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

E. Reinisch[1], G. Koller[1], P. Puschnig[1], T. Ules[1], M. Ostler[2], T. Seyller[2], M.G. Ramsey[1]

[1]Institute of Physics, Karl-Franzens-University Graz, AUSTRIA
[2]Technische Physik, University Erlangen Nürnberg, GERMANY

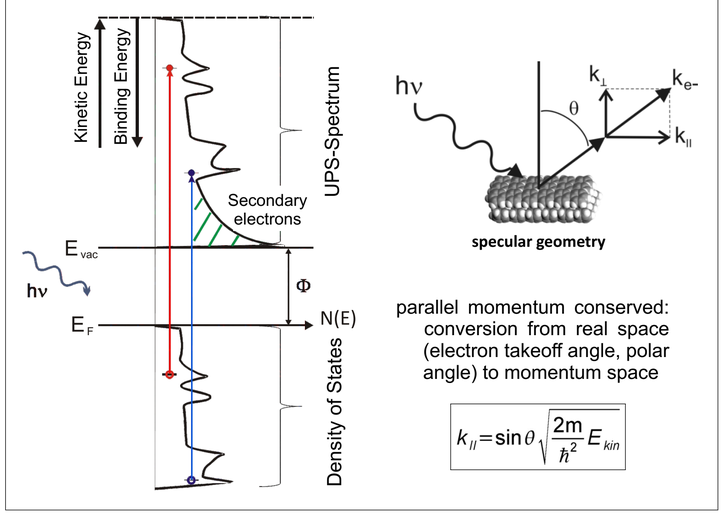
eva.reinisch@uni-graz.at
http://surface-science.uni-graz.at

FWF Der Wissenschaftsfonds.
FWF Project: „Electronic structure of doped epitaxial organic films"
Grant: P21330 – N20

method

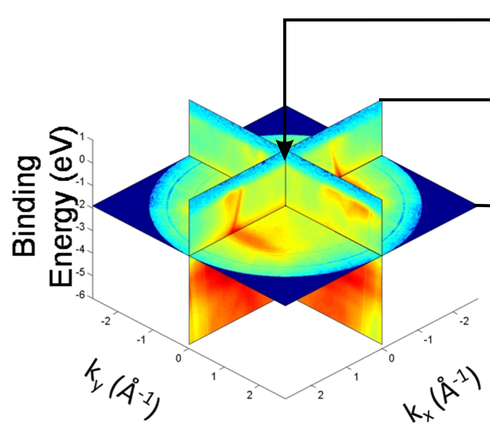
Angle Resolved UV Photoemission Spectroscopy

UV Photoemission Spectroscopy:



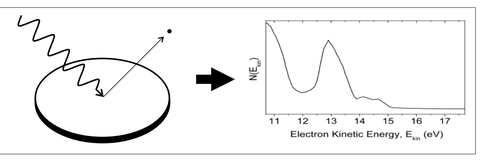
parallel momentum conserved: conversion from real space (electron takeoff angle, polar angle) to momentum space

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

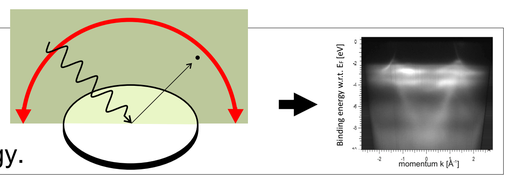


ARUPS provides a 4 dimensional dataset: Intensity, Energy, azimuthal angle, electron takeoff angle (polar angle)

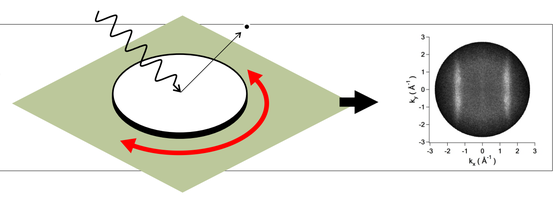
single SPECTRUM:
At fixed azimuthal angle we probe the kinetic energies of photoelectrons emitted at one defined polar angle.



BAND MAP:
In a fixed azimuthal orientation the photoelectrons from all takeoff angles in specular geometry are analysed after their energy.

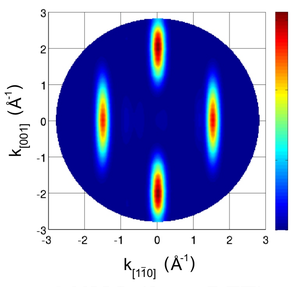


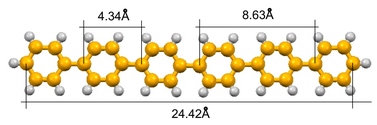
MOMENTUM MAP:
At a fixed energy we detect „specular" photoelectrons at varying azimuthal angles by rotating the sample.



results

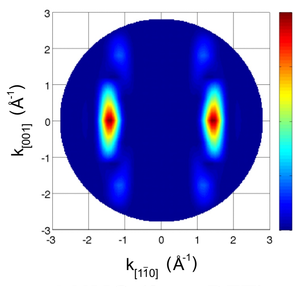
Sexiphenyl (6P)

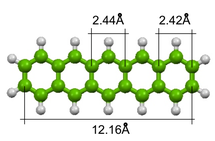




LUMO (from DFT)

Pentacene (5A)





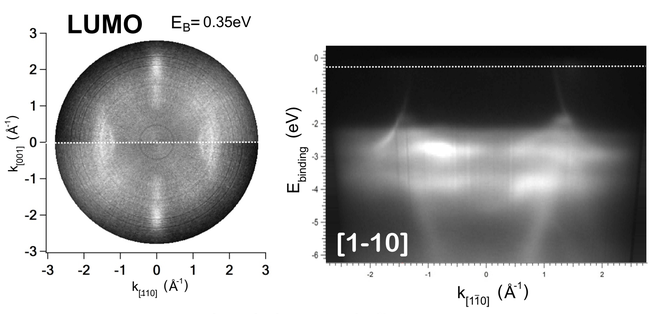
LUMO (from DFT)

discussion

Probing the momentum space structure with ARUPS requires highly ordered molecular films. In the presented experiments we use rodlike Sexiphenyl and Pentacene molecules which tend to align along or normal to the atomic rows on substrate surfaces with two-fold symmetry.
Thus ARUPS is an appropriate technique to analyse the modifications in energy and momentum space of the orbital configurations due to doping.
Although the investigated uniaxially oriented monolayers change their tilt angle on both Cu and Ag and their azimuthal orientation on Ag upon Cesium-doping, they remain ordered.

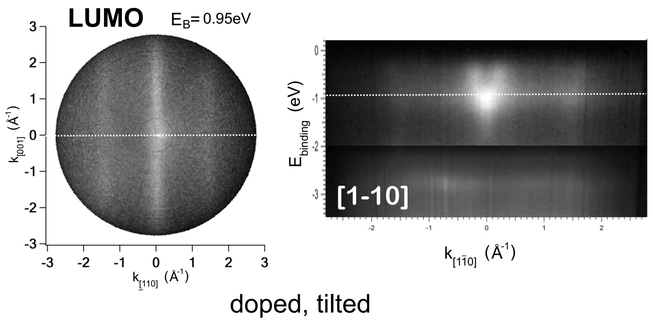
6P on Cu(110)

without Cs



backdonated, flat

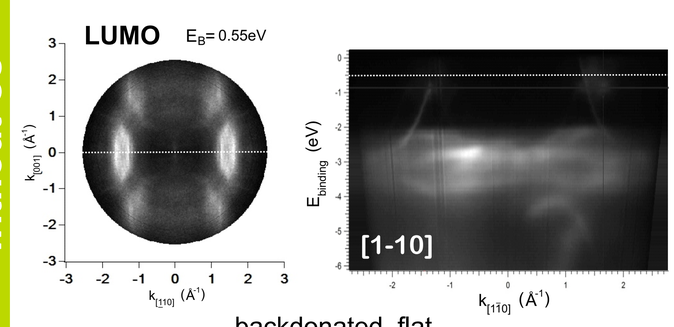
Cs doped



doped, tilted

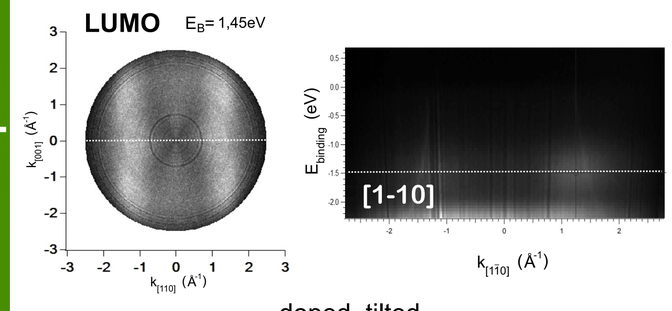
5A on Cu(110)

without Cs

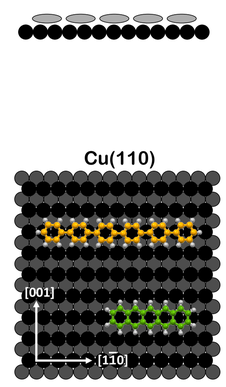


backdonated, flat

Cs doped



doped, tilted



On the pure **Cu(110)** substrate in both 6P and 5A monolayers the molecules align parallel to the Cu corrugation in [1-10] direction before and after Cs deposition.

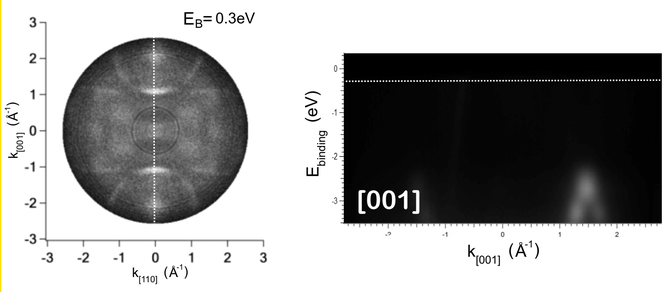
We observe flat lying molecules with the LUMO being filled by hybridisation and backdonation from the substrate.

Upon increasing Cs deposition the 6P molecules first are decoupled and tilted, followed by the filling of the LUMO and (LUMO+1 of 6P) by charge transfer from the alkali metal.

Also the 5A molecules are tilted after Cs deposition, the LUMO is occupied.

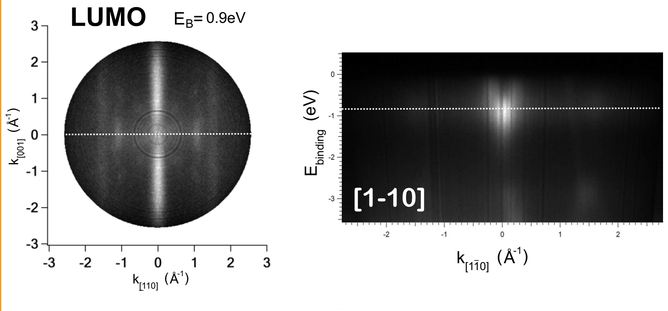
6P on Ag(110)

without Cs



undoped, flat

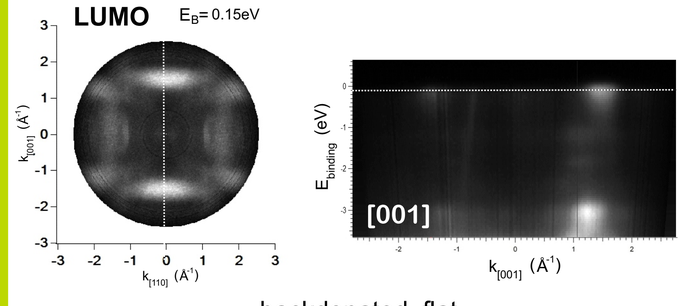
Cs doped



doped, tilted

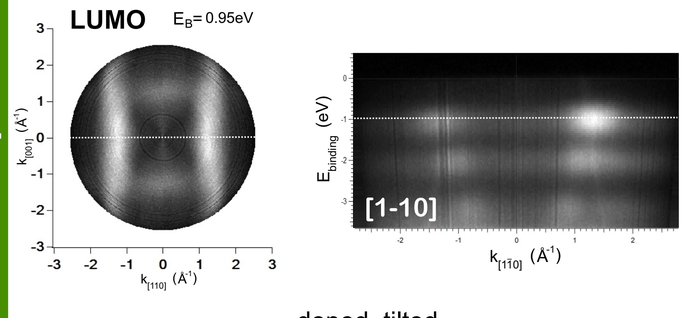
5A on Ag(110)

without Cs

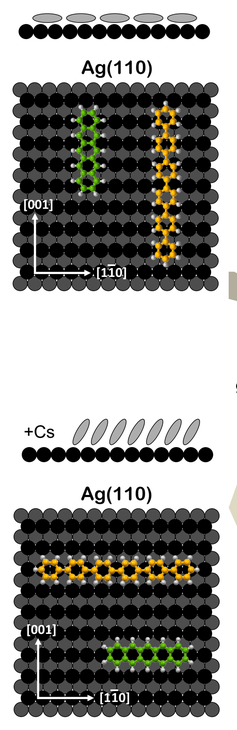


backdonated, flat

Cs doped



doped, tilted



On pure **Ag(110)** both 6P and 5A molecules lie flat in [001] direction, perpendicular to the substrate corrugation.

The LUMO of 5A on Ag(110) is filled but has a slightly different k-space distribution than on Cu(110).
In the momentum map of the undoped 6P monolayer on Ag(110) we see suppressed substrate features but no emissions from the 6P LUMO.

Prior to charge transfer from Cs to the organics the Cs exposure azimuthally reorients the molecules from perpendicular to parallel to the atomic rows of the substrate in [1-10] direction. Both molecules are tilted after reorientation.

Increasing Cs amounts cause a filling of the 6P LUMO and LUMO+1 by charge transfer, similar to 6P on Cu(110).