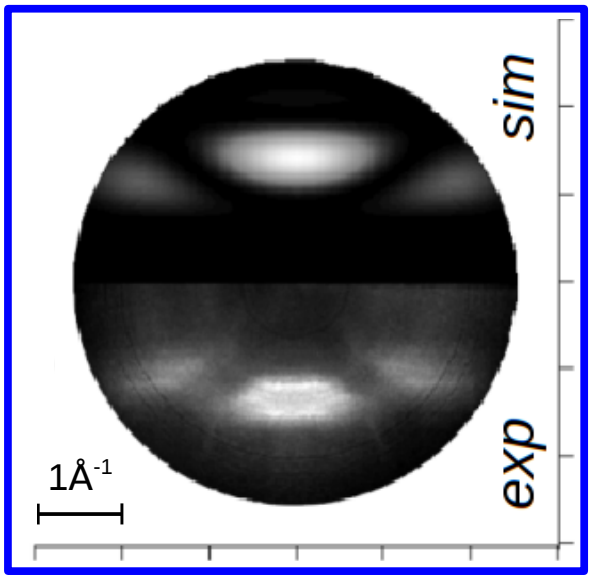


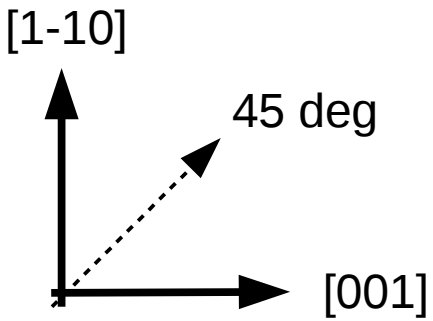
*Pentacene **along** the Cu-rows*

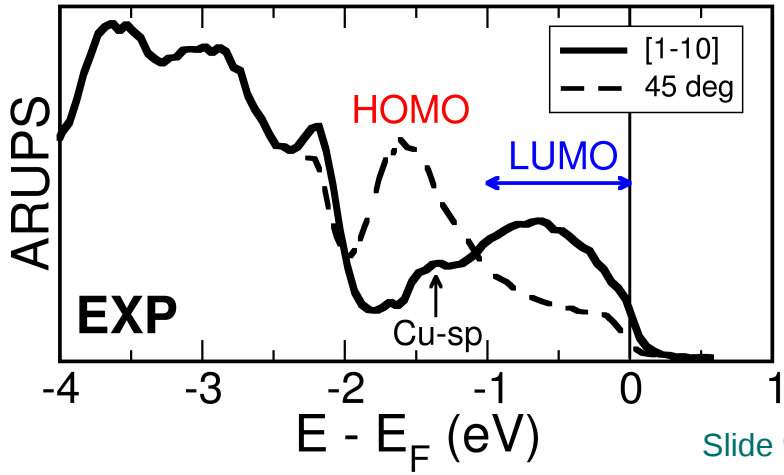
HOMO @ E_B = 1.5 eV



LUMO @ E_B = 0.8 eV

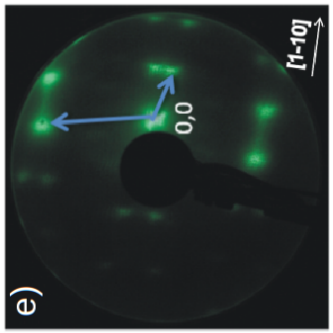




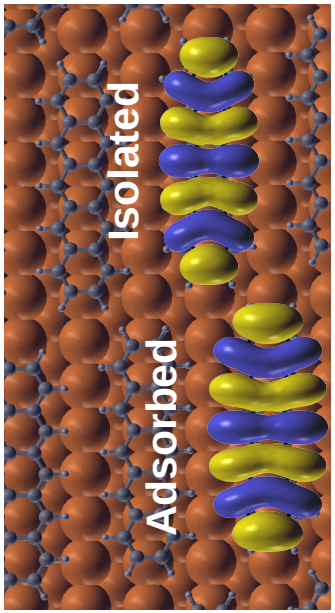


Modification of LUMO

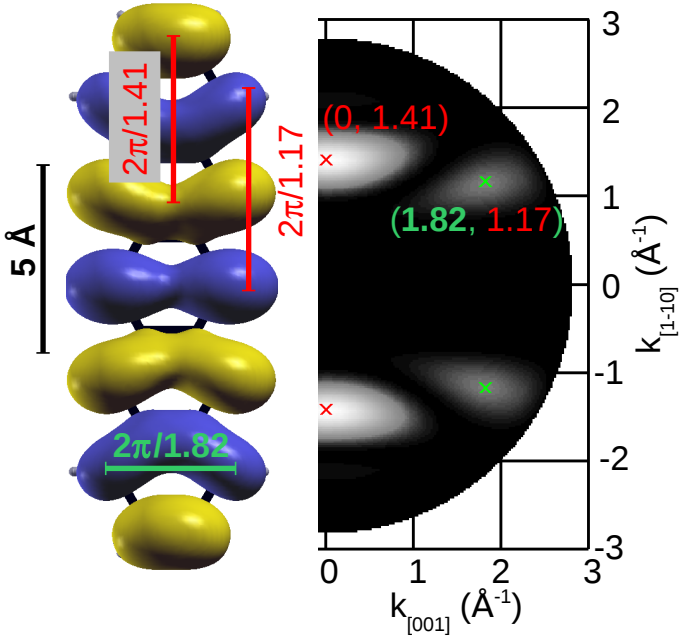
LEED



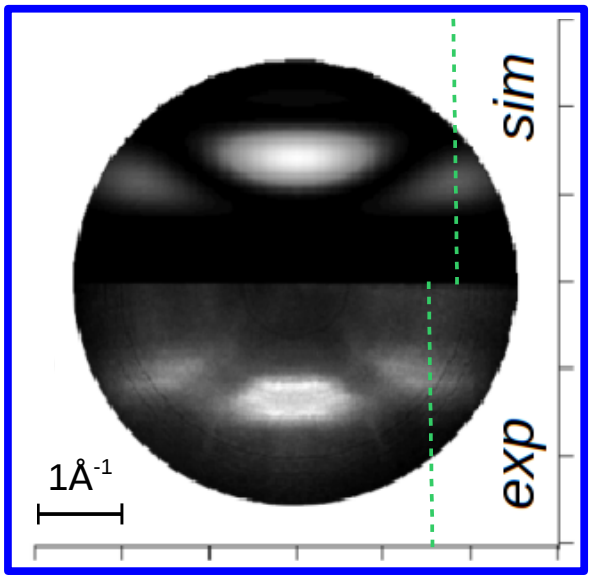
Non-Commensurate



*Pentacene **along** the Cu-rows*



LUMO @ E_B = 0.8 eV

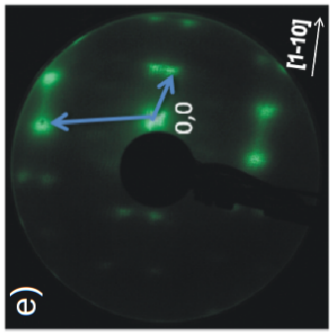


Isolated Pentacene *Pentacene / Cu(110)*

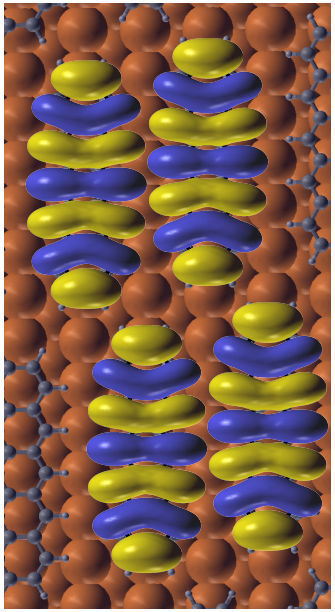
„Upon adsorption on Cu(110), the LUMO orbital of pentacene expands by ~20% across the long molecular axis.“

Dispersion of LUMO

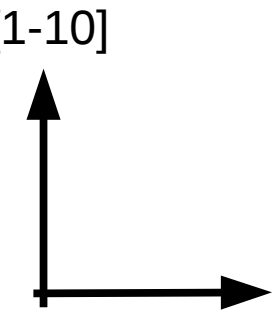
LEED



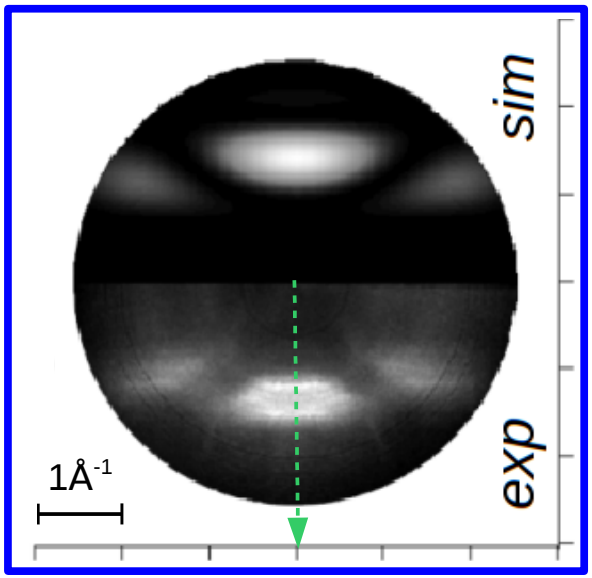
Non-Commensurate

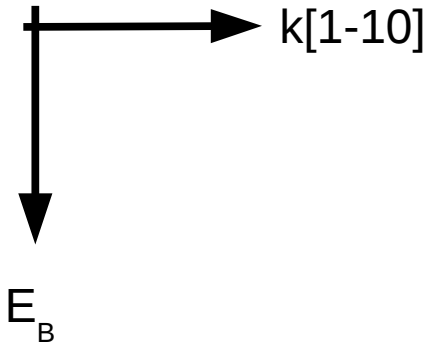


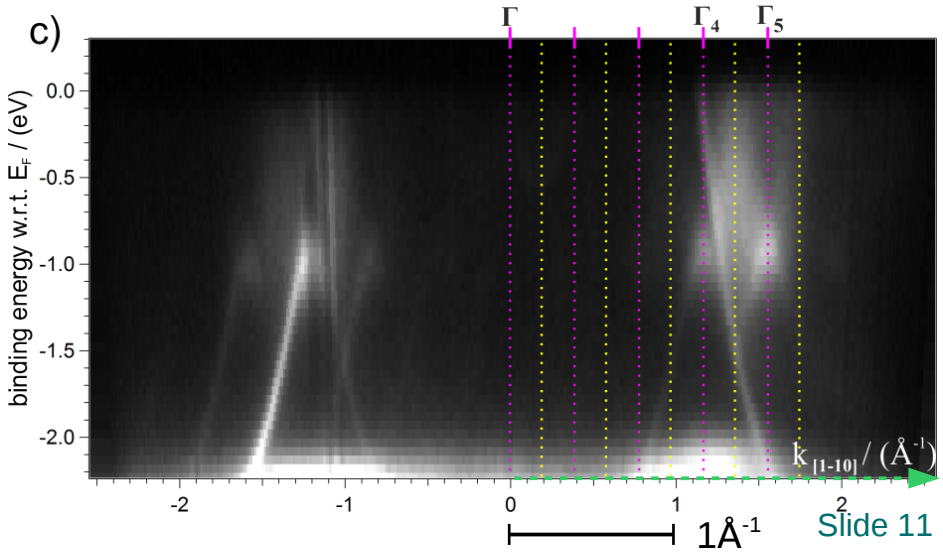
*Pentacene **along** the Cu-rows*



LUMO @ E_B = 0.8 eV





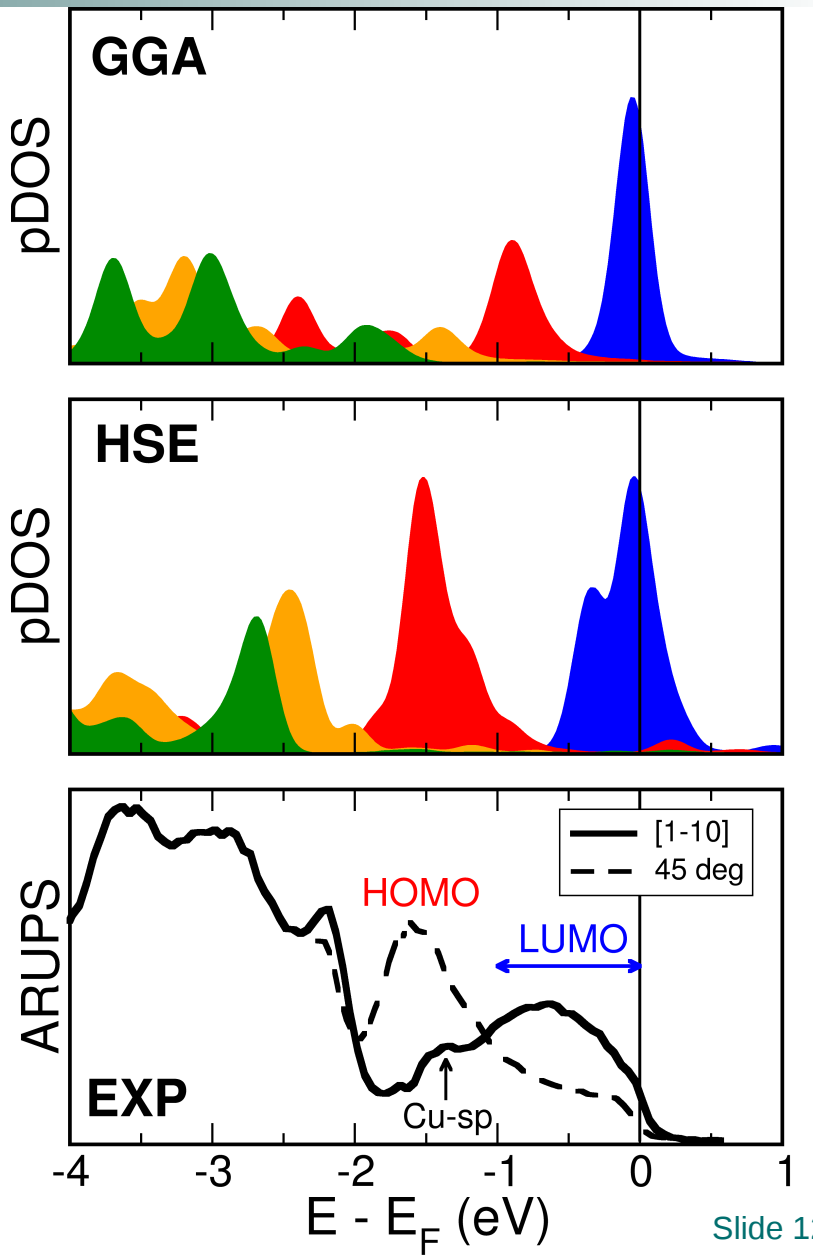


DFT-Result: Pentacene/Cu(110)

DFT-results for Pentacene/Cu(110) are problematic

- A commensurate structure had to be chosen
- GGA yields HOMO too close to E_F, LUMO at E_F (*)
- HSE yields some improvement regarding HOMO, but LUMO is still too close to E_F

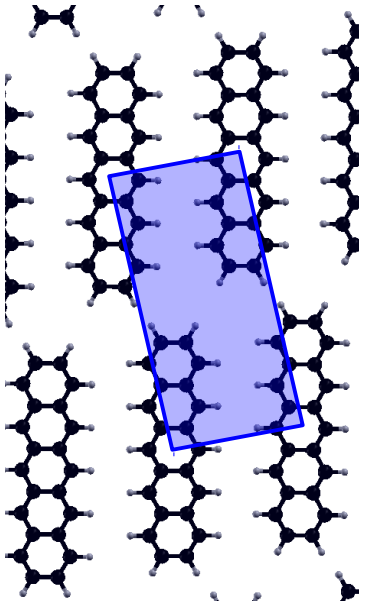
➡ analyze dispersion of free-standing layer



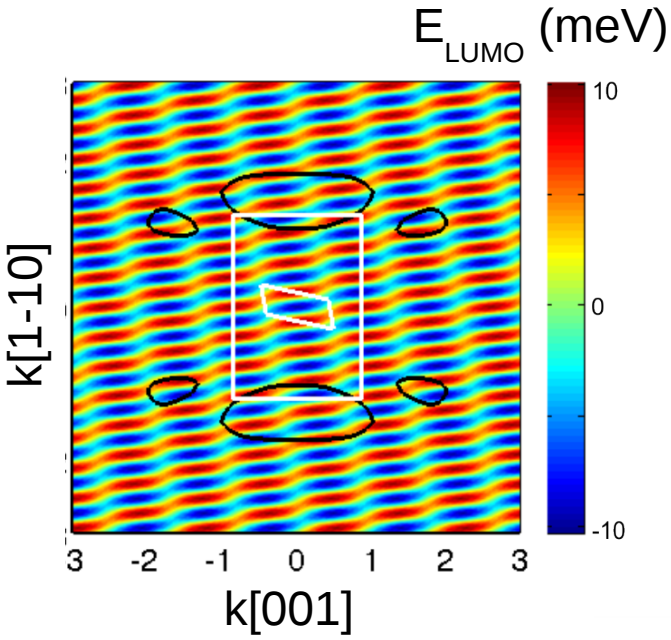
(*) A similar DFT-result of Müller et al. in [*J. Phys. Chem. C* **116**, 23465 (2012)] led to a wrong assignment of experimentally observed peaks

Dispersion of LUMO

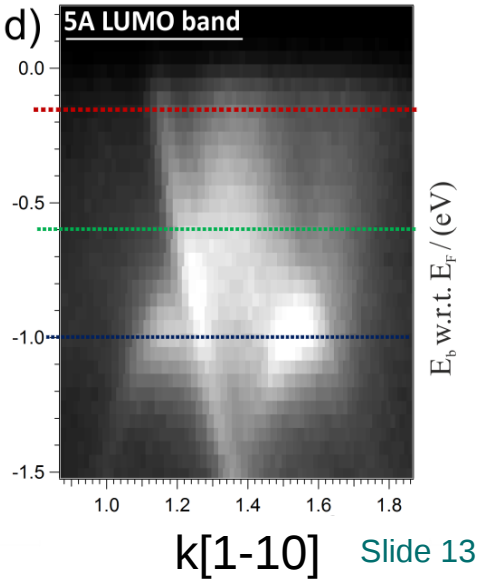
Free-standing layer



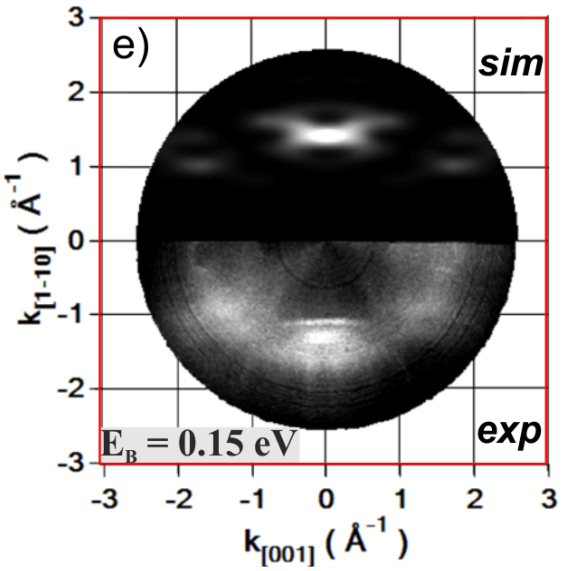
Color-coded 2D -dispersion

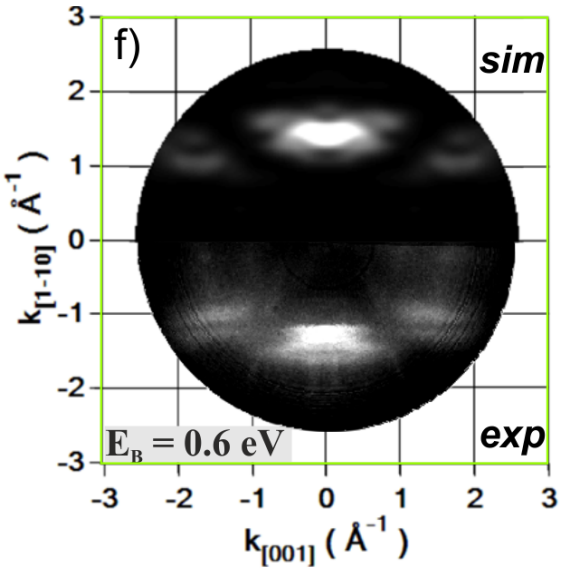


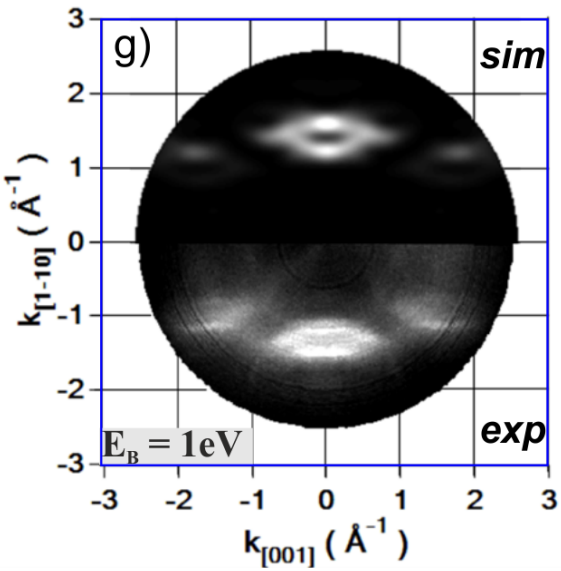
ARUPS band map

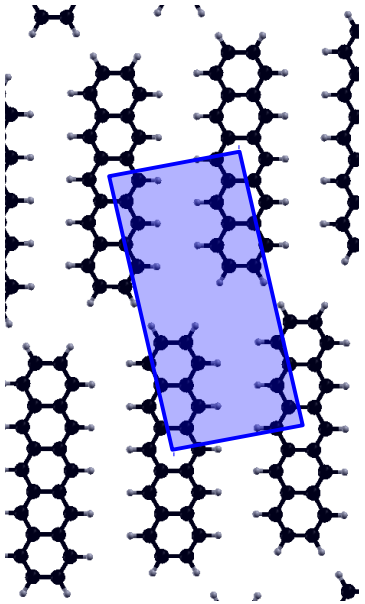


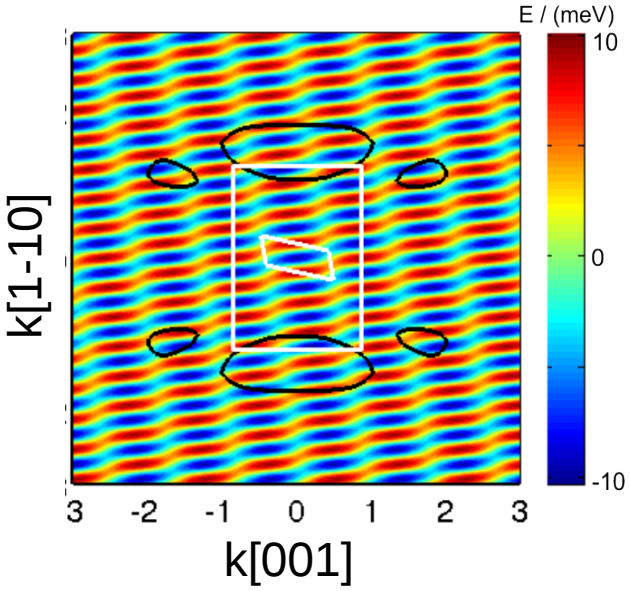
Dispersion of LUMO

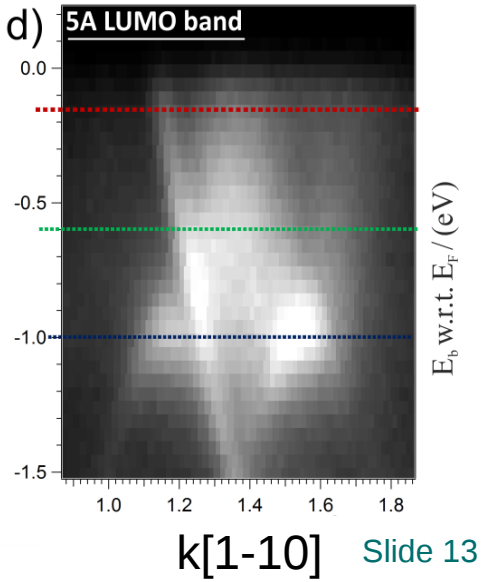






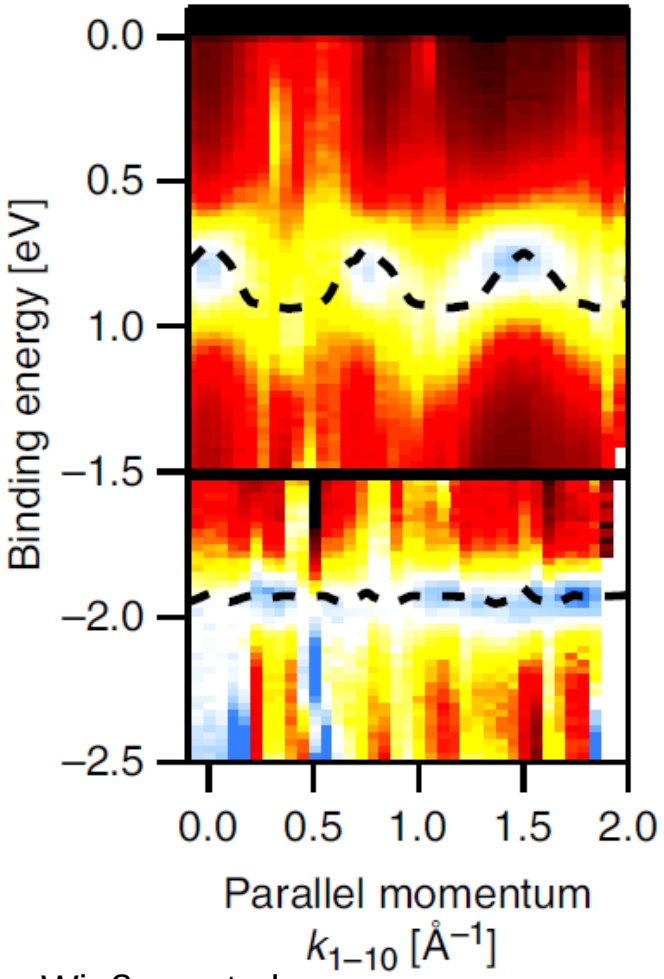






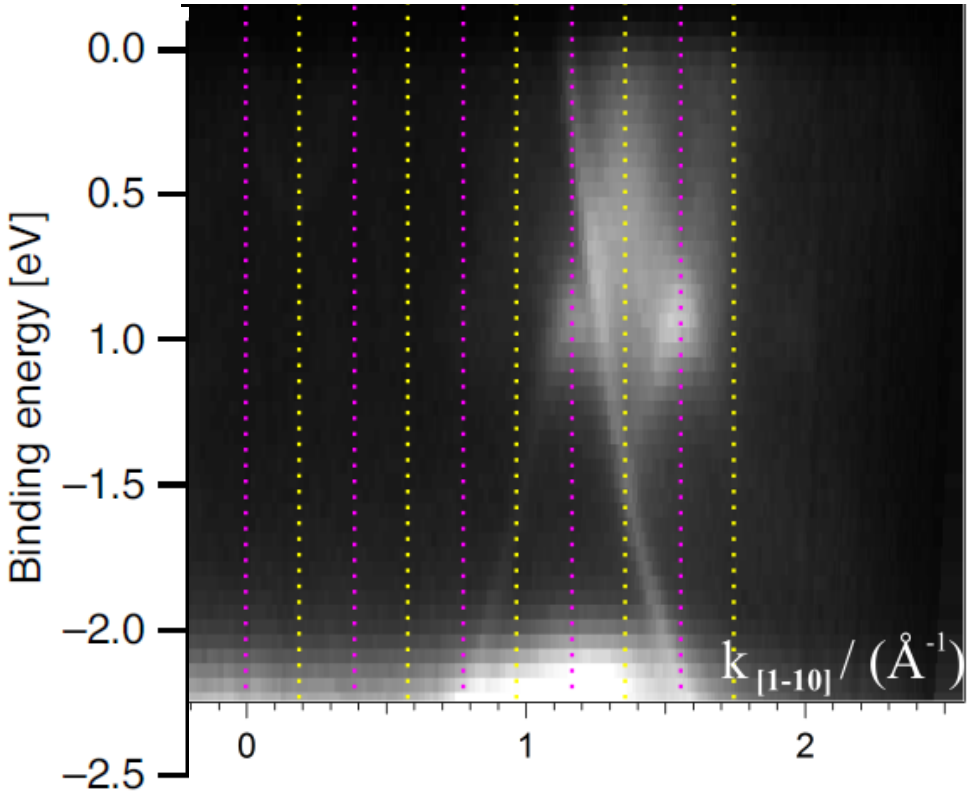
Substrate-Enhanced Dispersion

PTCDA/Ag(110)



Wießner et al.,
Nature Communications **4**, 1514 (2013).

Pentacene/Cu(110)



Thomas Ules et al.,
submitted

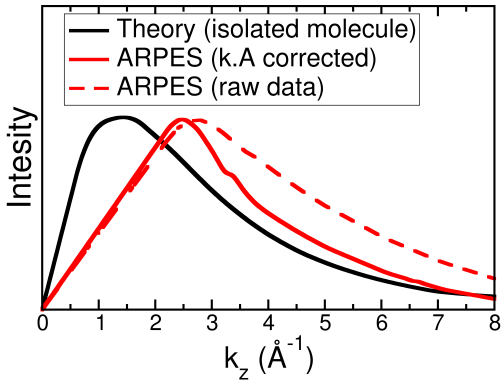
Conclusion and Outlook

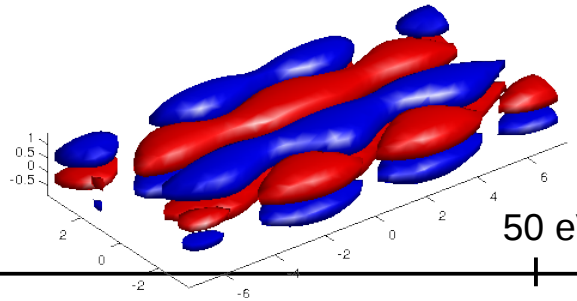
Conclusion

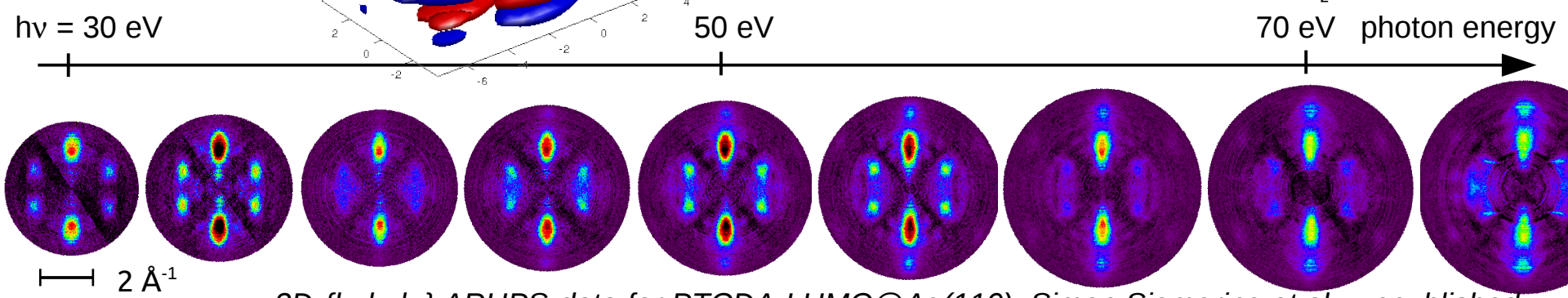
- Orbital tomography yields molecular orientation and unambigous assignment of states
- Pentacene/Ag(110): weak interaction, orbitals remain gas-phase like
- Pentacene/Cu(110): modification of orbital size and strong substrate-induced dispersion

Future Perspectives of Orbital Tomography

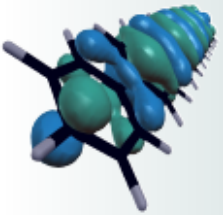
- Complex systems, e.g. PTCDA/CuPc mixed monolayer: Stadtmüller et al., *Nature Comm.* ***5****, 3685* (2014)
- Benchmark for theory with unprecedented richness of information
- Orbital modification / hybridization of molecular orbitals upon adsorption
- Three-dimensional mapping of molecular orbitals





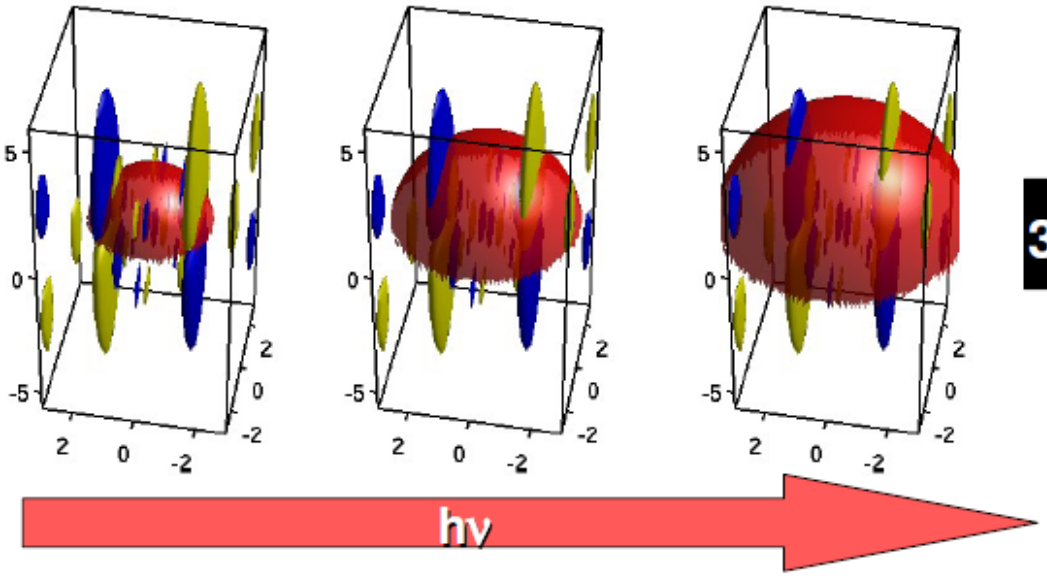


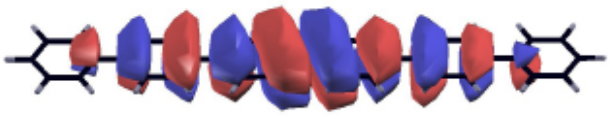
3D-{k_x,k_y,k_z} ARUPS-data for PTCDA-LUMO@Ag(110): Simon Siemering et al., unpublished



Conclusions and Outlook

- Simple theory for PE intensity
- Azimuthal scans provide fingerprints of molecular orbitals
- Works also for rather strongly bound monolayers on metals
- **Yes, we can!** - reconstruct molecular orbitals from PE ;-)





Collaborations and Funding

Theoretical Physics – University Graz, Austria
Daniel Lüftner

Claudia Draxl: formerly at Chair of Atomistic Modelling, MU Leoben, now at HU Berlin

Experimental Surface Science Group – University Graz, Austria
Thomas Ules, Eva-Maria Reinisch, Stephen Berkebile, Alexander Fleming
Georg Koller, Mike Ramsey

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

Peter Grünberg Institut (PGI-3), JARA, Forschungszentrum Jülich,
Sergey Soubatch, Benjamin Stadtmüller, Martin Willenbockel, Simon Siemering,
Christian Kumpf, Stefan Tautz

The work is part of the single project P23190-N16
„Understanding photoemission of organic thin films“

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

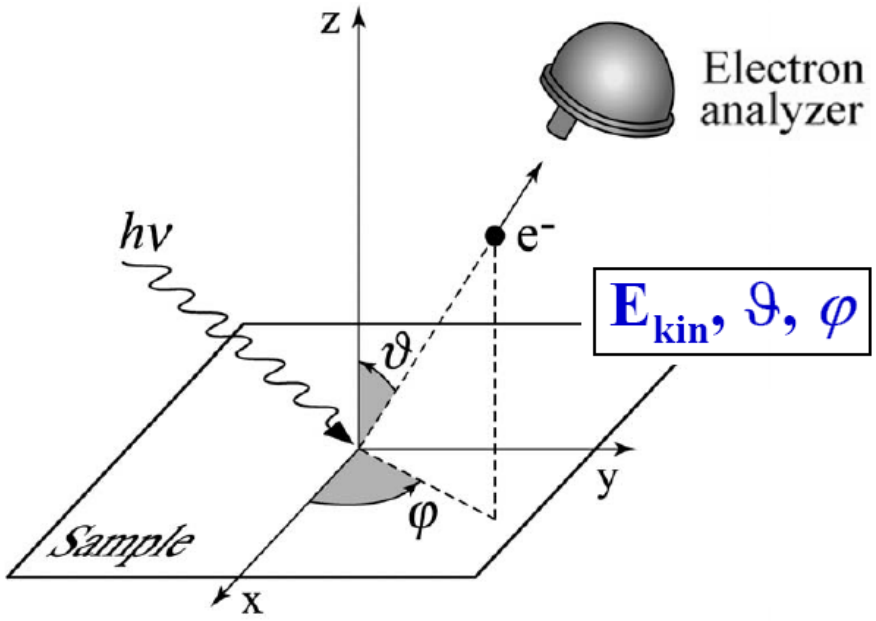
$$I(\boldsymbol{k}, \omega) = I_0(\boldsymbol{k}, \nu, \boldsymbol{A}) f(\omega) A(\boldsymbol{k}, \omega)$$

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

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 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

$\boldsymbol{E_B}$

$\mathbf{k}$