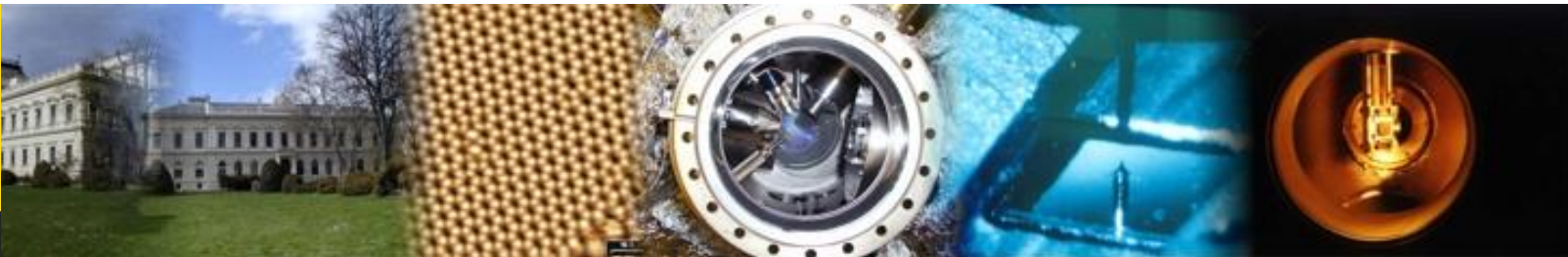


Contrasting Pentacene on Cu(110) and Ag(110): interactions revealed by valence band tomography

Ules Thomas

Surface Science Group, KFUni Graz



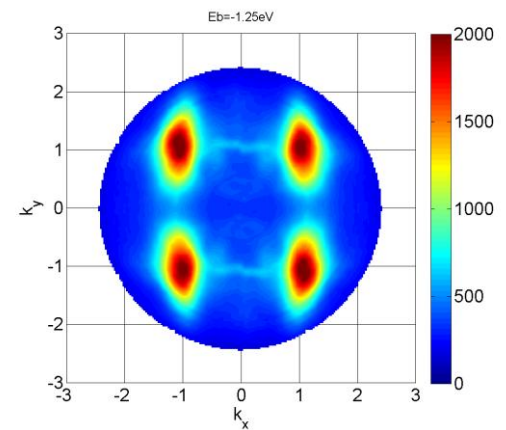
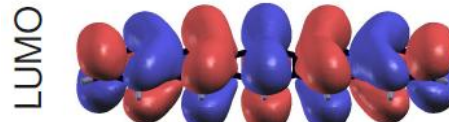
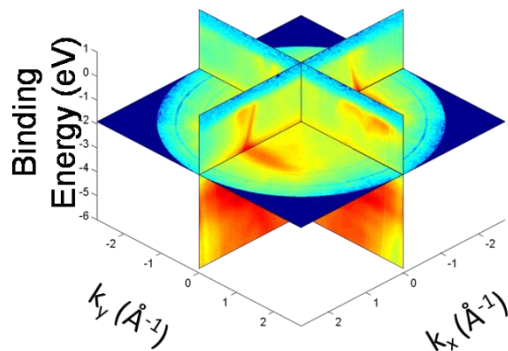
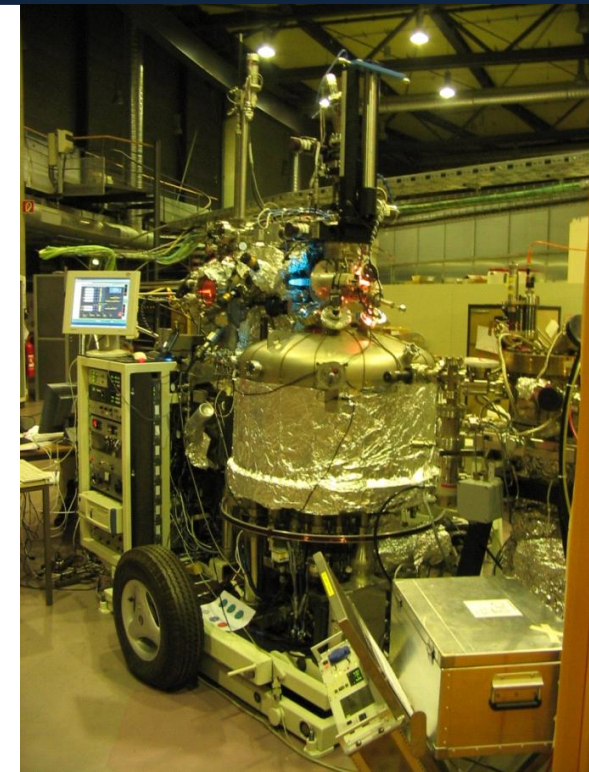
Outline

Angle Resolved UPS; Orbital Tomography

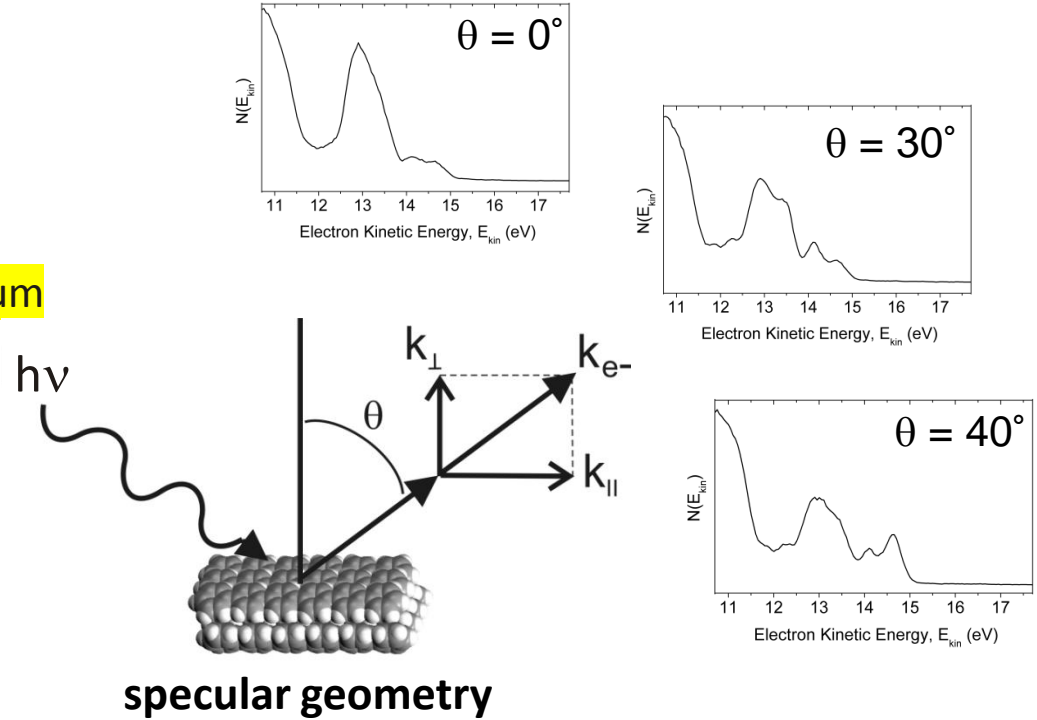
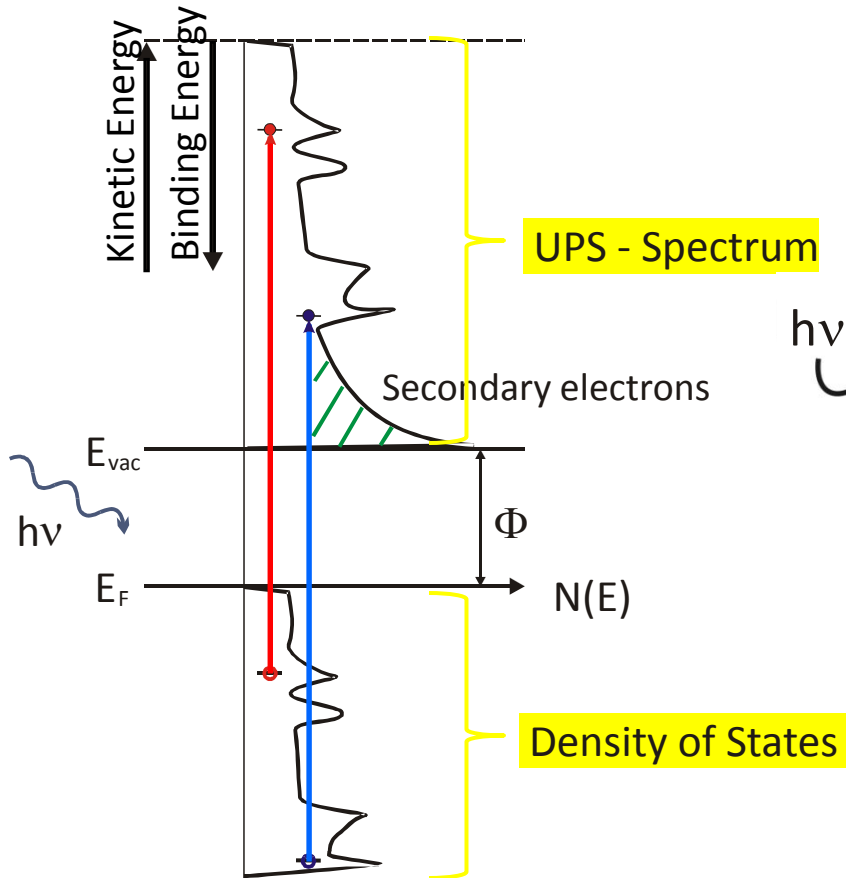
Influence of the substrate on the orbital structure ?

- Pentacene on Ag(110) vs. on Cu(110)

similar but different



UV Photoemission Spectroscopy (UPS)

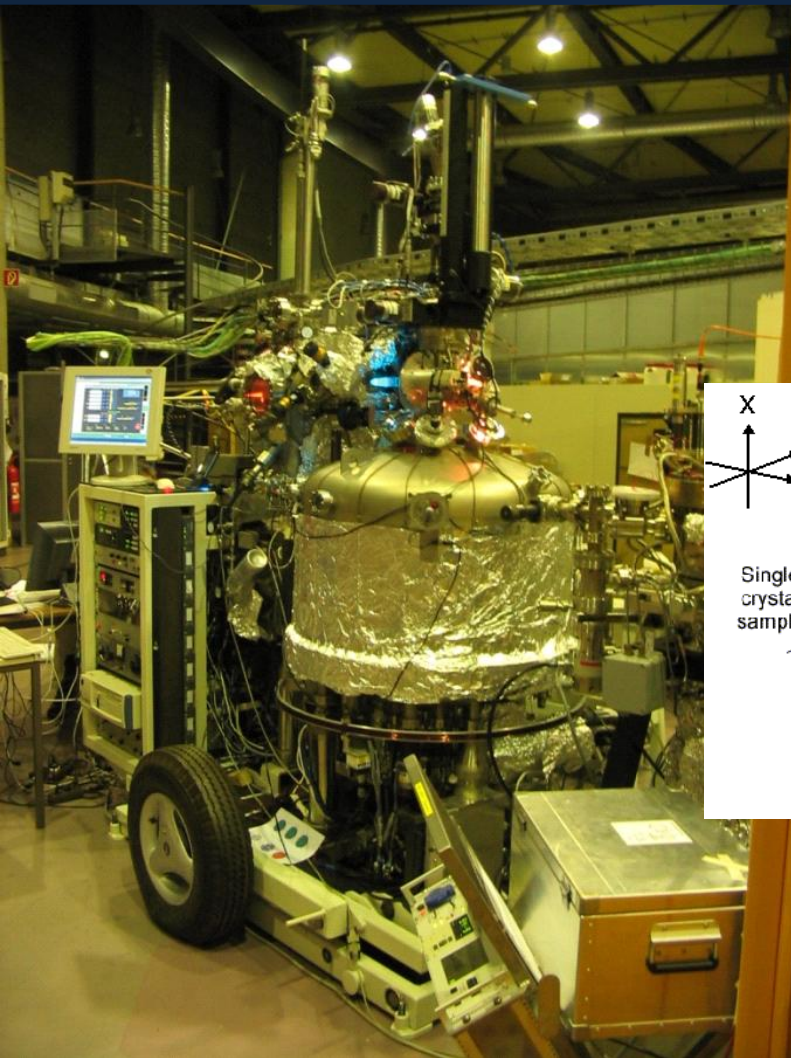


Growth of ordered molecular layers is essential for the determination of the band structure.

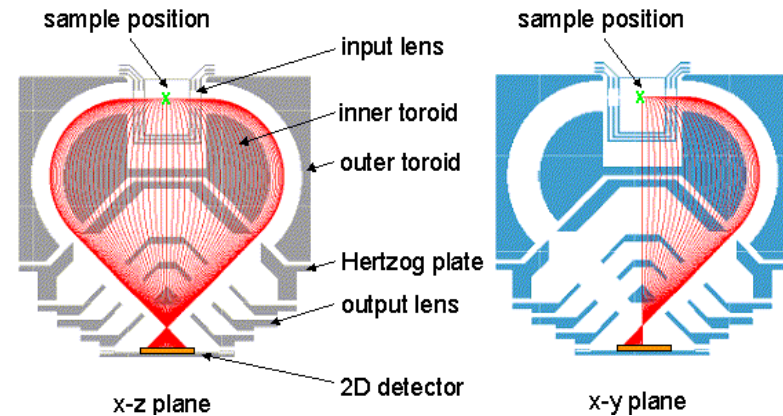
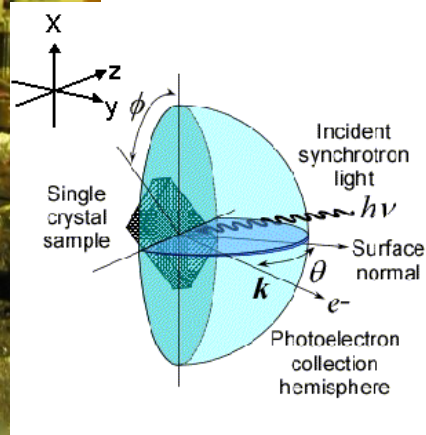
only parallel momentum k_{\parallel} conserved

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

Method



ARUPS; Tomography

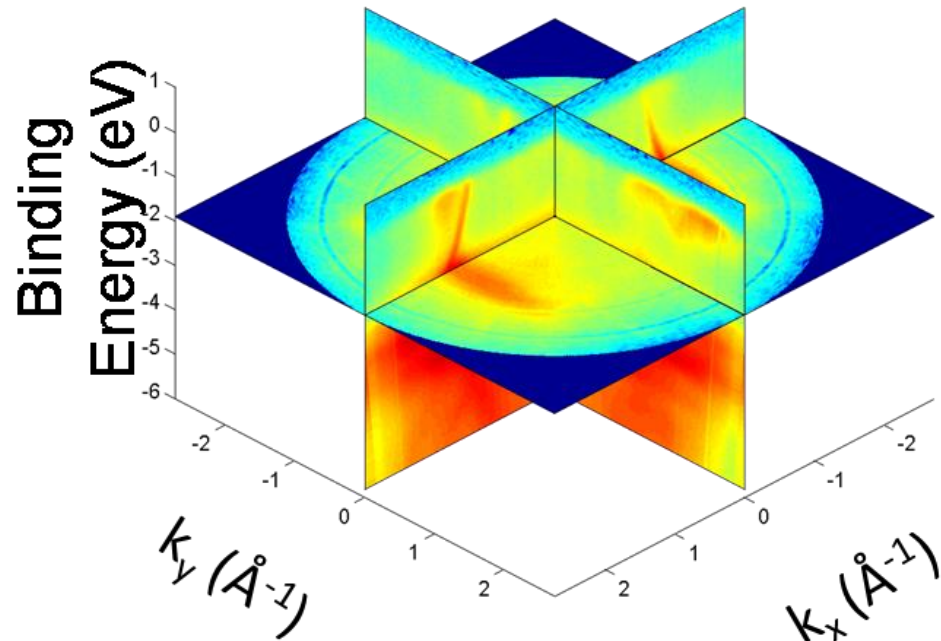


The Toroidal Analyzer collects Photoelectrons with takeoff angles of $\pm 80^\circ$ with one shot!

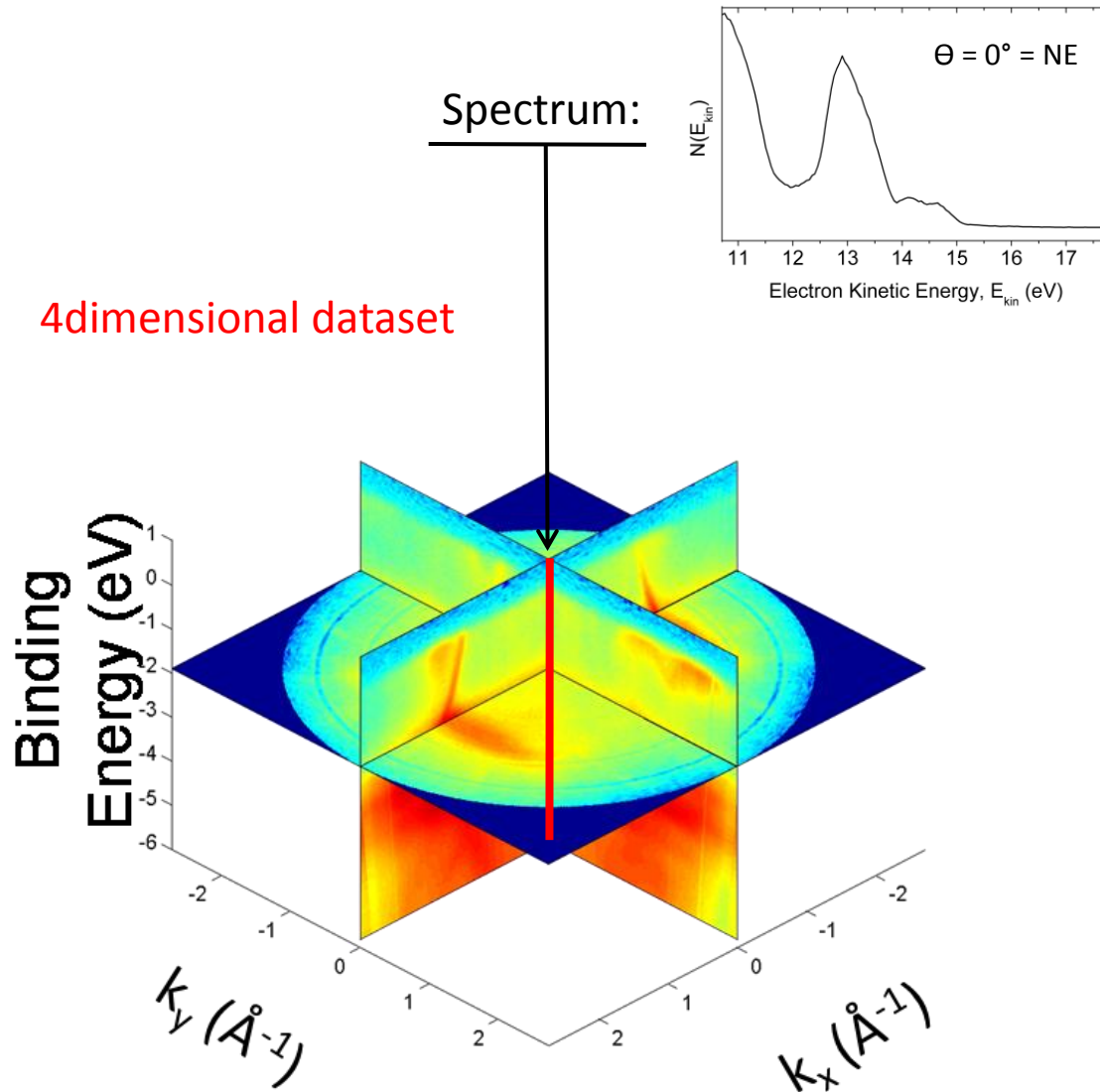
Toroidal Electron Spectrometer for Angle Resolved Photoelectron Spectroscopy with Synchrotron Radiation at BESSY II

Angle Resolved UV Photoemission Spectroscopy (ARUPS)

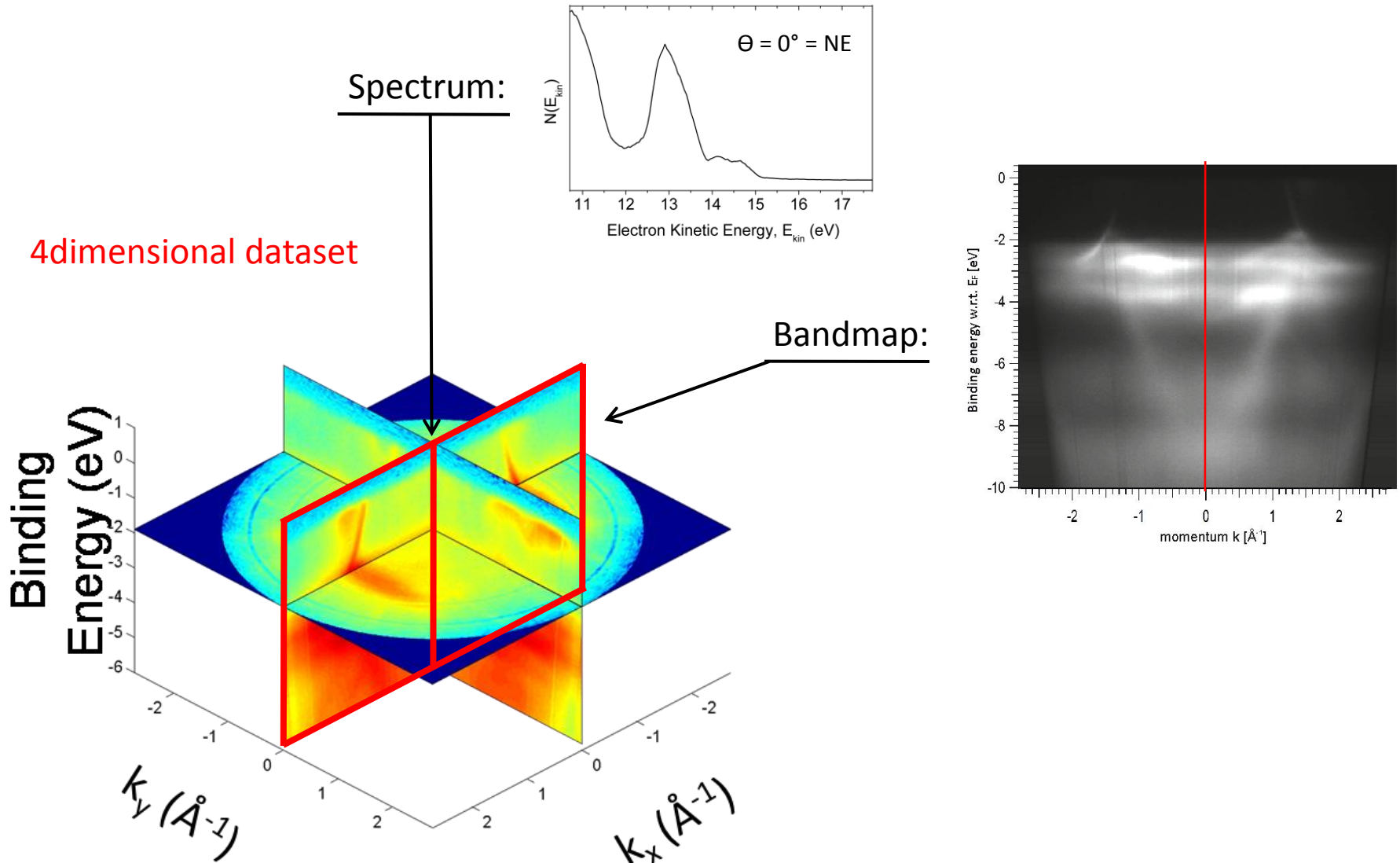
4dimensional dataset



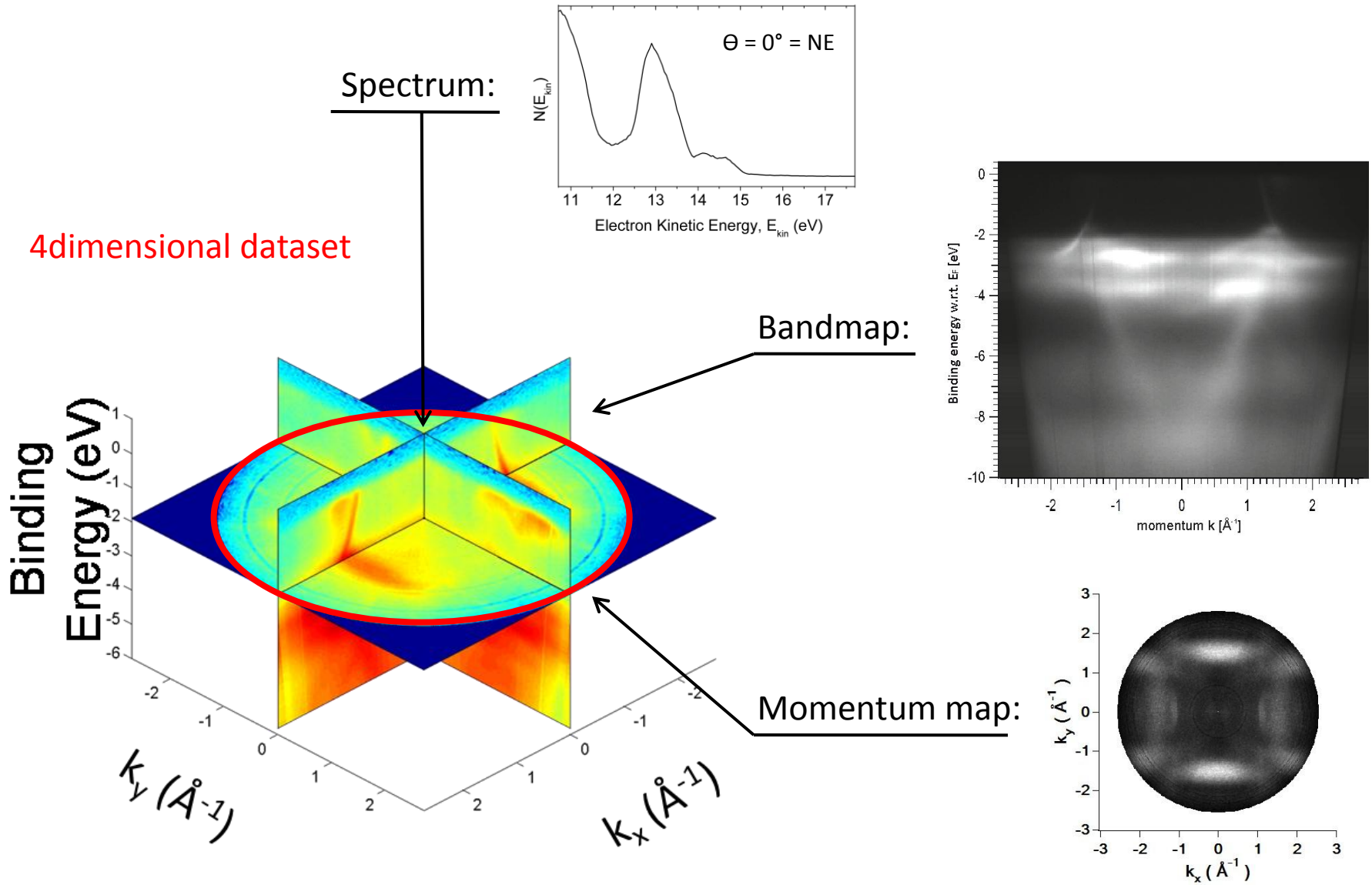
Angle Resolved UV Photoemission Spectroscopy (ARUPS)



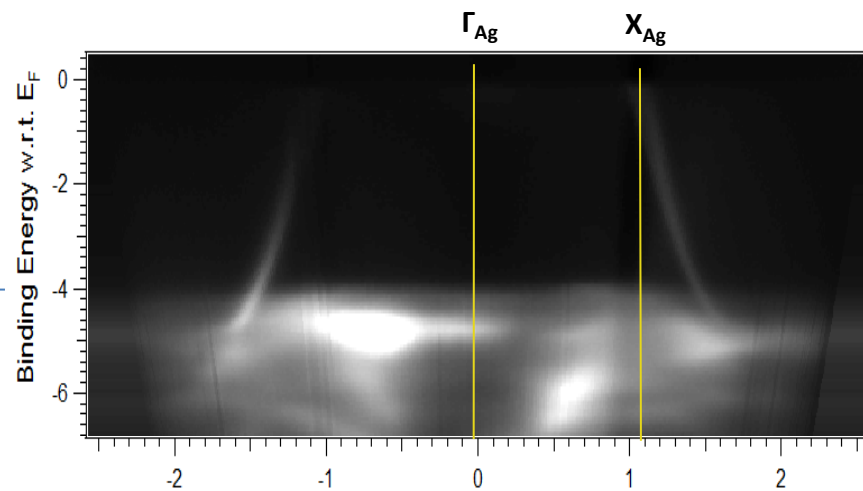
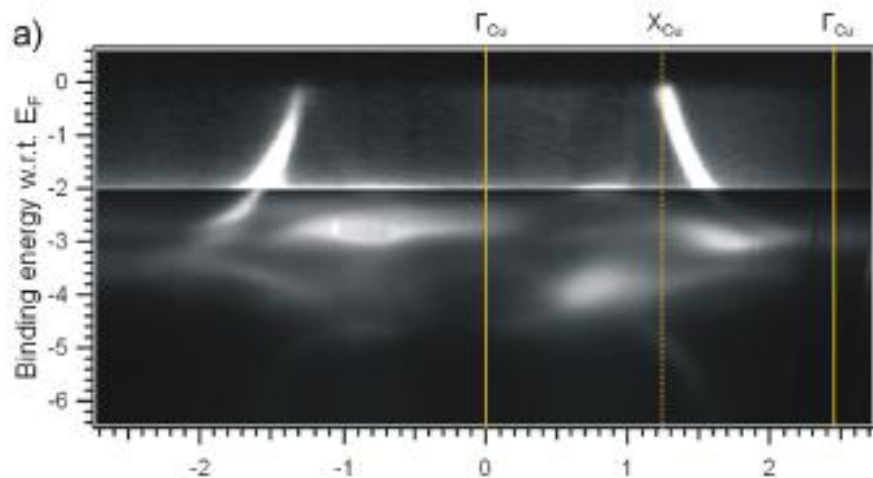
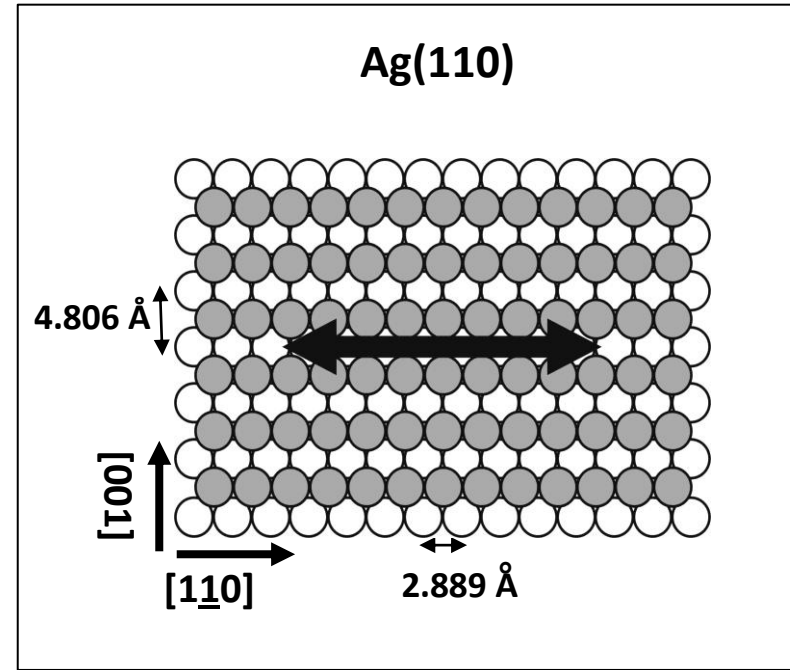
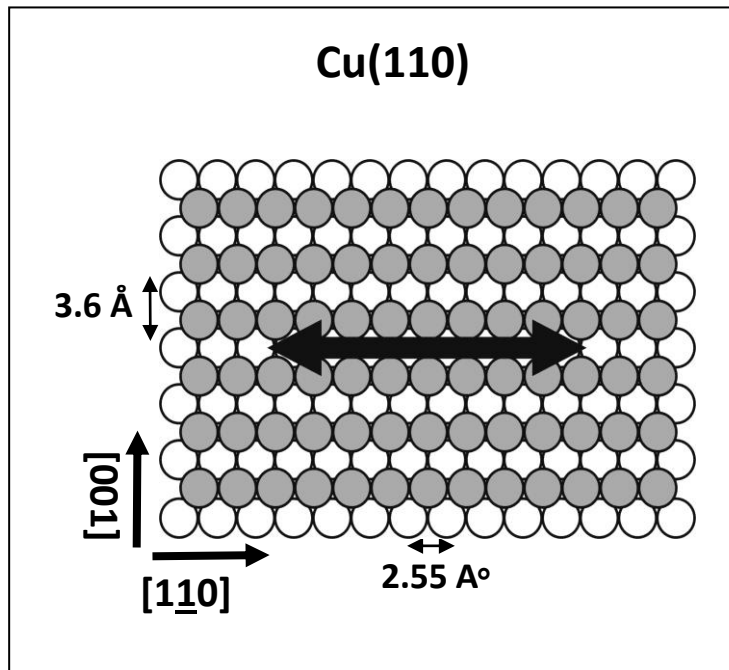
Angle Resolved UV Photoemission Spectroscopy (ARUPS)



Angle Resolved UV Photoemission Spectroscopy (ARUPS)

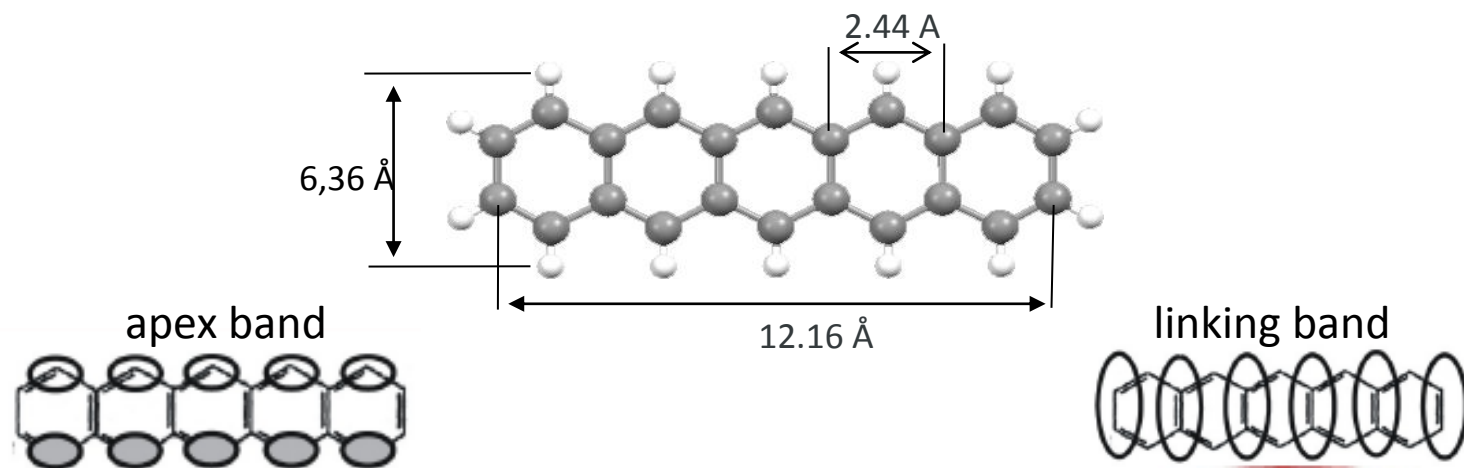


The system: Substrates

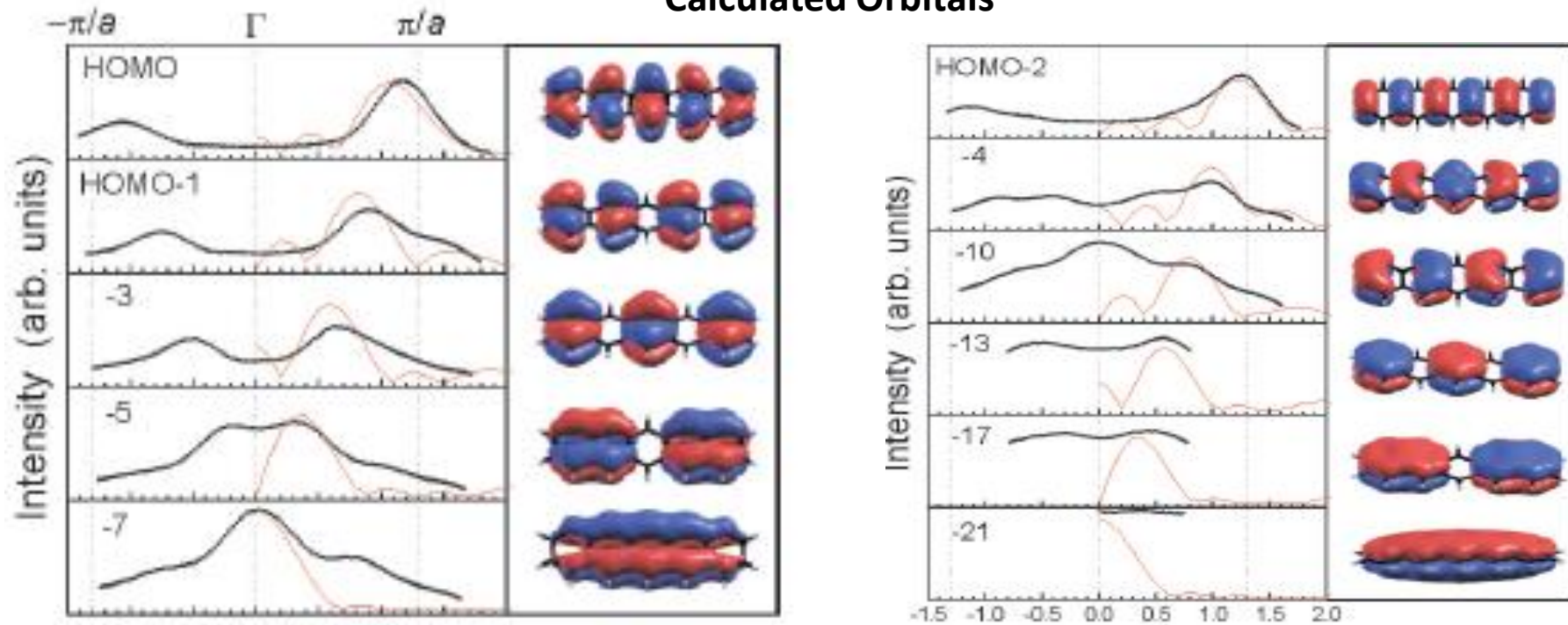


The system: Molecule

Pentacene (5A)



Calculated Orbitals



Pentacene (5A) + Photoemission

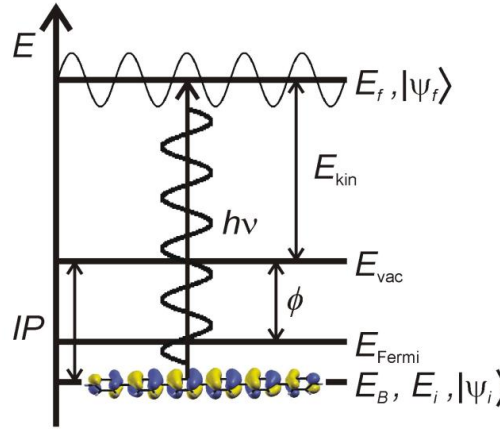
Fermis Golden rule formula

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

Assumption: Final state is a plane wave

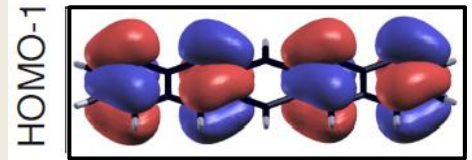
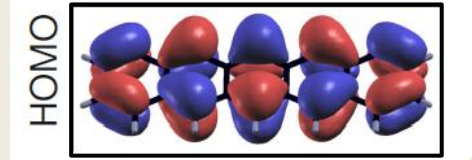
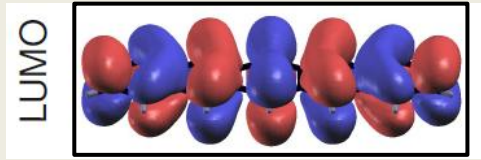
$$I_i(\theta, \phi) \propto |(\mathbf{A} \cdot \mathbf{k})|^2 \times \left| \tilde{\psi}_i(\mathbf{k}) \right|^2$$

Fourier Transform of initial state

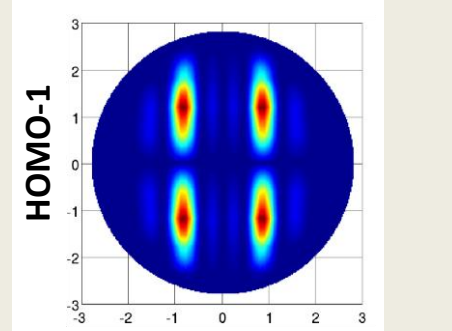
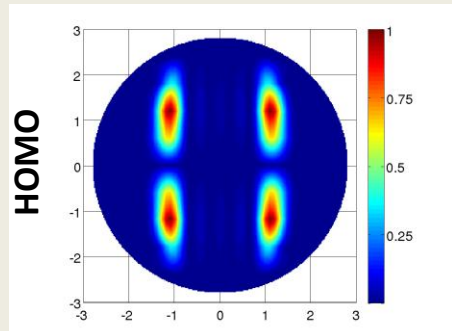
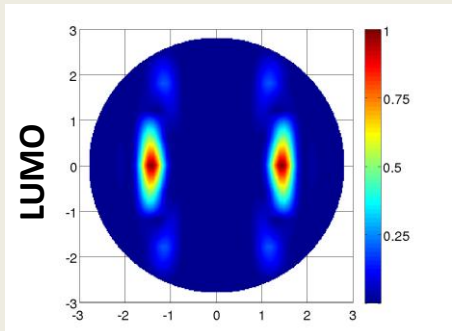


Berkebile S. Doctoral thesis, 2009

DFT of molecular orbitals

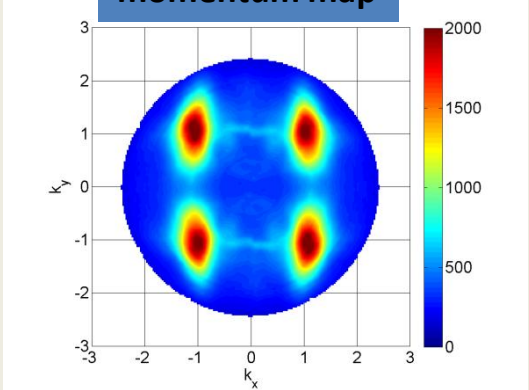


Fourier Transform of DFT orbitals

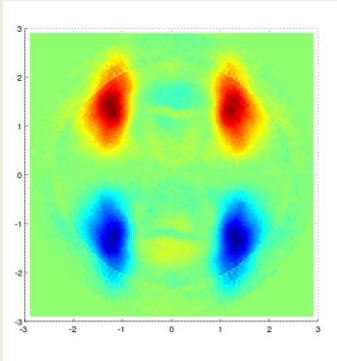


From momentum space to real space

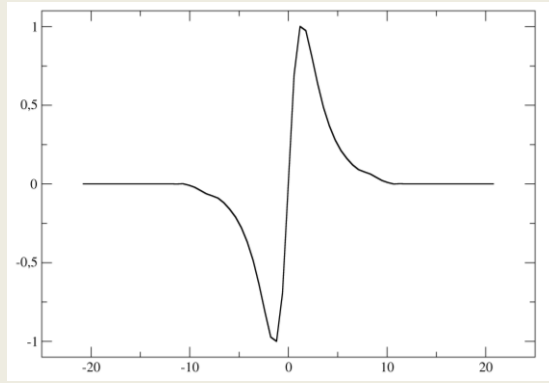
momentum map



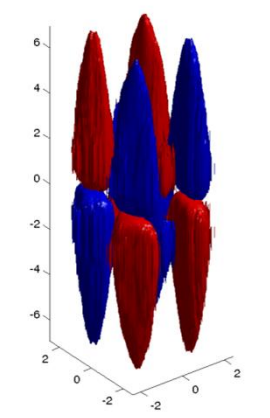
add phase info



1 D F.T. in z direction



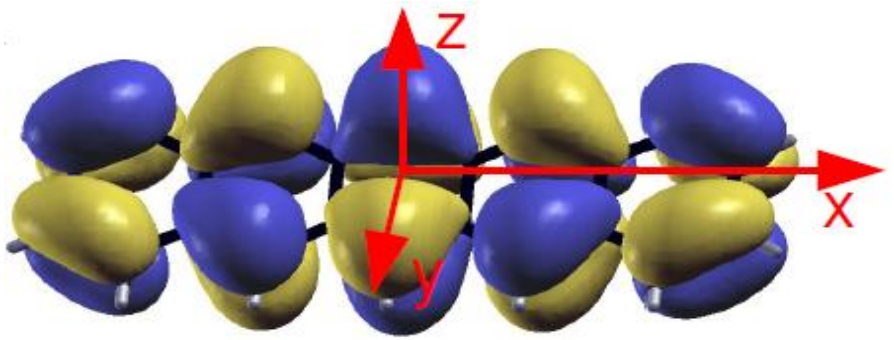
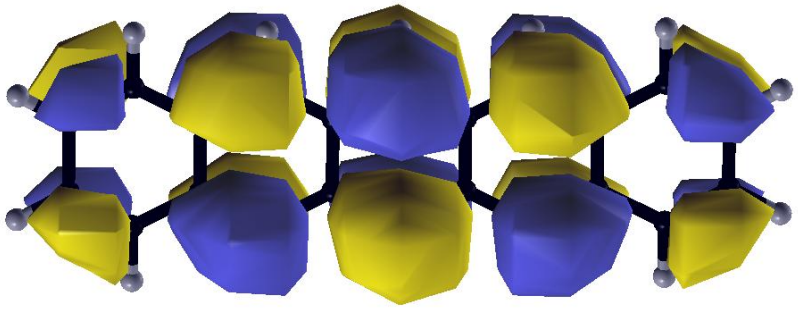
Extrapolation of 2dim. in z



Exp. back F.T.

HOMO

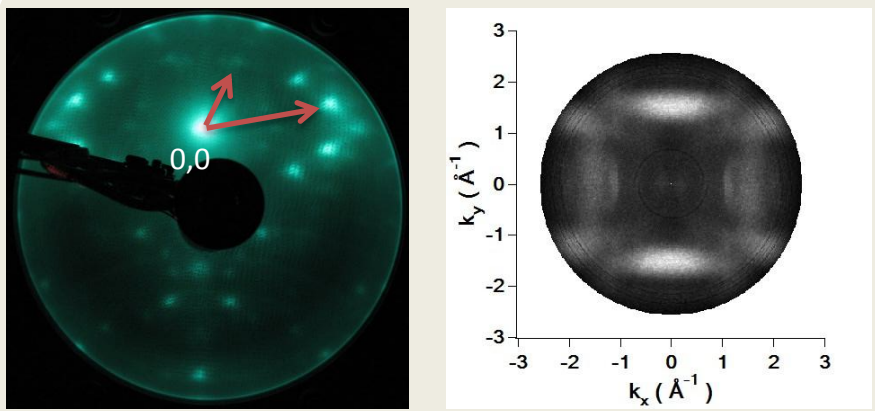
DFT orbital



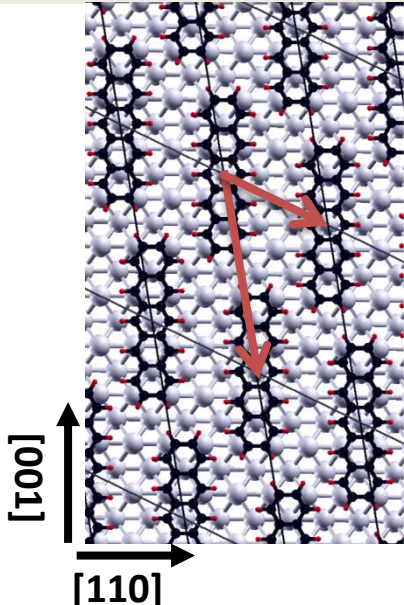
Plane wave approximation for the final state is good!

5A on the two substrates

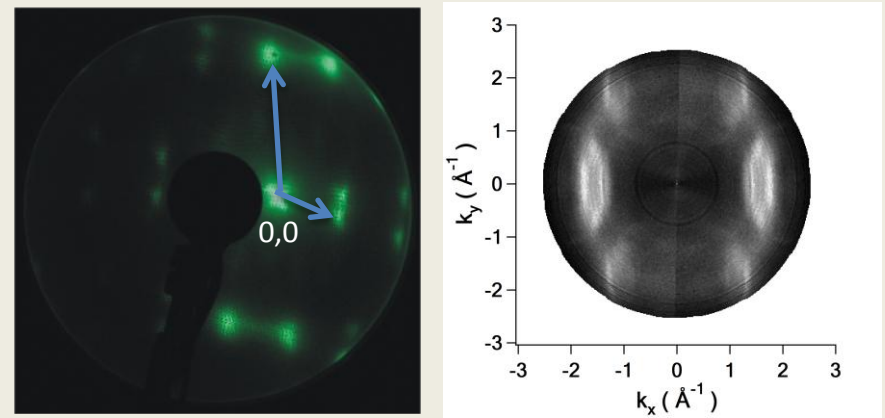
5A monolayer on Ag(110)



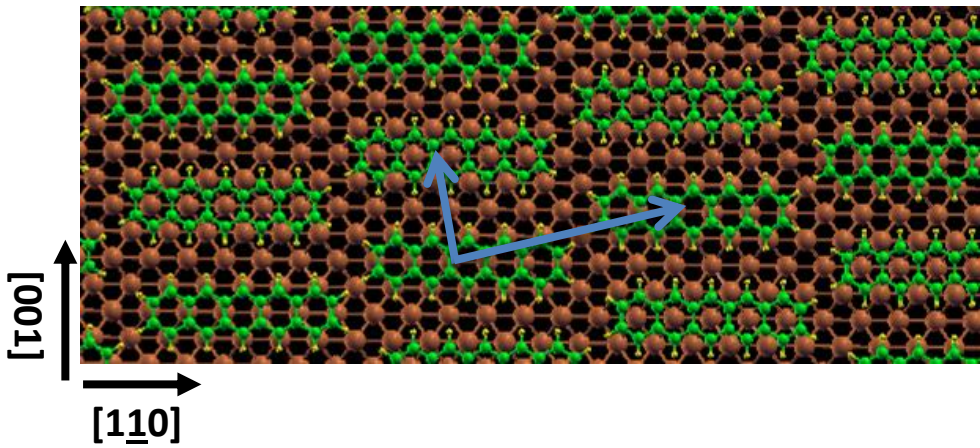
$$M = \begin{pmatrix} 3 & -1 \\ -1 & 4 \end{pmatrix} \xrightarrow{[1-10]}$$



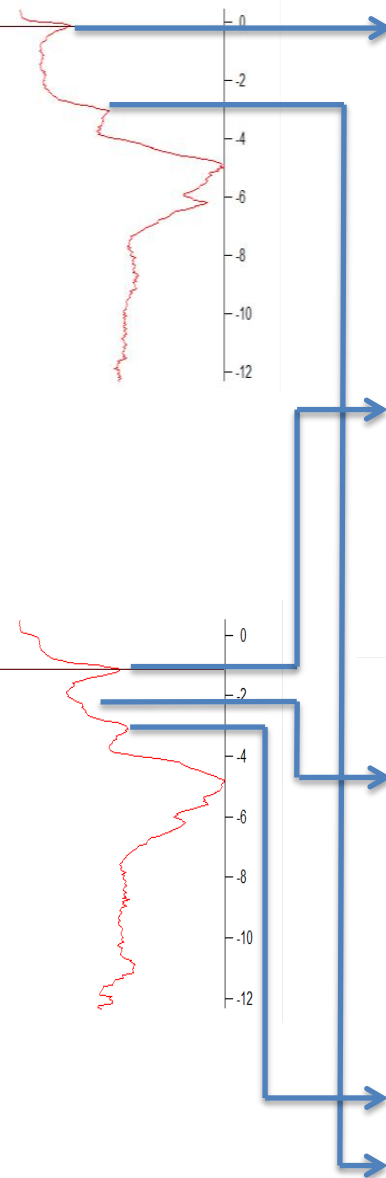
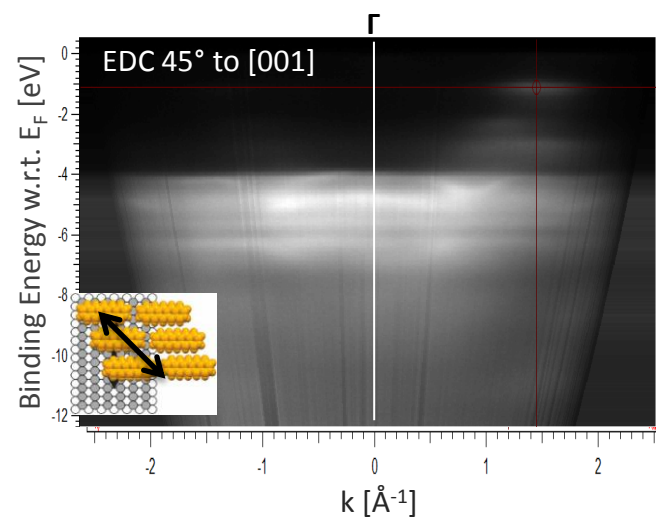
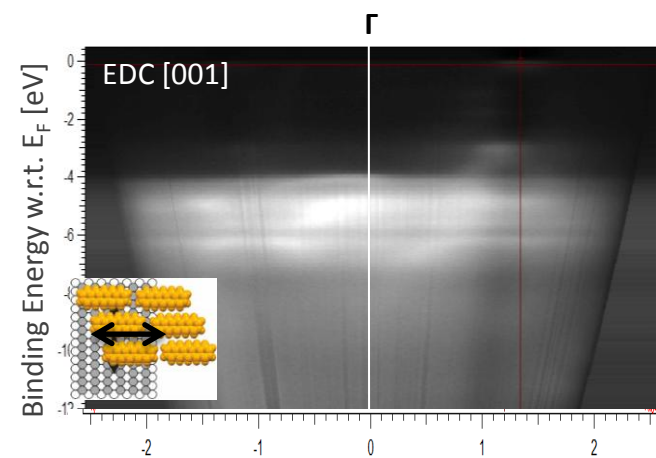
5A monolayer on Cu(110)



$$M = \begin{pmatrix} 6.5 & -1 \\ -0.5 & 2 \end{pmatrix} \xrightarrow{[1-10]}$$

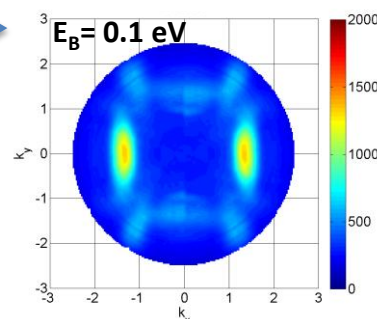


5A on Ag(110)

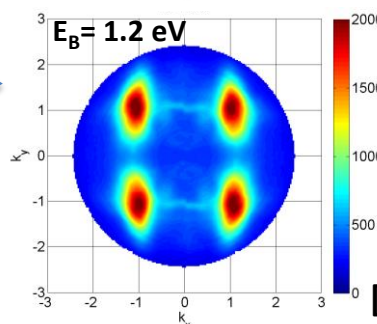
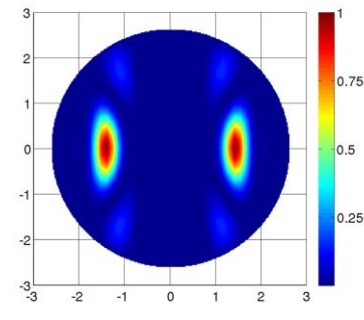


Experiment

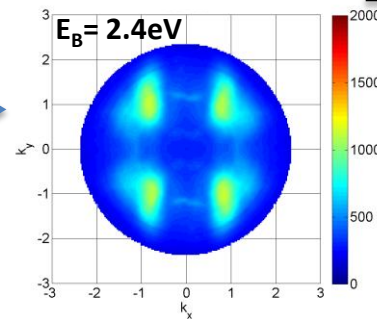
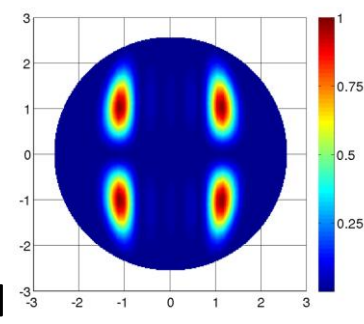
Theory



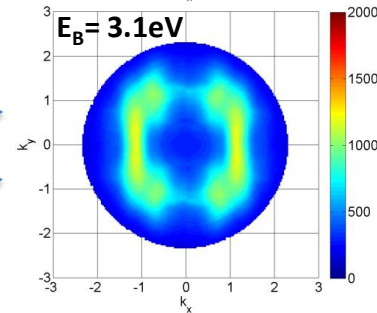
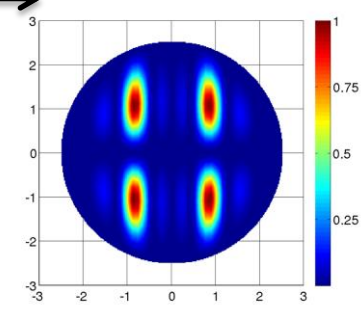
LUMO



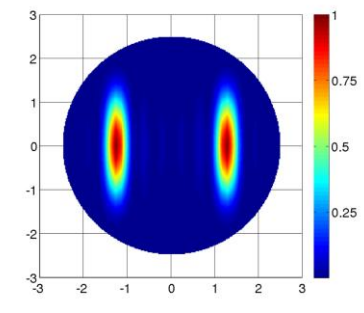
HOMO



HOMO-1



HOMO-2



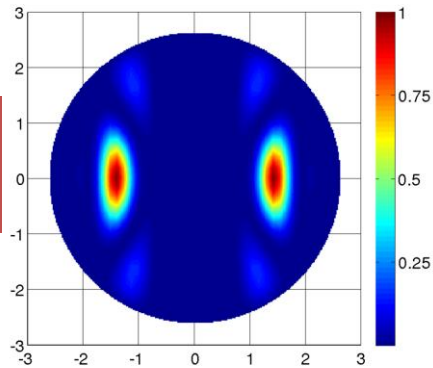
[001]

Momentum maps of 5A on Ag(110)

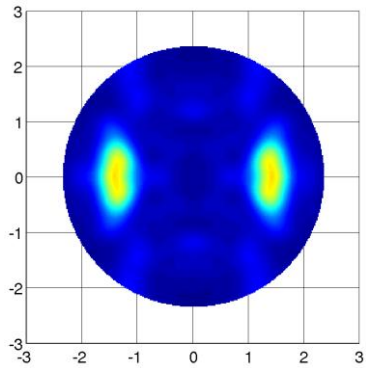
Theory

Experiment

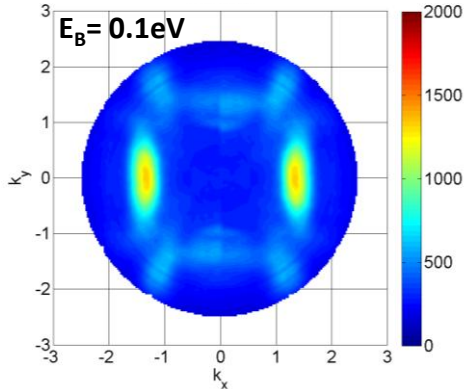
Isolated molecule



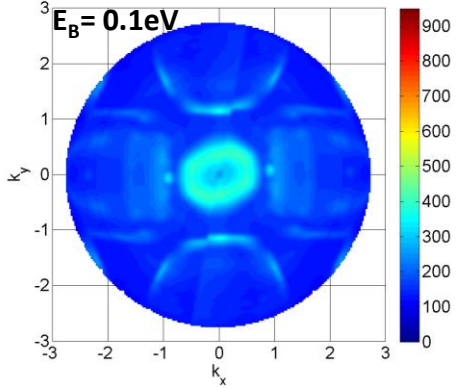
Monolayer structure + substrate



5A monolayer

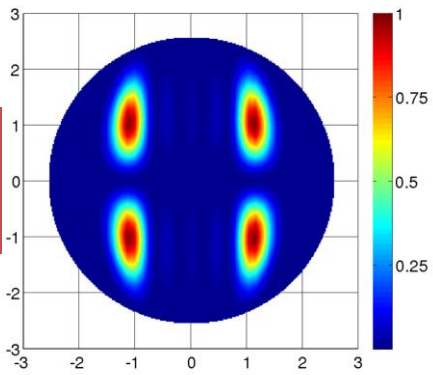


Substrate

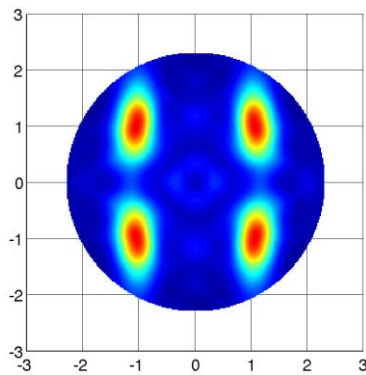


LUMO

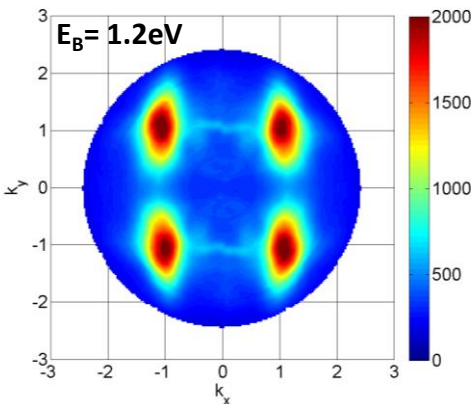
Isolated molecule



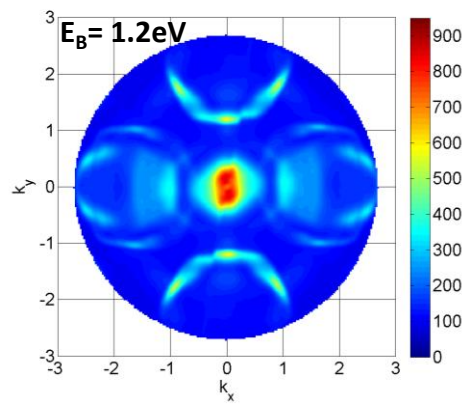
Monolayer structure + substrate



5A monolayer



Substrate



HOMO

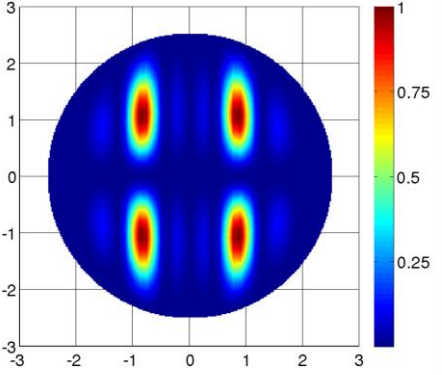
Momentum maps of 5A on Ag(110)

Theory

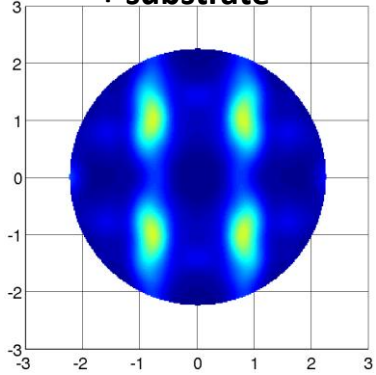
Experiment

HOMO-1

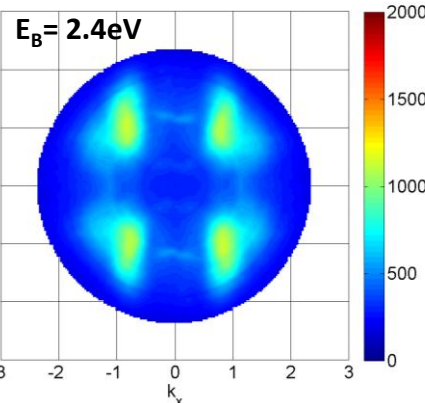
Isolated molecule



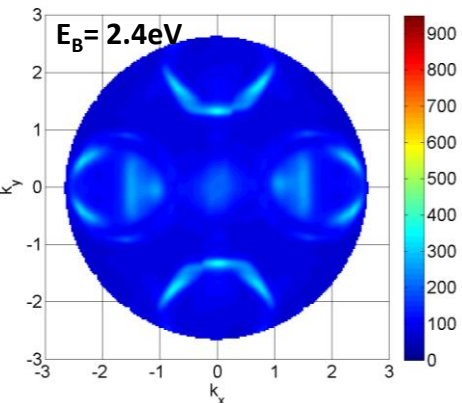
Monolayer structure + substrate



5A monolayer

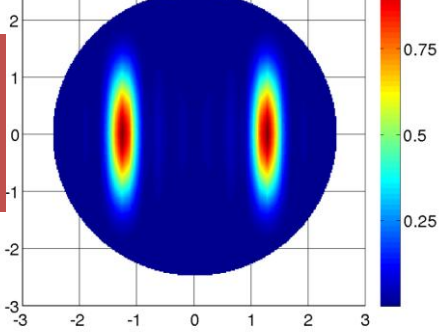


Substrate

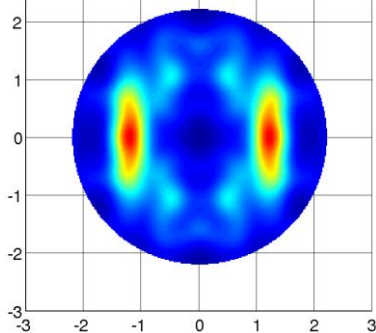


HOMO-2

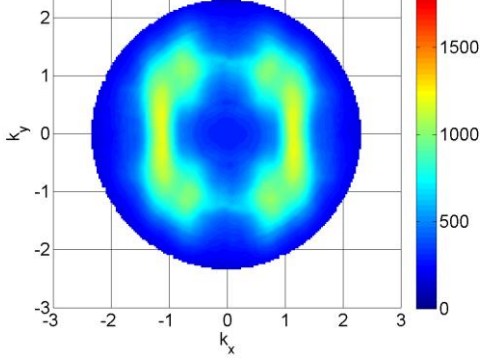
Isolated molecule



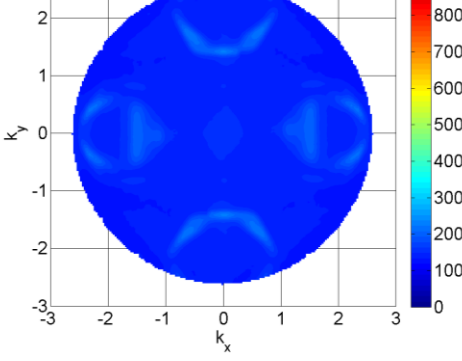
Monolayer structure + substrate



$E_B = 3.1\text{eV}$



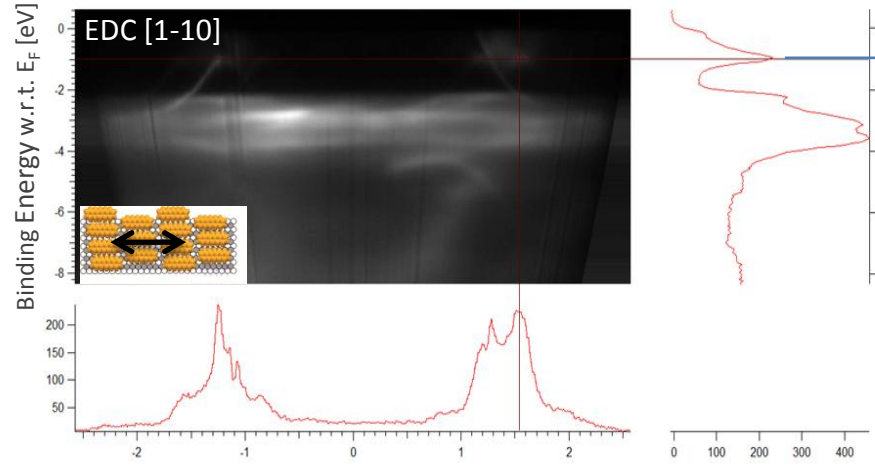
$E_B = 3.1\text{eV}$



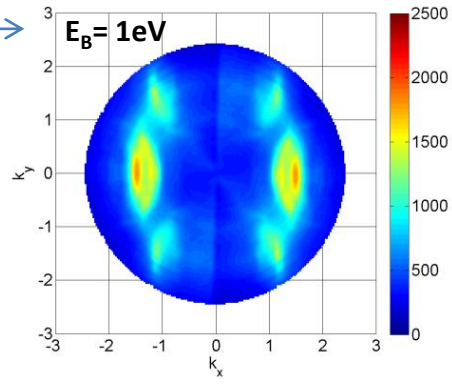
5A on Ag(110)

- Momentum maps compare well to the theoretical maps of the isolated molecule

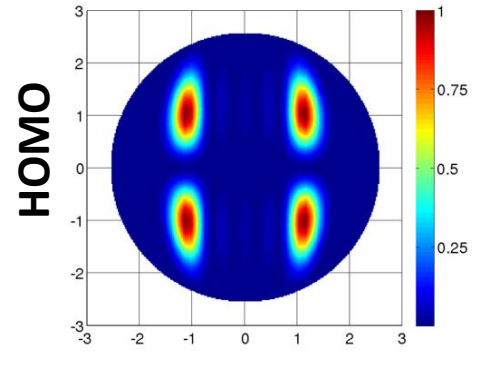
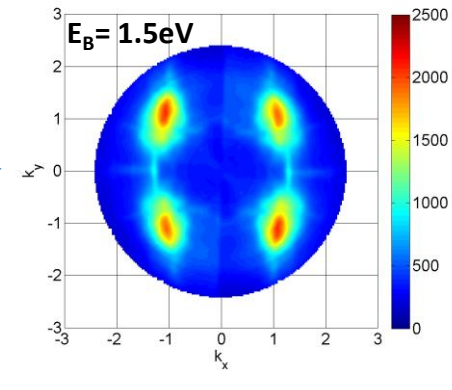
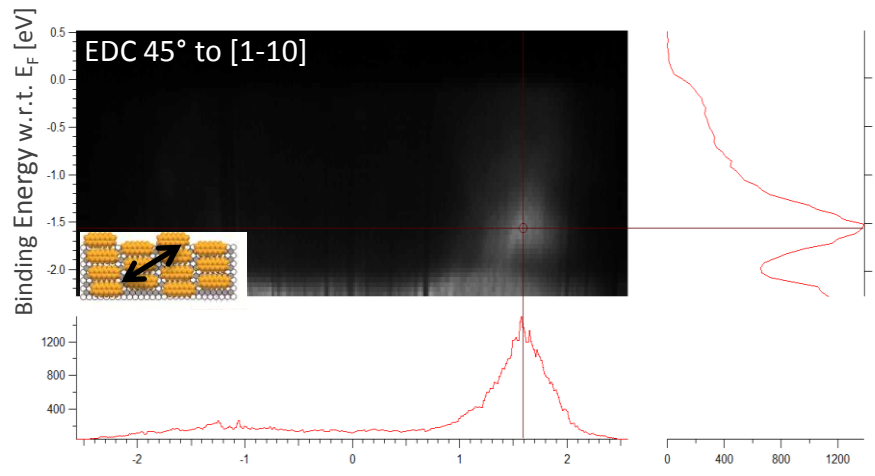
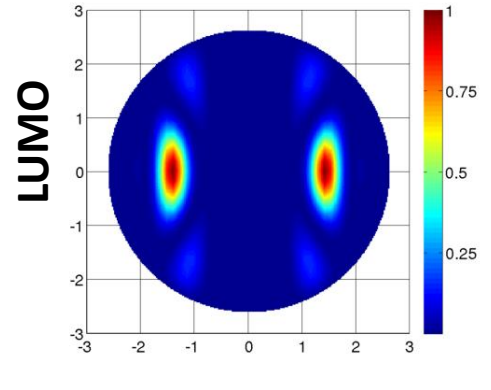
5A on Cu(110)



Experiment



Theory



Closer look at the LUMO

Compare to DFT

Theory

Experiment

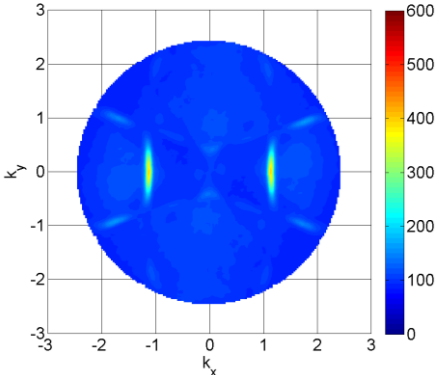
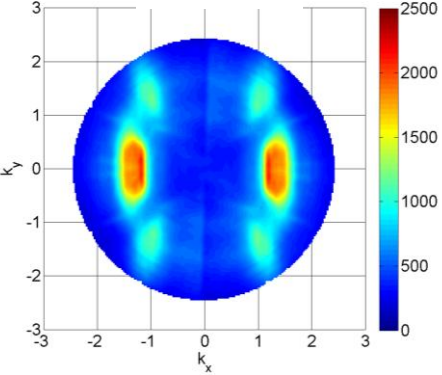
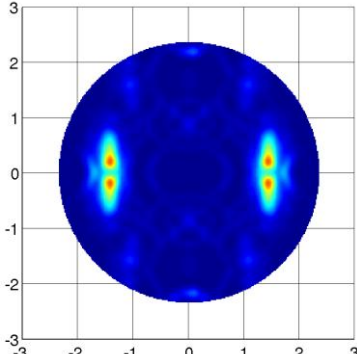
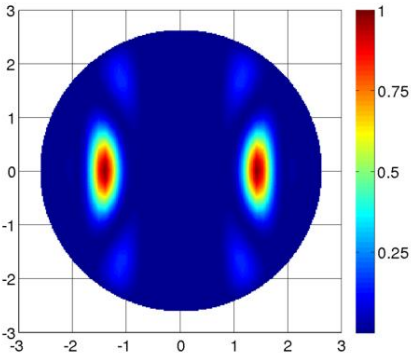
Isolated molecule

Monolayer structure + substrate

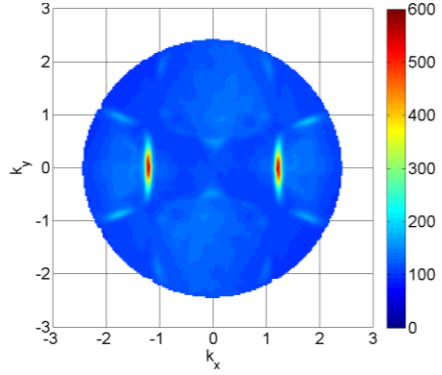
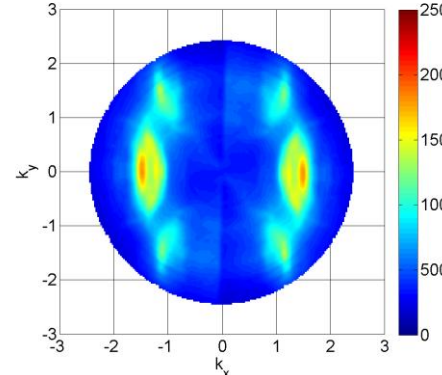
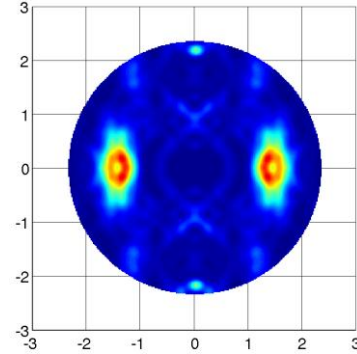
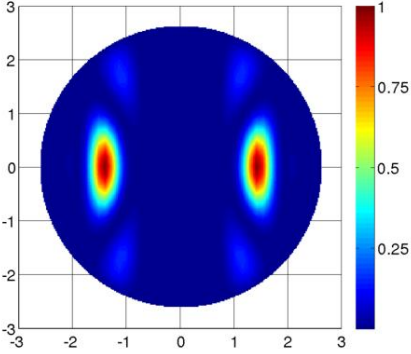
5A monolayer

Substrate

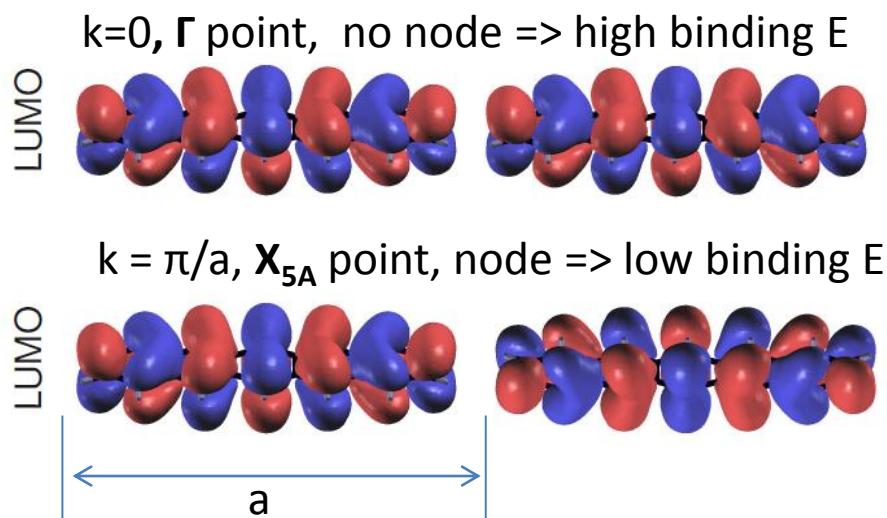
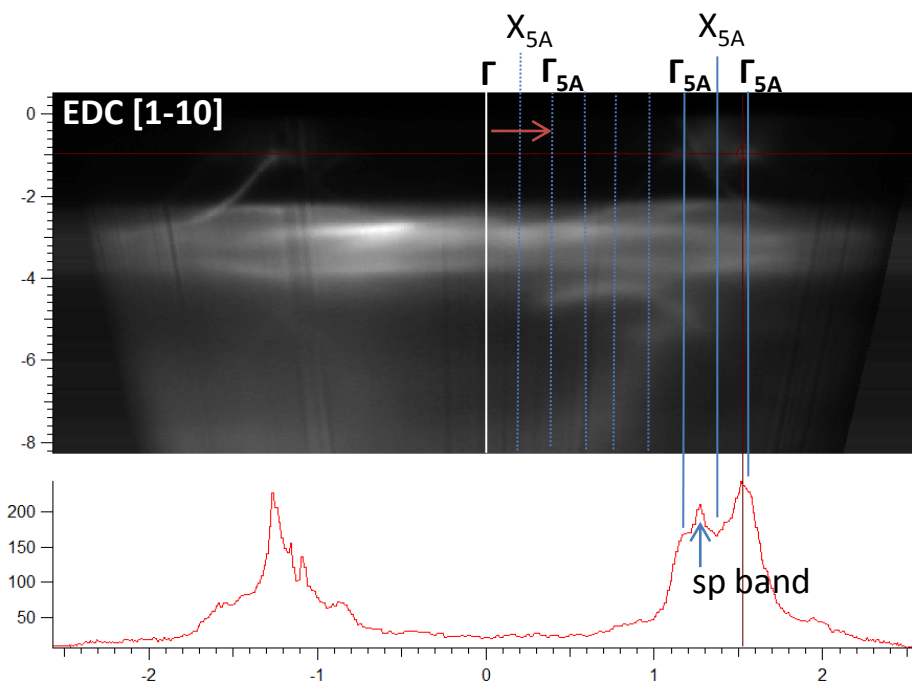
LUMO, - 0.8 eV



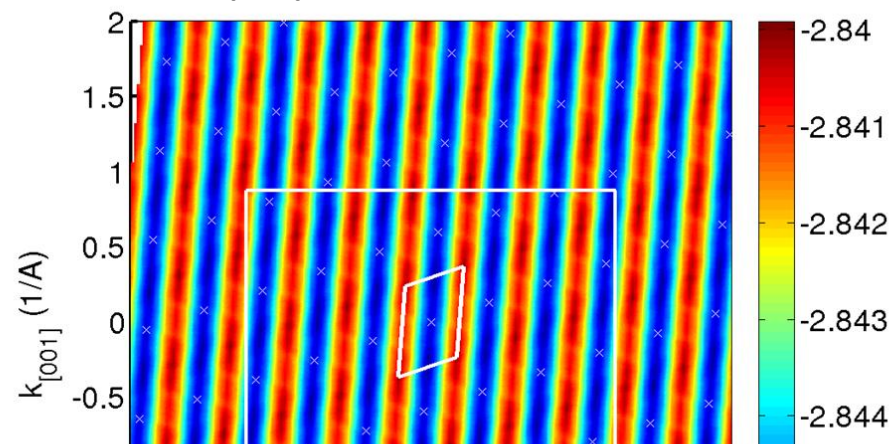
LUMO, - 1 eV



What is the origin of the structured LUMO ? Intermolecular Dispersion ?



Dispersion of the LUMO calculated for the 5A Cu(110) unit cell without the substrate



Theory: Dispersion without the substrate only $\sim 10\text{meV}$!

Experiment: $\sim 200\text{meV}$!

5

6

Summary

- Simple FT of orbitals explains ARUPS very well
- **Weakly bound: 5A on Ag(110)**
orbitals are \sim as isolated molecule
- **Strongly bound: 5A on Cu(110)**
 - modification in energy and momentum
 - intermolecular dispersion mediated through substrate interaction

Acknowledgements

Eva Reinisch
Michael Ramsey
Georg Koller
Margareta Wagner
Stephen Berkebile

Daniel Lüftner
Peter Puschnigg

Markus Ostler
Thomas Seyller

FWF

Der Wissenschaftsfonds.

BESSY II

HZB Helmholtz
Zentrum Berlin



European **L**ight **S**ources **A**ctivities

Thank you for your attention!!



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GRAZ**

