Cs doping of organic semiconducting monolayers: probing the electronic and geometric structure with Angle Resolved UPS

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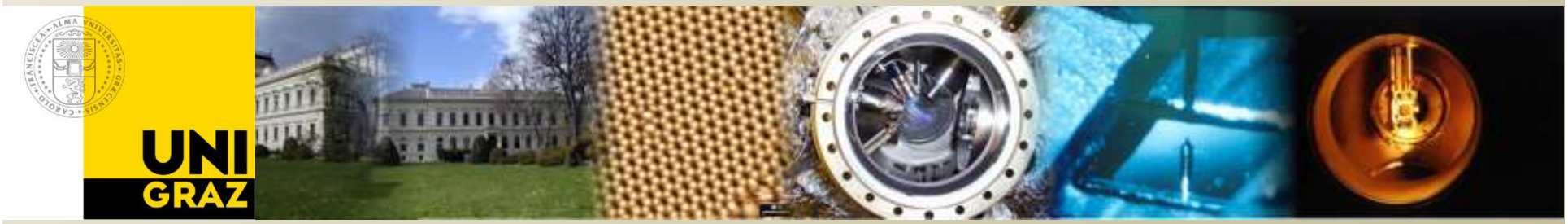
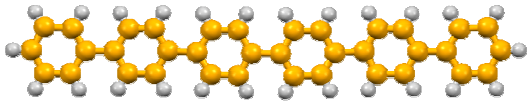
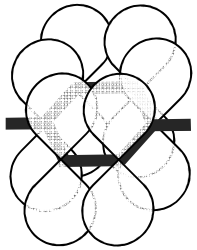


INTRODUCTION

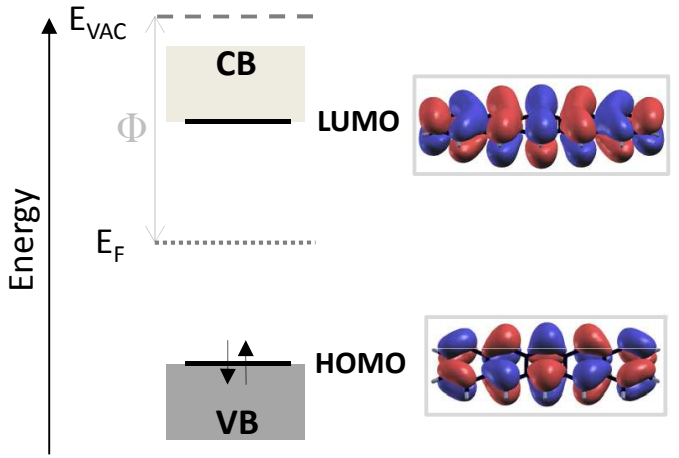
para-Sexiphenyl (6P)



Organic molecules have a conjugated π-electron system delocalised along the molecular backbone:



Electronic states in the molecular band gap region



Why are we interested in the Cesium-doping experiments?

- Modify electronic structure and thus optoelectronic properties of the organic layers
  => „move“ (un)occupied states in(to) the band gap

- Investigate changes of the geometric configurations in the molecular films

OUTLINE

I. System

II. Probing the electronic and geometric structure
    => ARUPS technique

III. What means „Doping“ of organic molecules with Cs?

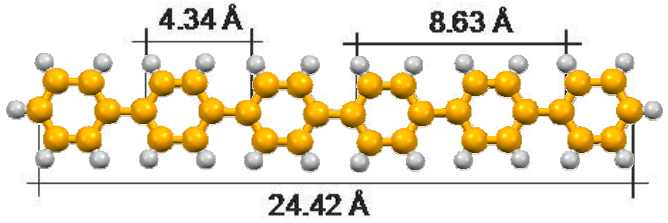
VI. Experiments:
    6P and 5A on Cu(110)
    6P and 5A on Ag(110)
    => Doping of the organic monolayers

I. The System

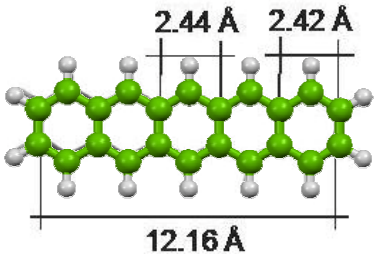
I. The system

Conjugated organic molecules:

para-Sexiphenyl (6P)

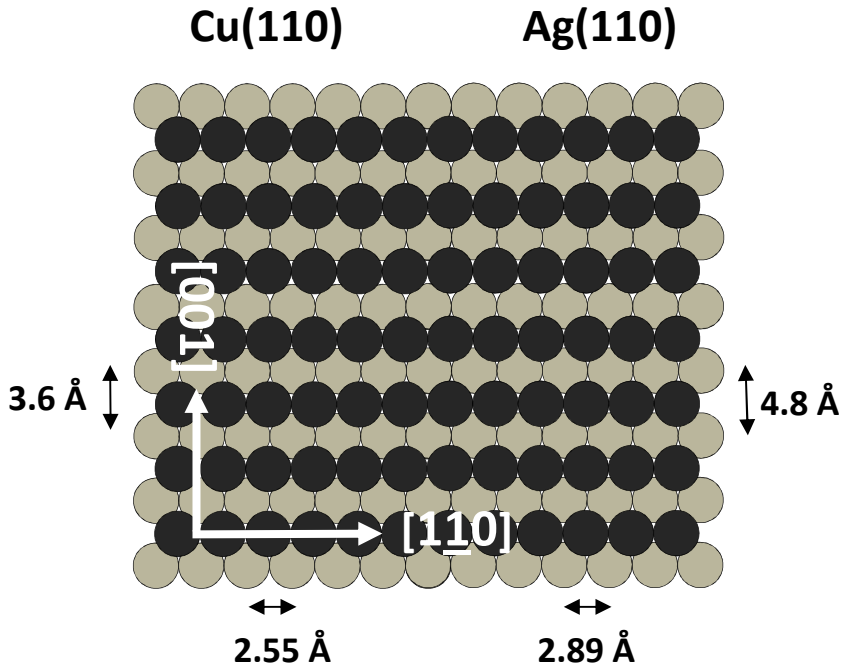


Pentacene (5A)



Cesium: alkali metal
one weakly bound 6s-electron
=> n-dopant

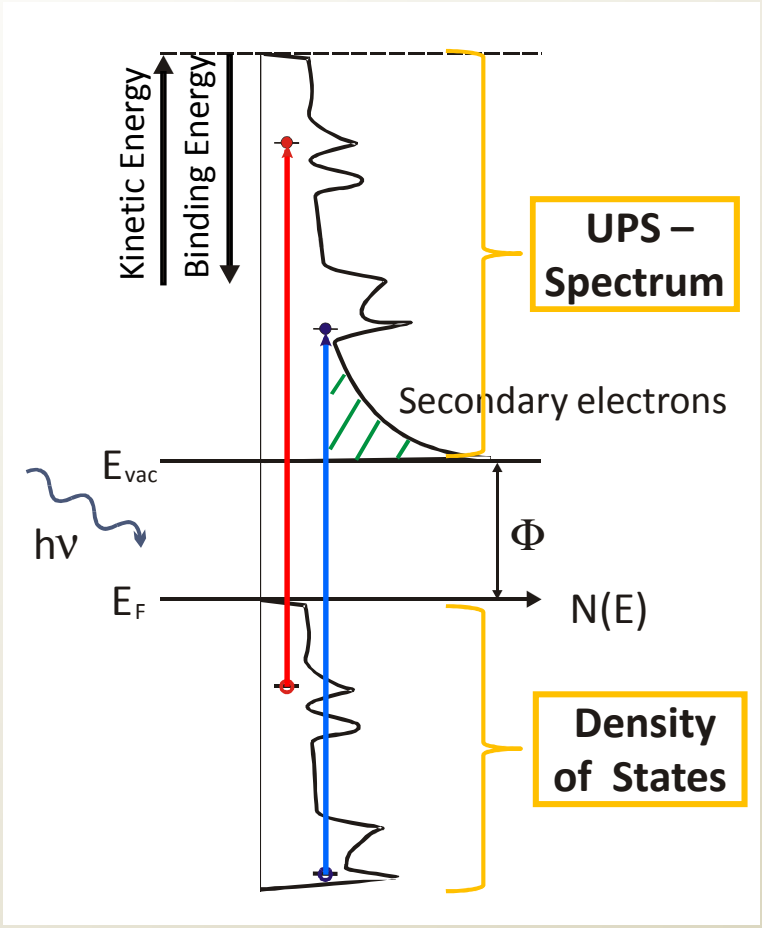
Substrates with two-fold symmetry:



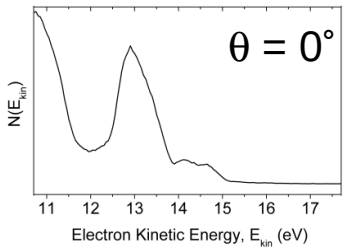
The rodlike molecules tend to grow ordered and oriented along/perpendicular to the substrate corrugation.

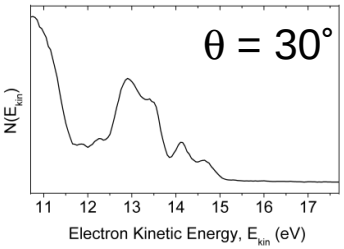
II. ARUPS technique

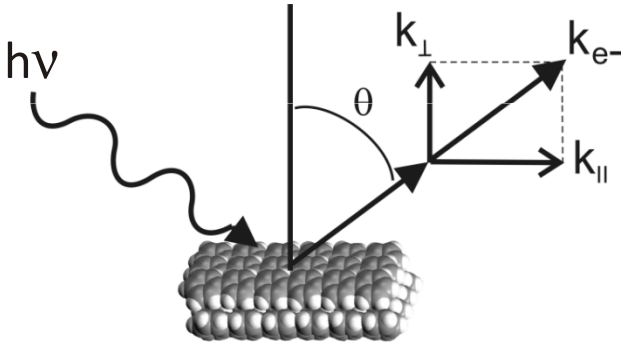
UV Photoemission Spectroscopy (UPS)

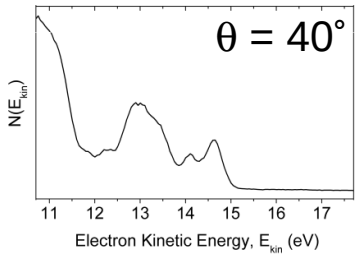


Angular dependence in ordered molecular layers:







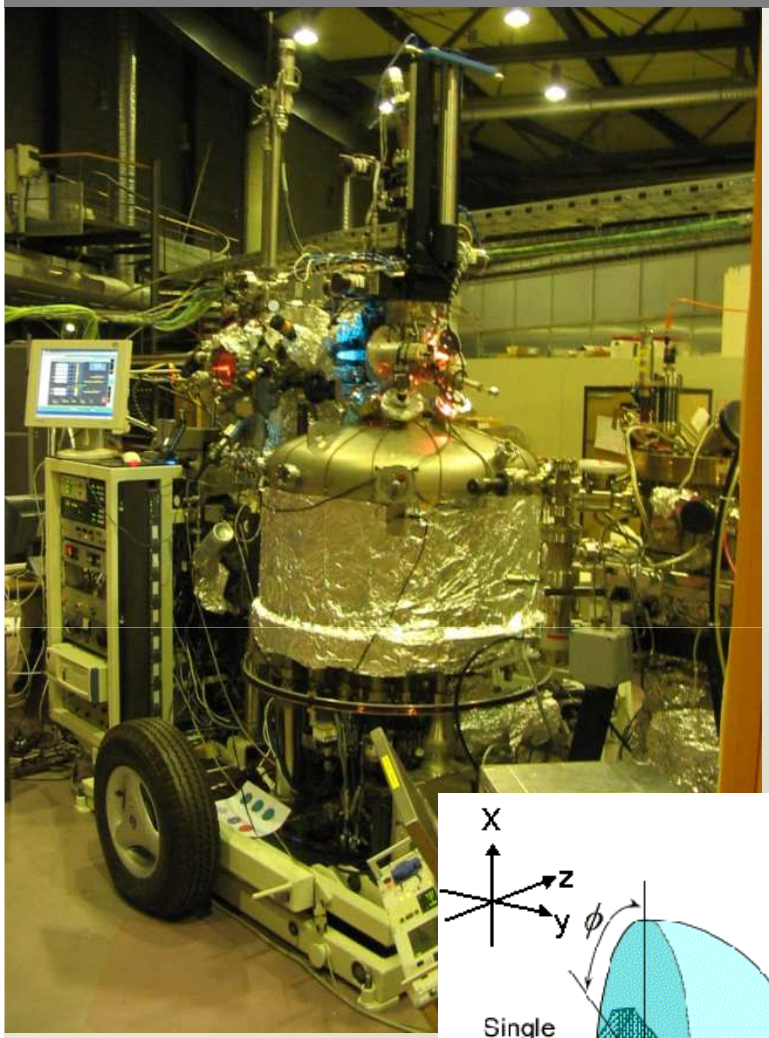


Growth of ordered molecular layers is essential for the determination of the band structure.

only parallel momentum k_{II} conserved

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

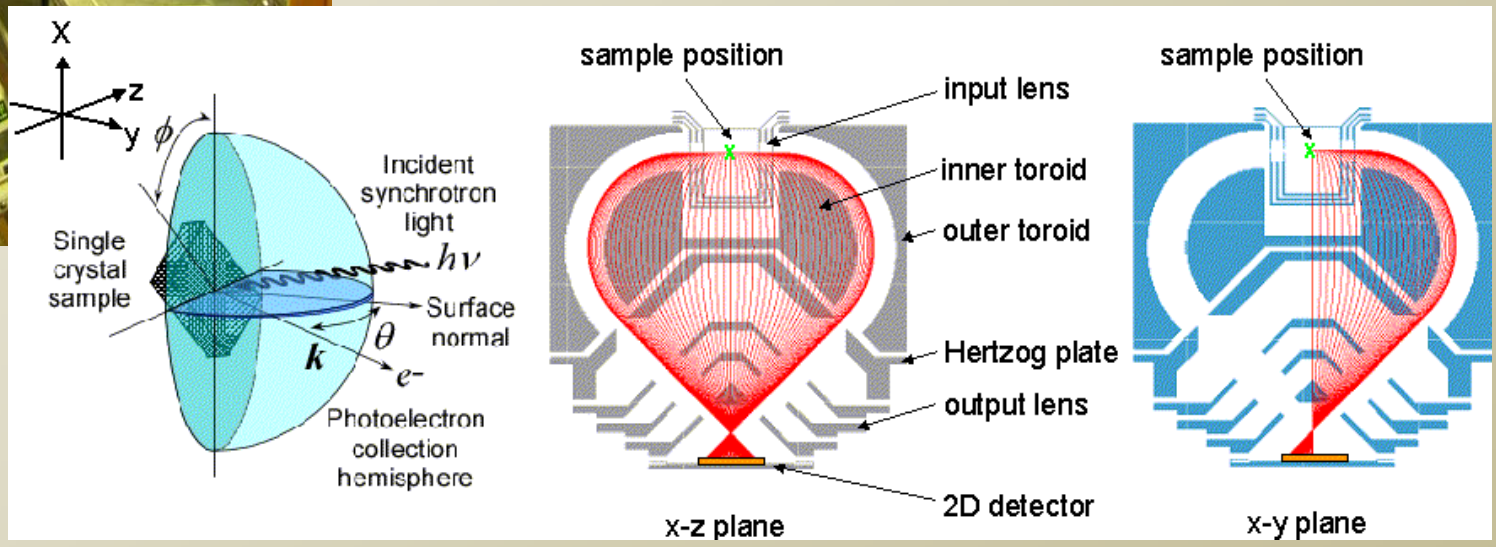
II. ARUPS TECHNIQUE



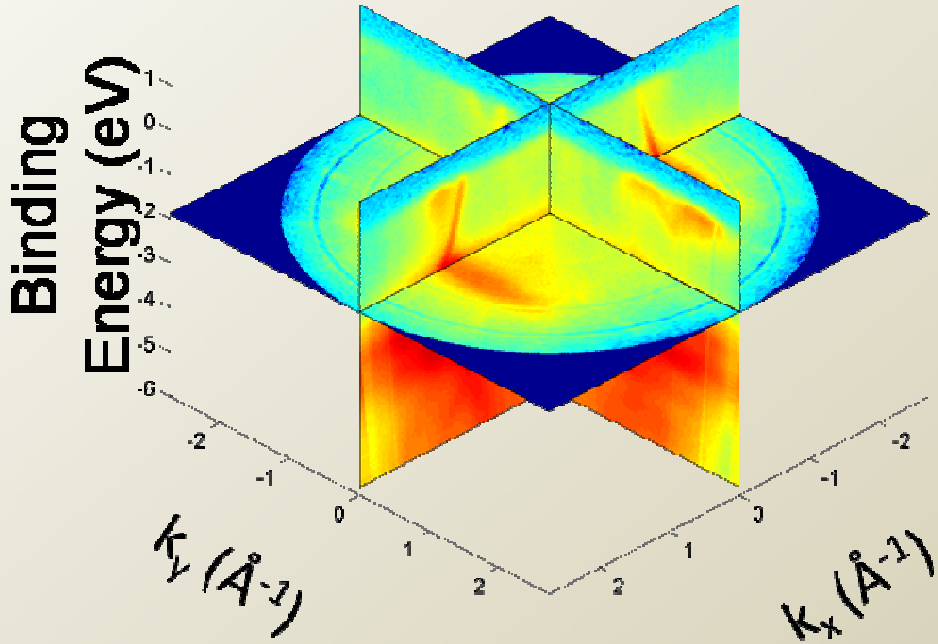
Toroidal Electron Spectrometer

for Angle Resolved Photoelectron Spectroscopy
with Synchrotron Radiation at BESSY II

The Toroidal Analyzer collects Photoelectrons
with takeoff angles of ±80° with one shot!

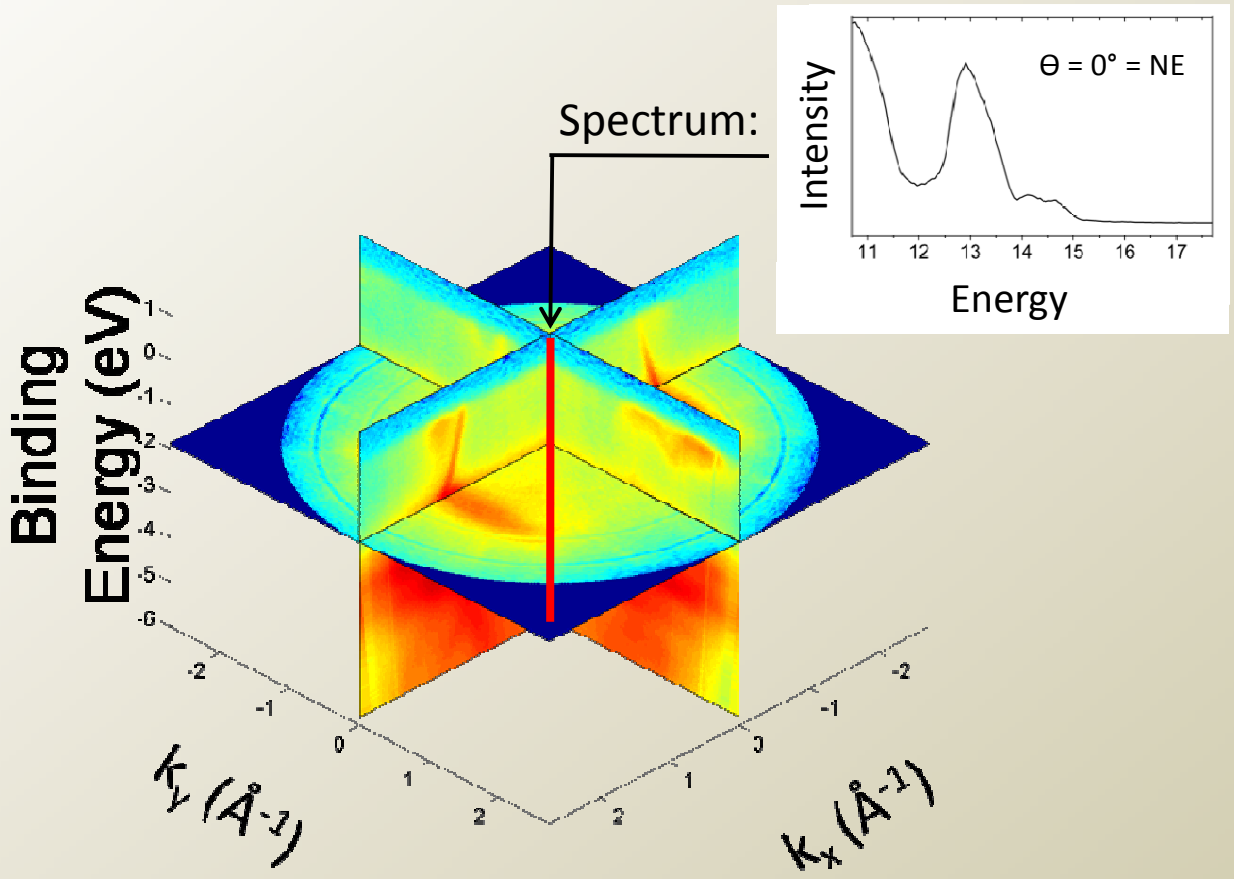


Angle Resolved UV Photoemission Spectroscopy (ARUPS)



4-dimensional dataset
- **Intensity**
- **Energy**
- **2-dim polar angle / momentum**

Angle Resolved UV Photoemission Spectroscopy (ARUPS)



4-dimensional dataset
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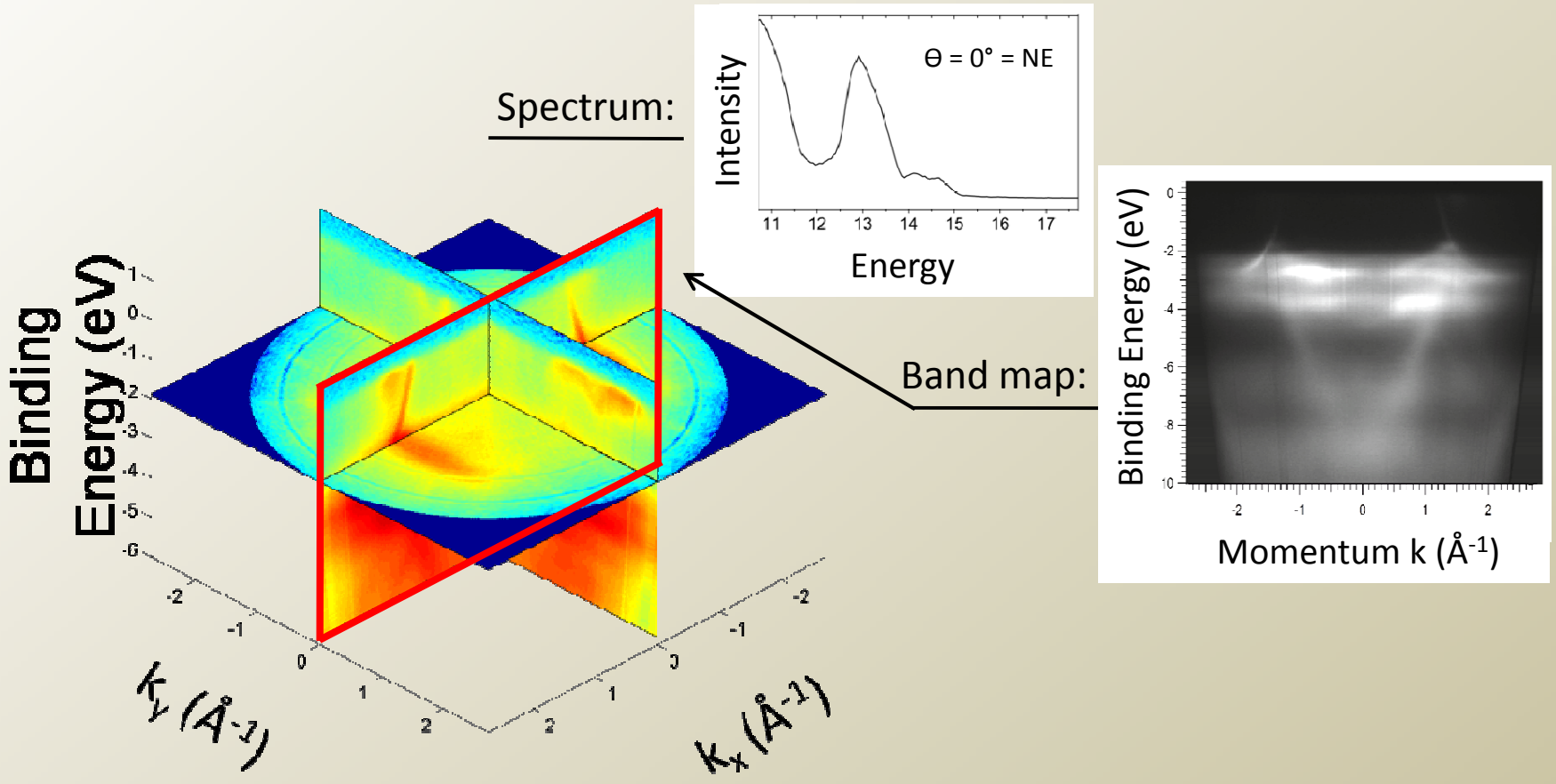
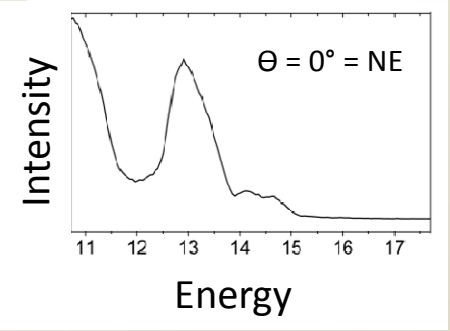
Angle Resolved UV Photoemission Spectroscopy (ARUPS)



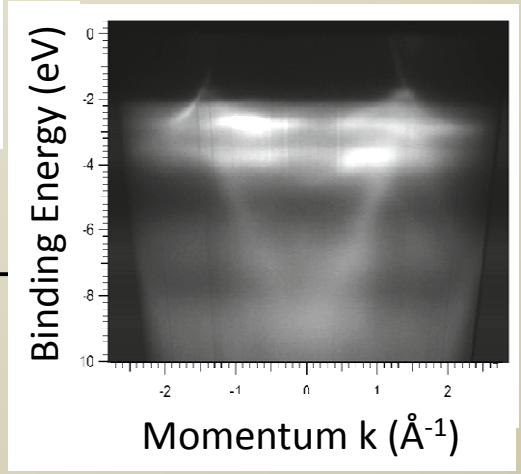
4-dimensional dataset
- **Intensity**
- **Energy**
- **2-dim polar angle / momentum**

Angle Resolved UV Photoemission Spectroscopy (ARUPS)

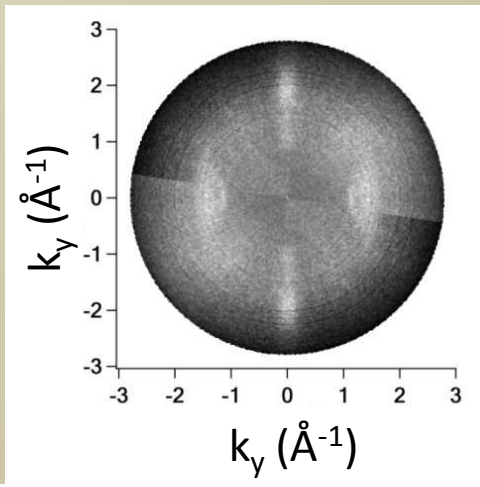
Spectrum:

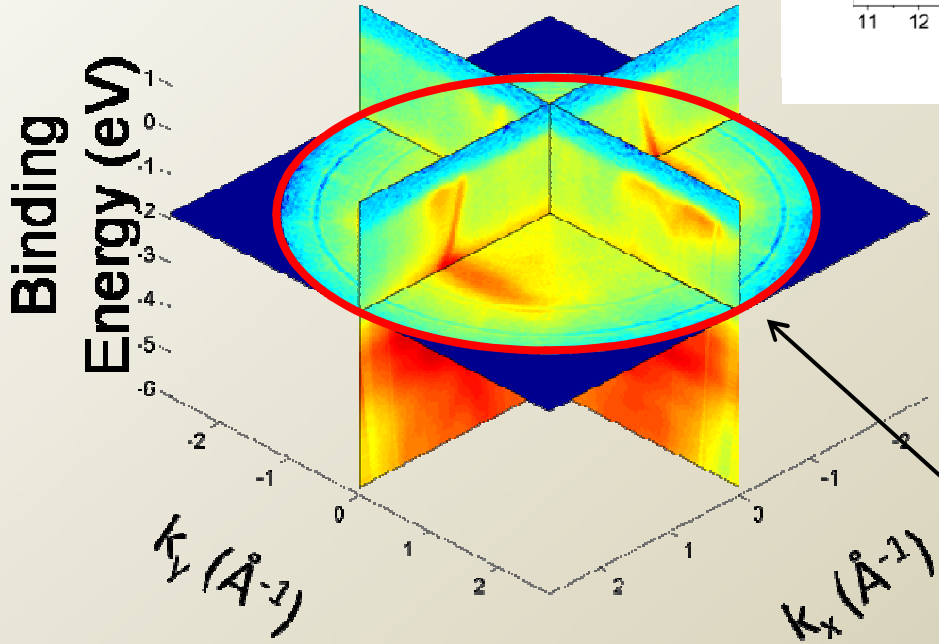


Band map:



Momentum map:





4-dimensional dataset
- **Intensity**
- **Energy**
- **2-dim polar angle / momentum**

III. What does „Doping“ with Cs mean?

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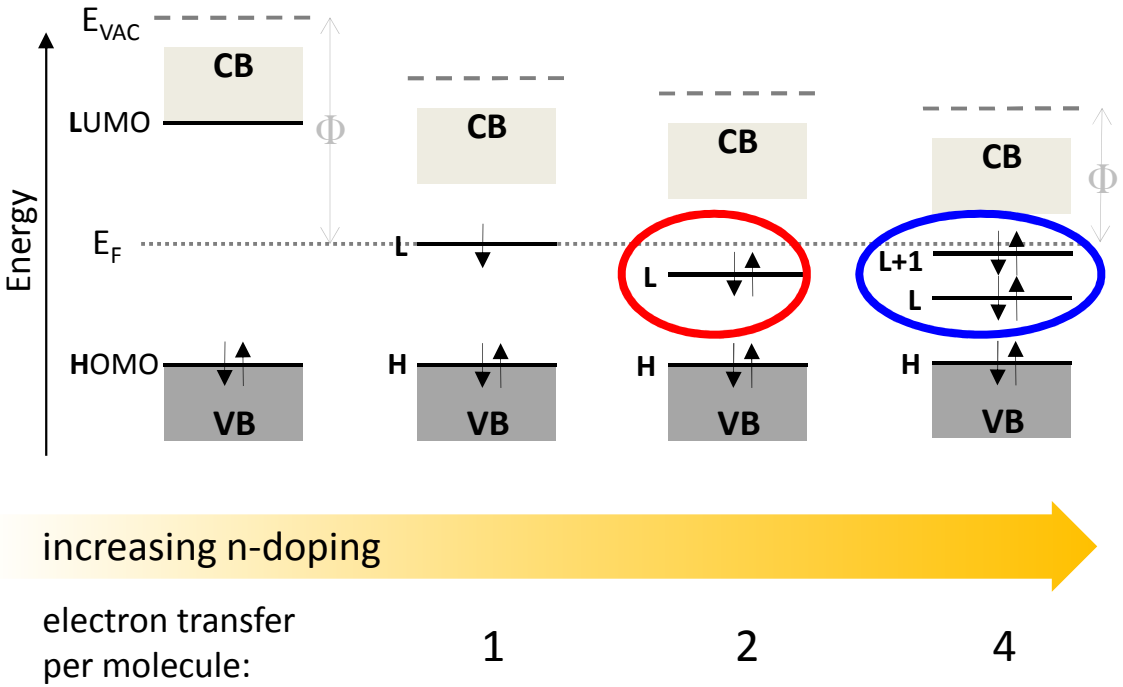
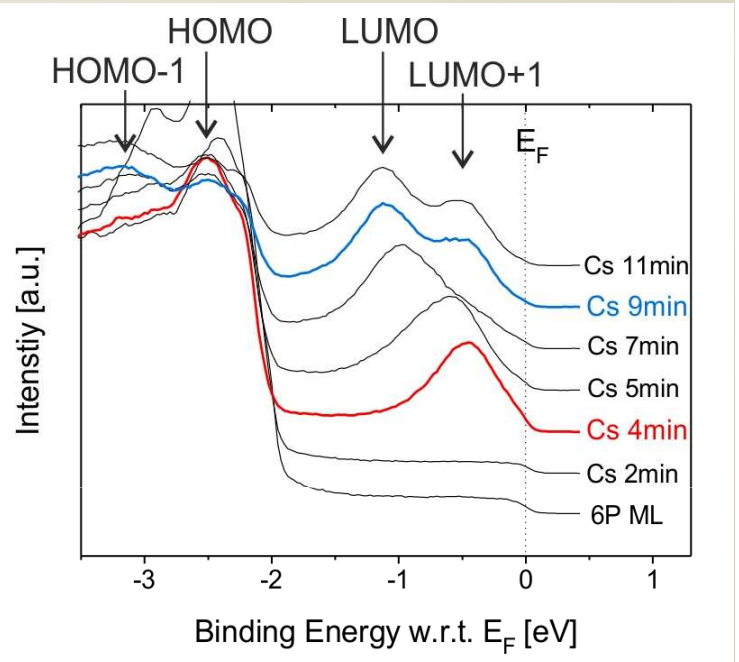
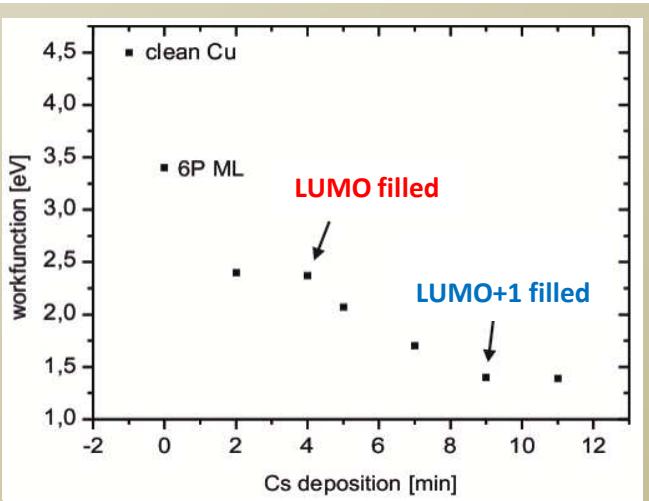
Filling of unoccupied Molecular orbitals:



UPS of doped 6P on Cu(110):



Workfunction Φ lowers with increasing Cs exposure:

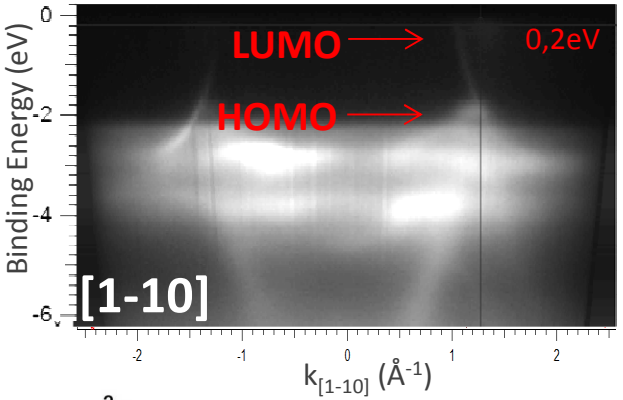


IV. Experiments

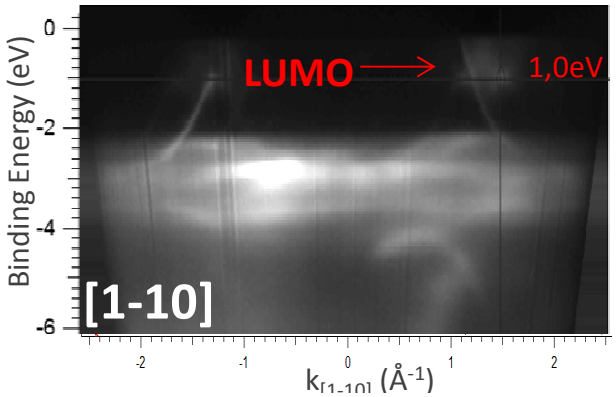
IV. Experiments

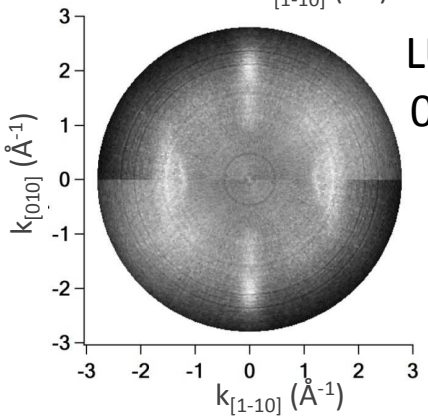
Cu(110)

6P on Cu(110)

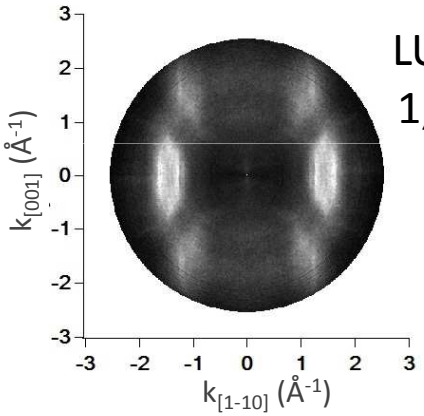


5A on Cu(110)

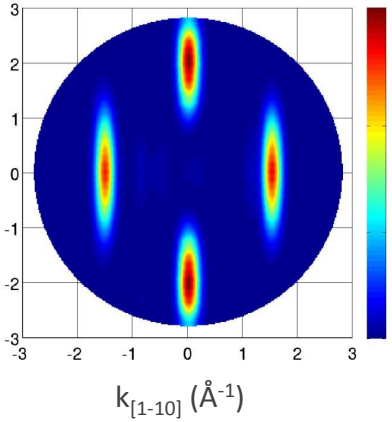




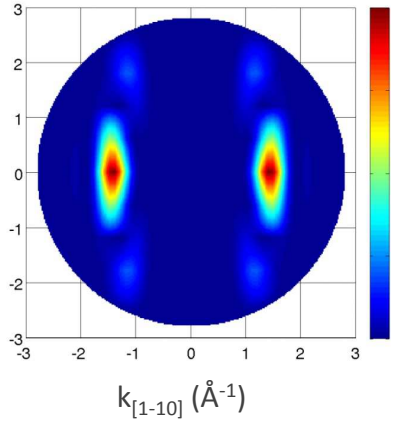
LUMO
0,2eV

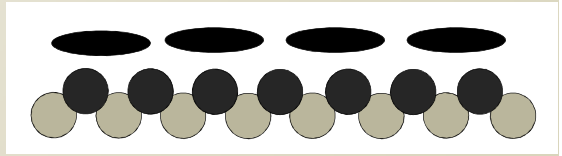


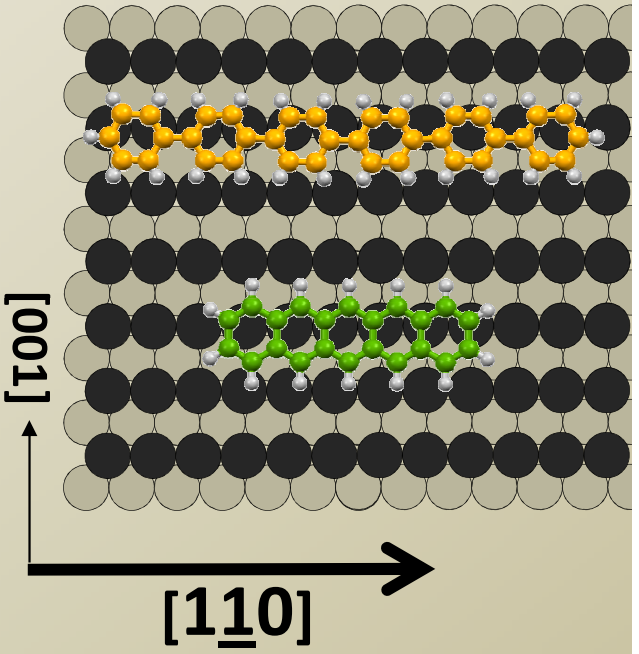
LUMO
1,0eV



DFT
Calculation
of
LUMOs







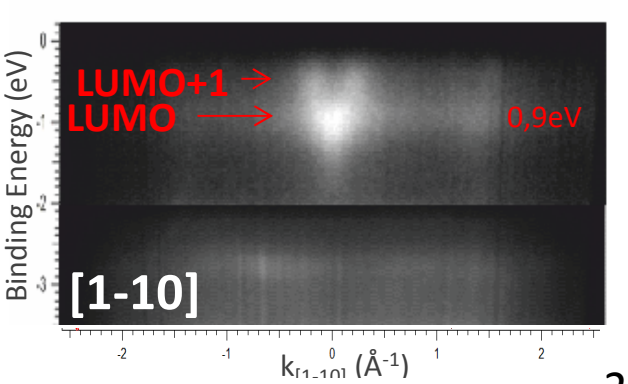
- LUMO hybridised and backdonated
  => strongly bound to the substrate

- k-map features of isolated molecule
  => molecules lie flat on the surface

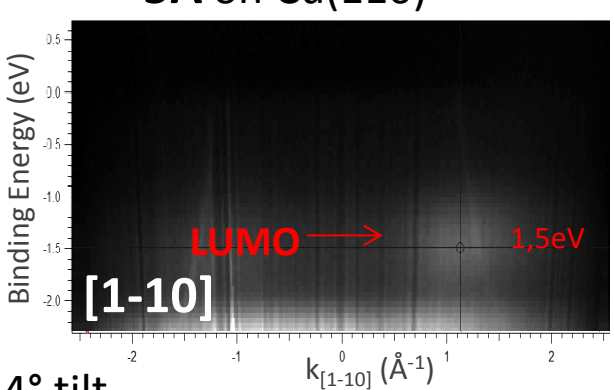
IV. Experiments

Cu(110) + Cesium

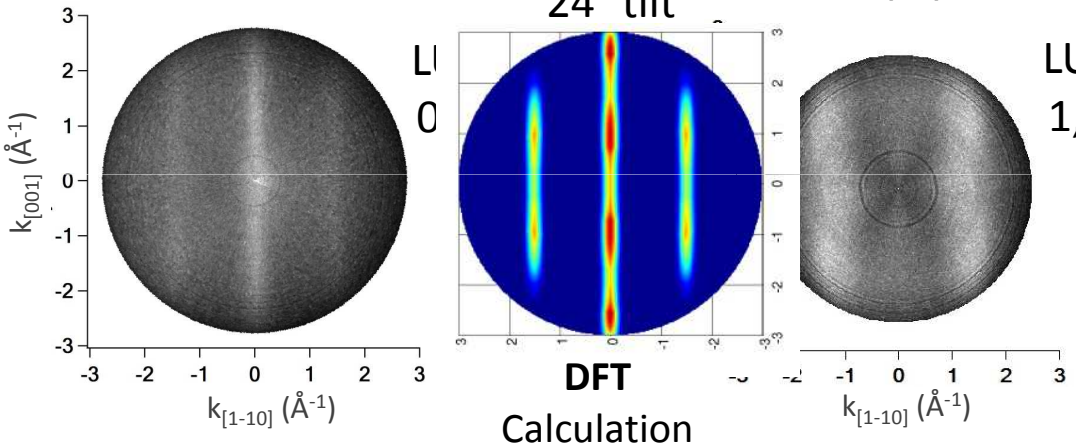
6P on Cu(110)



5A on Cu(110)



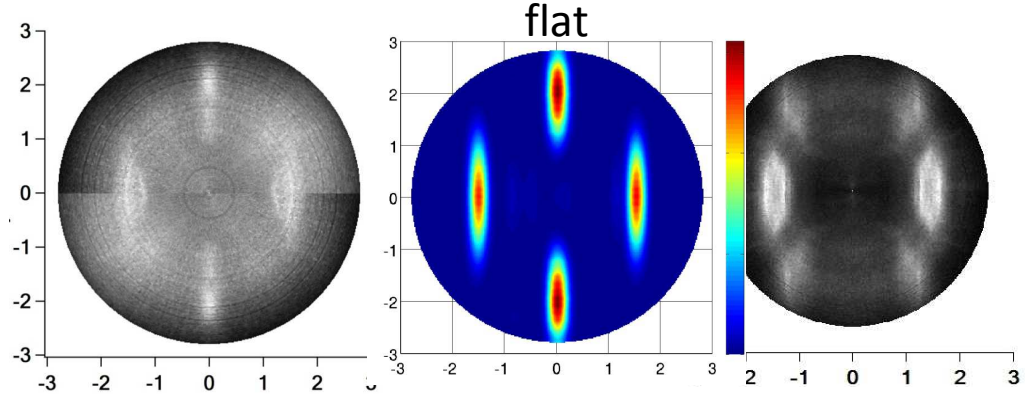
24° tilt

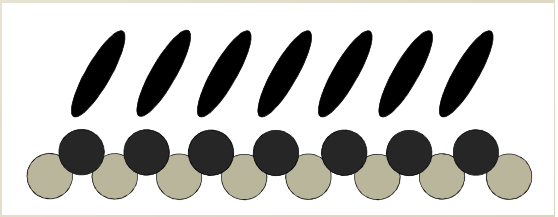


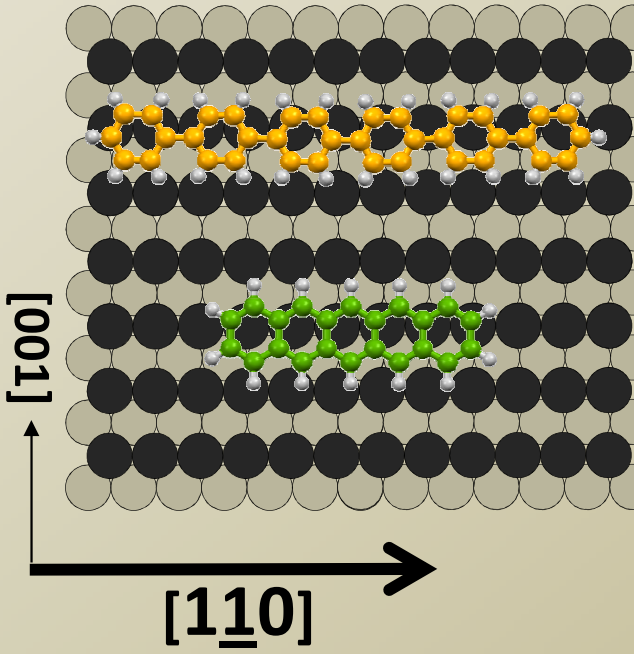
LUMO
1,5eV

DFT
Calculation

flat







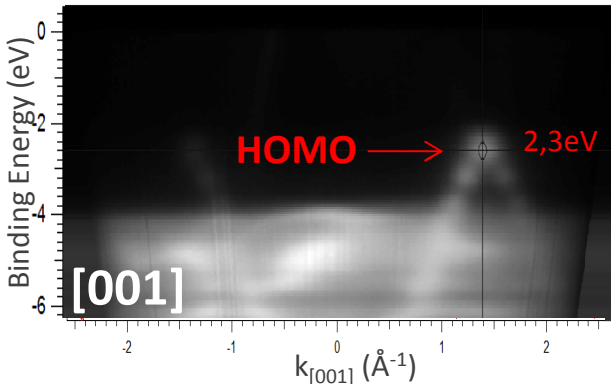
- -orbitals shifted in energy
- -6P LUMO doped from Cs

- -Elongated features in k-map
  => molecules are tilted

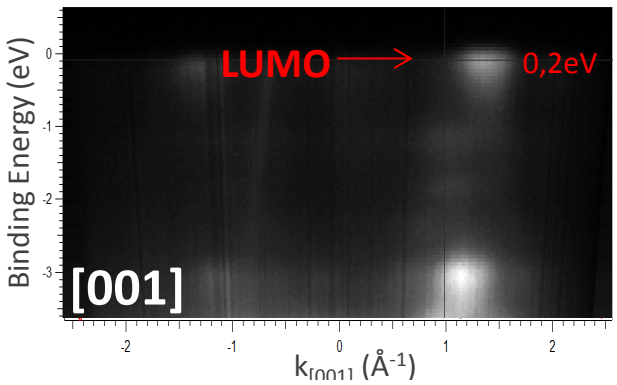
IV. EXPERIMENTS

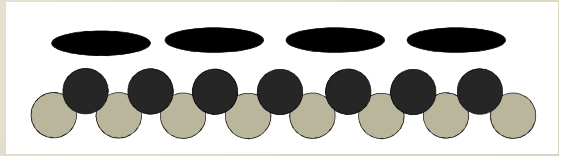
Ag(110)

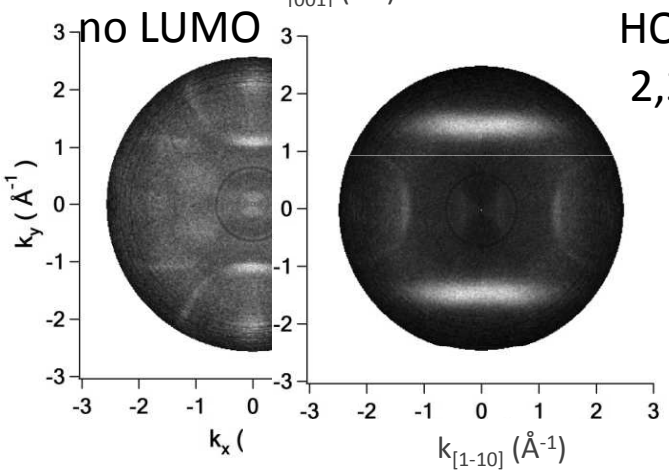
6P on Ag(110)

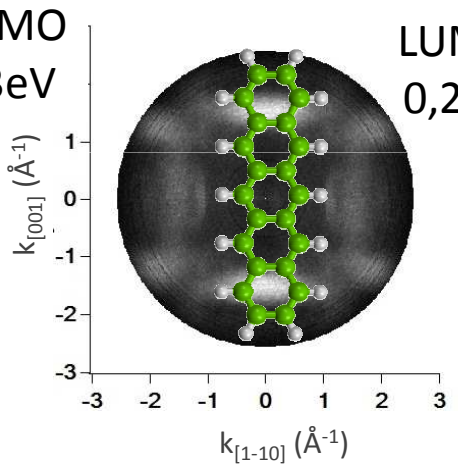


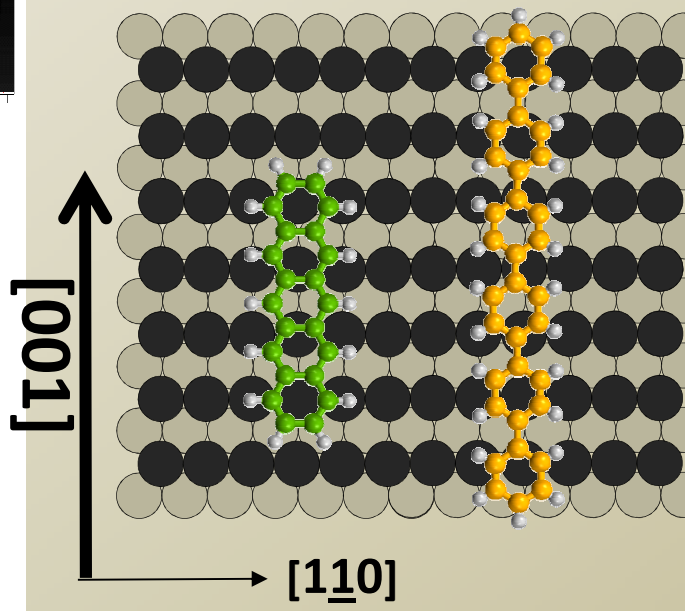
5A on Ag(110)

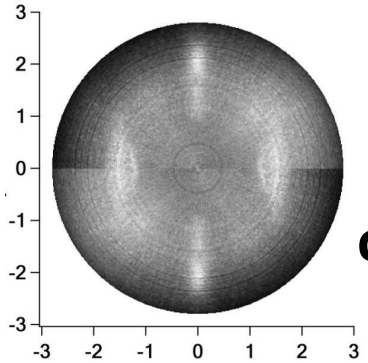




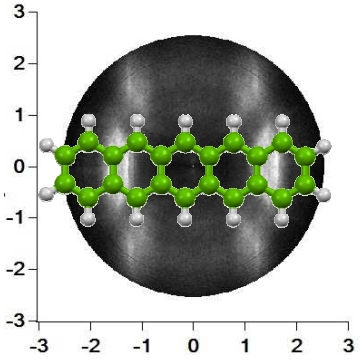








COMPARISON:
undoped
6P and 5A
on Cu(110)



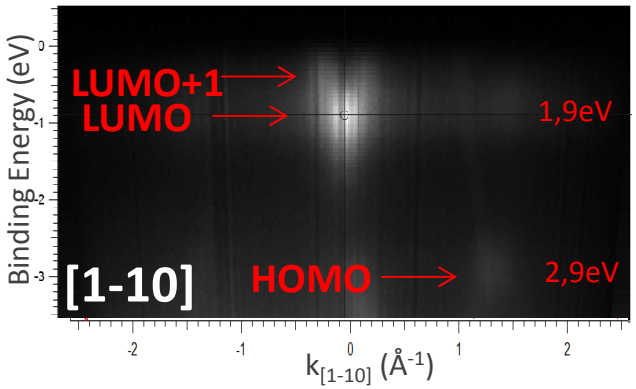
-Different orientation
-6P LUMO not backdonated
=> weaker bound to the Ag substrate

- molecules lie flat on the surface

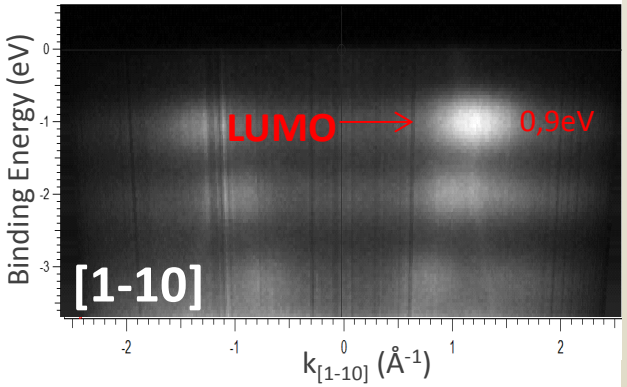
IV. Experiments

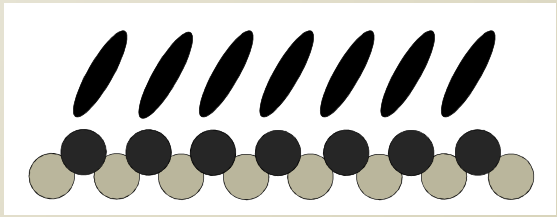
Ag(110) + Cesium

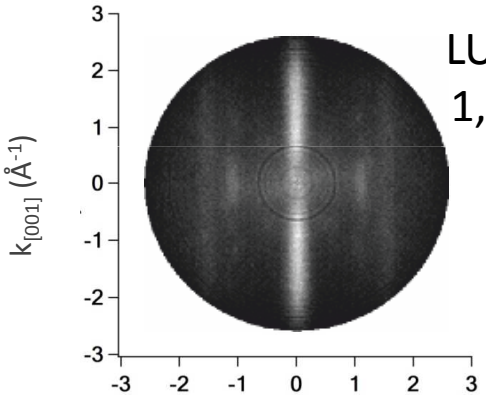
6P on Ag(110)

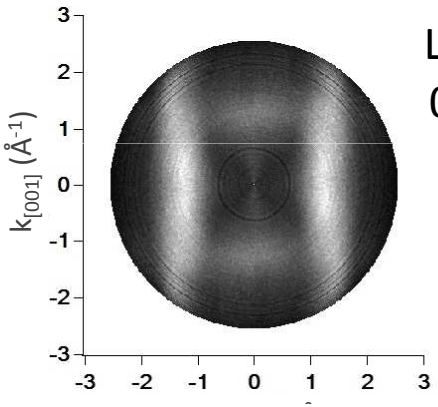


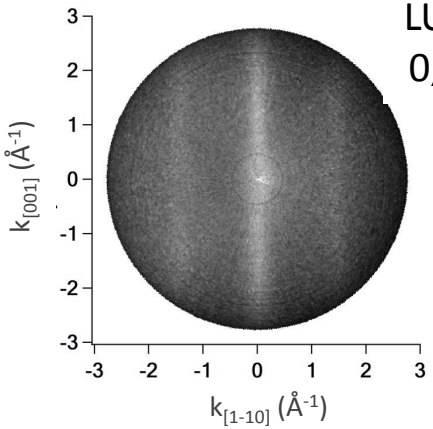
5A on Ag(110)







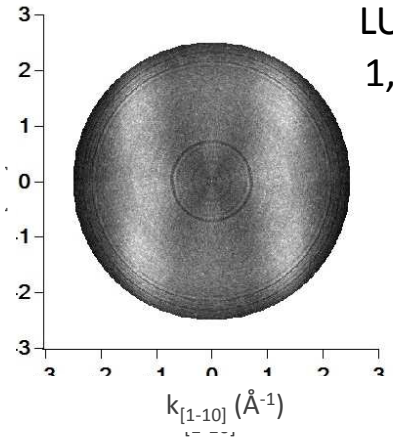


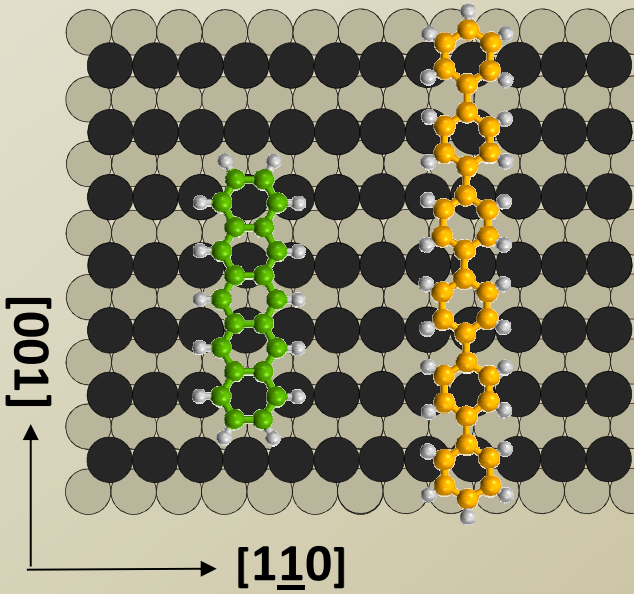


COMPARISON:

doped

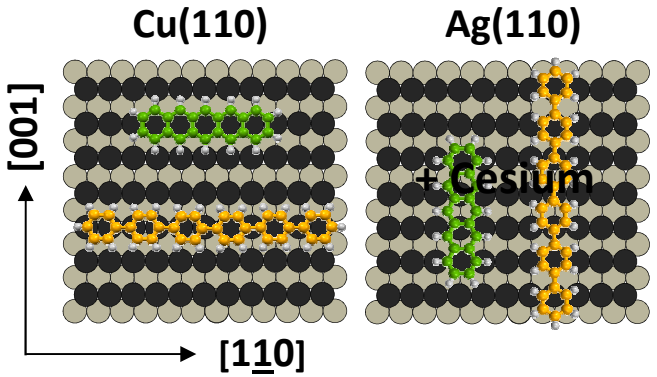
6P and 5A on Cu(110)





- REORIENTATION, layer remains ordered
- tilted molecules
-orbitals shifted in energy
- LUMO doped from Cs

SUMMARY



ARUPS can tell us about …

… how molecules arrange on different substrates:

- 6P and 5A are **flat** and ordered but **differently aligned** on the two investigated substrates:
  stronger interaction with Cu(110) than with Ag(110)

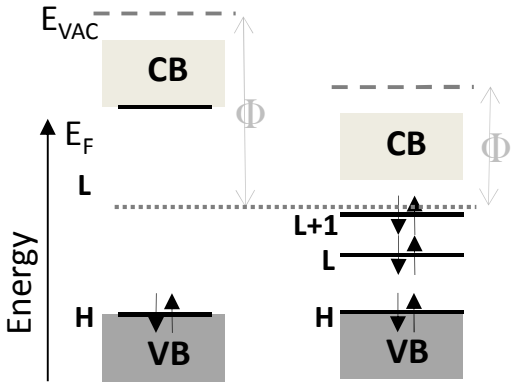
- after Cs deposition both molecules are **tilted** and **ordered along the substrate corrugation**!
  (substrate reconstruction by Cesium?)

=> Cesium influences the geometric structure of molecules (substrate-molecule interaction)

… the changes in the electronic structure of the molecules induced by Cesium deposition:

- 6P features shift in energy (decreasing workfunction)
- 6P molecules become n-doped (LUMO and LUMO+1 occupied)

- 5A features shift in energy
- no filling of unoccupied orbitals observed (LUMO backdonated)



=> Cesium can modify the optoelectronic properties by shifting/filling the band gap states

Thank you for your attention!!

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