Bonding, Structure und Function of Molecular Adsorbate Layers at Solid Surfaces

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International University Bremen

Regensburg, 13.10. 2006

Organic Electronics

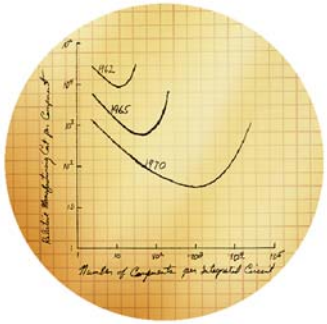
Electronics on the basis of organic adsorbate layers

Key technology for future electronics

New application areas

Fraunhofer Institut Dresden and UDC

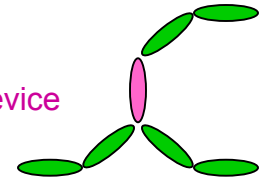
Miniaturisation



Moores Law 1965

Molecular Electronics

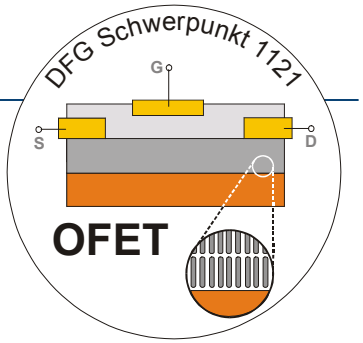
- complete devices constructed from the tool box of chemistry
- networks of these devices created by self assembly.



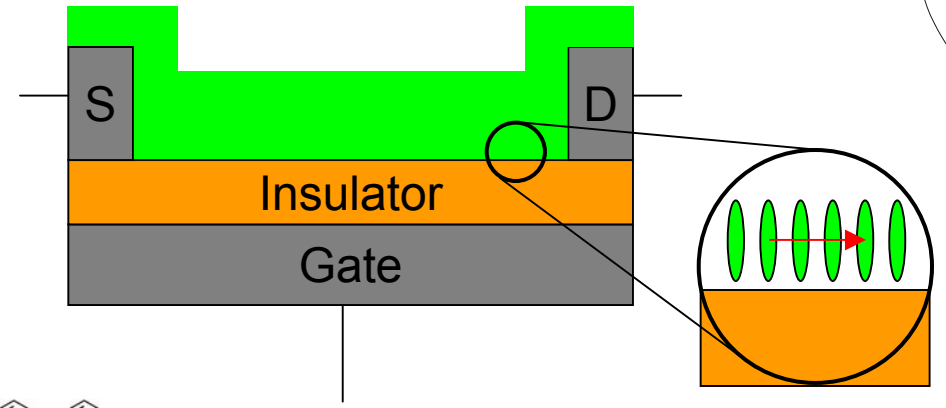
molecular device

molecular wire

Organic Field Effect Transistor

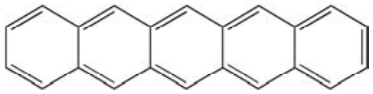


Organic Field Effect Transistor

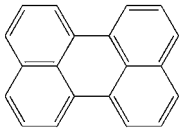


direction of transport

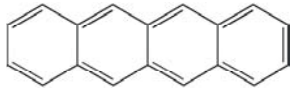
Molecules:



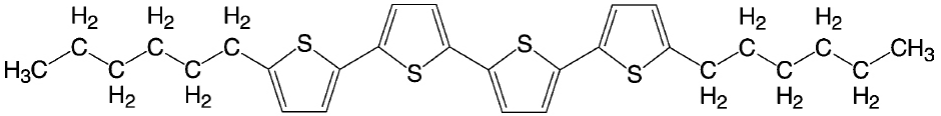
Pentacene



Perylene



Tetracene



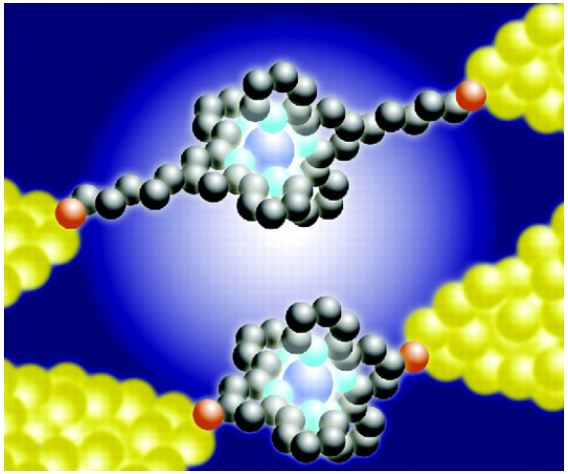
DH4T

Functionality: π-electron system
(luminescence, transport, bonding)

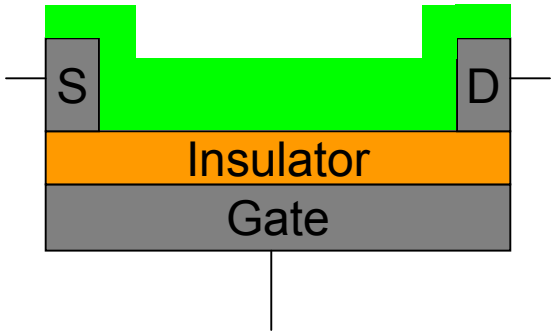
Interfaces in OFETs are responsible for functionality:

- charge carrier injection at the contacts
- film growth starts at surface of insuator
- charge carrier transport at the interface organic layer / insulator (traps for electrons and holes)

The Problem of Contacts in Molecular Electronics



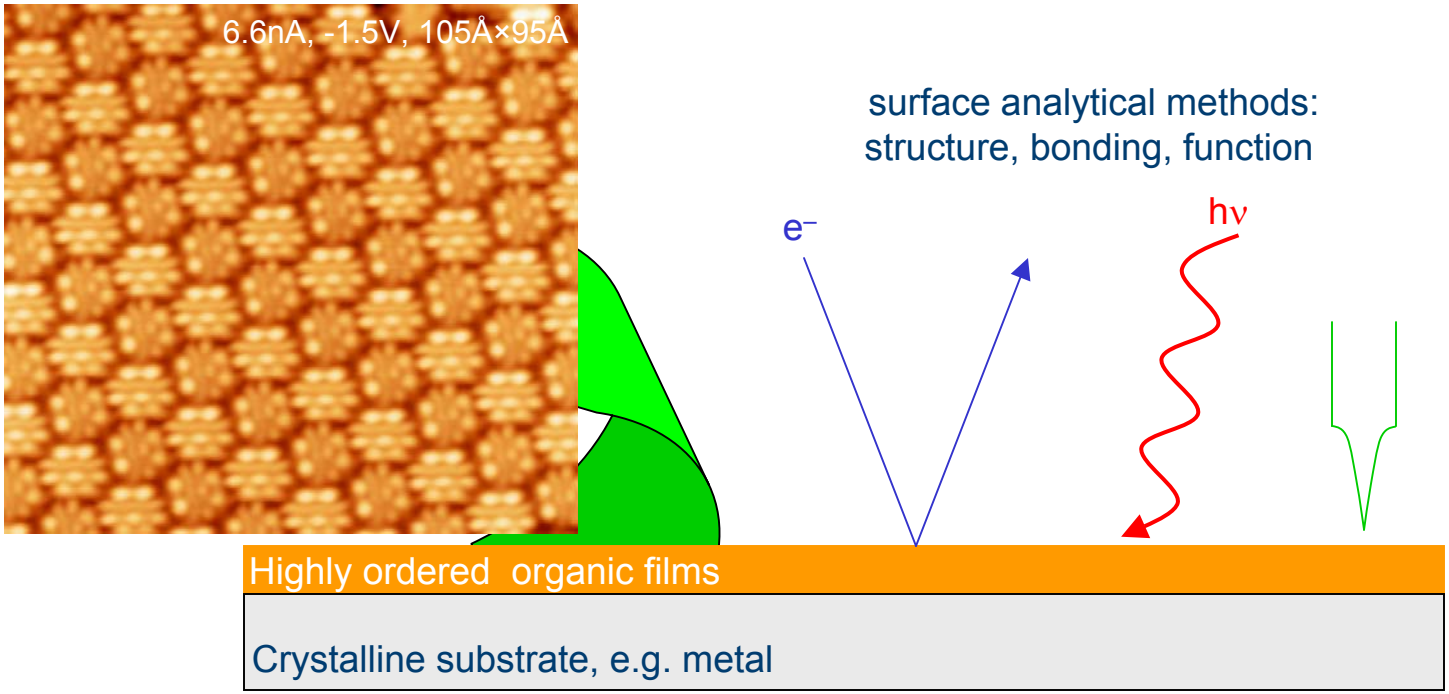
„In such junctions, the **connection** between the **molecule** and the **electrode** greatly affects the current-voltage characteristics.“
A. Nitzan & M. A. Ratner, Science 300, 1384 (2003)



„A major unsolved problem ... is that there are currently **no robust methods** to image and determine the **precise adsorption site** and **conformation** of the molecule on this length scale..... At the current stage of experimental uncertainty, one expects to see **fluctuations** from measurement to measurement or even within the same test system over time. “
C. Joachim & M. A. Ratner, PNAS 102, 8800 (2005)

Strategy and Work Programme

Strategy: Use highly ordered interfaces between relevant materials



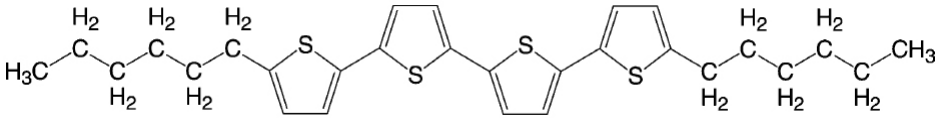
Work programme:
Under which conditions do highly ordered layers form?
Compehensive characterisation of highly ordered layers (with their functions in mind)

Combination of interface physics and chemistry with organic / molecular electronics

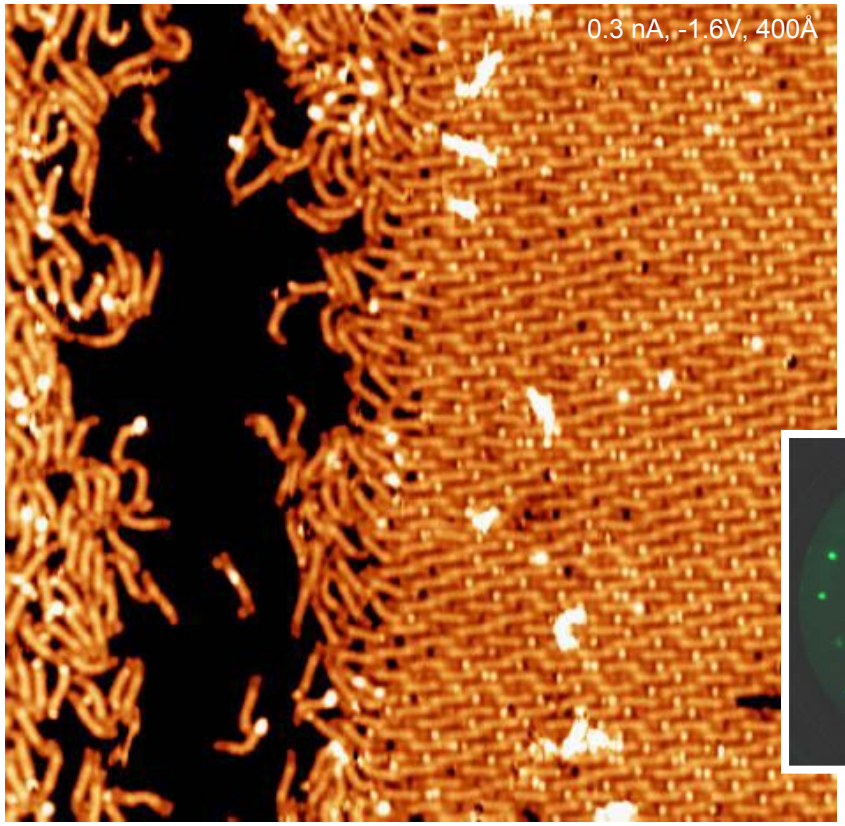
Experimental Methods

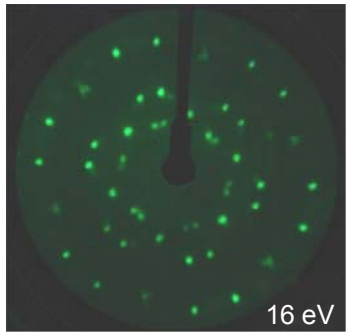
STM / STS:	**Scanning tunnelling microscopy / spectroscopy**
XPS/UPS:	Photoelectronen spectroscopy
NEXAFS:	X-ray absorption spectroscopy
NIXSW:	**X-ray standing waves**
HREELS / EELS:	**Electron energy loss spectroscopy**
LEED:	Low energy electron diffraction
PL:	Photoluminescence spectroscopy
Raman:	Raman spectroscopy

STM

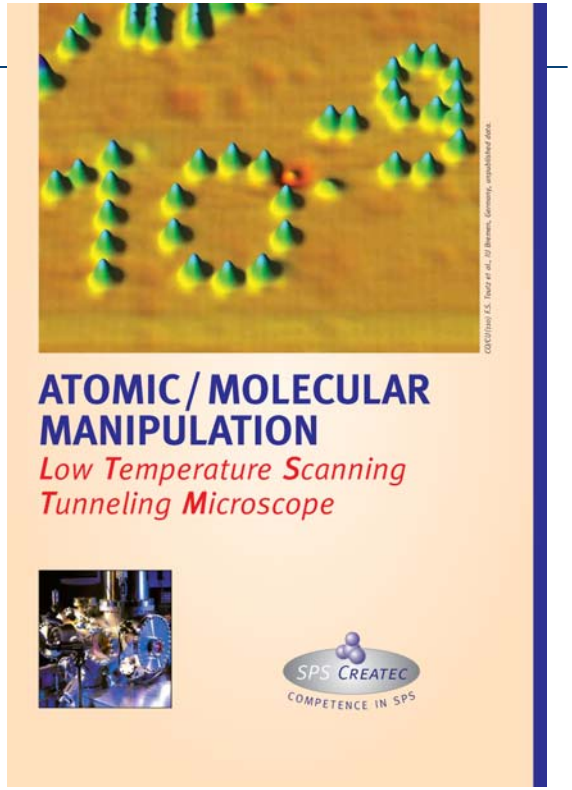


DH4T – Dihexyl-Quaterthiophene / Ag(111)





Soubatch, Temirov, FST, Langmuir in press (2006)



STM

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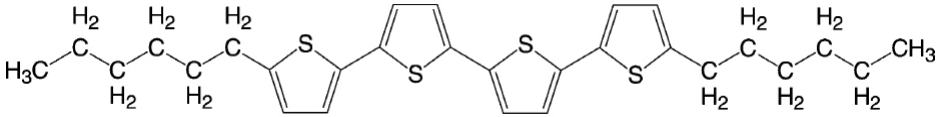

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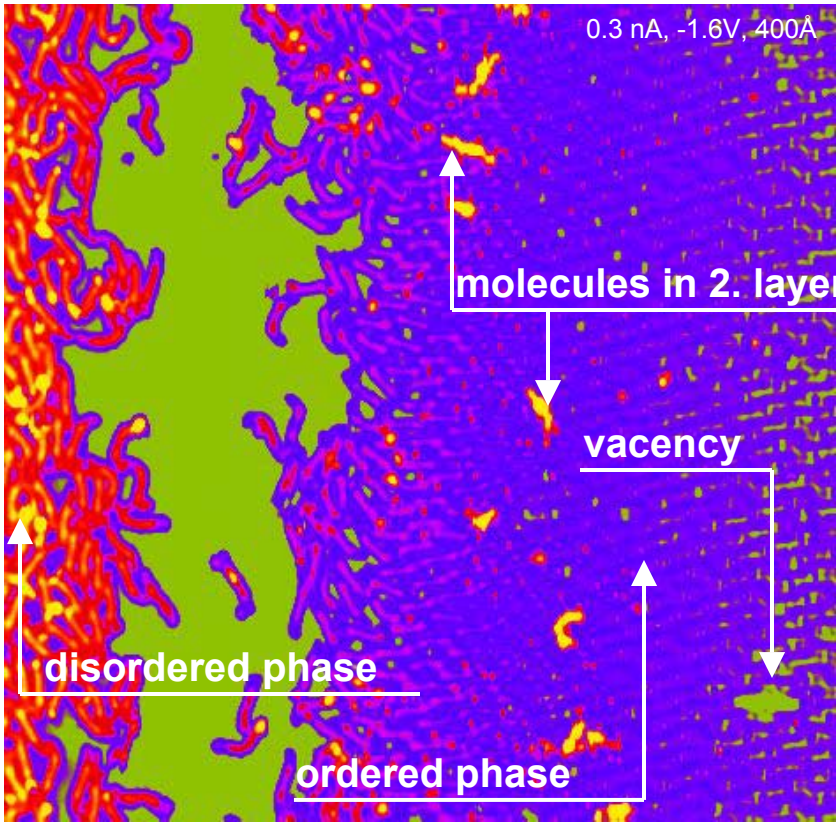
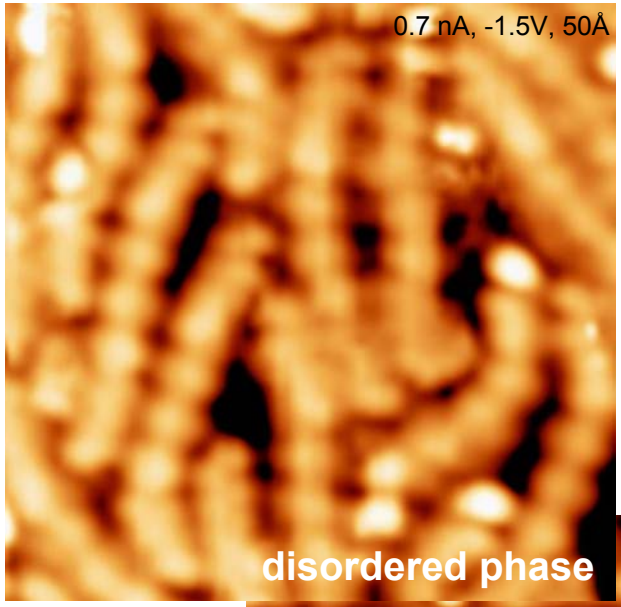
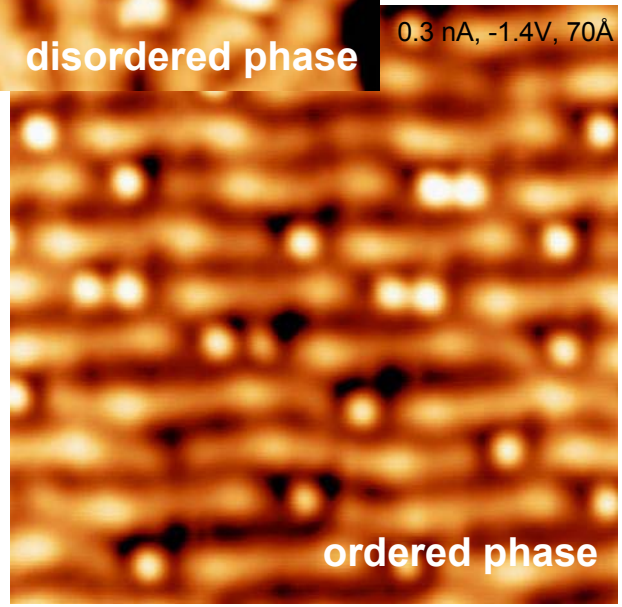
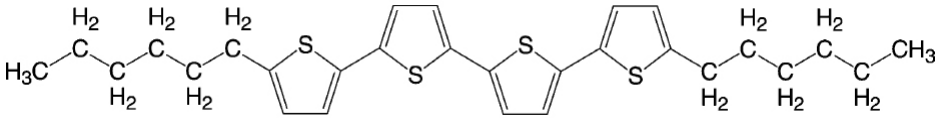






STM



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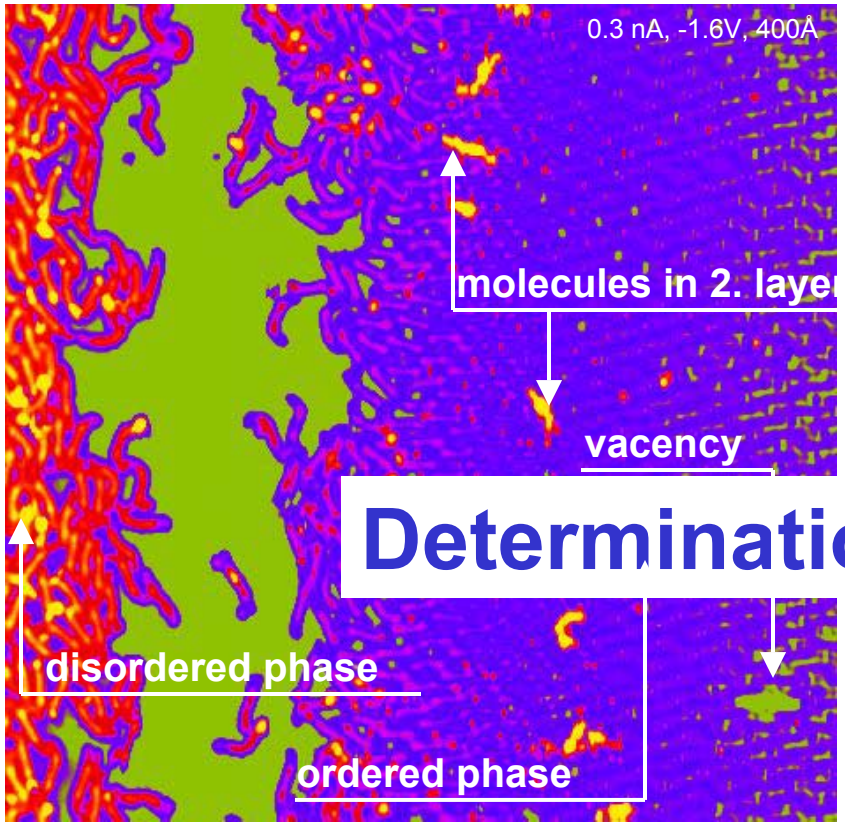
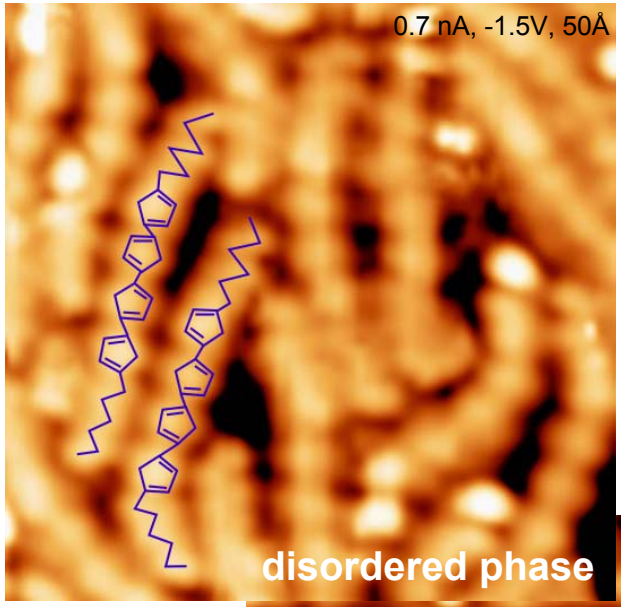
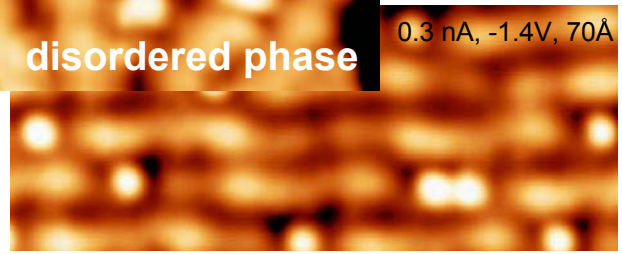
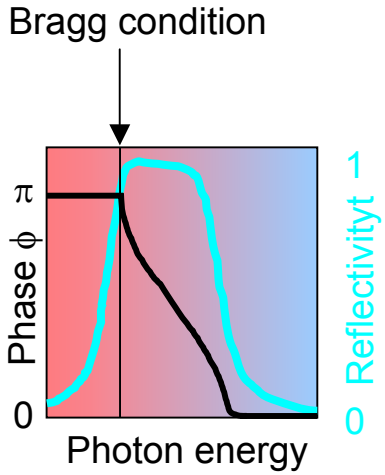


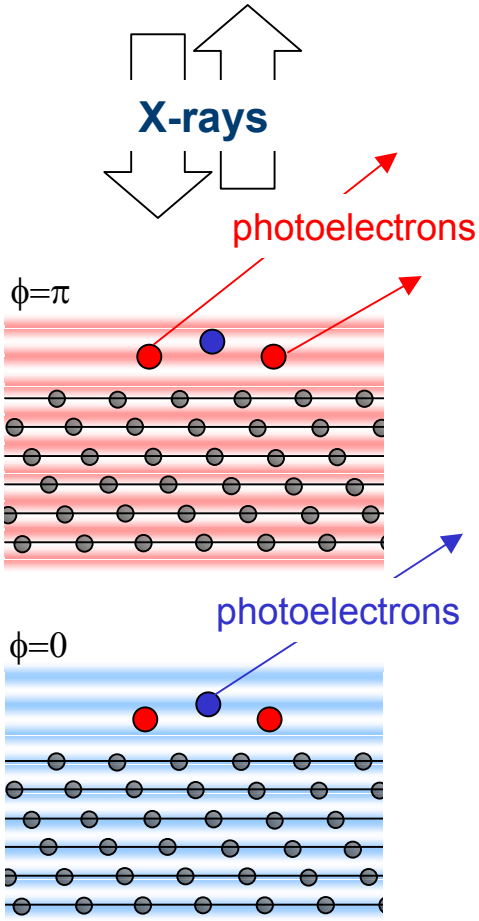




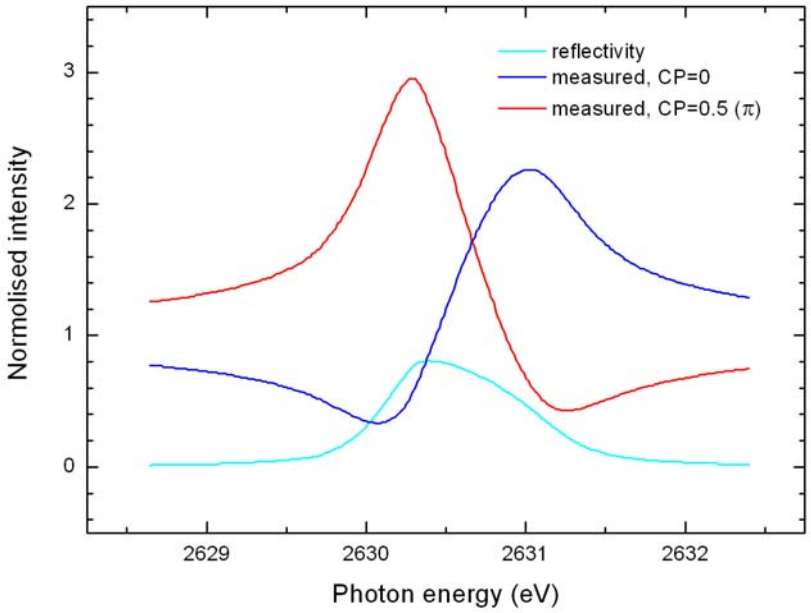
Determination of lateral structures

X-Ray Standing Waves (NIXSW)





NIXSW photoelectron yield



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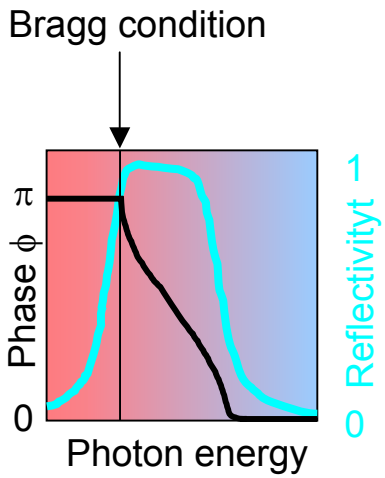
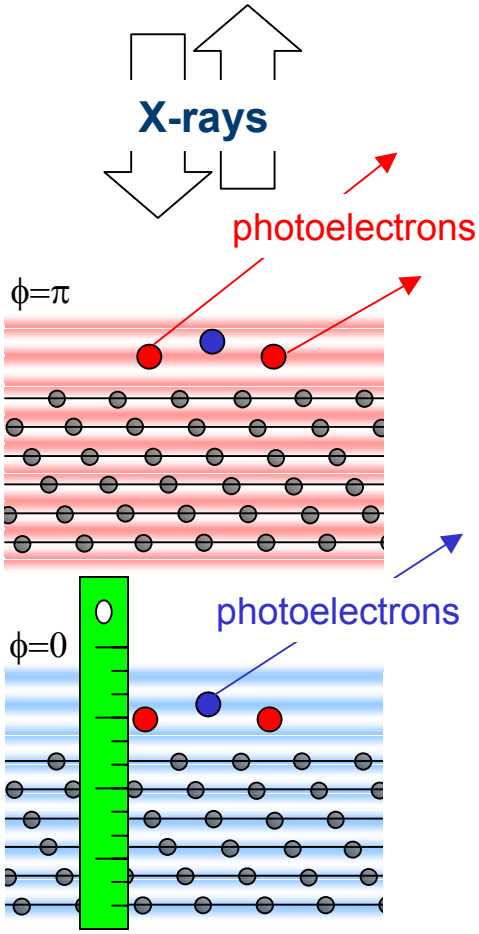
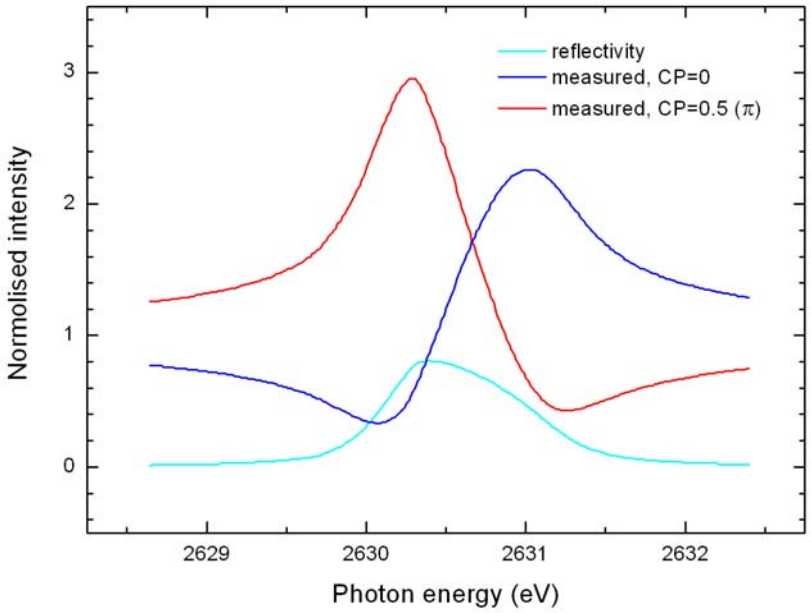


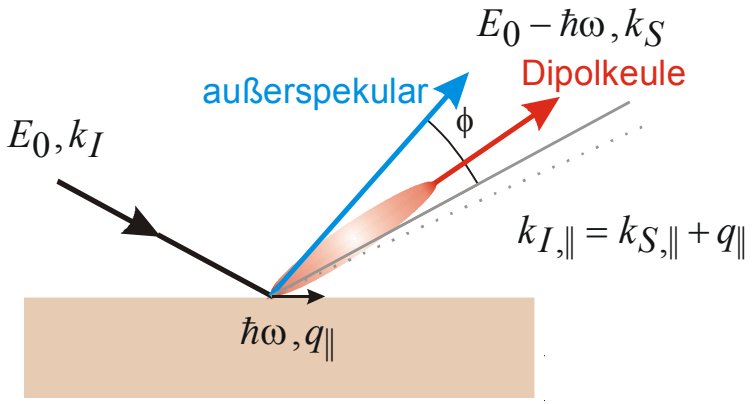


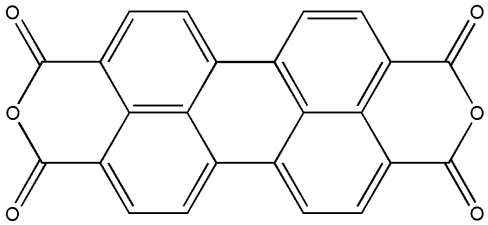
NIXSW photoelectron yield



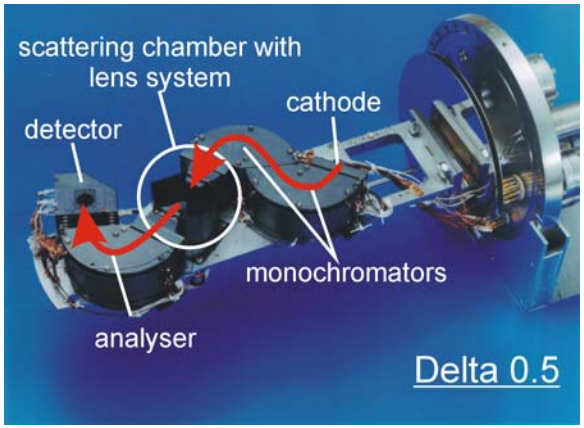
Atomic scale ruler (~0.05 Å)

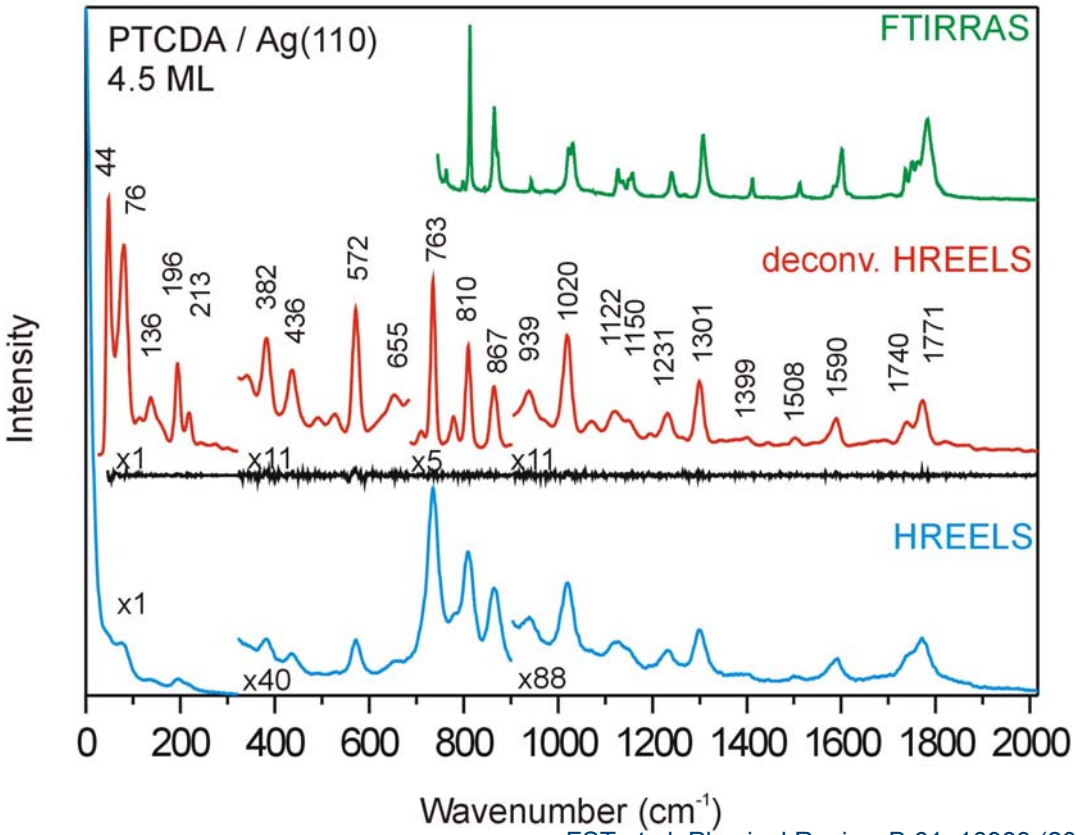
Inelastic Electron Scattering (HREELS)





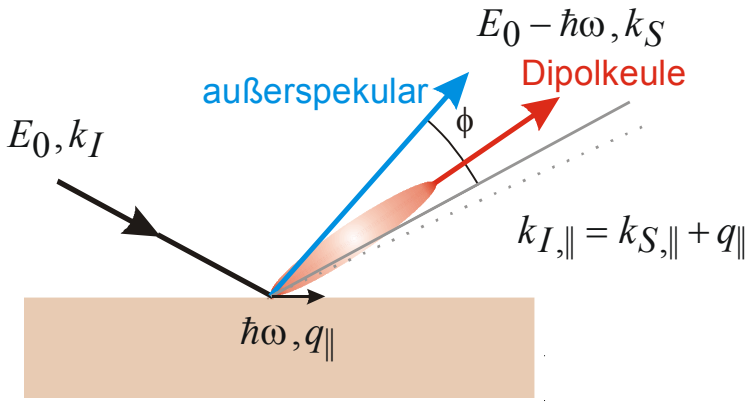
3,4,9,10 - Perylene - Tetracarboxylic Dianhydride

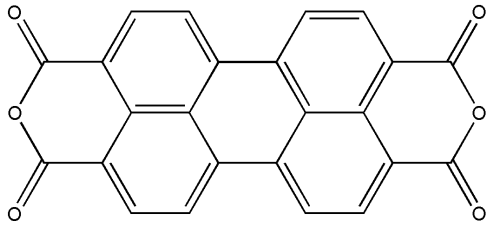




FST et al. Physical Review B 61, 16933 (2000)

Inelastic Electron Scattering (HREELS)





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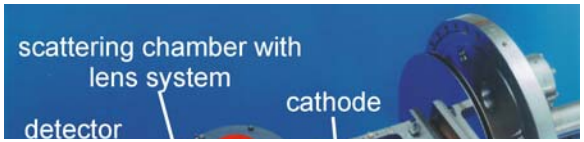
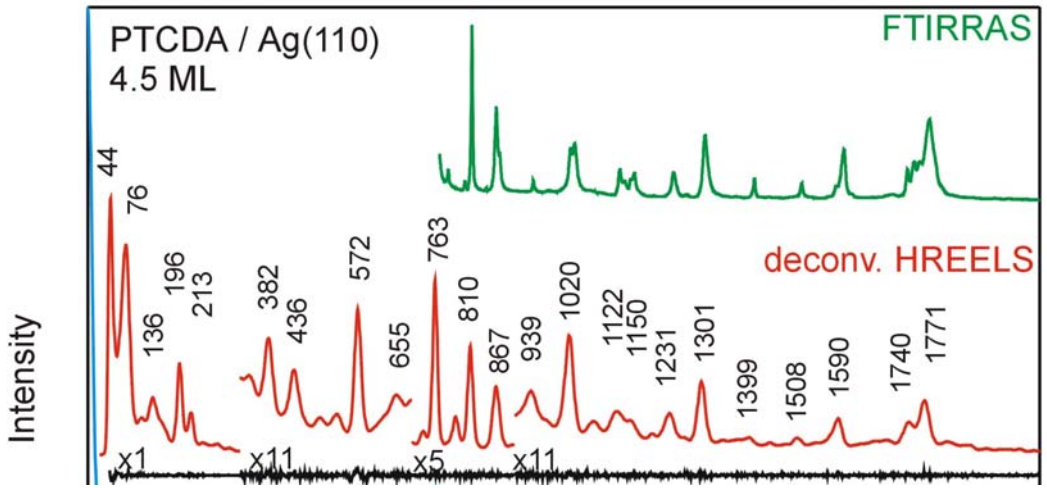
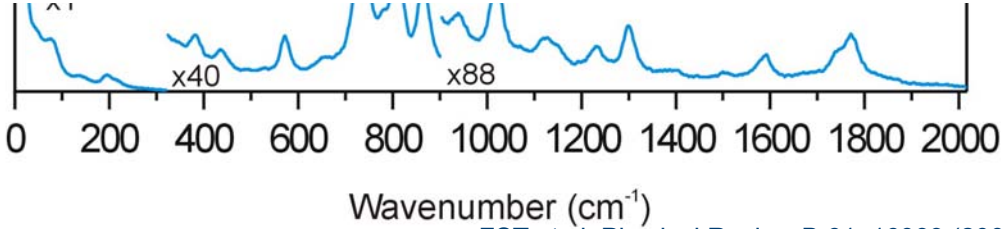




Probes of the molecule substrate interaction



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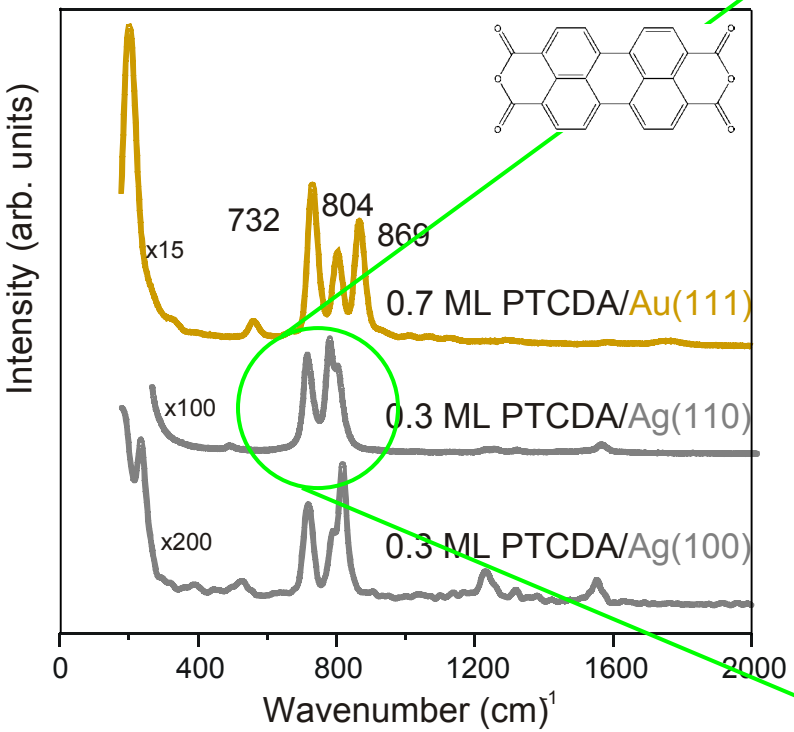
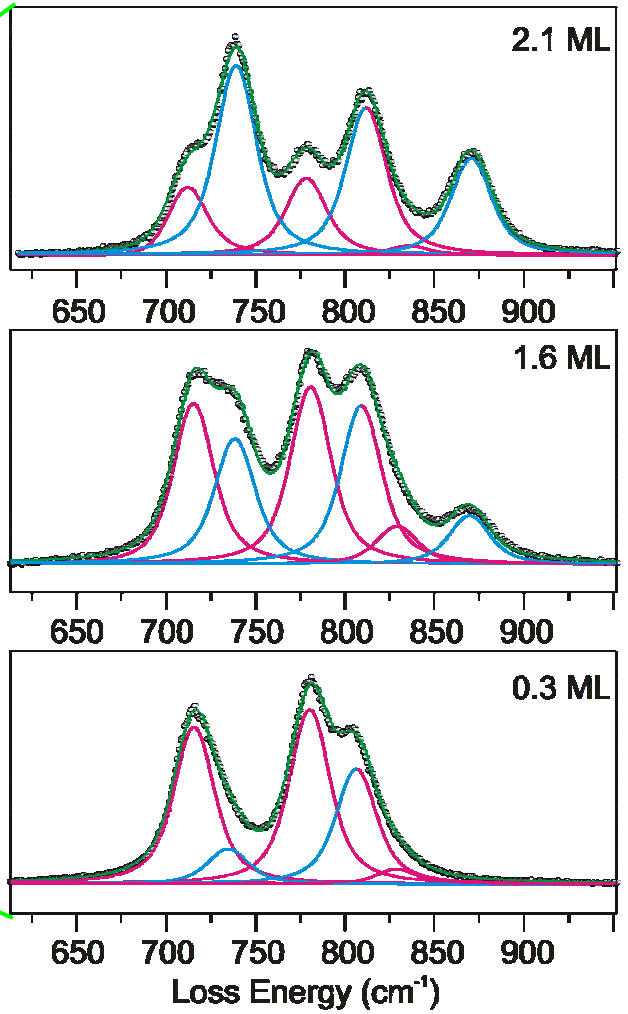
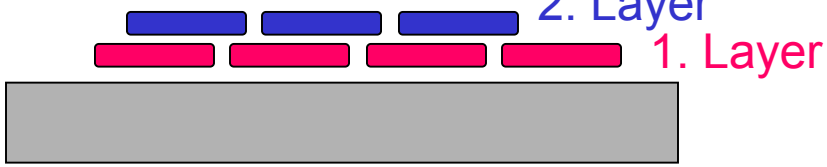
Inelastic Electron Scattering (HREELS)

molecule-substrat interaction

example: PTCDA/Ag







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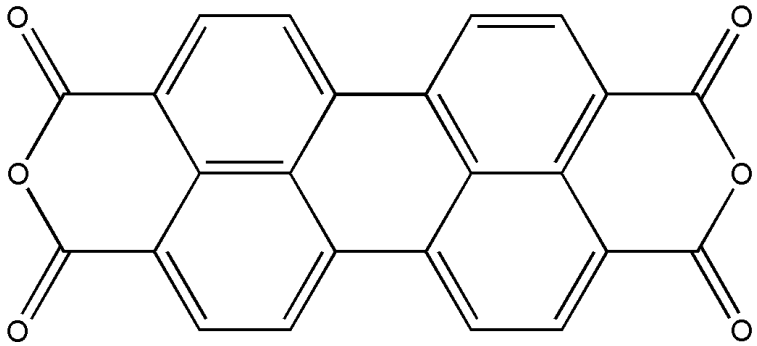
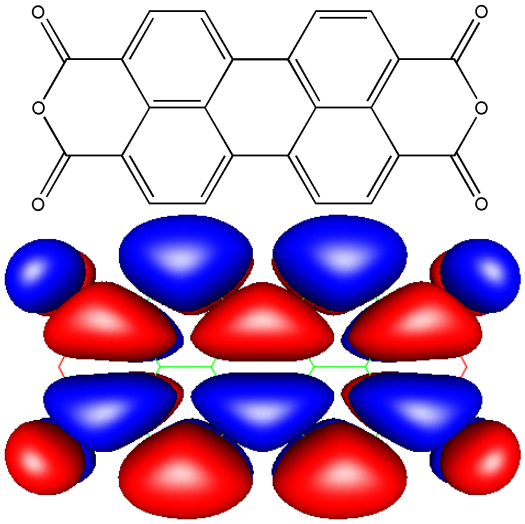
Substrate Bonding of Organic Molecules

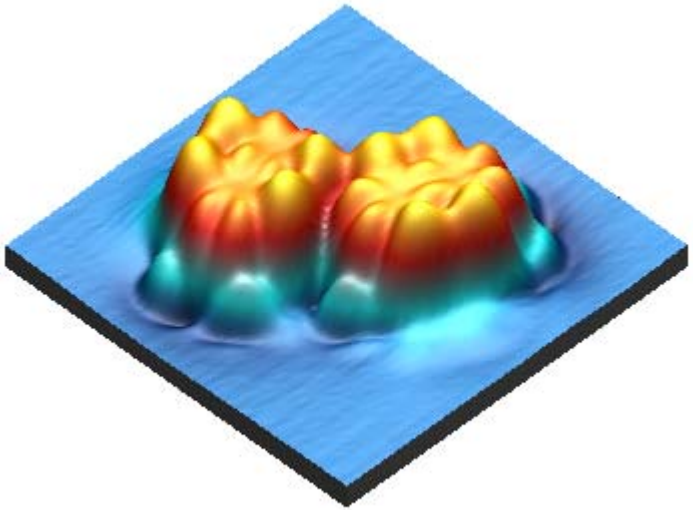


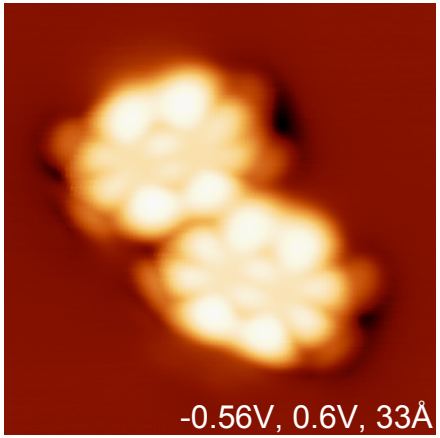
Chemisorption PTCDA / Ag(111)

PTCDA/Ag(111) Interface Structure

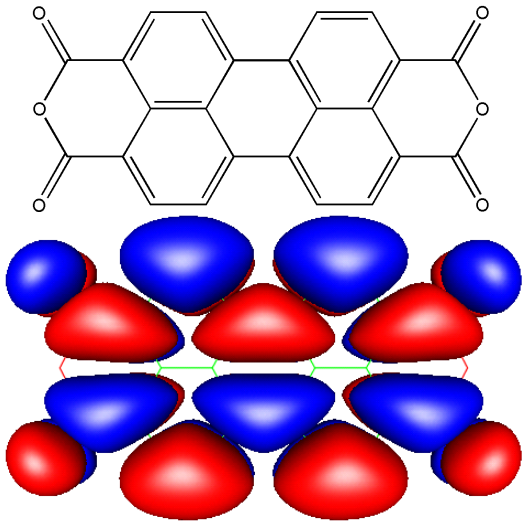


Lowest **U**noccupied **M**olecular **O**rbital





PTCDA/Ag(111) Interface Structure



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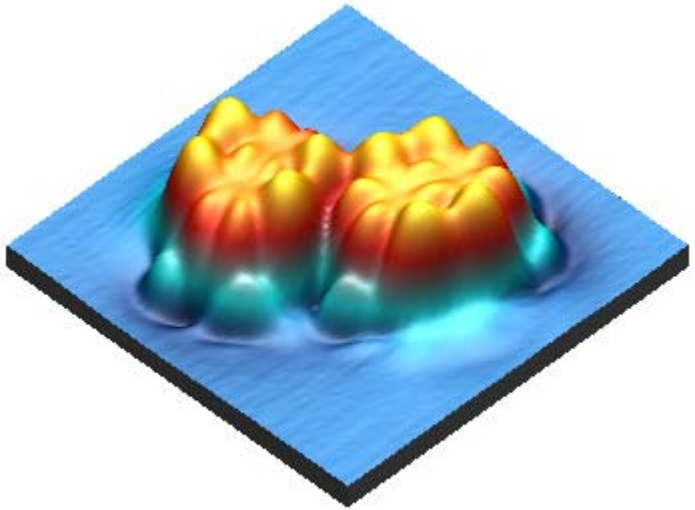
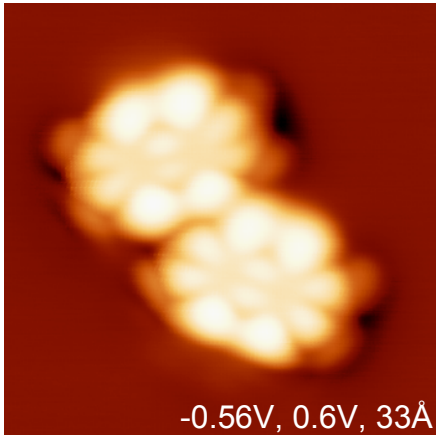


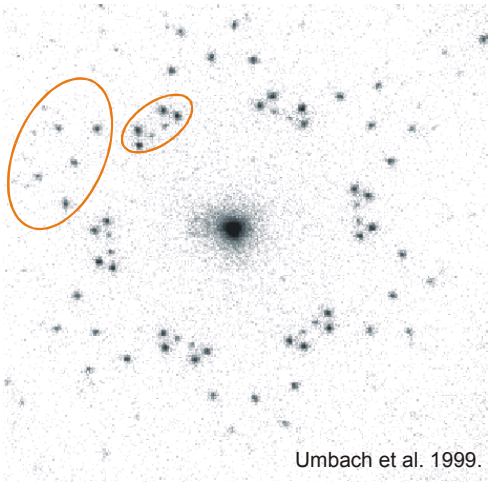


PTCDA / Ag(111):
commensurate,
chemisorbed monolayer

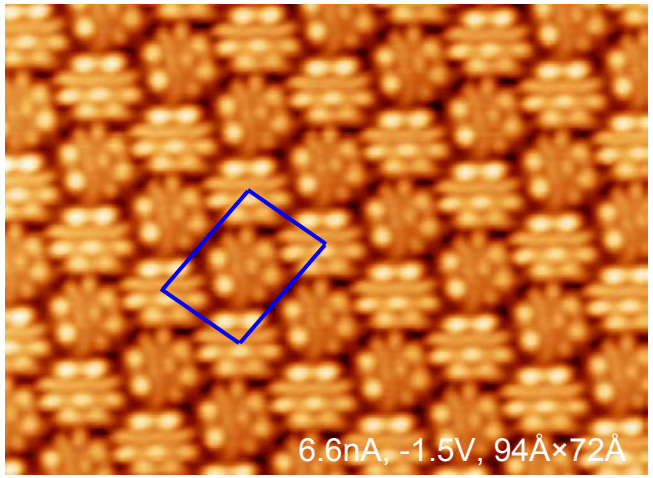
Superstructure matrix:

$$\begin{pmatrix} 6 & 1 \\ 5 & -3 \end{pmatrix}$$

slightly compressed
as compared to
bulk structure



Kraft, FST et al. Physical Review B 74, 041402(R) (2006)



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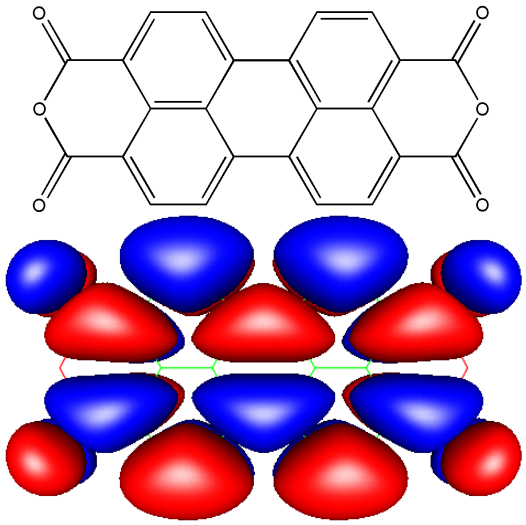

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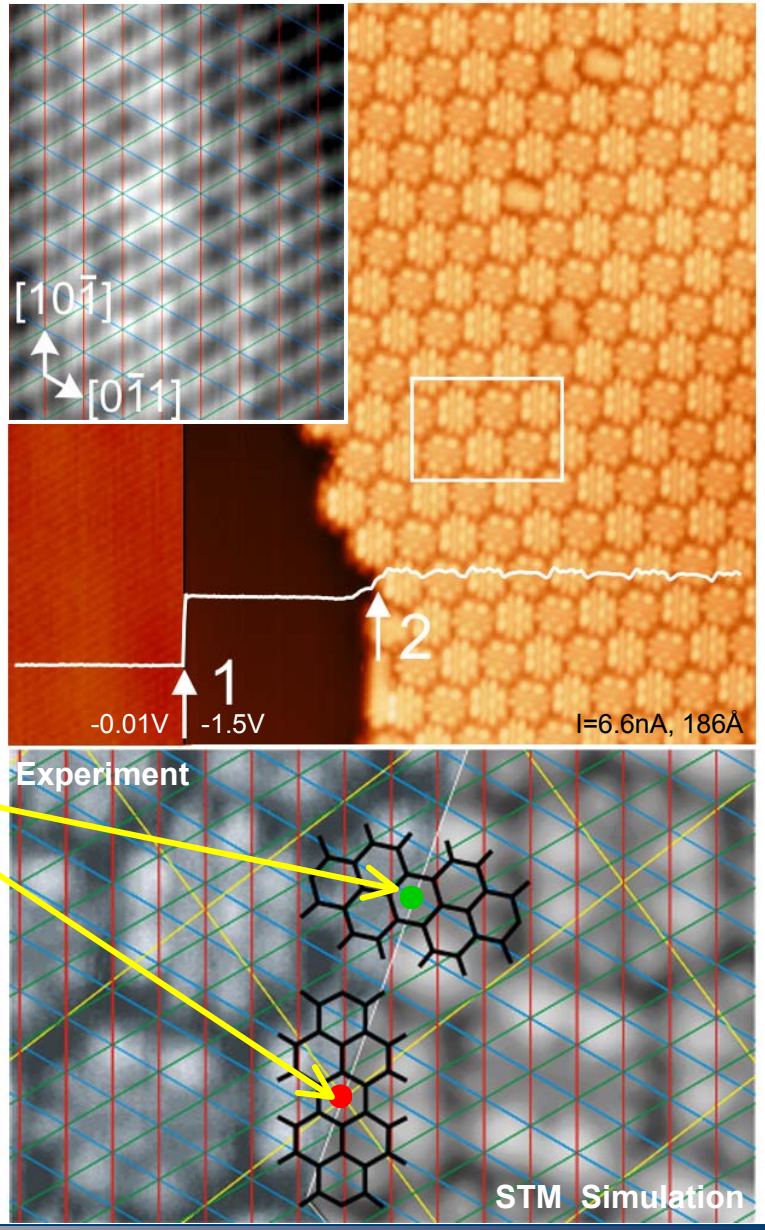
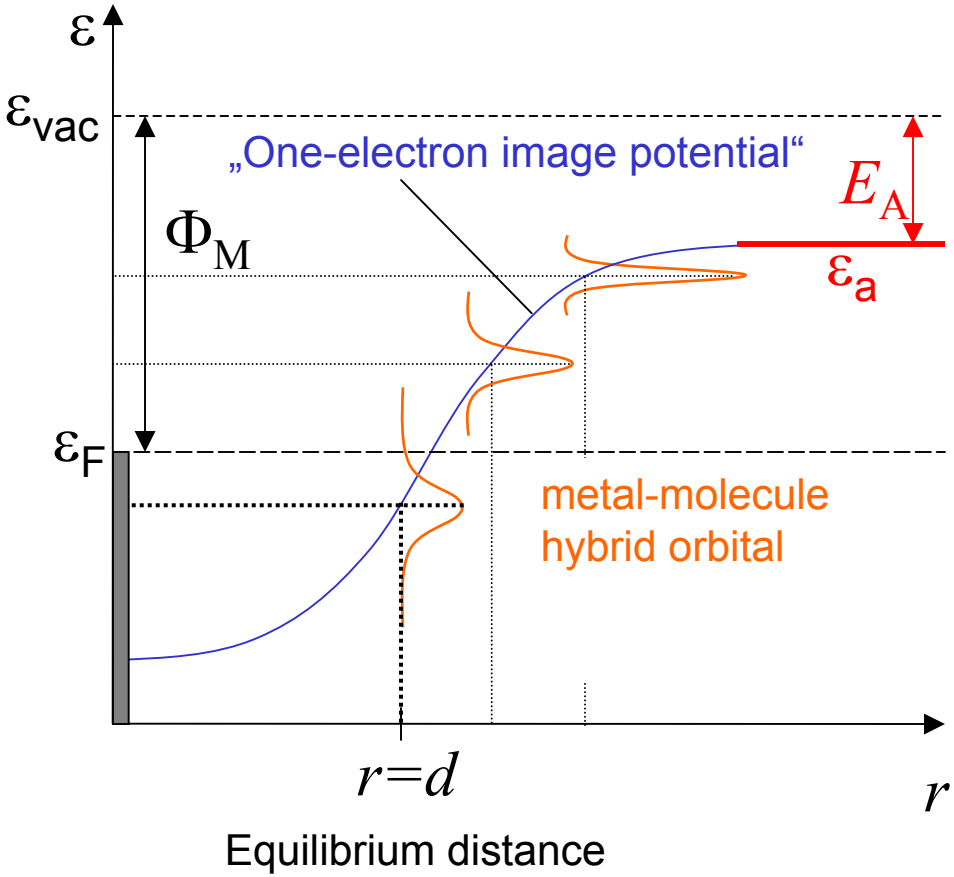
slightly compressed
as compared to
bulk structure

Adsorption site:
bridge site

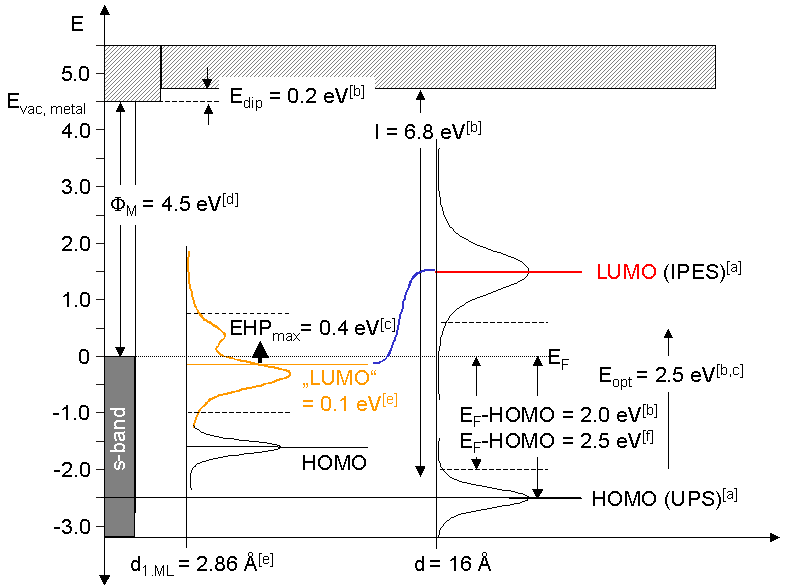


Kraft, FST et al. Physical Review B 74, 041402(R) (2006)

Electronic Structure: Newns-Anderson Model



Affinity level of
the free molecule

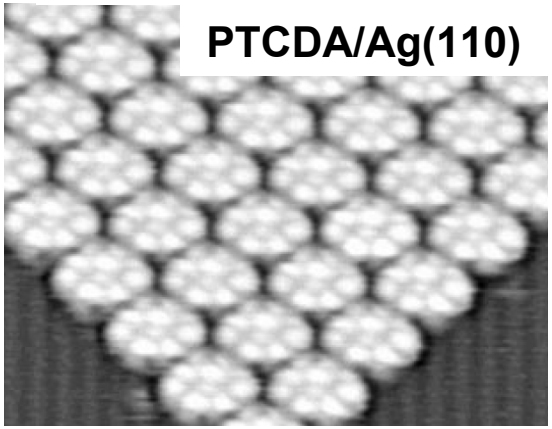


The ability of a metal surface to bind an electron accepting molecule is directly related to its ability to stabilise the molecular affinity level below the Fermi-level.

Structure and Dynamic Properties

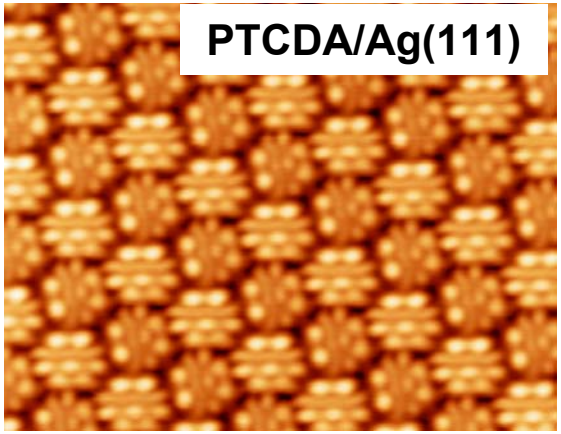
M. Böhringer et al.,Surf. Sci. 419 (1998) L95–L99

PTCDA/Ag(110)



3.0nA, -0.36V

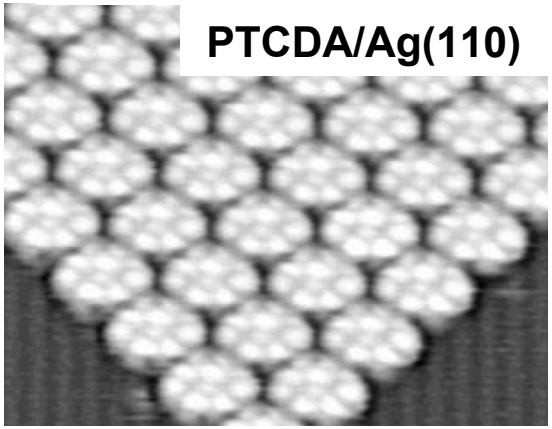
PTCDA/Ag(111)



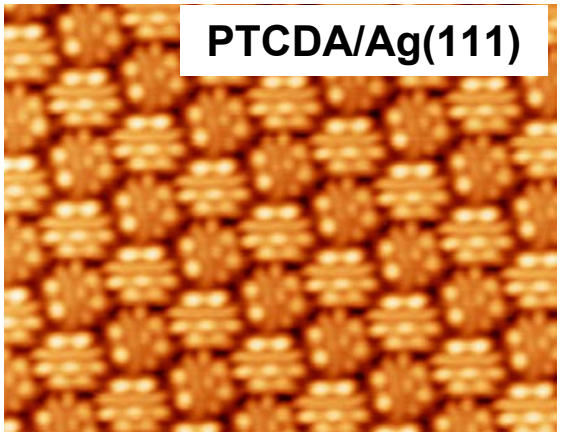
6.6nA, -1.5V, 94Å×72Å

Structure and Dynamic Properties

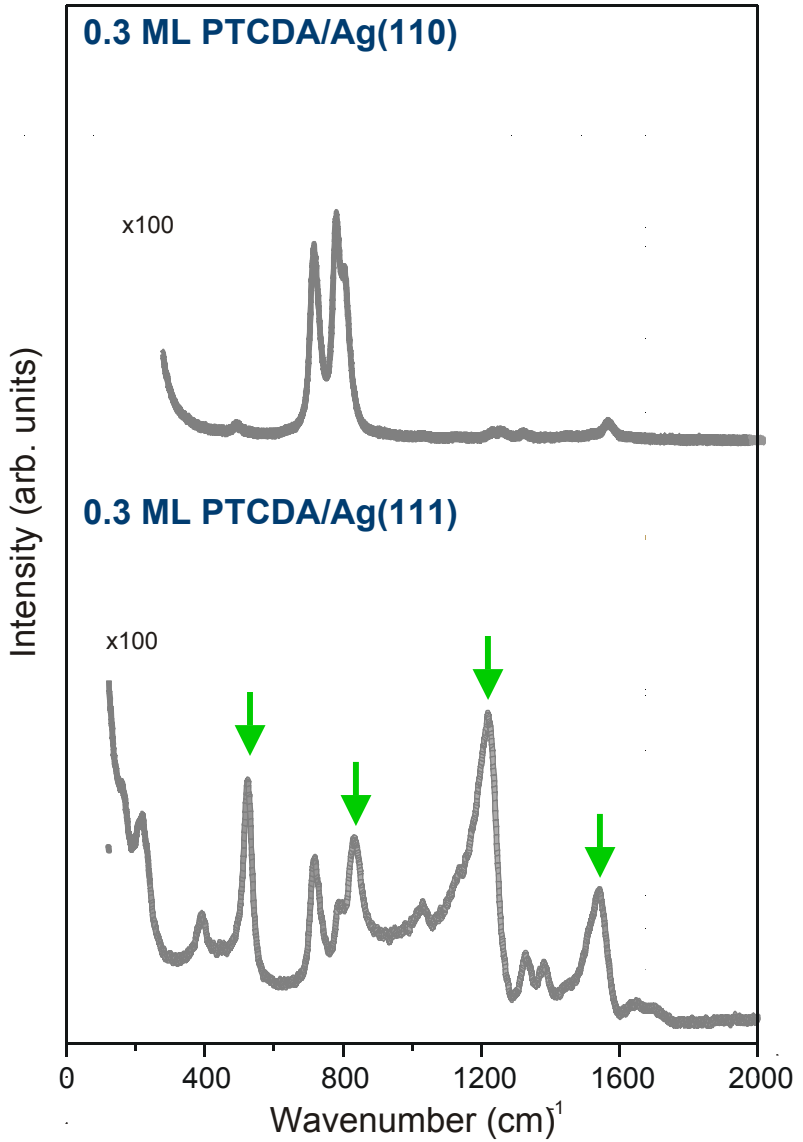
M. Böhringer et al.,Surf. Sci. 419 (1998) L95–L99



3.0nA, -0.36V



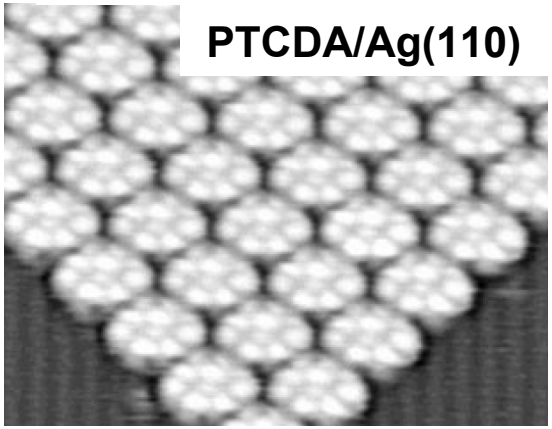
6.6nA, -1.5V, 94Å×72Å



FST et al. Physical Review B 65, 125405 (2002)

Structure and Dynamic Properties

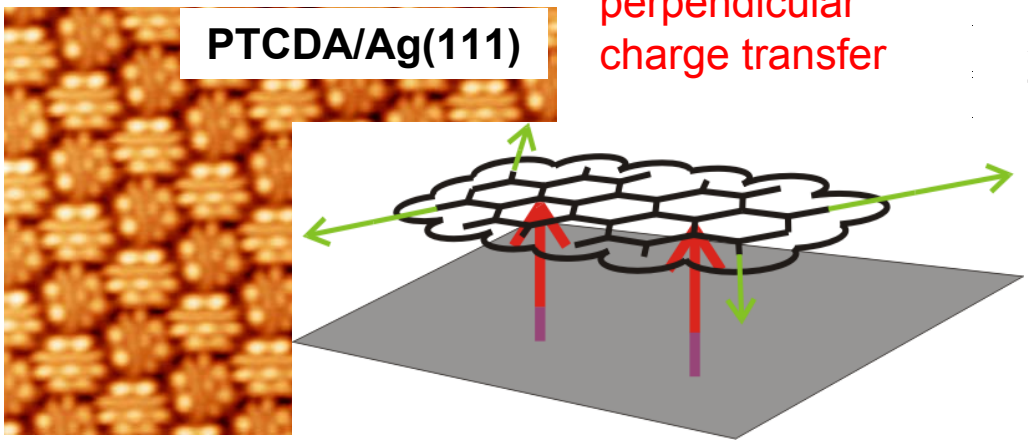
M. Böhringer et al.,Surf. Sci. 419 (1998) L95–L99



3.0nA, -0.36V

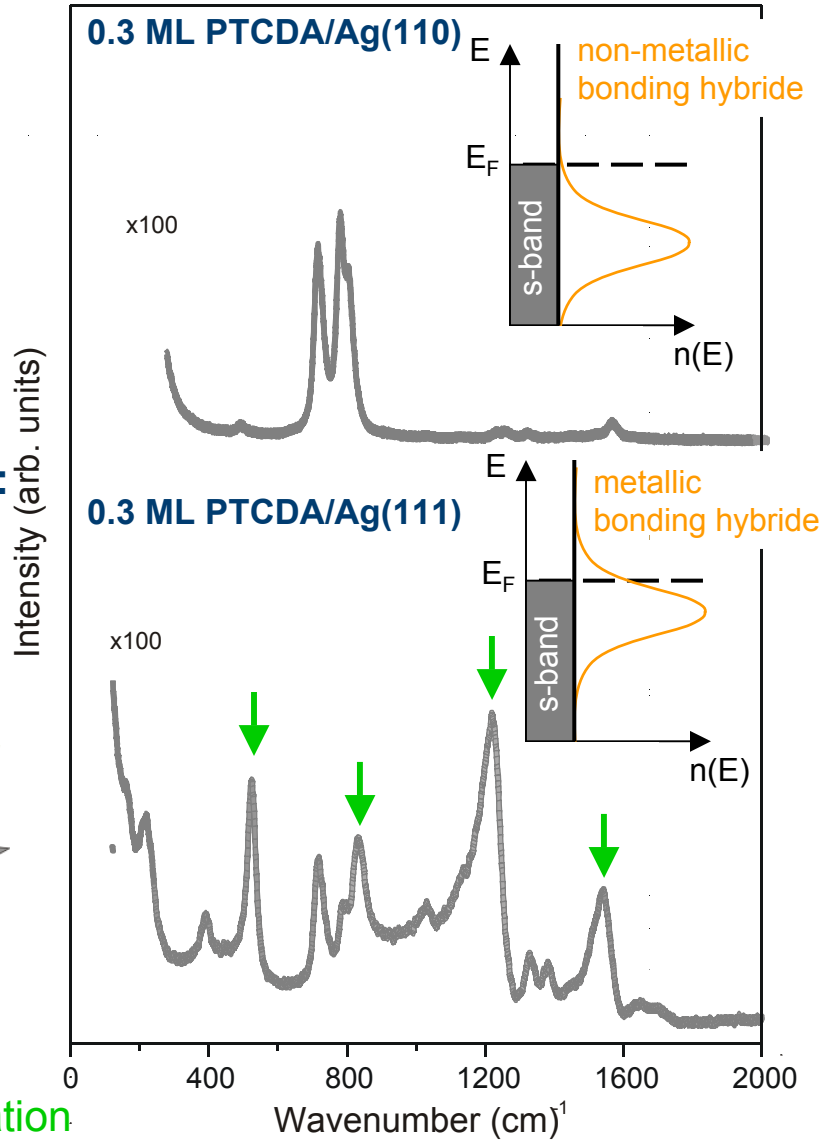
Interfacial Dynamic Charge transfer (IDCT):

perpendicular charge transfer



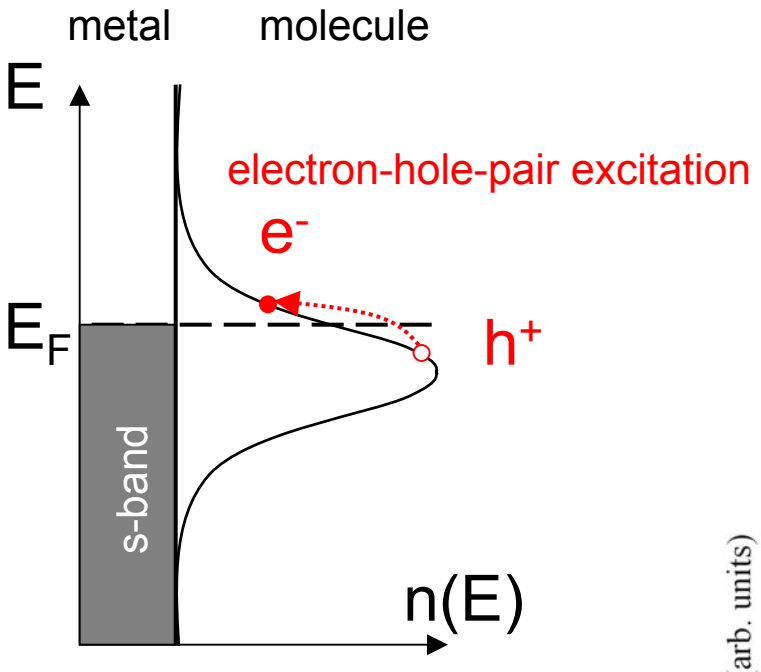
6.6nA, -1.5V, 94Å×72Å

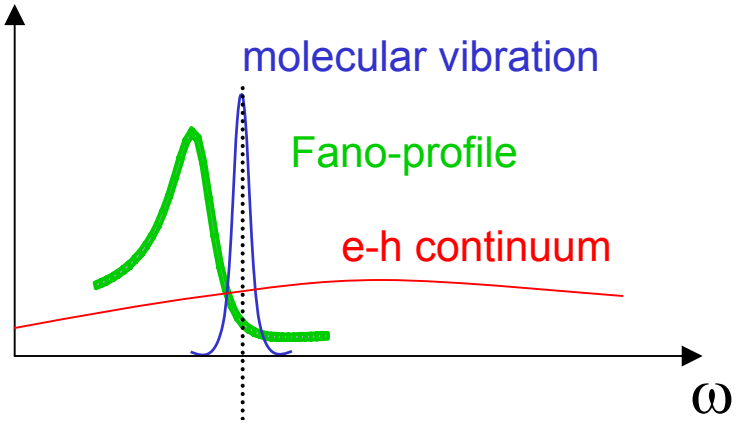
molecular vibration with paralell polarisation



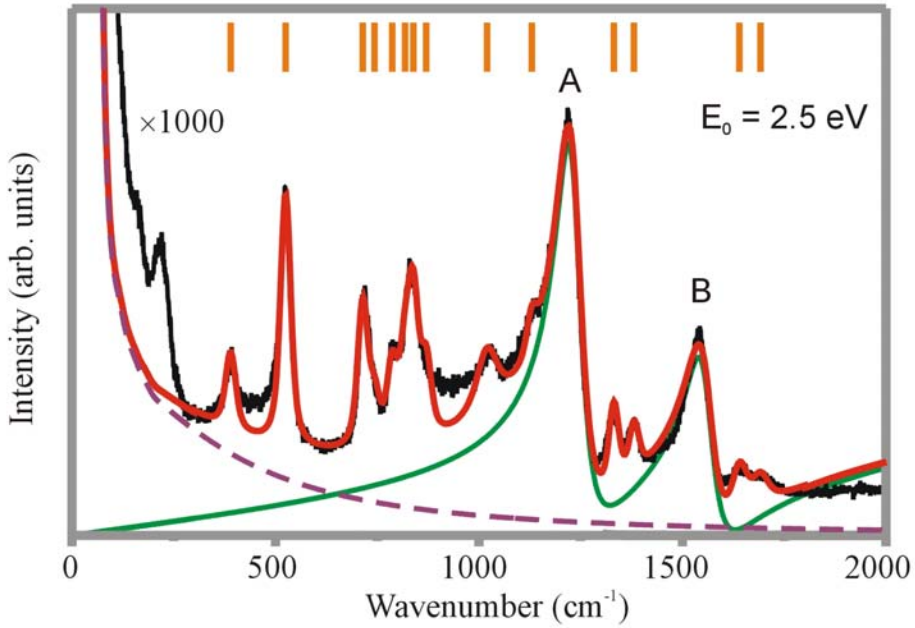
FST et al. Physical Review B 65, 125405 (2002)

Dynamic Charge Transfer: Line Shape Analysis





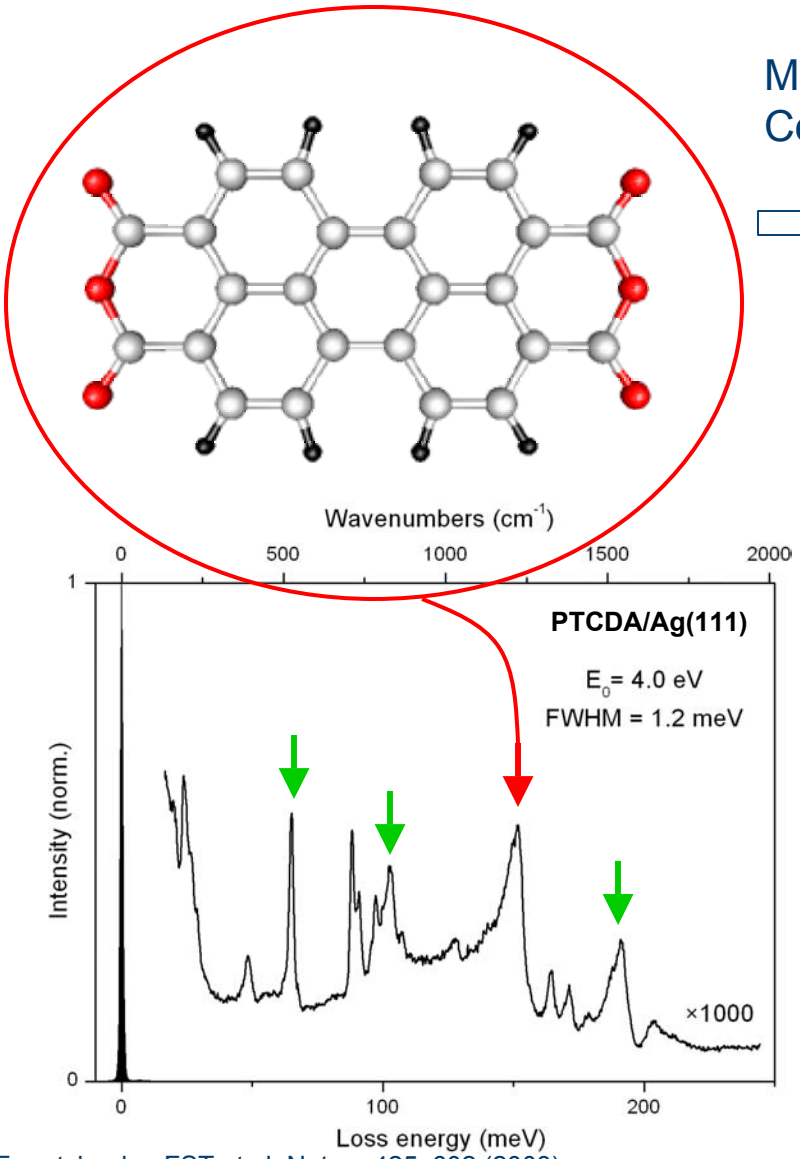
$$\tilde{\varepsilon}(\omega) = \varepsilon_\infty + \frac{4\pi\chi_1(0)\omega_{CT}^2 edN}{\omega_{CT}^2(1-\lambda_\alpha D_\alpha(\omega)) - \omega^2 - i\omega\gamma}$$



electro-phonon-coupling: V = 140 ± 30 meV

FST et al. Physical Review B 65, 125405 (2002)

Analysis of Molecular Dynamics : Bonding in the Centre

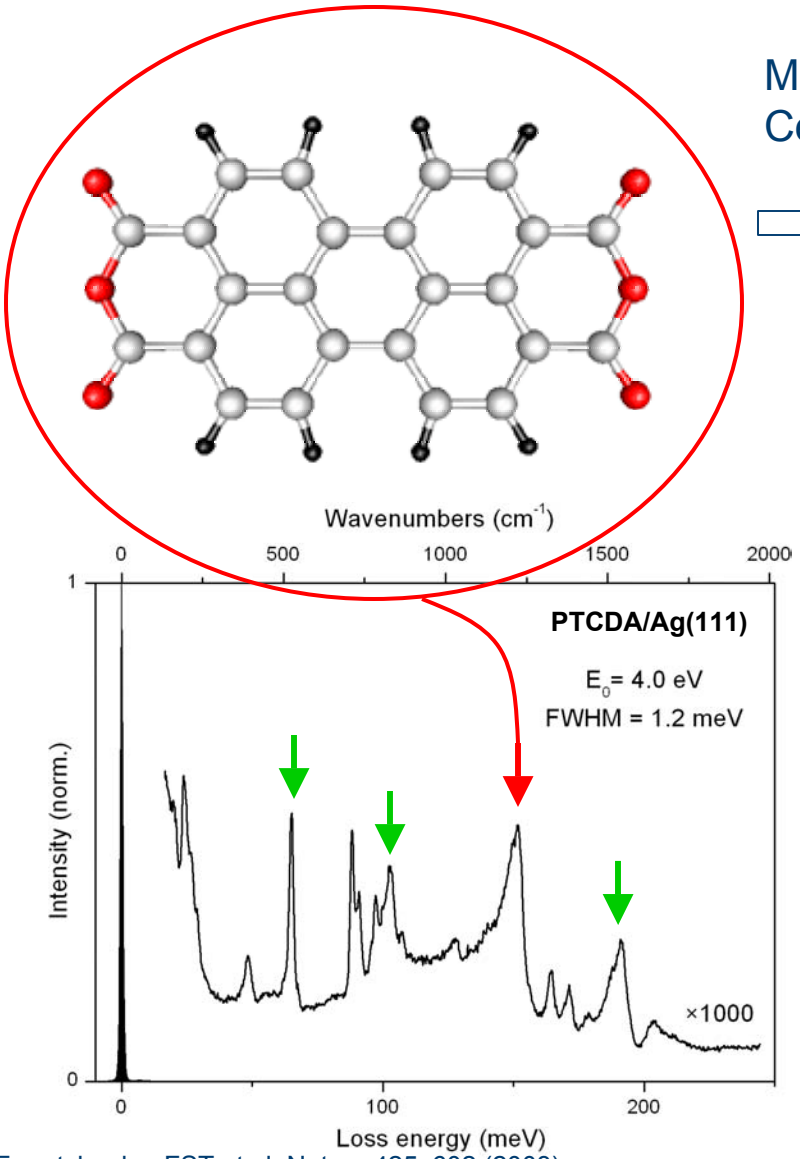


Modes which modulate the electron density in the Centre of the molecule are particularly enhanced

⇨ **Bonding in the centre** (“Saugnapf”-model)

Eremtchenko, FST et al. Nature 425, 602 (2003)
Eremtchenko, FST et al. New Journal of Physics 6, 4(2004)

Analysis of Molecular Dynamics : Bonding in the Centre



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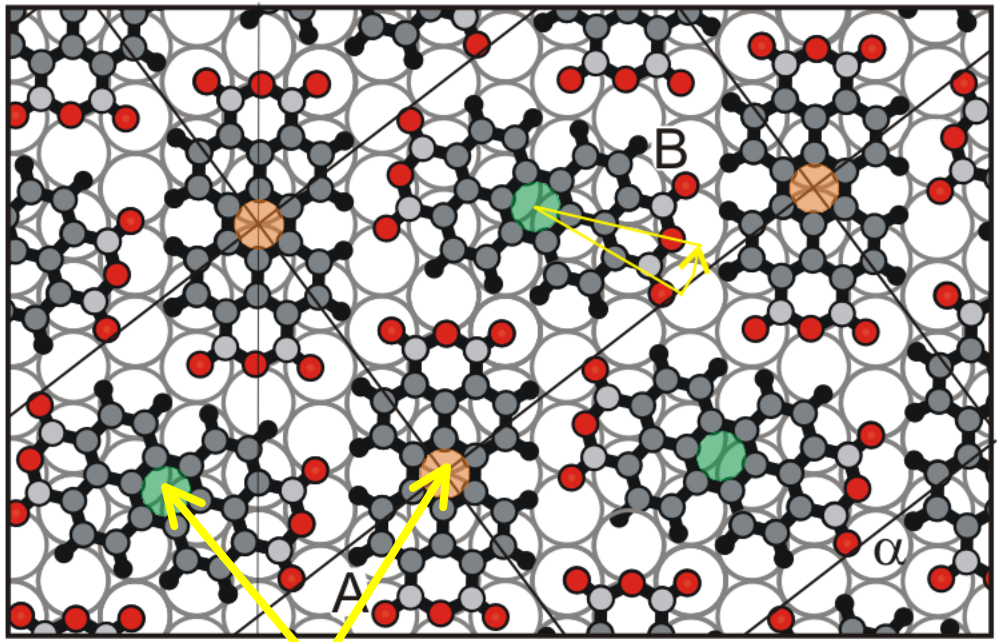
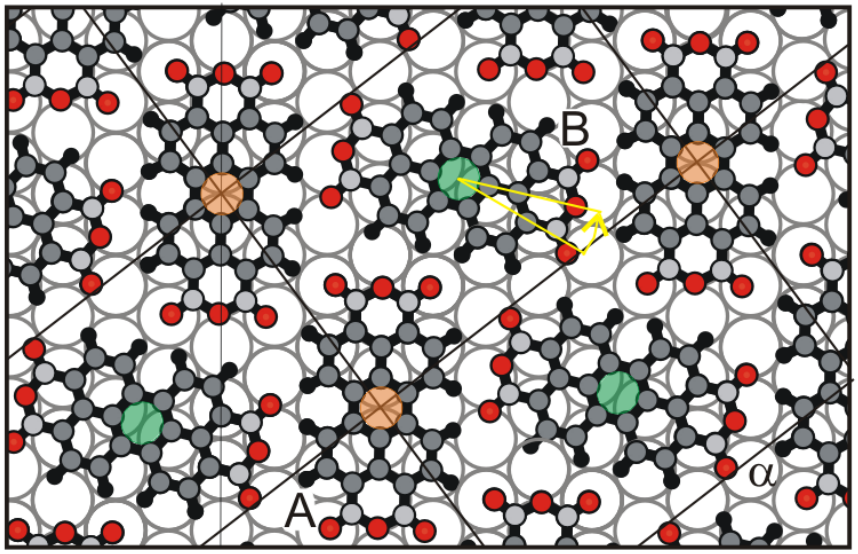


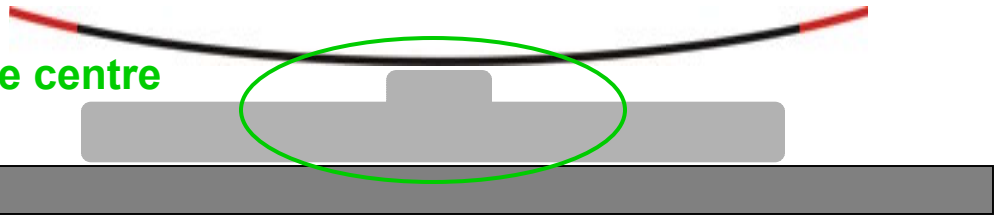
Adsorption site determination:
Molecules anchored with their centres

Eremtchenko, FST et al. Nature 425, 602 (2003)
Eremtchenko, FST et al. New Journal of Physics 6, 4(2004)

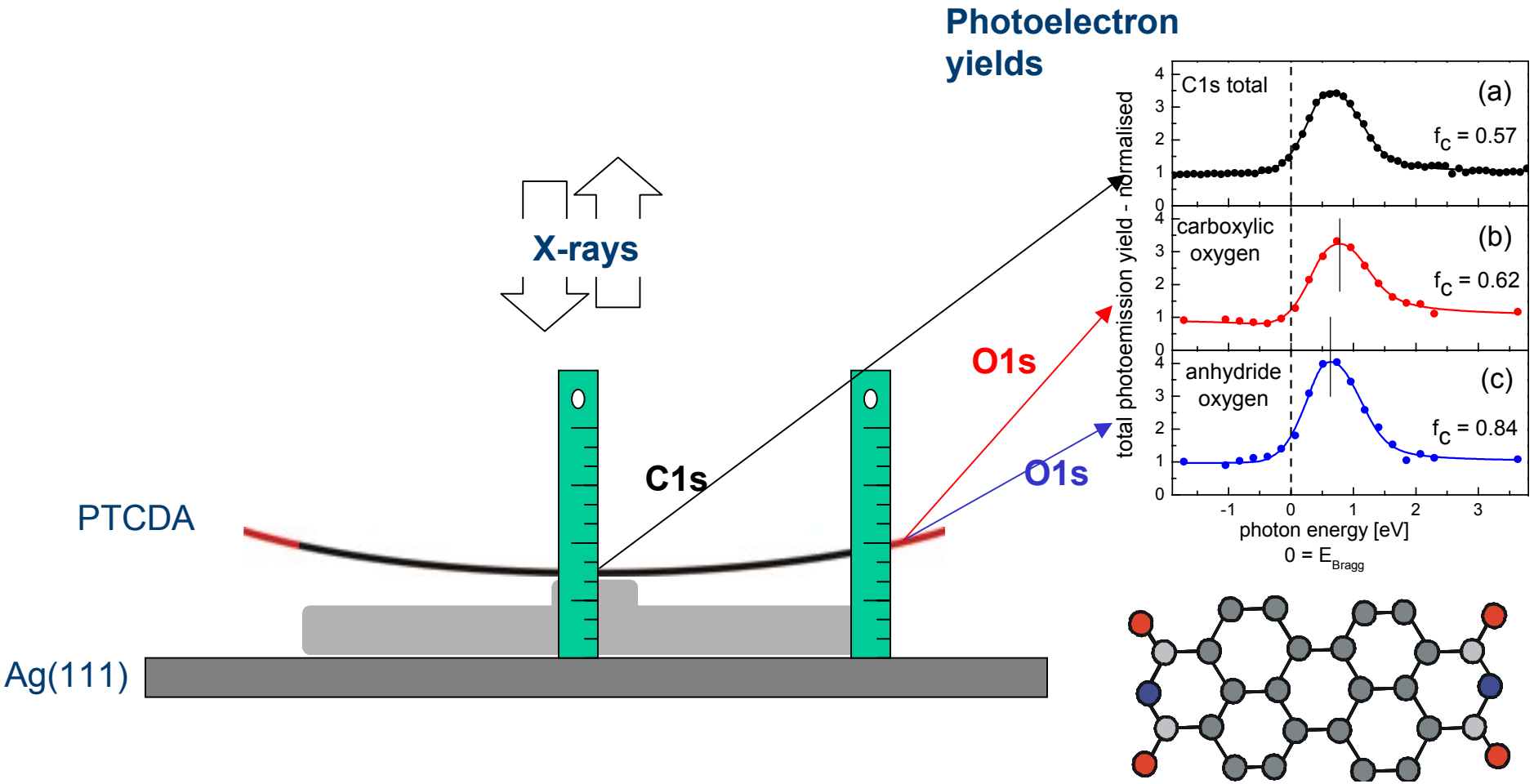
Does the Bonding lead to a Molecular Distortion ?



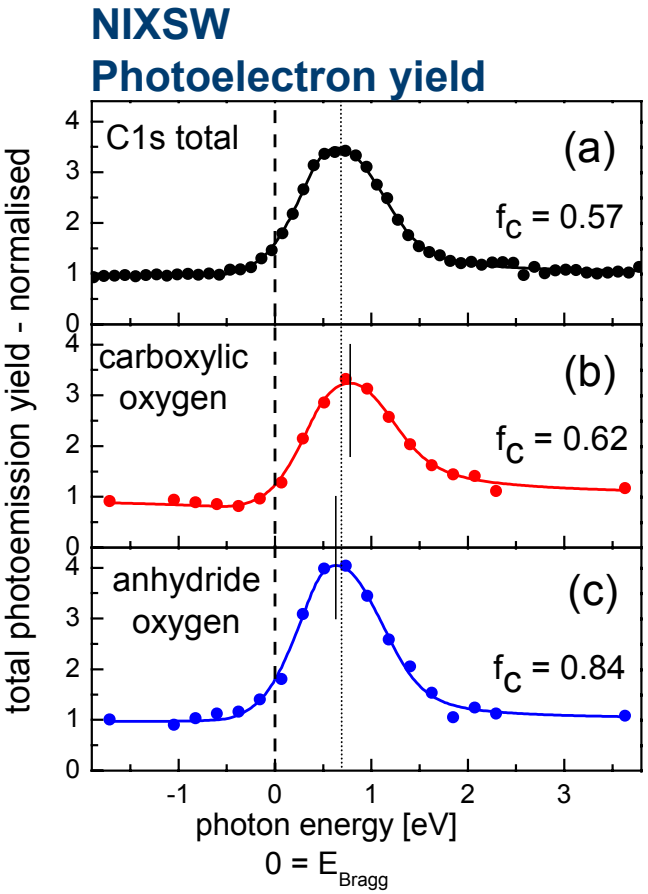
?

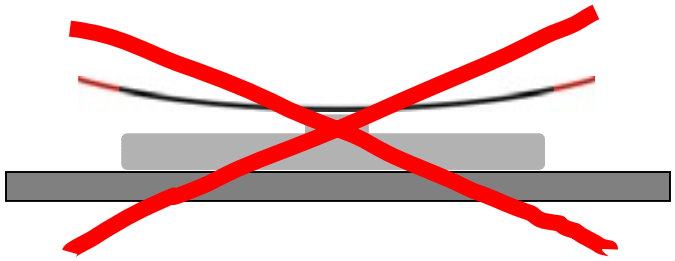


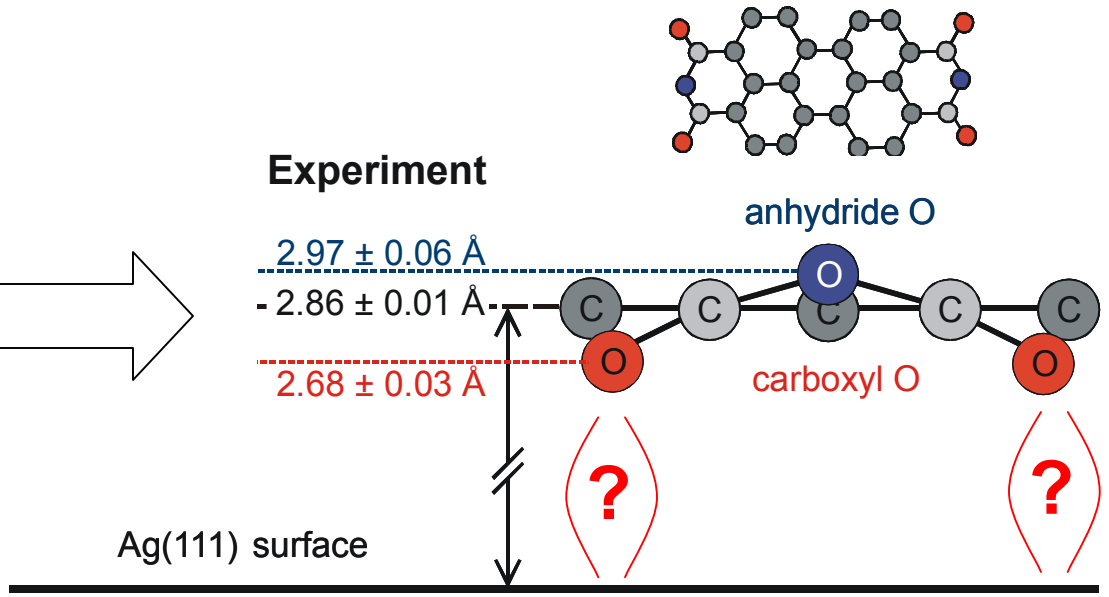
"Atomic Scale Ruler": NIXSW



Result: Bond Length and Molecular Structure







Physical Review Letters 94, 036106 (2005)
Physical Review Letters 95, 209602 (2005)

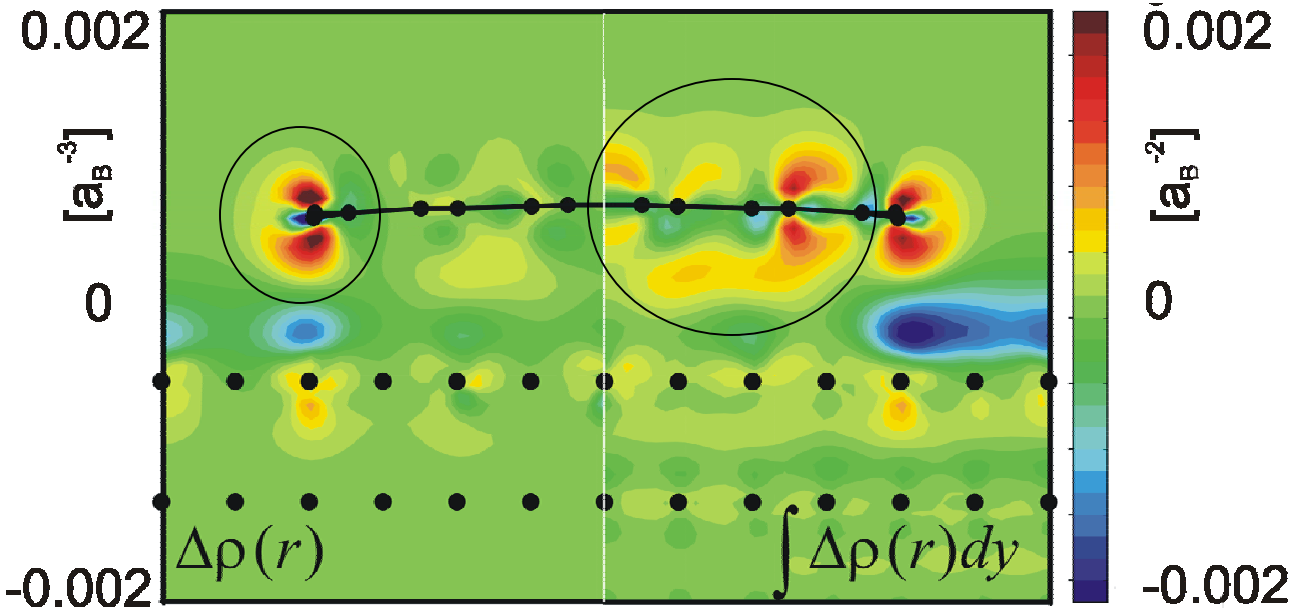
Bond length is relatively short
(cf. 3.22 Å distance between molecular layers in bulk)

Which is the mechanism of the KONVEX distortion?

Result: Bonding Mechanism

Physical Review Letters 94, 036106 (2005)
Physical Review Letters 95, 209602 (2005)

Charge displacements

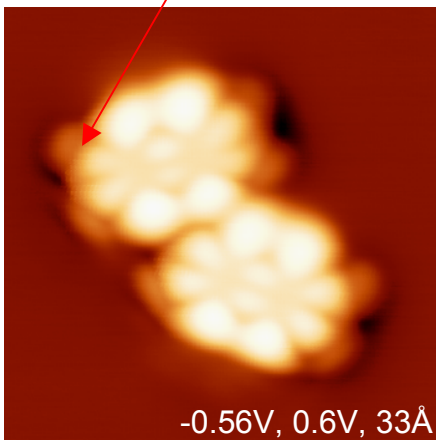


partial valences
of the carboxylic oxygens:
sekundary bond

primary bond:
charge transfer into LUMO

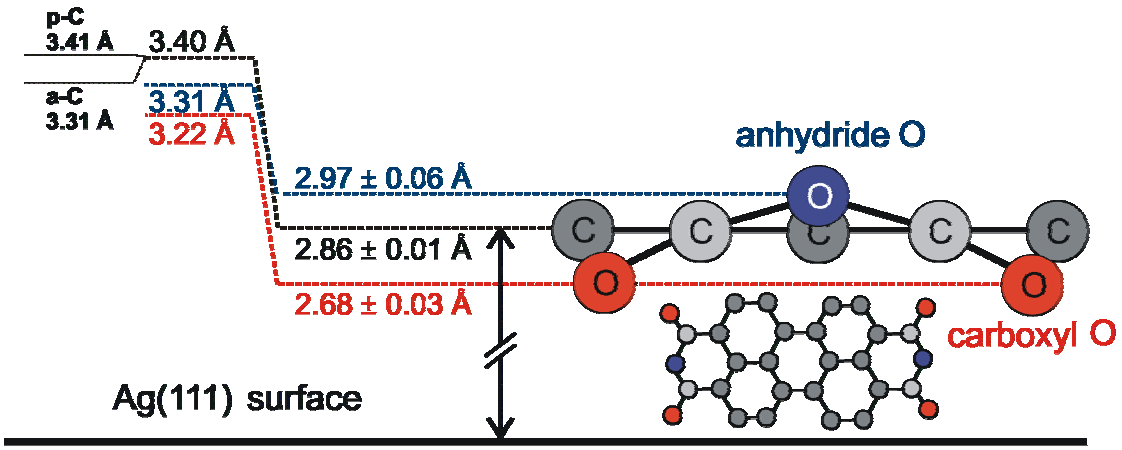
distortion

C=O double bond is
weakened



Summary: Density Functional Calculation

Physical Review Letters 94, 036106 (2005)
Physical Review Letters 95, 209602 (2005)

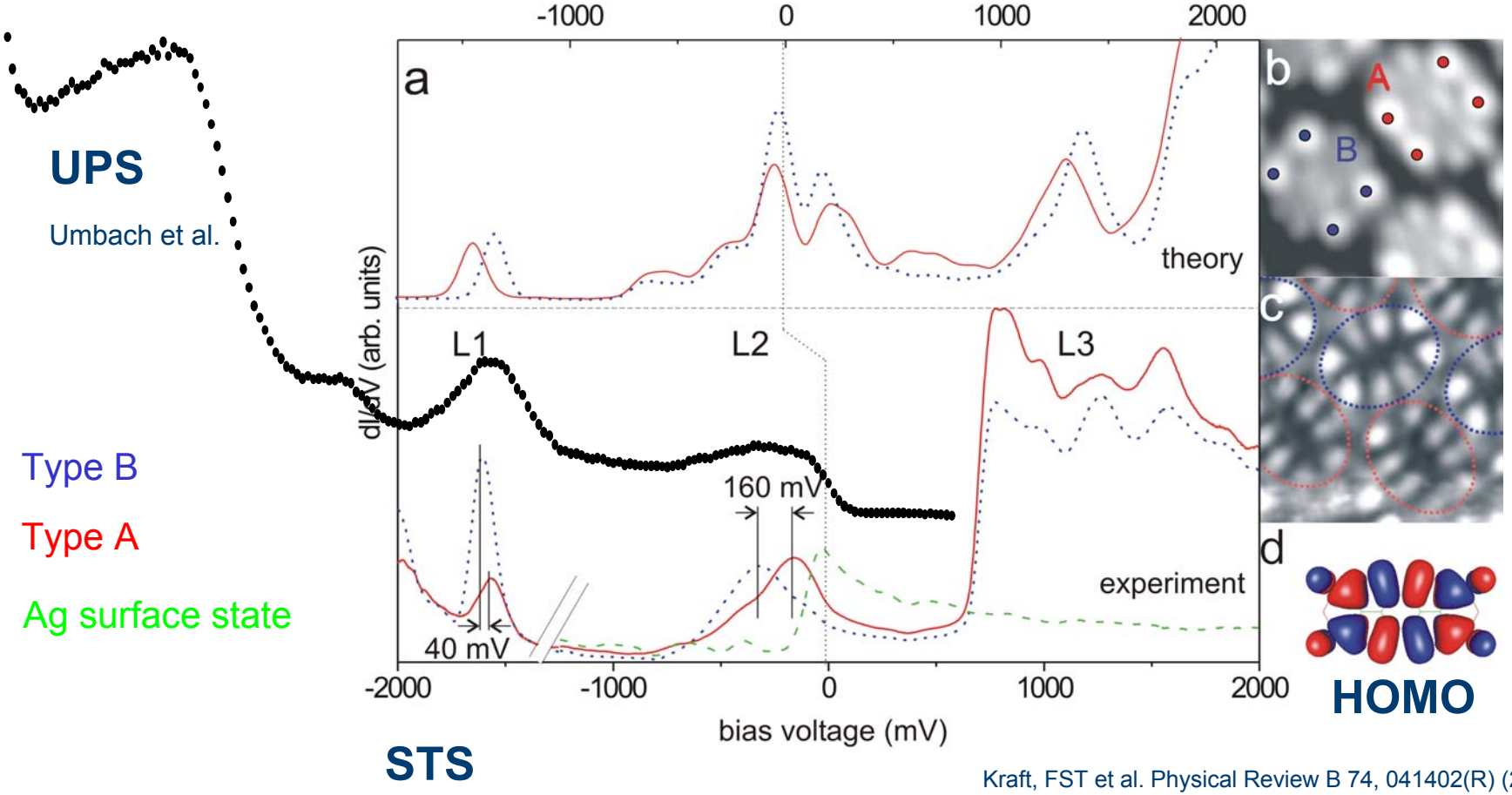


Theorie:

DFT-GGA (SIESTA)
Standard double zeta basis with polarisation (DZP) for Ag and H, Triple zeta basis for O and C

Bond length	✗
Adsorption site	✓
Distortion of the molecule	✓
Metallicity of the molecule	✓
STM image contrast	✓
Site-specific electronic structure	✓

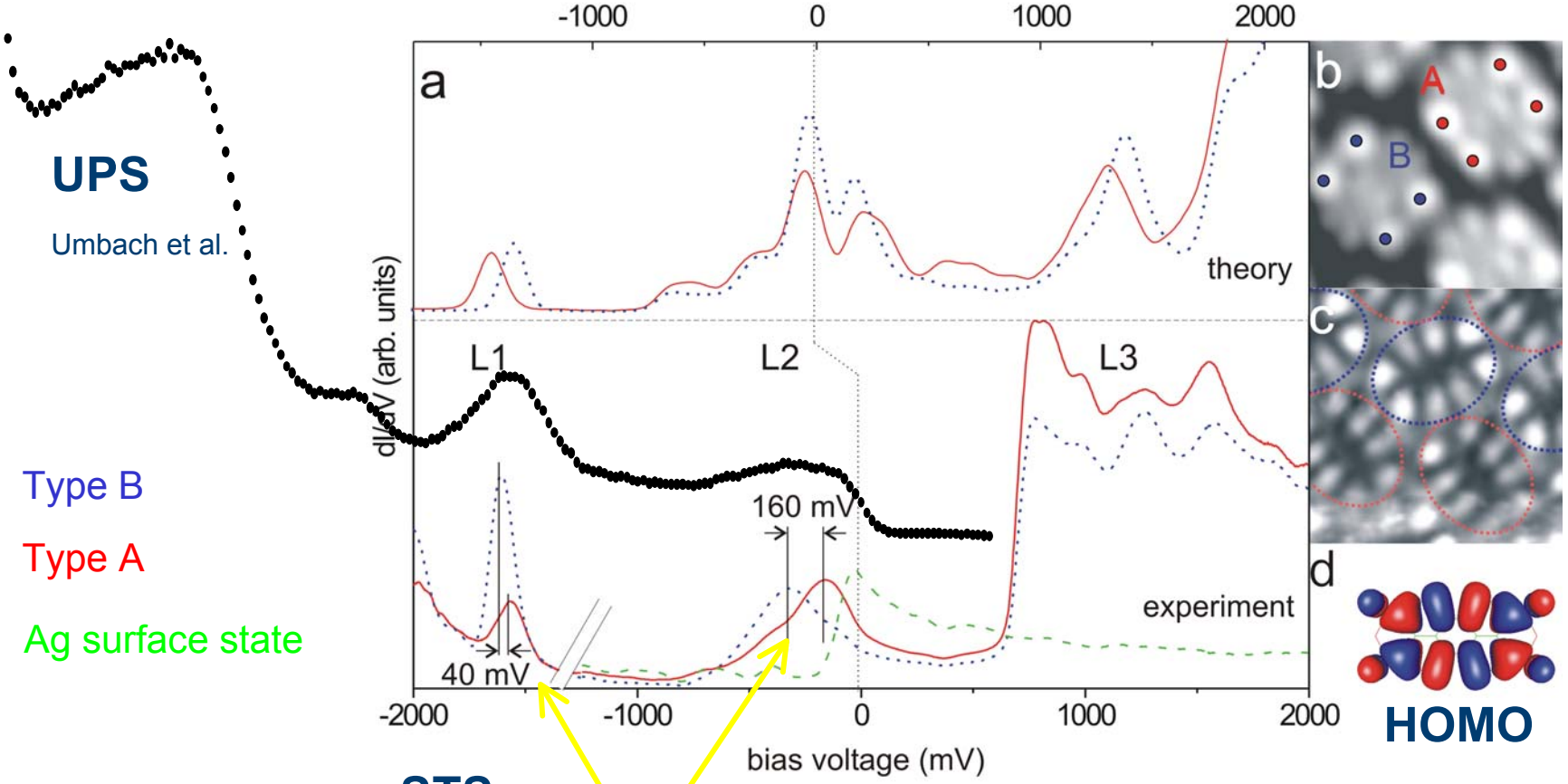
Electronic Structure: Hybridisation



Kraft, FST et al. Physical Review B 74, 041402(R) (2006)

L1 = former HOMO (sharp) L2 = former LUMO (broad)

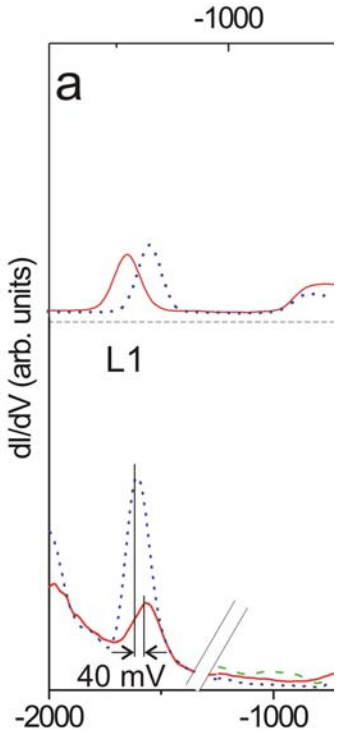
Electronic Structure: Site-specific



Kraft, FST et al. Physical Review B 74, 041402(R) (2006)

Site-specific electronic structure

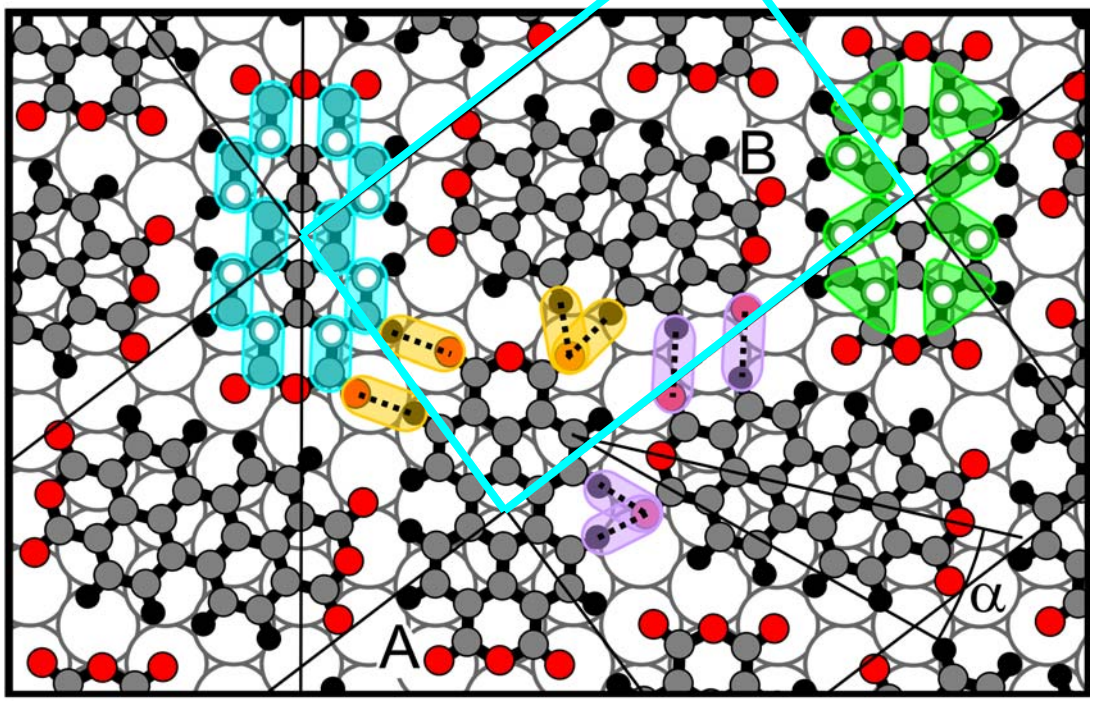
Electronic Structure: Site-specific



Type B

Type A

Kraft, FST et al. Physical Review B 74, 041402(R) (2006)



Due to distortion of **unit cell** from orthogonality, hydrogen bridges A-A and B-B are different from each other, as are A-B and B-A

O-H	distance
A-A	2.36Å
B-B	2.55Å
A-B	2.15Å
B-A	2.04Å

For a free-standing herringbone layer, different O-H bonds lead to:

$E_{HOMO}(A)=E_{HOMO}(B) + 120$ meV

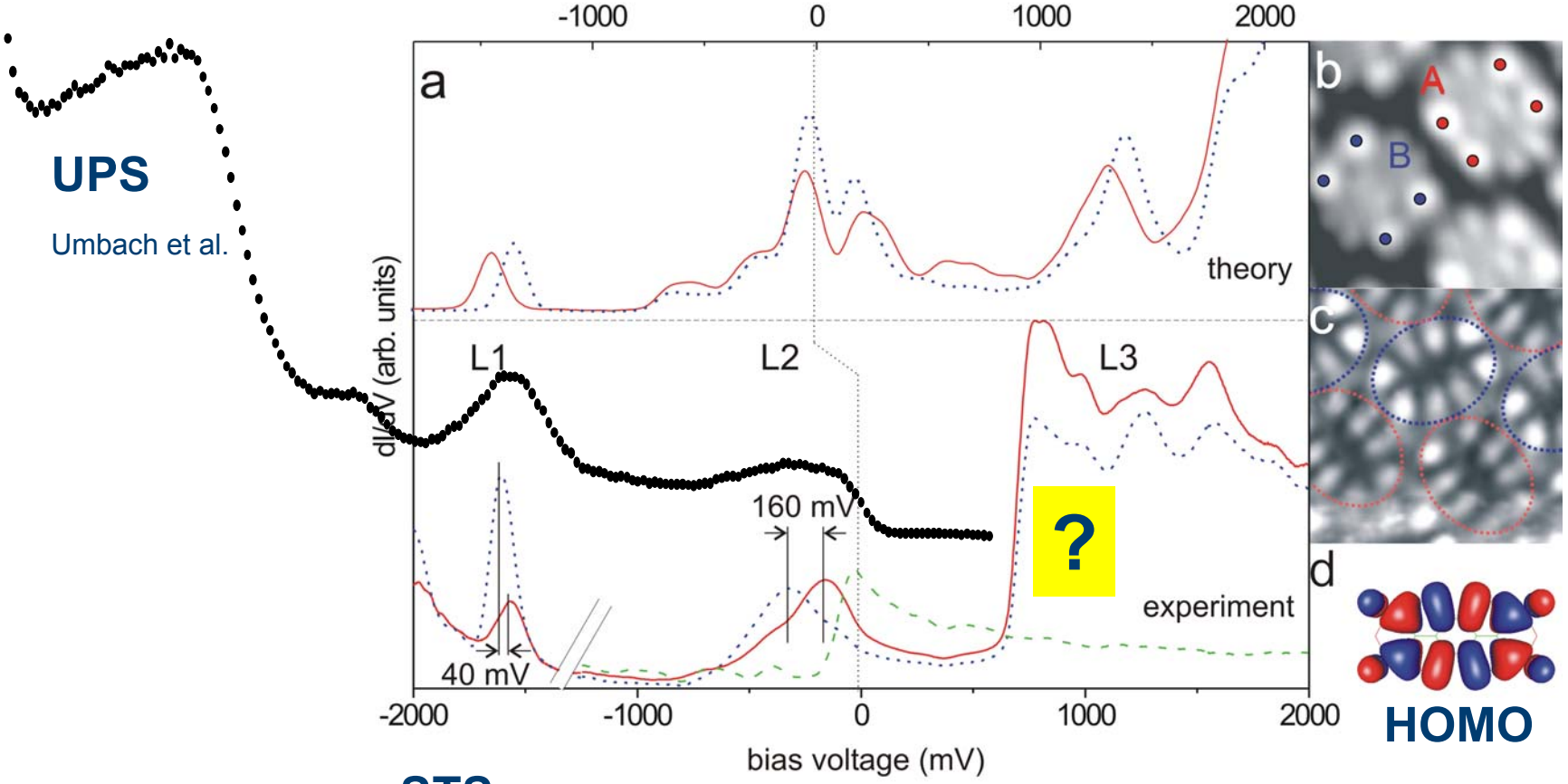
The metal overcompensates this shift to

$E_{HOMO}(A)=E_{HOMO}(B) - 100$ meV

Experiment:

$E_{HOMO}(A)=E_{HOMO}(B) + 40$ meV

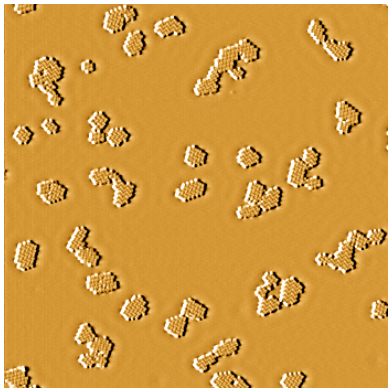
Electronic Structure: Continuum?

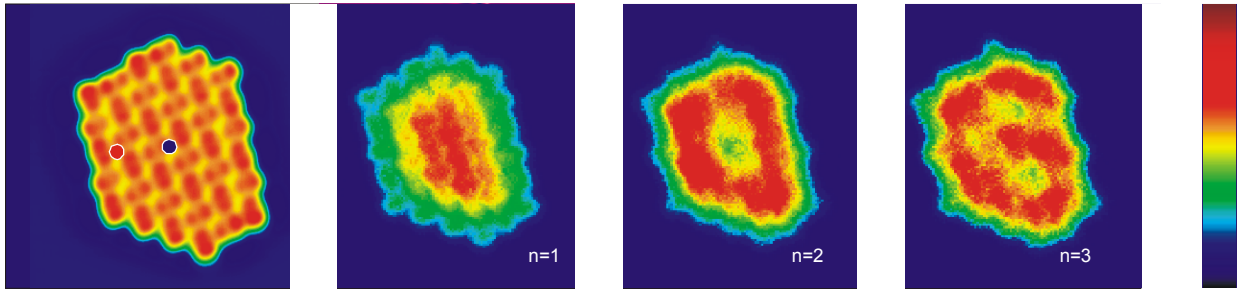


Kraft, FST et al. Physical Review B 74, 041402(R) (2006)

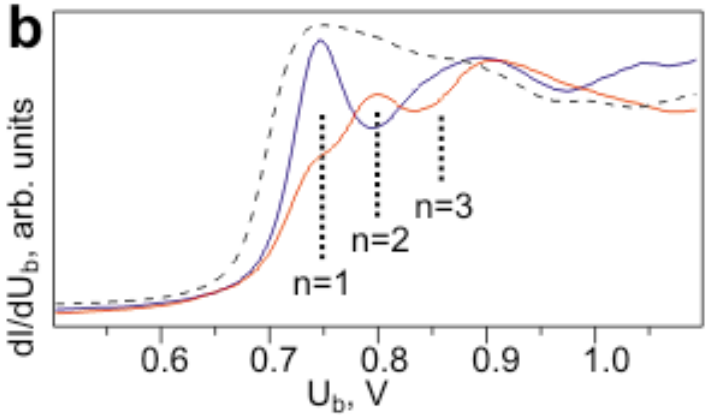
Study small islands!

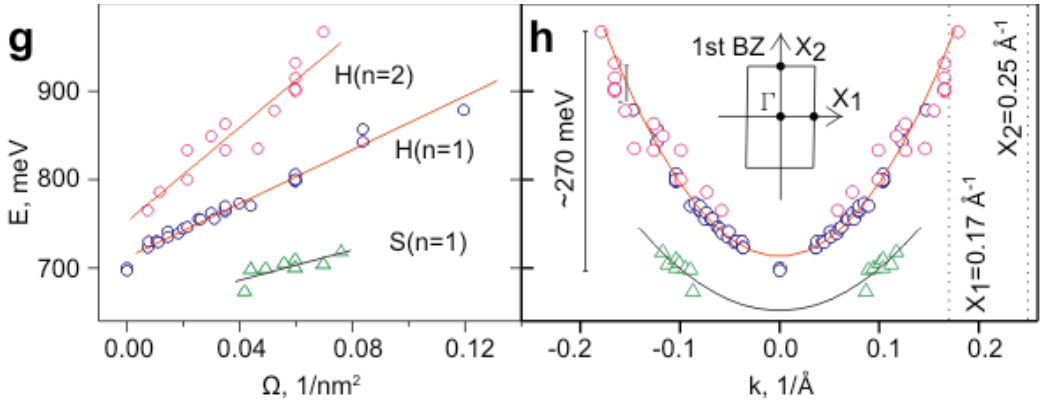
Electronic Structure: PTCDA/Ag(111) interface state





Confinement of free-electron-like PTCDA/Ag(111) interface state

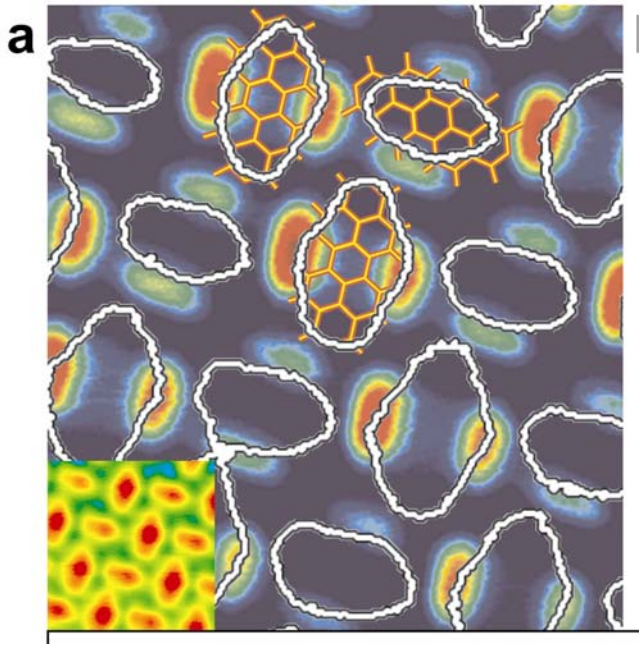


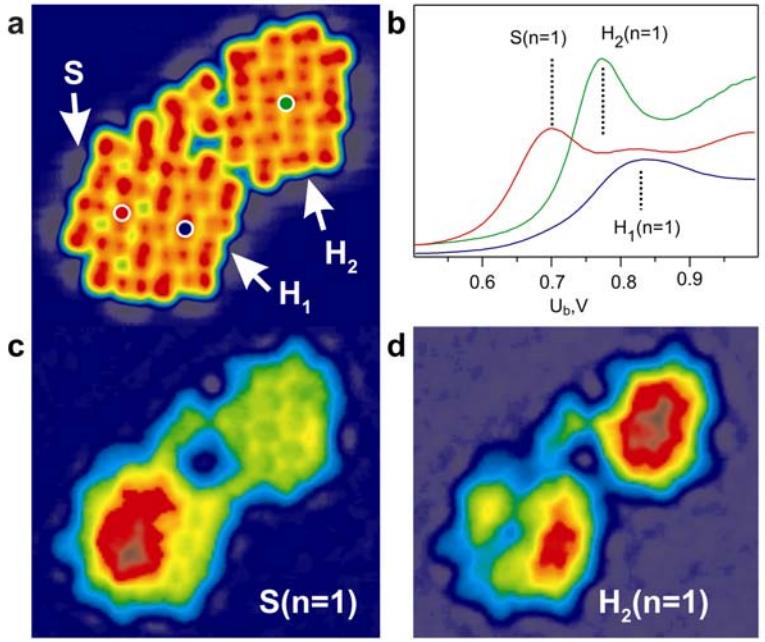


Temirov, FST et al. Nature in press (2006)

Parabolic dispersion with m*=0.47 similar to Ag surface state (m*=0.42)

Electronic Structure: PTCDA/Ag(111) interface state



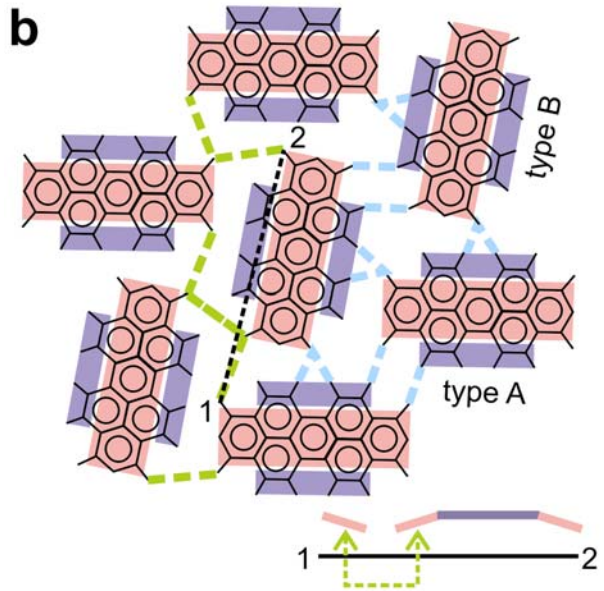


At k=0, the delocalised state is concentrated on the molecules

The delocalised state depends very sensitively on molecular coordination

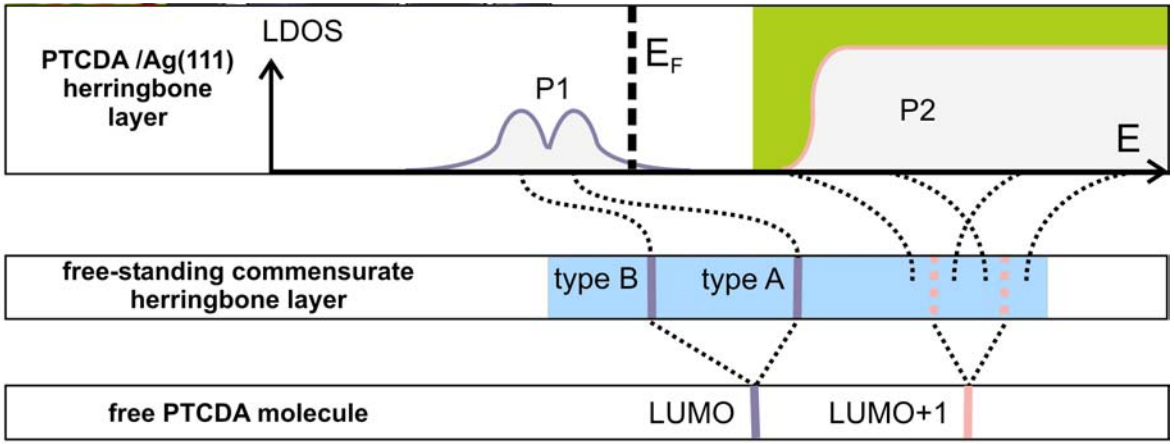
Temirov, FST et al. Nature in press (2006)

Electronic Structure: Summary



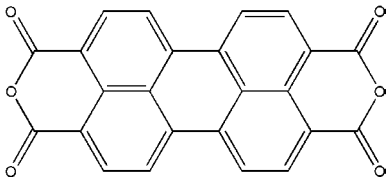
intermolecular interaction

substrate-mediated interaction



Temirov, FST et al. Nature in press (2006)

Summary: Substrate Bonding

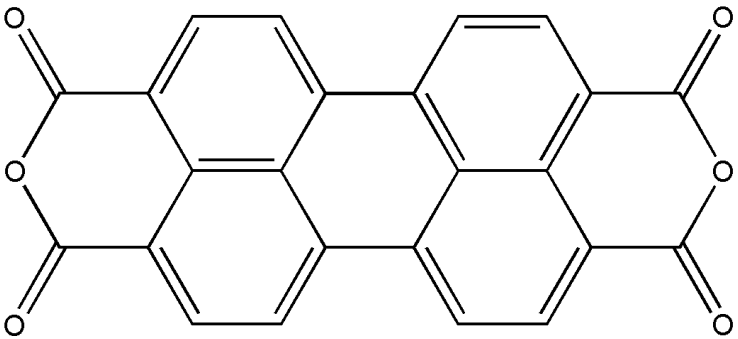


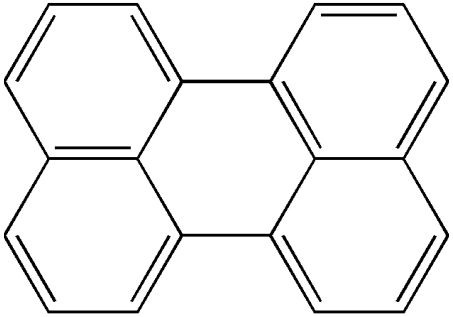
a. Chemisorption
b. Interface structure
c. Dynamic charge transfer: bonding centre
d. Interfacial electronen-phononen-coupling
e. Bond length and molecular configuration
f. Detailed electronic structure

⇩

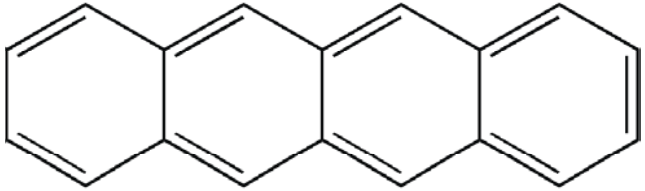
Comprehensive characterisation of a model system

Molecules without Additional Functional Groups

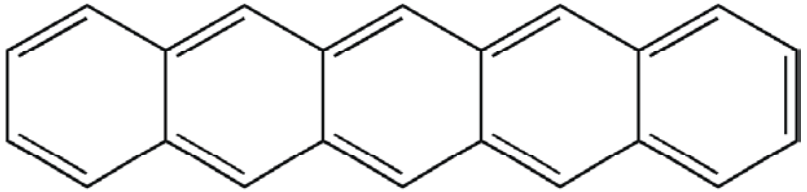




Perylene

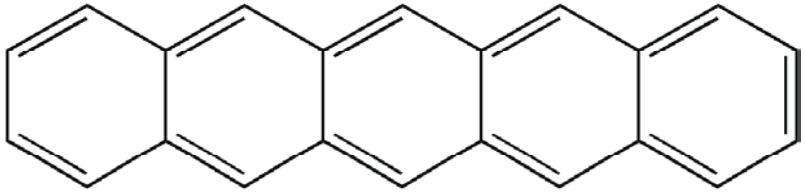


Tetracene



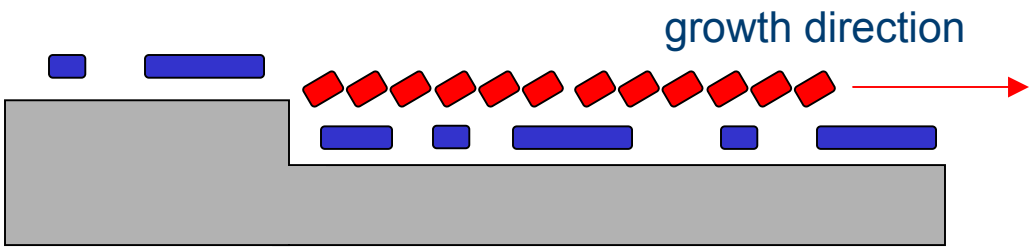
Pentacene

Structures and Ordering Processes

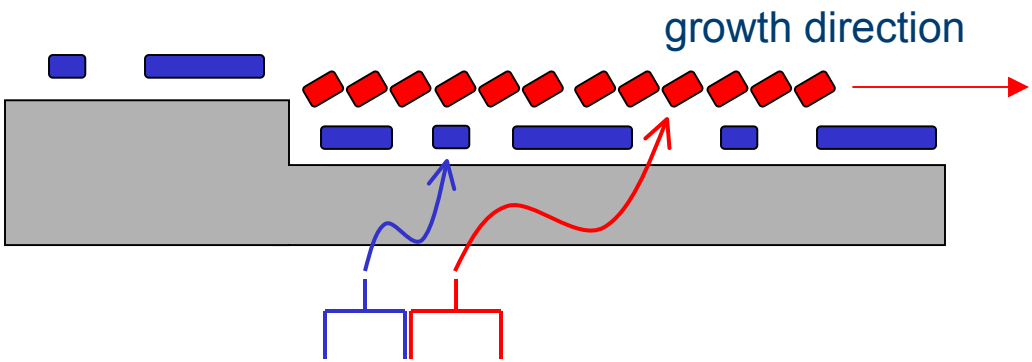


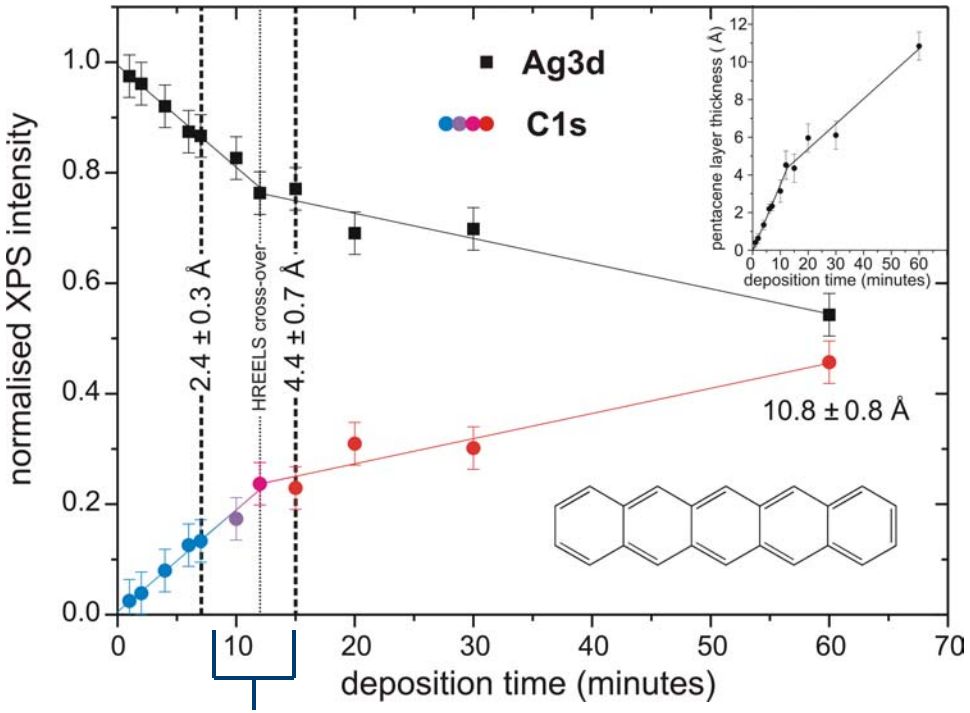
a. Structures: Ordered molecular layers on a disordered interface layer: Pentacene / Ag(111)

Ordering on a Disordered Monolayer



Pn / Ag(111) @ 300 K: Two Phases of Growth

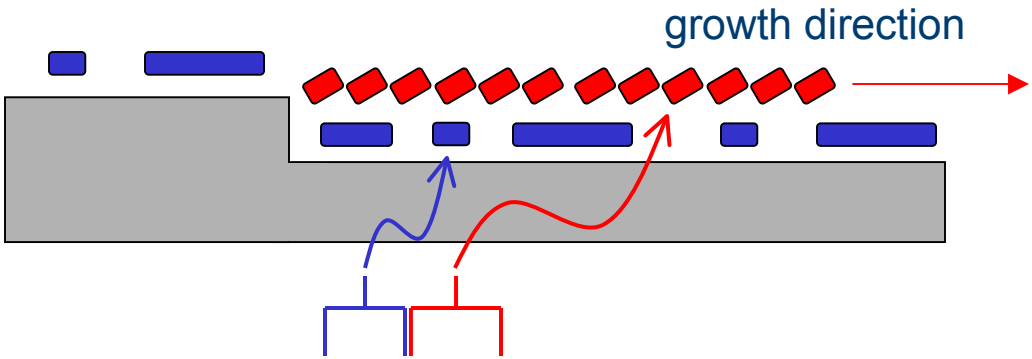


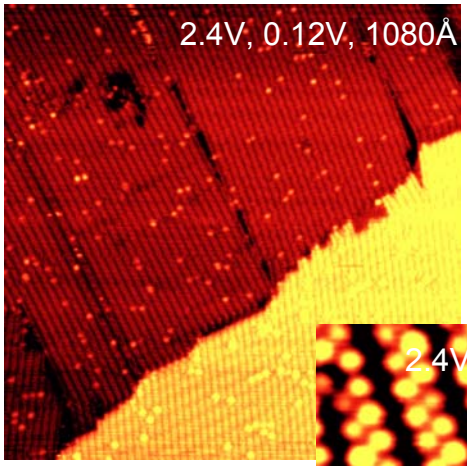


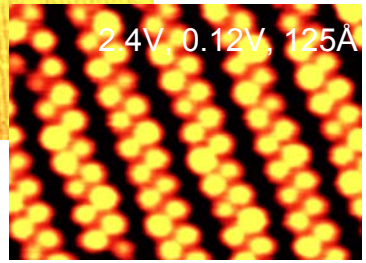
Decrease of the sticking coefficient

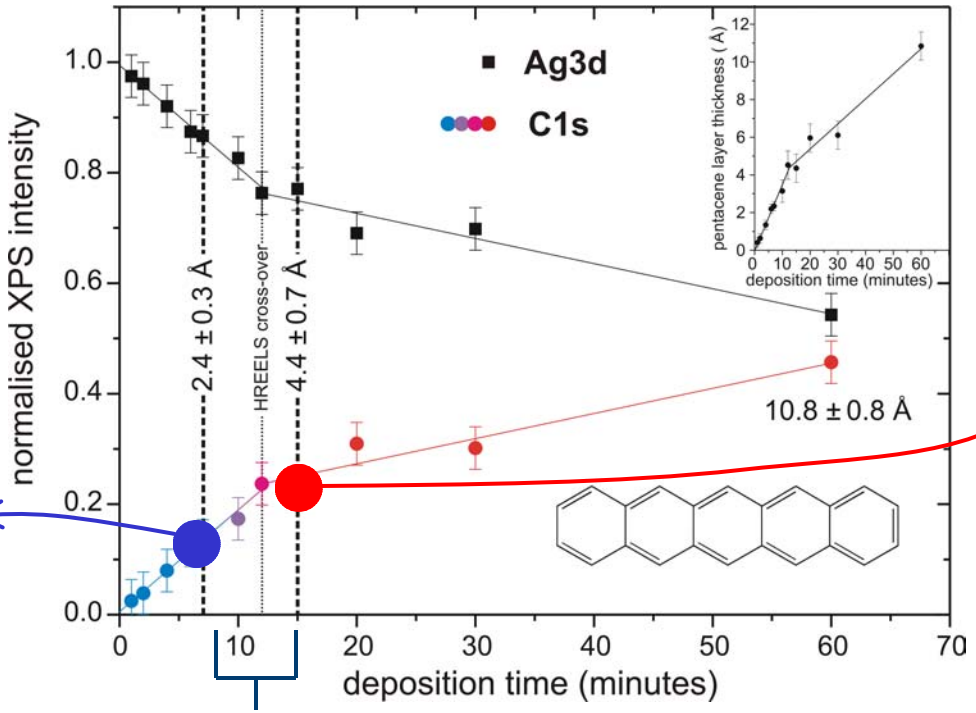
Eremtchenko, FST, et al. Physical Review B 72, 115430 (2005)

Pn / Ag(111) @ RT: Order on a Disordered Contact Layer









STM

Decrease of the sticking coefficient

Eremtchenko, FST, et al. Physical Review B 72, 115430 (2005)

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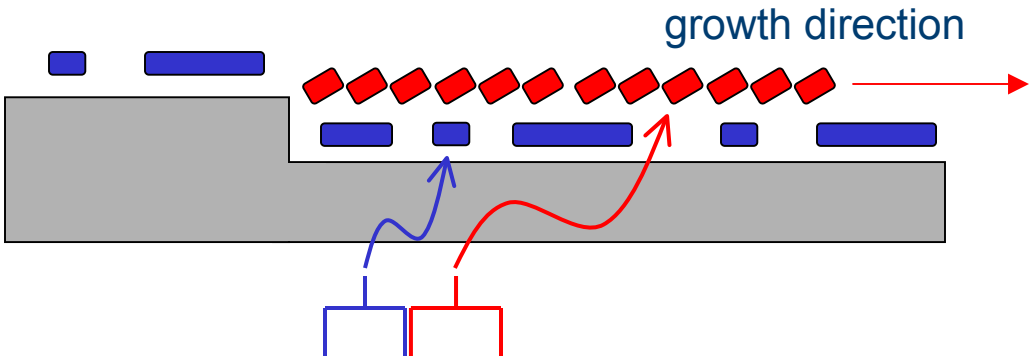
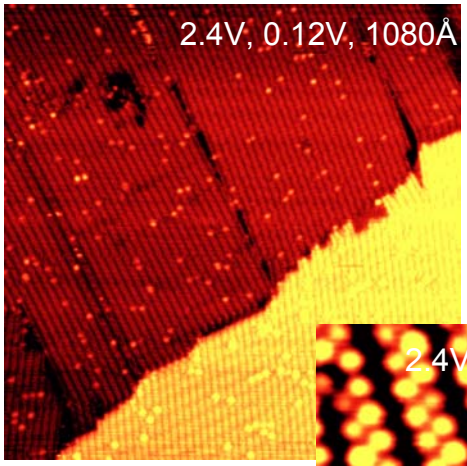
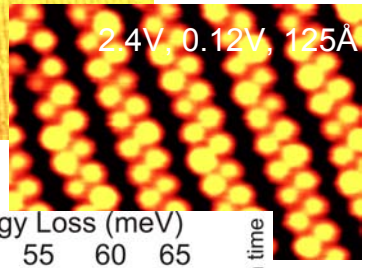
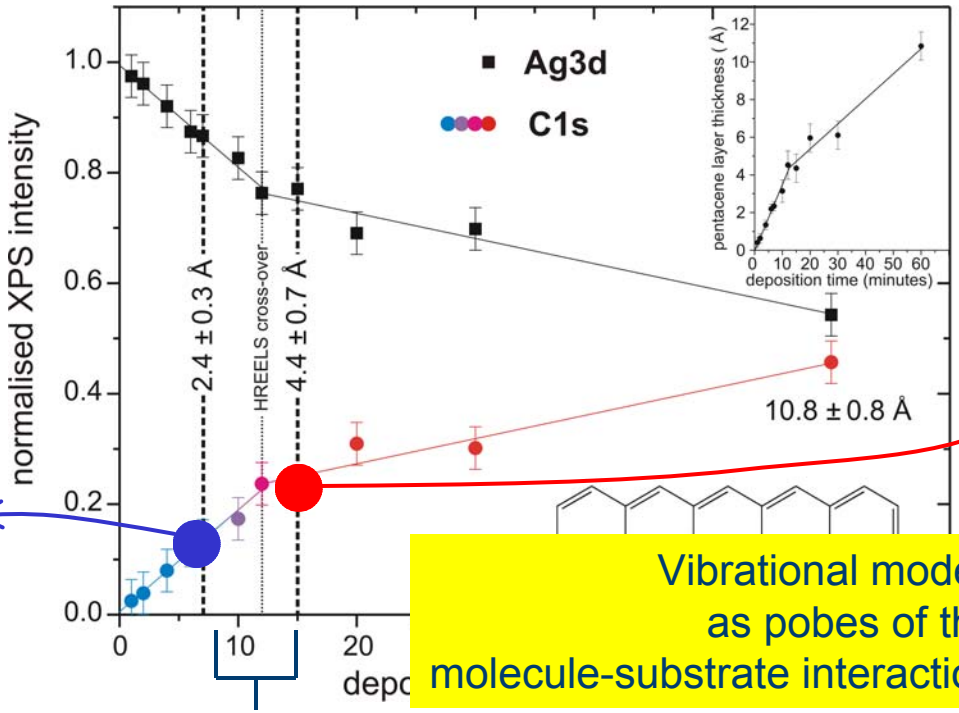


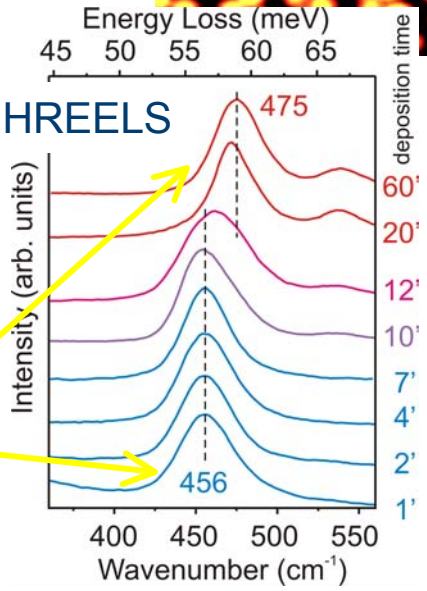






STM

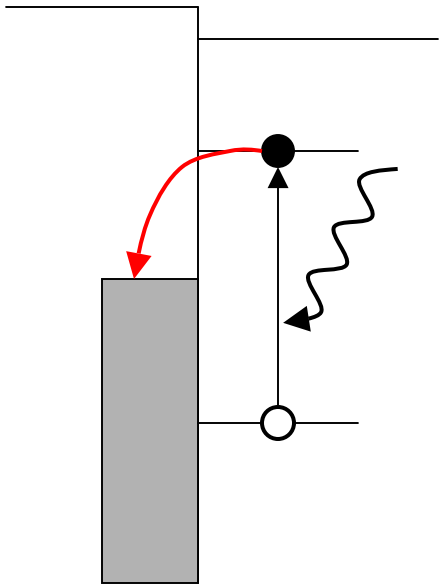
Vibrational modes as pobes of the molecule-substrate interaction



Decrease of the sticking coefficient

Eremtchenko, FST, et al. Physical Review B 72, 115430 (2005)

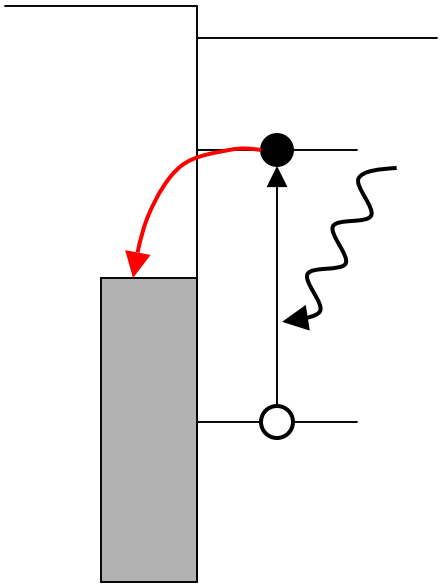
Luminescence Properties at Interfaces



metal molecule

PL is quenched

Luminescence Properties at Interfaces



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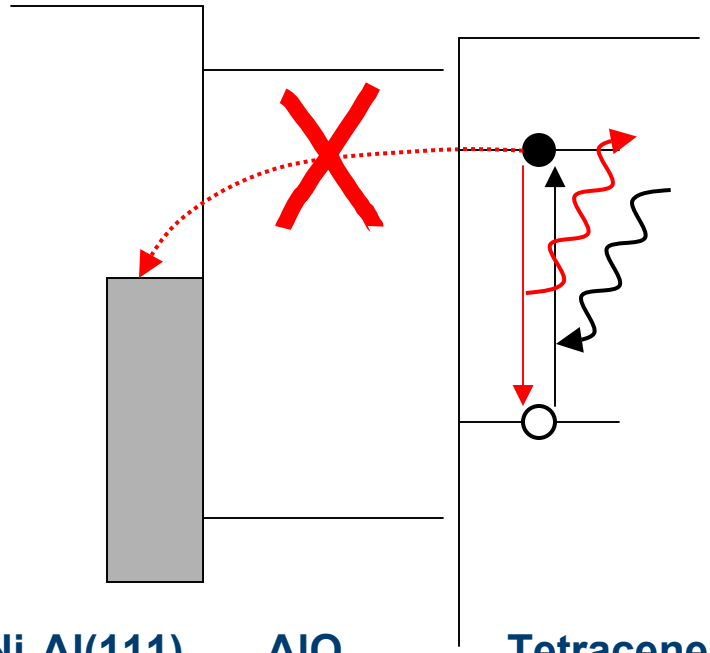


$Ni_3Al(111)$ AlO_x Tetracene

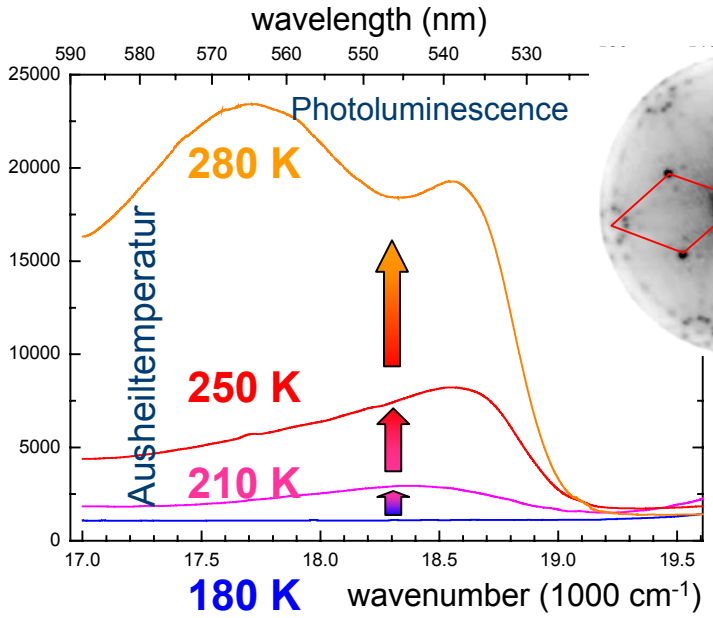
free molecule PL?

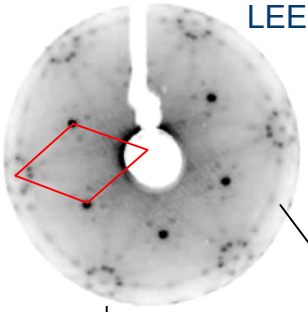
Luminescence is quenched for Tetracene on $AlO_x/Ni_3Al(111)$ at 80 K deposition, luminescence reappears after annealing of the film.

M. Schneider at al., J. Luminescence 110 (2004) 275

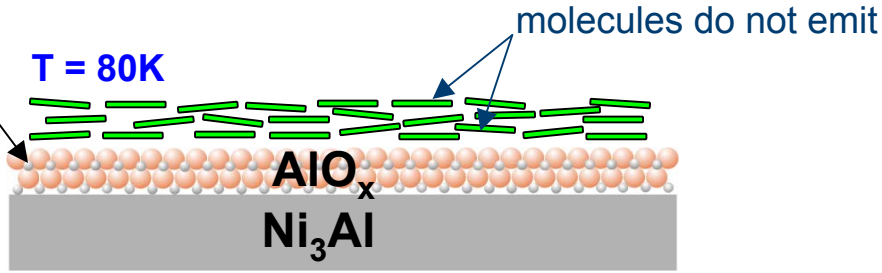
Do molecular orientation and film morphology influence the luminescence behaviour?

AlO_x / $Ni_3Al(111)$: Luminescence and Film Morphology

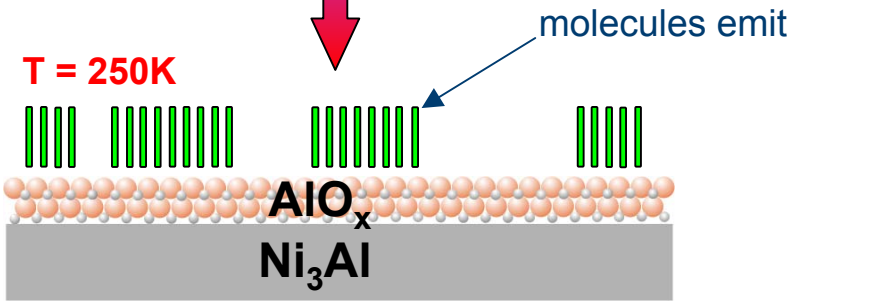




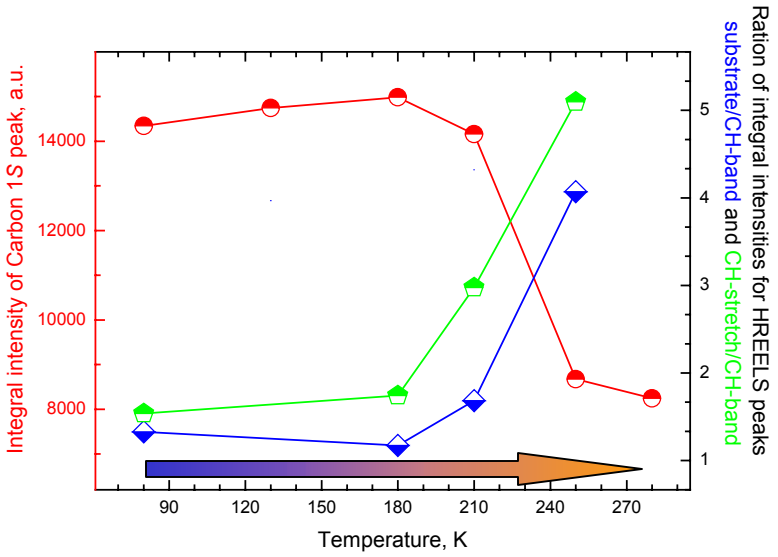
Double layer of epitaxial AlO_x
LEED 58 eV



~ 3 flat lying tetracene layers



~ 0.6 upright tetracene layers



Model on the basis of ARXPS and HREELS

Soubatch, FST et a. Surface Science, in press (2006), published online 17. August 2006

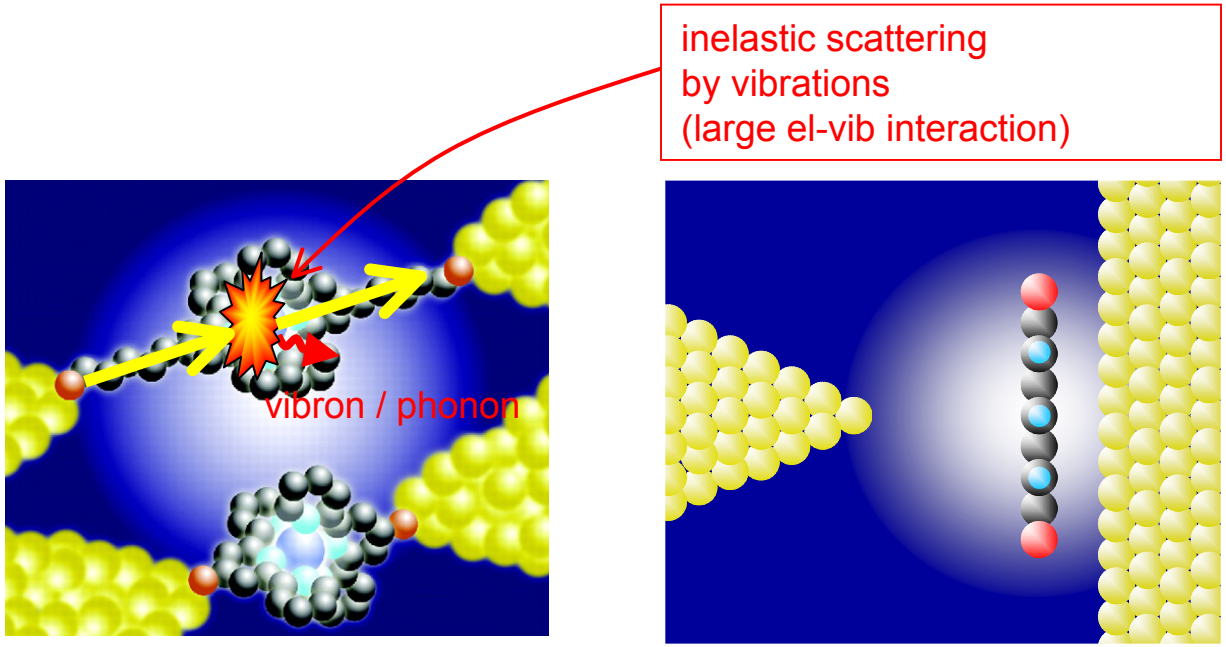
Functions of Molecular Adsorbate Layers

a. Luminescence properties at interfaces

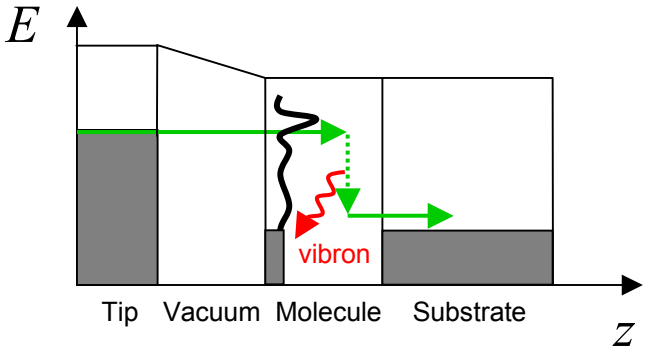
b. Transport through molecules

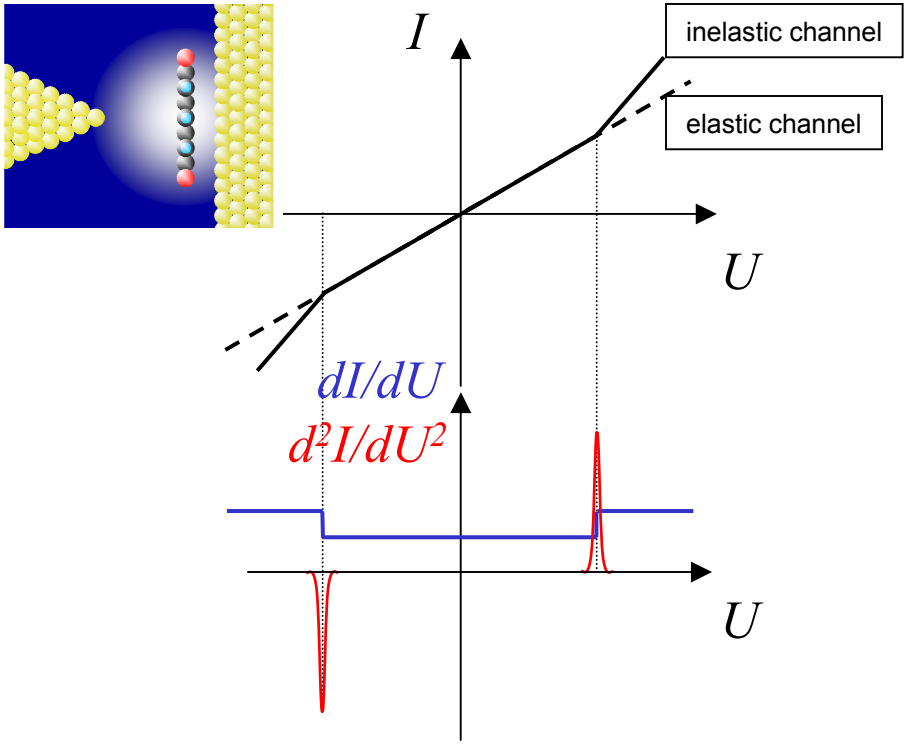
Transport through Molecules

Challenge: measuring conductance of single molecules



Inelastic Tunnelling Spectroscopy (IETS)





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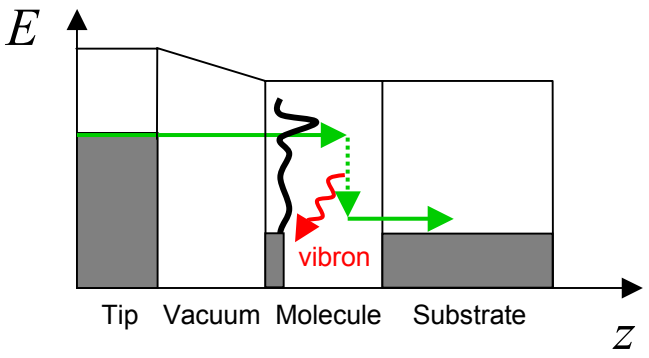

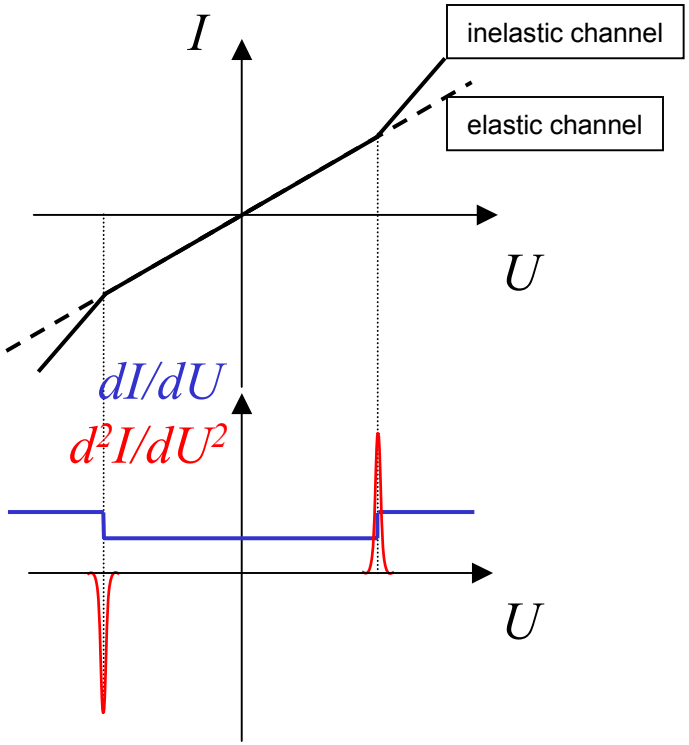

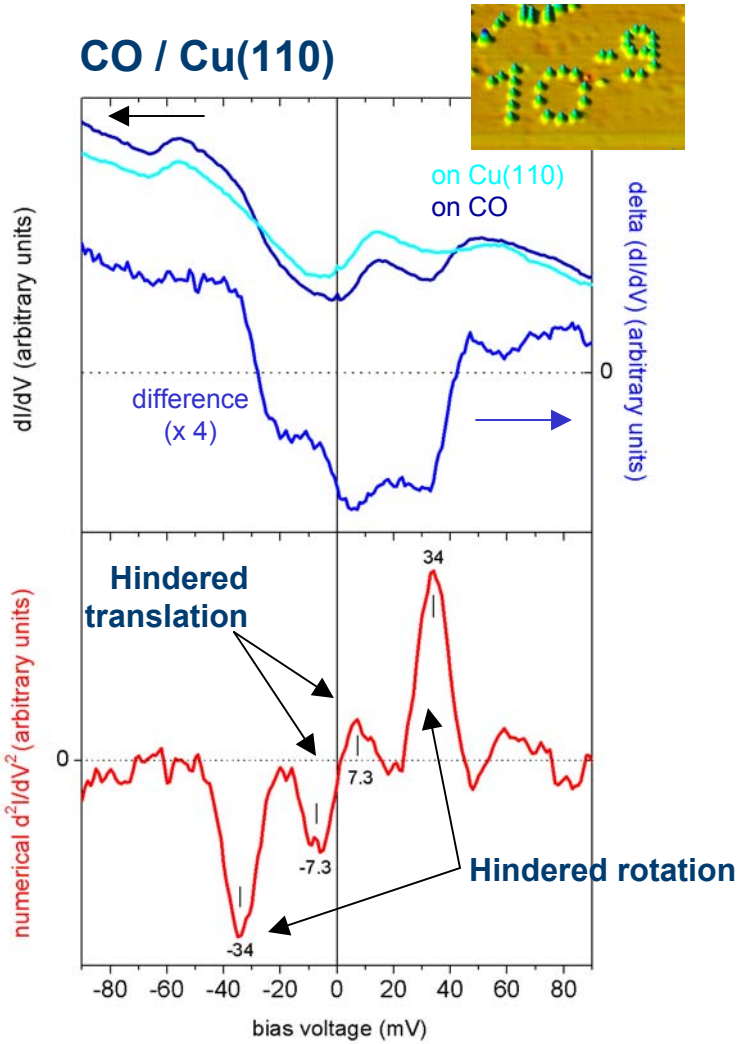

Summary: Bonding – Structure – Functions

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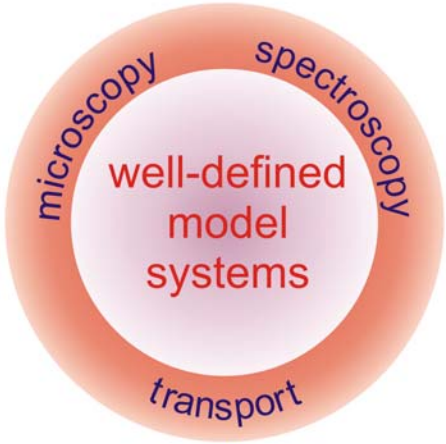

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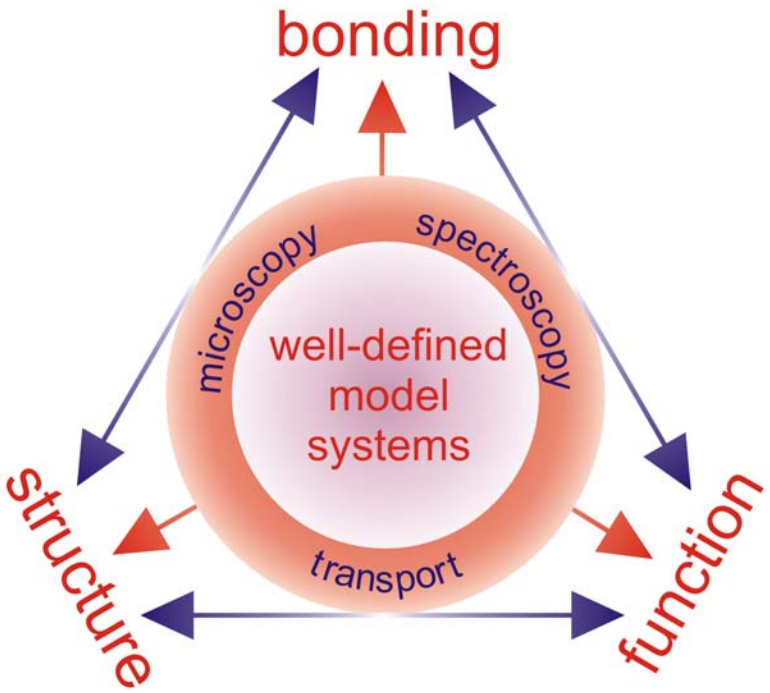

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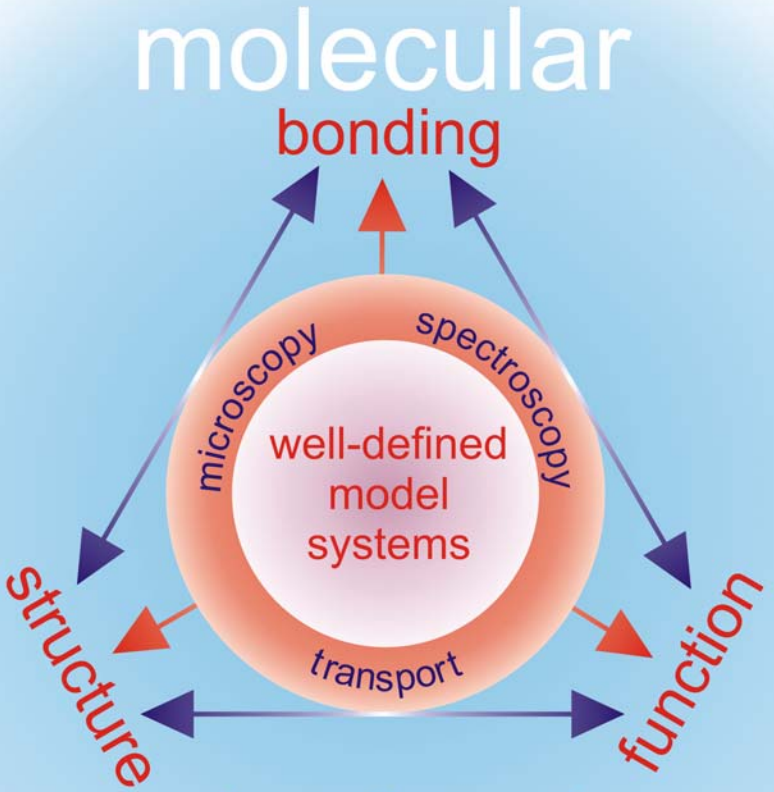

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