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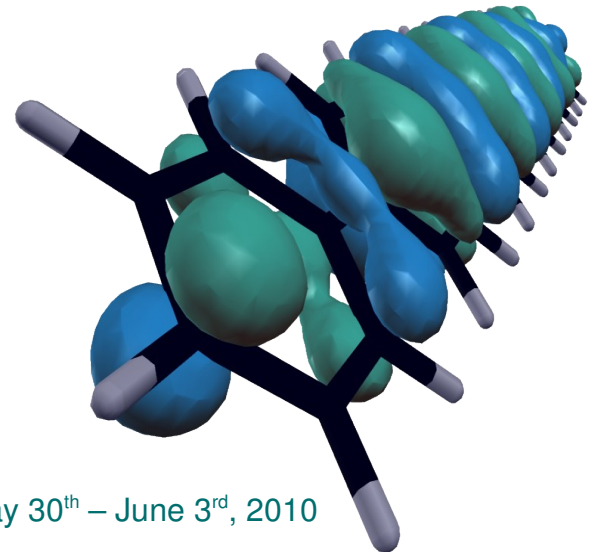
Structural and Electronic Properties of Organic Molecular Films from Density Functional Theory



Collaborations and Funding

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Institut für Festkörperphysik, TU Graz
Paul Frank
Adolf Winkler
Roland Resel

The work is part of the National Research Network
„Interface controlled and functionalized organic films“

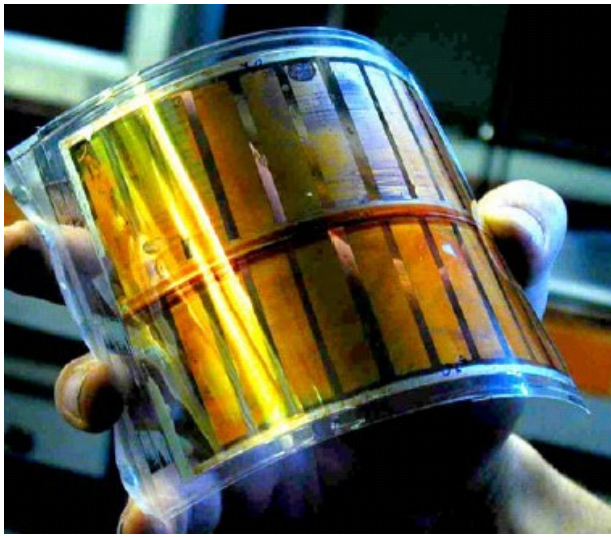
Motivation

White OLED

Area = 10x10 cm2 (from HC Starck CleviosTM PH510 PEDOT layer)

OLED display

(from Samsung, ultra-thin 0.05mm, 4-inch 480×272 resolution, 100,000:1 contrast , 200cd/m^2)



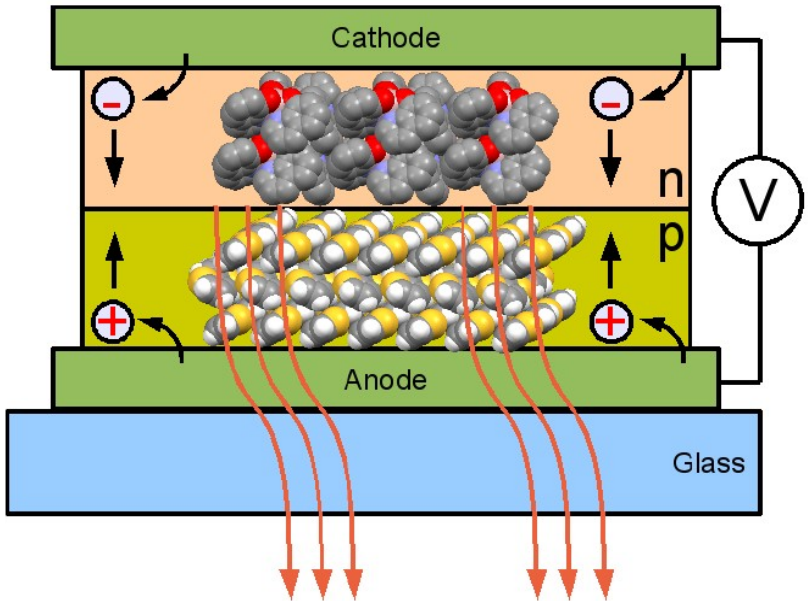
Organic Solar Cell

(Linz Institute for Solar Cells)

Advantages: large areas, mechanically flexible, low cost

Motivation

OLED



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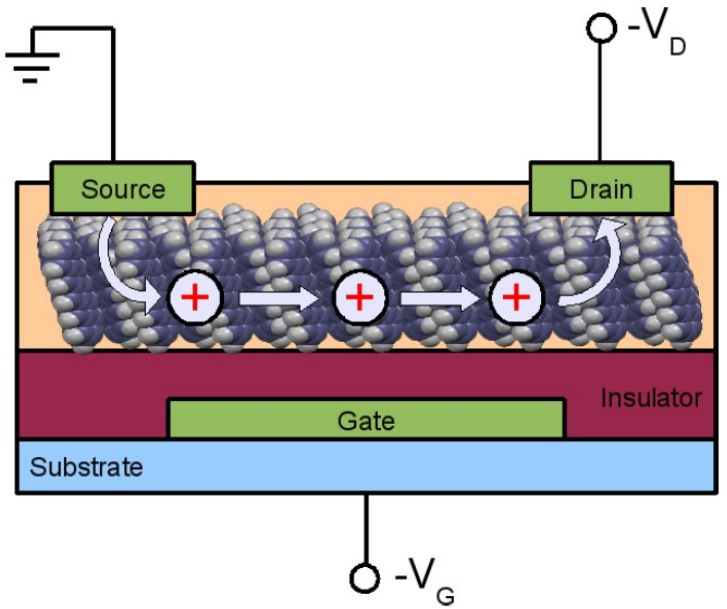
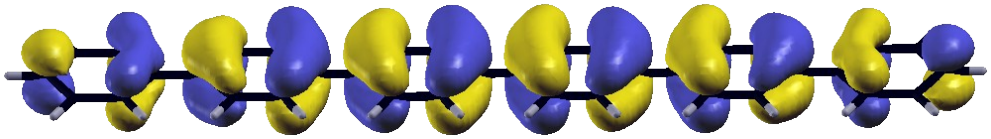
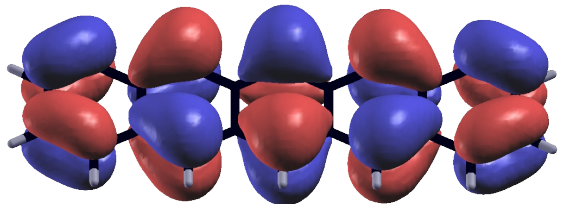




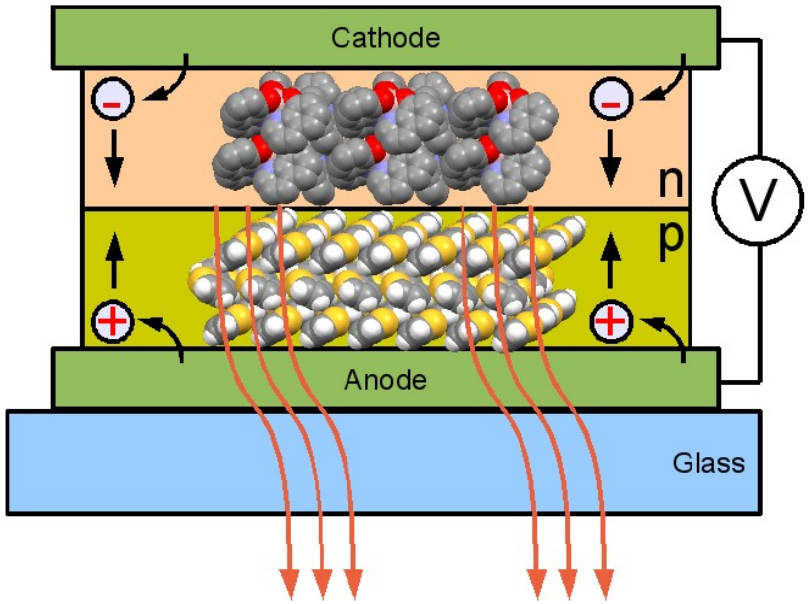
para-Sexiphenyl (6P) ($C_{36}H_{26}$)



Pentacene (5A) ($C_{22}H_{14}$)

Motivation

OLED



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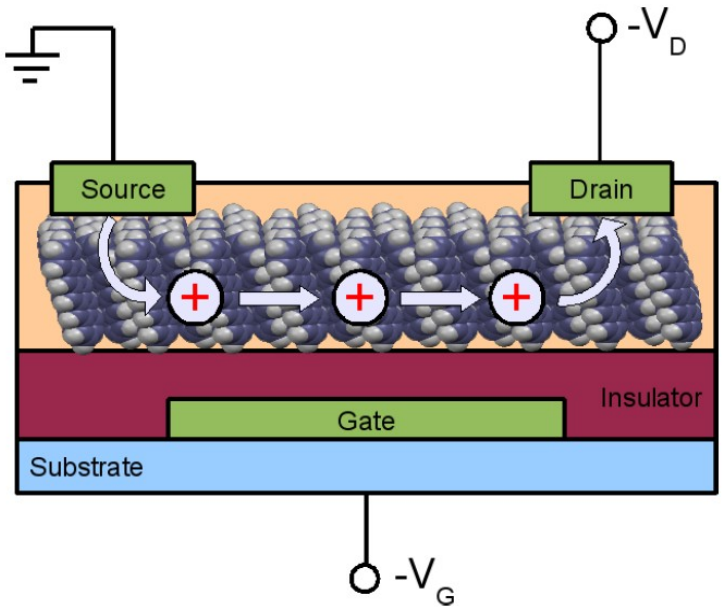
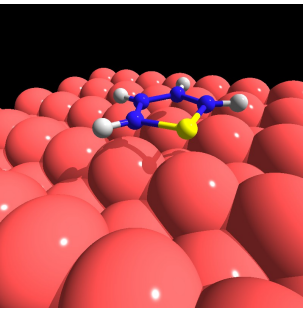


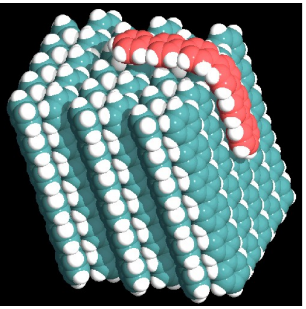
Challenges for Theory

– **Cohesive properties:** between molecules and at organic / metal interface
– **Thin film growth:** molecular orientation, morphology, growth modes
– **Electronic structure:** band gaps, level alignment, electronic states at the interfaces
– **Optical properties:** excitonic effects

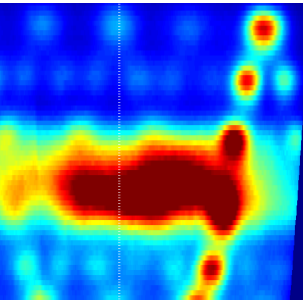
Overview



I. Cohesive Properties



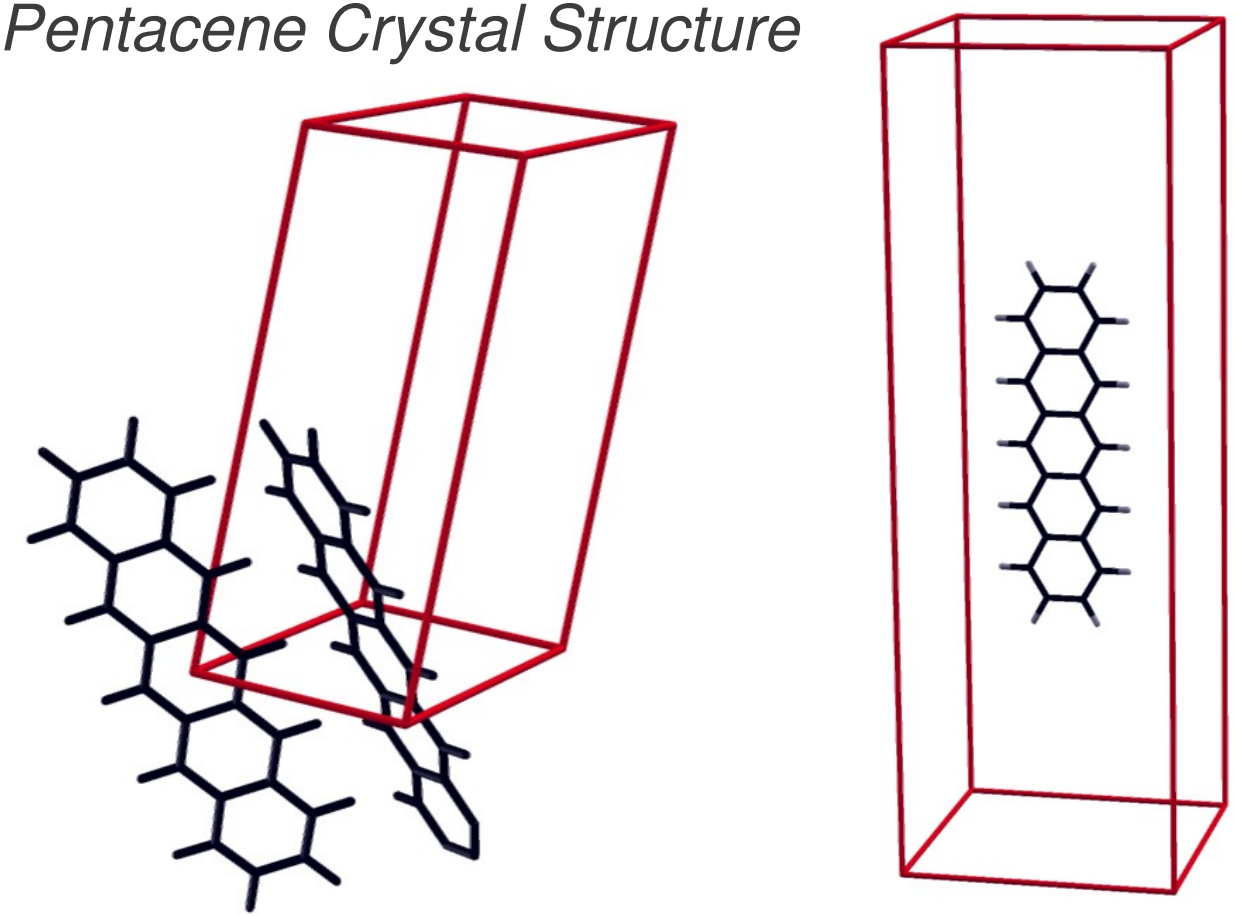
II. Kinetic Barriers in Growth



III. Electronic Structure

Cohesive Energy of Molecular Crystals

Pentacene Crystal Structure



$$E_{cohesive} = -[\ (1/2)E_{crystal} - E_{molecule}\ ]$$

DFT in a Nutshell

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

Kohn-Sham Equations

DFT in a Nutshell

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

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

atomic nuclei *Hartree potential* *exchange-correlation potential*

DFT in a Nutshell

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

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Self-consistency

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

DFT in a Nutshell

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

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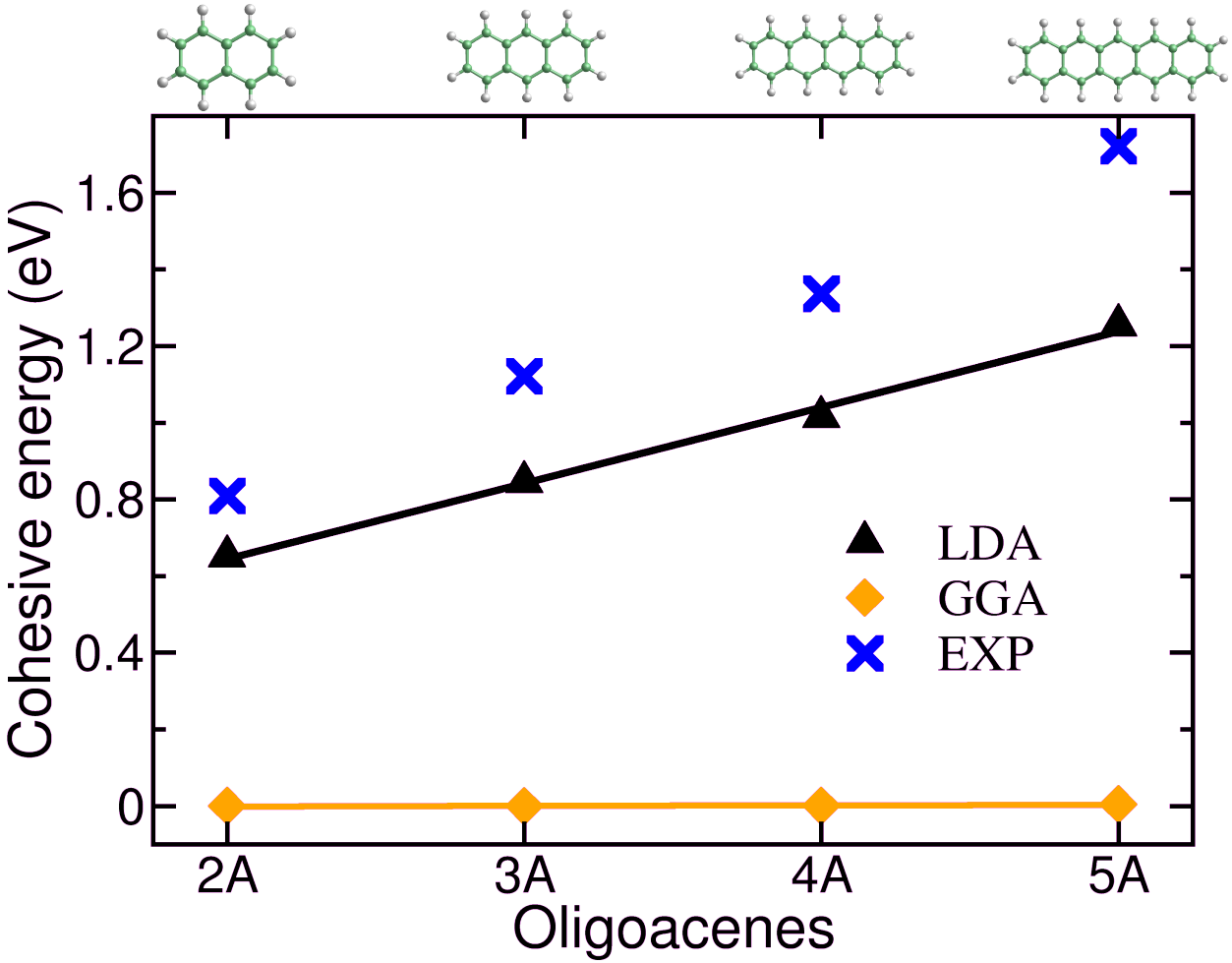
Approximations:
e.g.: LDA, GGA, ...

Self-consistency

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

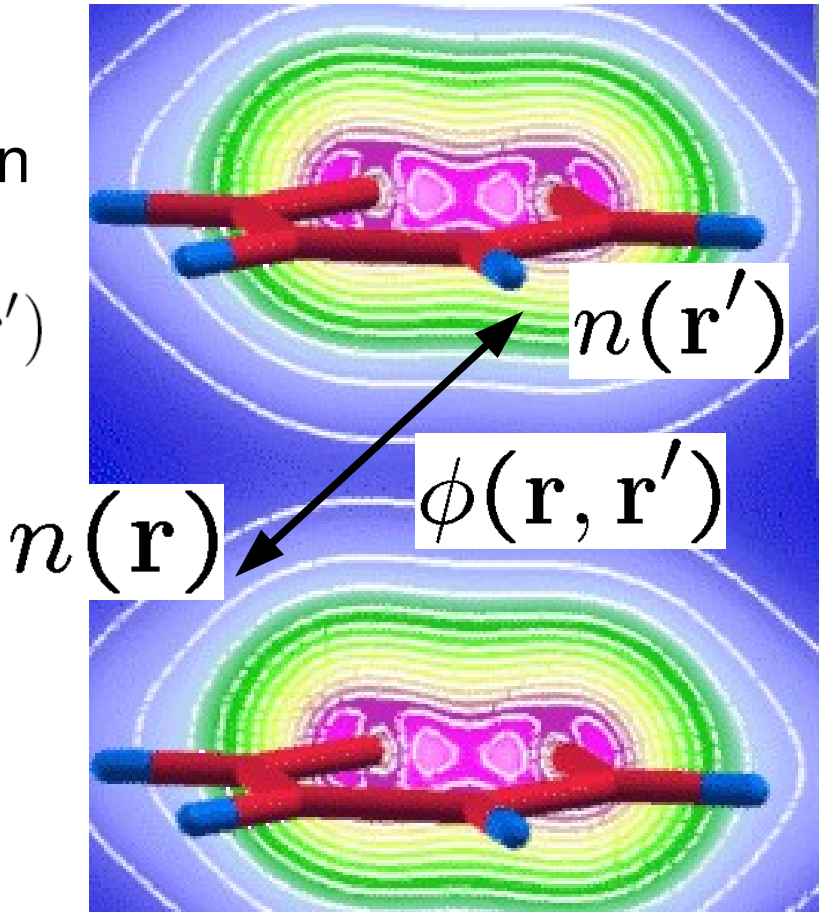
Cohesive Energy of Molecular Crystals



Van der Waals Density Functional

Nonlocal Correlation Energy
leading to van-der-Waals interaction

$$E_c^{\mathrm{nl}} = \frac{1}{2} \int d^3r d^3r' n(\mathbf{r}) \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}')$$

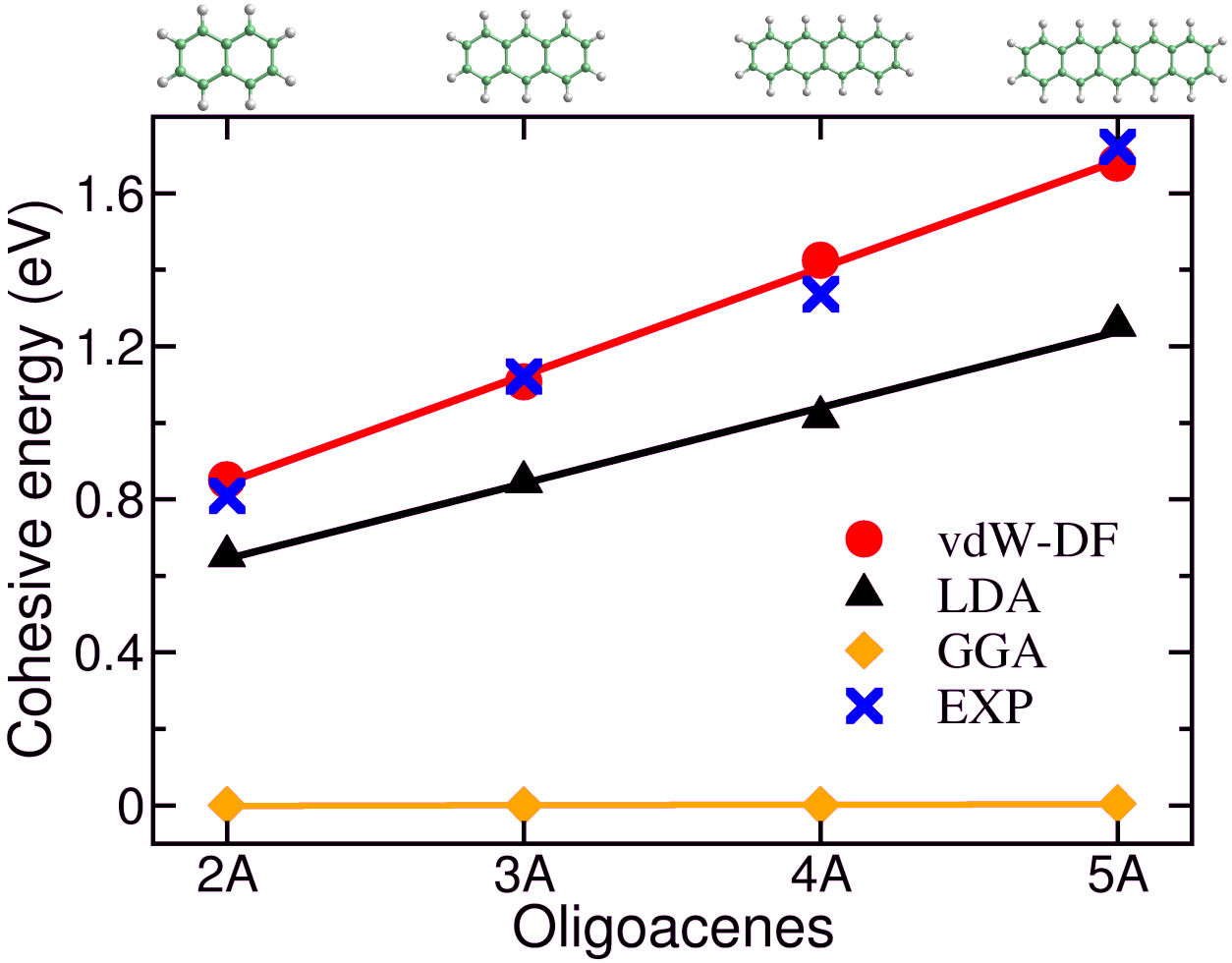


Exchange-Correlation Energy

$$E_{xc}^{\mathrm{vdWDF}} = E_x^{\mathrm{GGA}} + E_c^{\mathrm{LDA}} + E_c^{\mathrm{nl}}$$

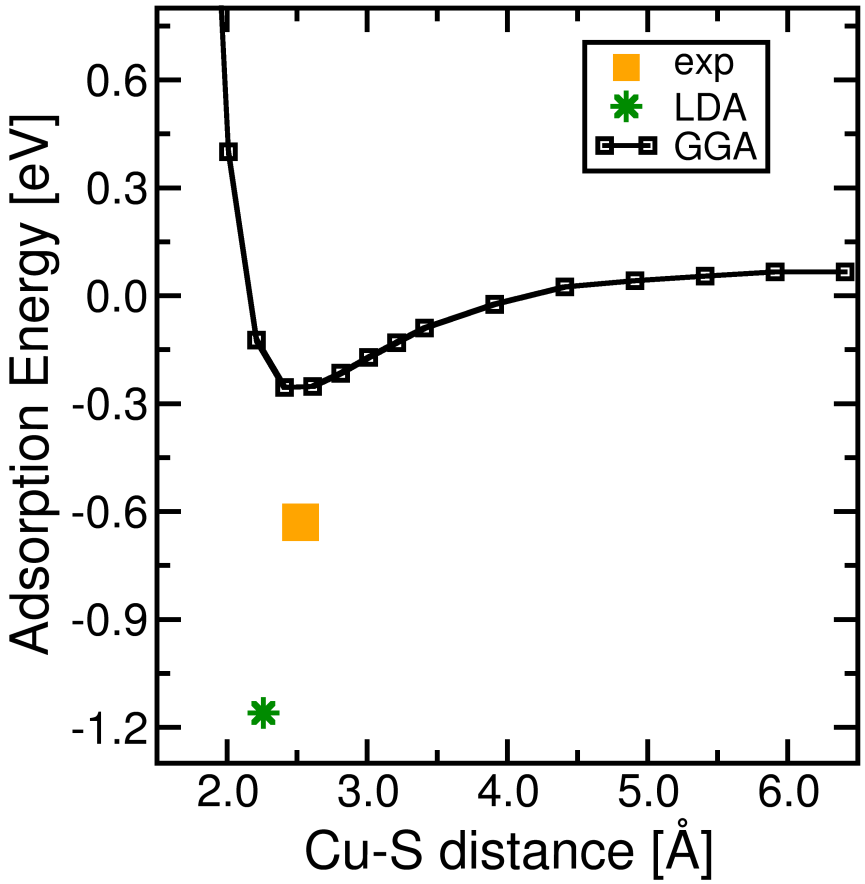
Dion et al, *Phys. Rev. Lett.* ***92****, 246401 (2004).*

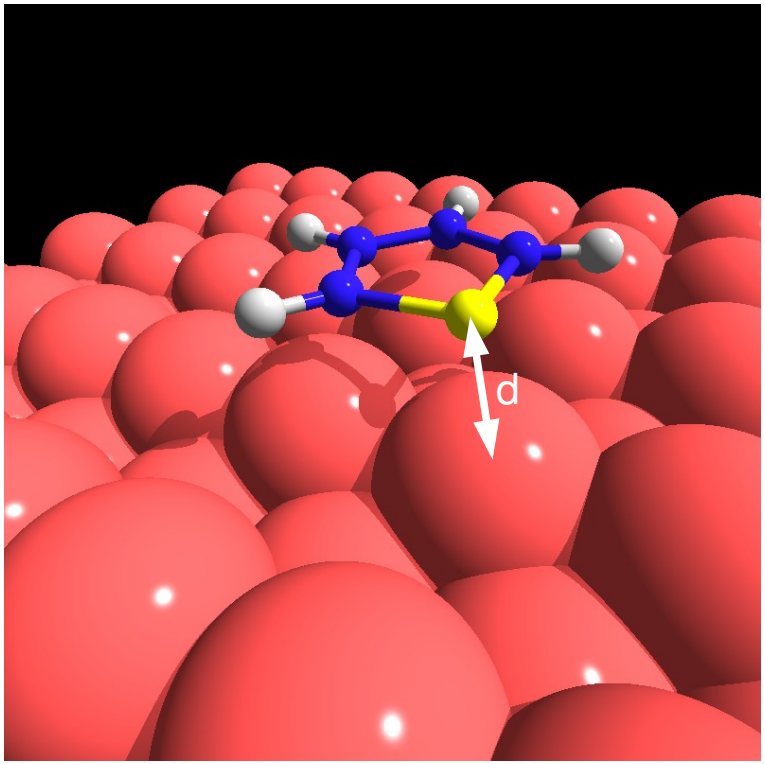
Cohesive Energy of Molecular Crystals



Nabok, Puschnig, Ambrosch-Draxl, *Phys. Rev. B* ***77****, 245316 (2008).*

Thiophene / Cu(110)





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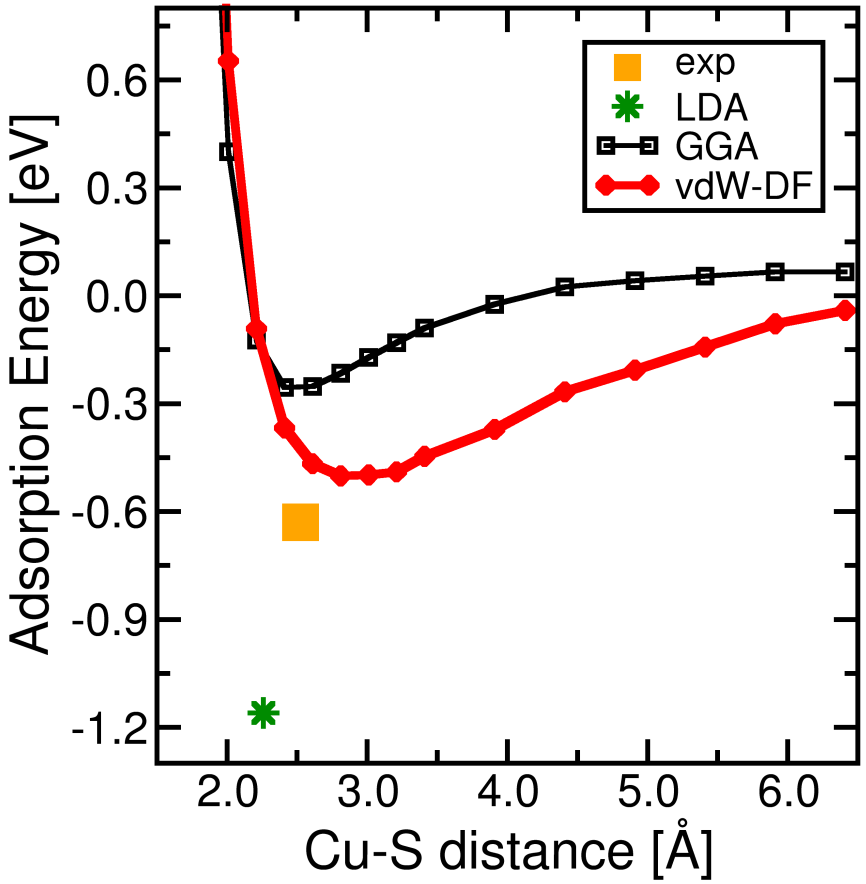
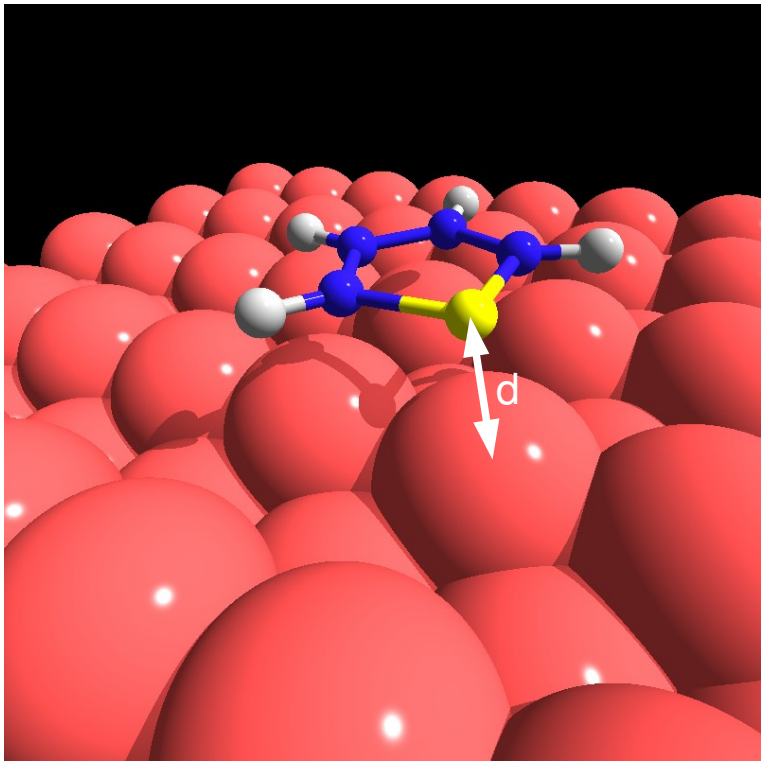
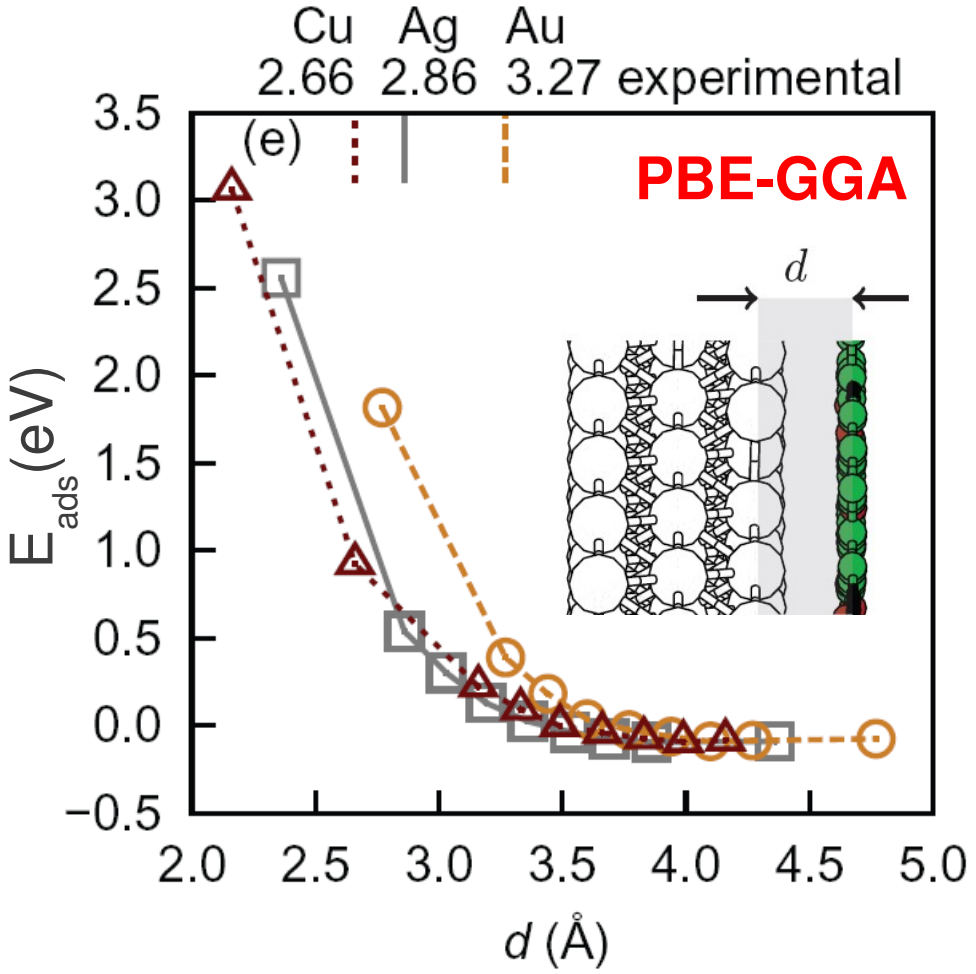
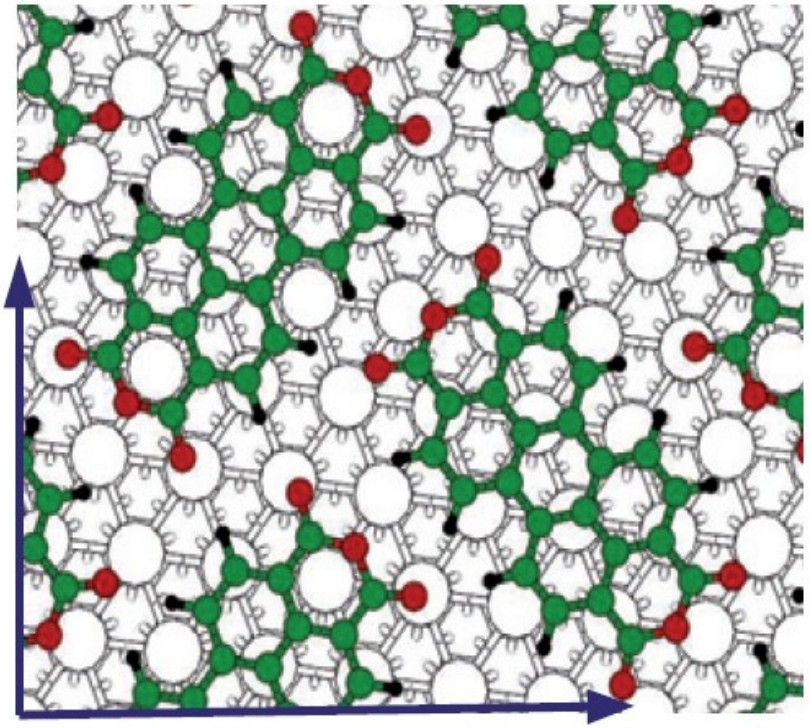




Sony, Puschnig, Nabok, Ambrosch-Draxl, *Phys. Rev. Lett.* ***99****, 176401 (2007).*

PTCDA / Coinage Metals

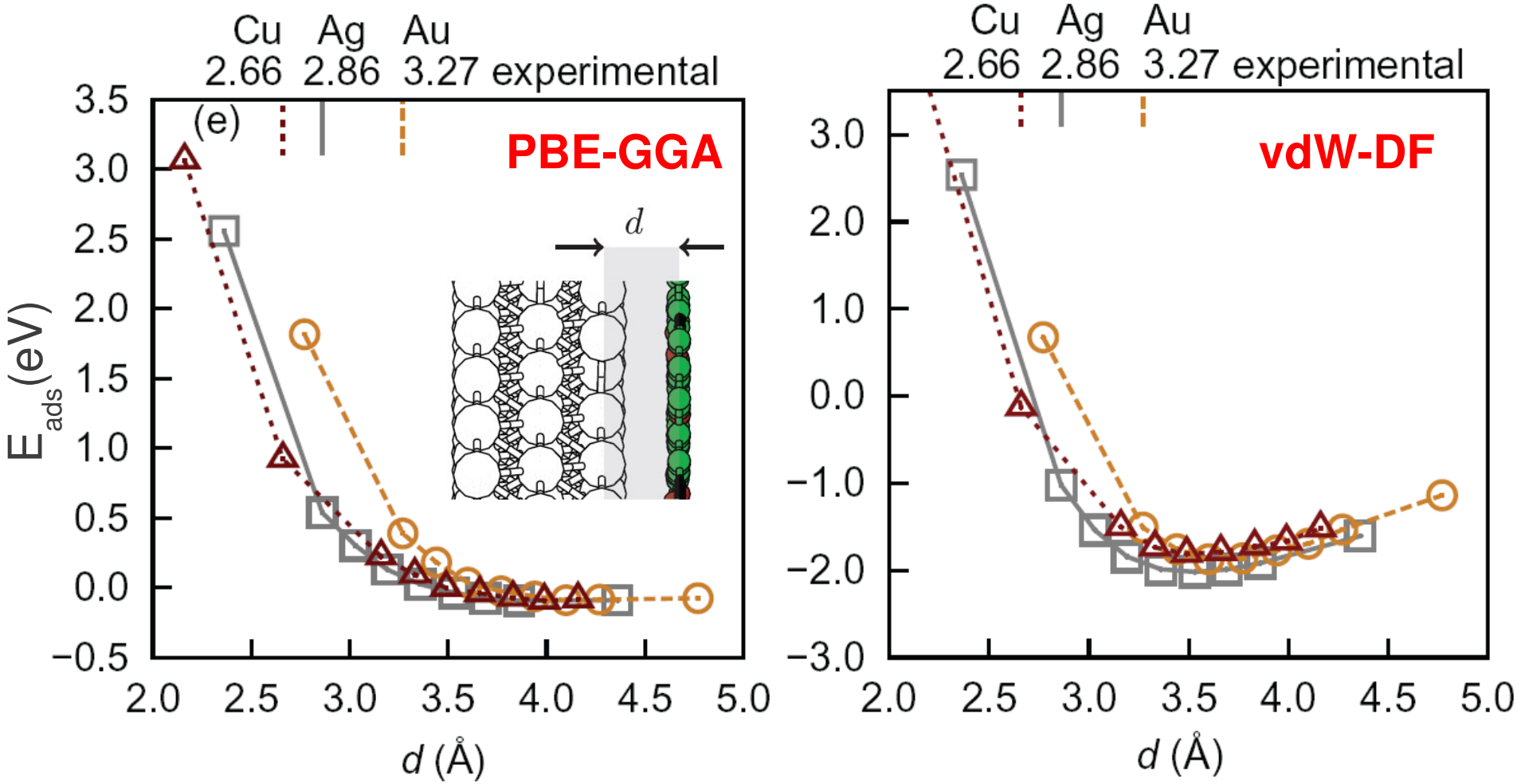




PTCDA / Ag(111)

Romaner, Nabok, Puschnig, Zojer, Ambrosch-Draxl, *New. J. Phys.* **11**, 053010 (2009).

PTCDA / Coinage Metals



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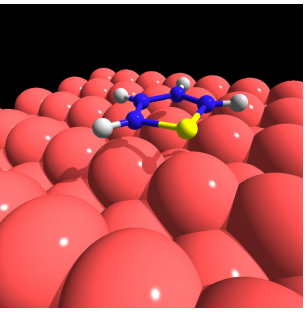
Overview



Van der Waals Interactions within DFT

Organic / organic works fine; organic / metal interactions still problematic

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Sony et al., *PRL.* **99**, 176401 (2007).

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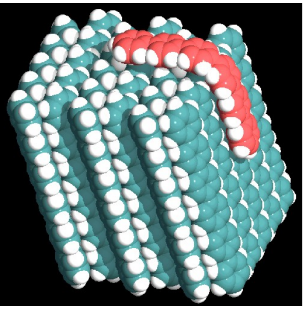

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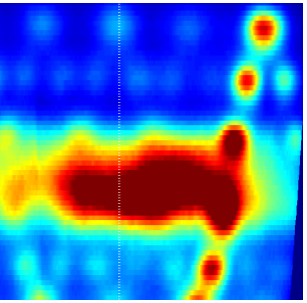
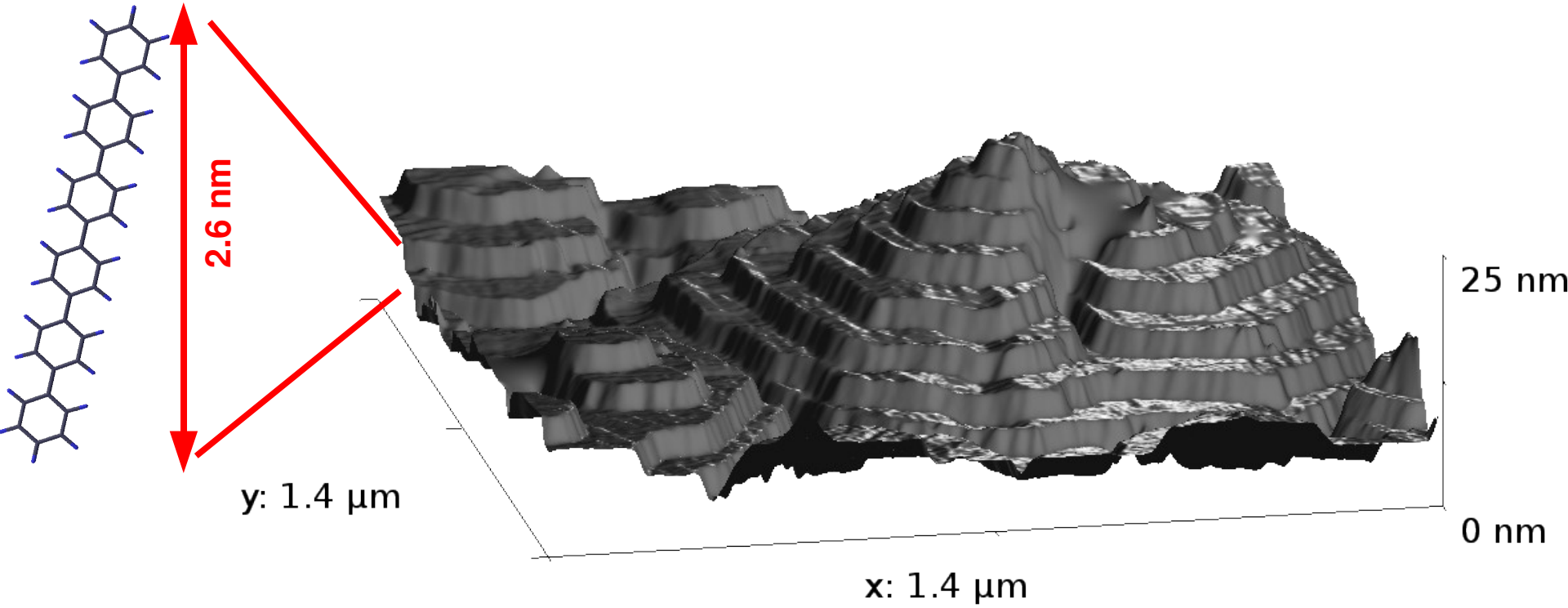


III. Electronic Structure

Molecular Mounds



AFM image: Sexiphenyl grown on a disordered mica surface

Molecular Mounds

Der Steirische Erzberg (Iron Ore Mine)

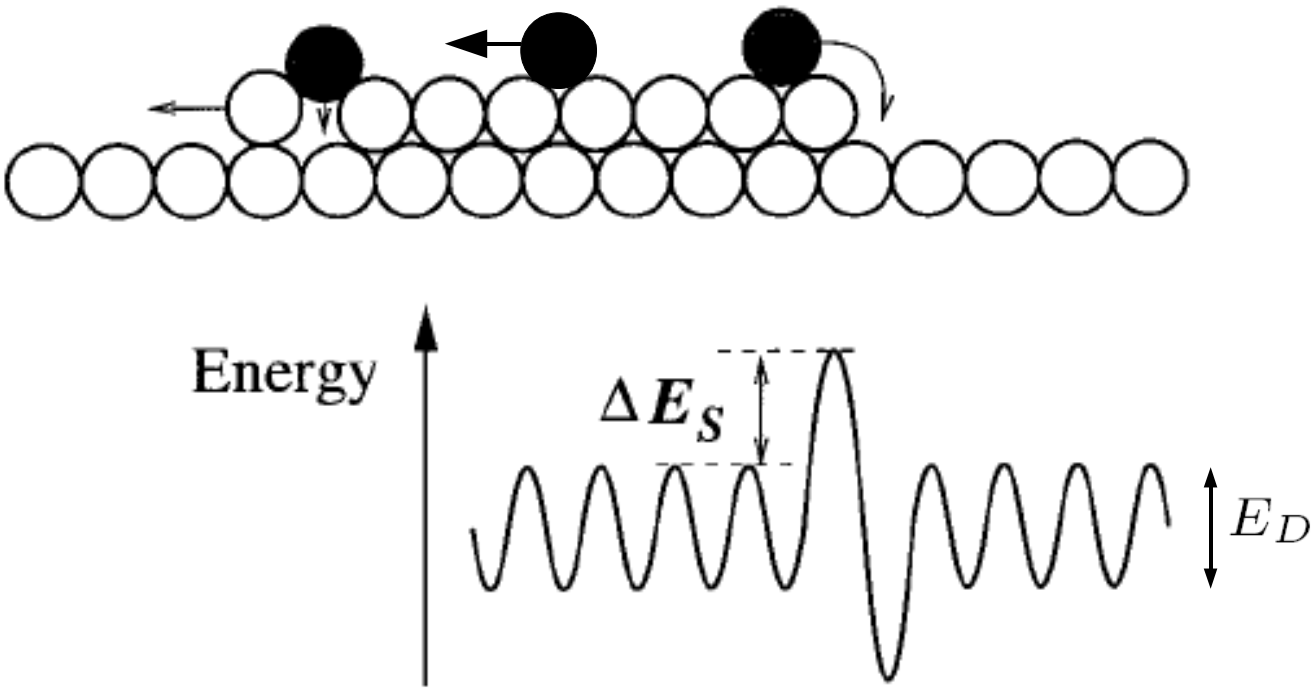
Ehrlich-Schwoebel Barrier (ESB)

Diffusion on a terrace

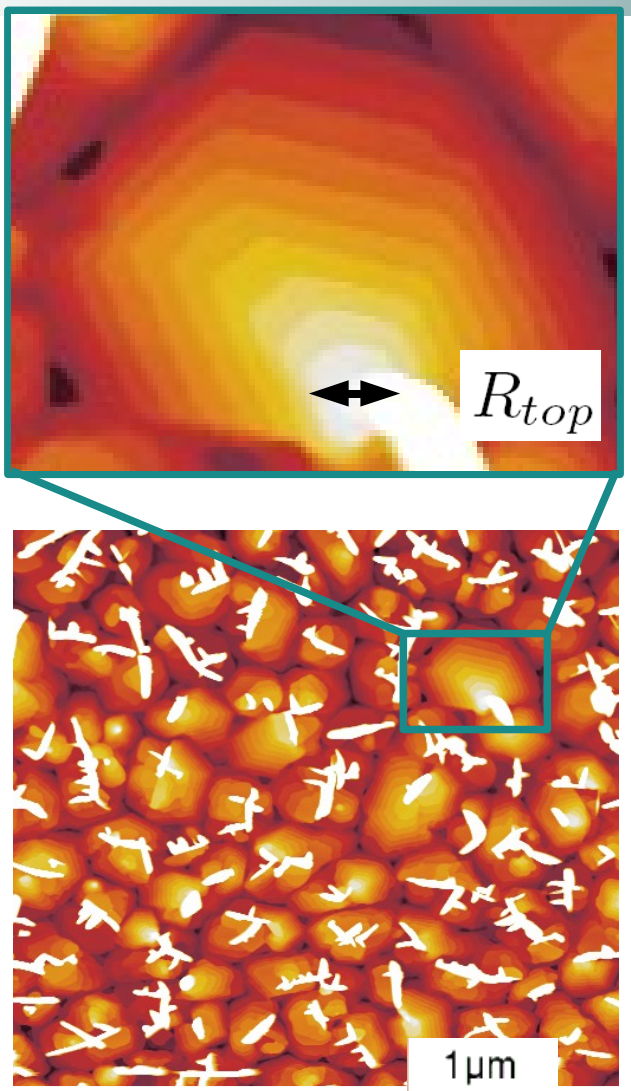
$$\nu = \nu_0 e^{-E_D/k_B T}$$

Interlayer jump rate

$$\nu' = \nu'_0 e^{-E_S/k_B T}$$



Sexiphenyl on Mica



AFM image: Film thickness = 30 nm

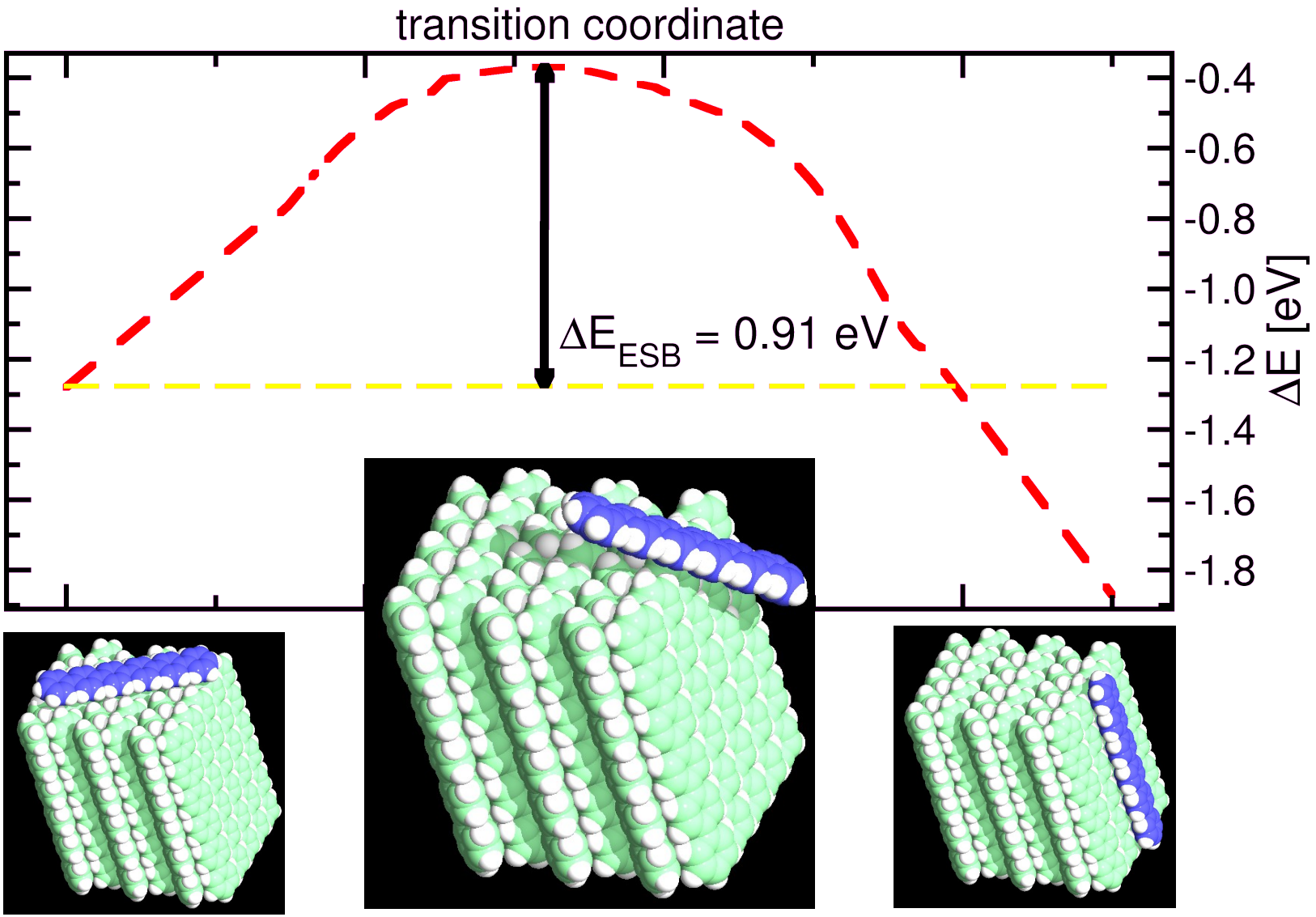
Ehrlich-Schwoebel Barrier = 0.67 eV

$$R_{top} \propto \left(\frac{\nu'}{F}\right)^{1/5} \approx 20 - 50nm$$

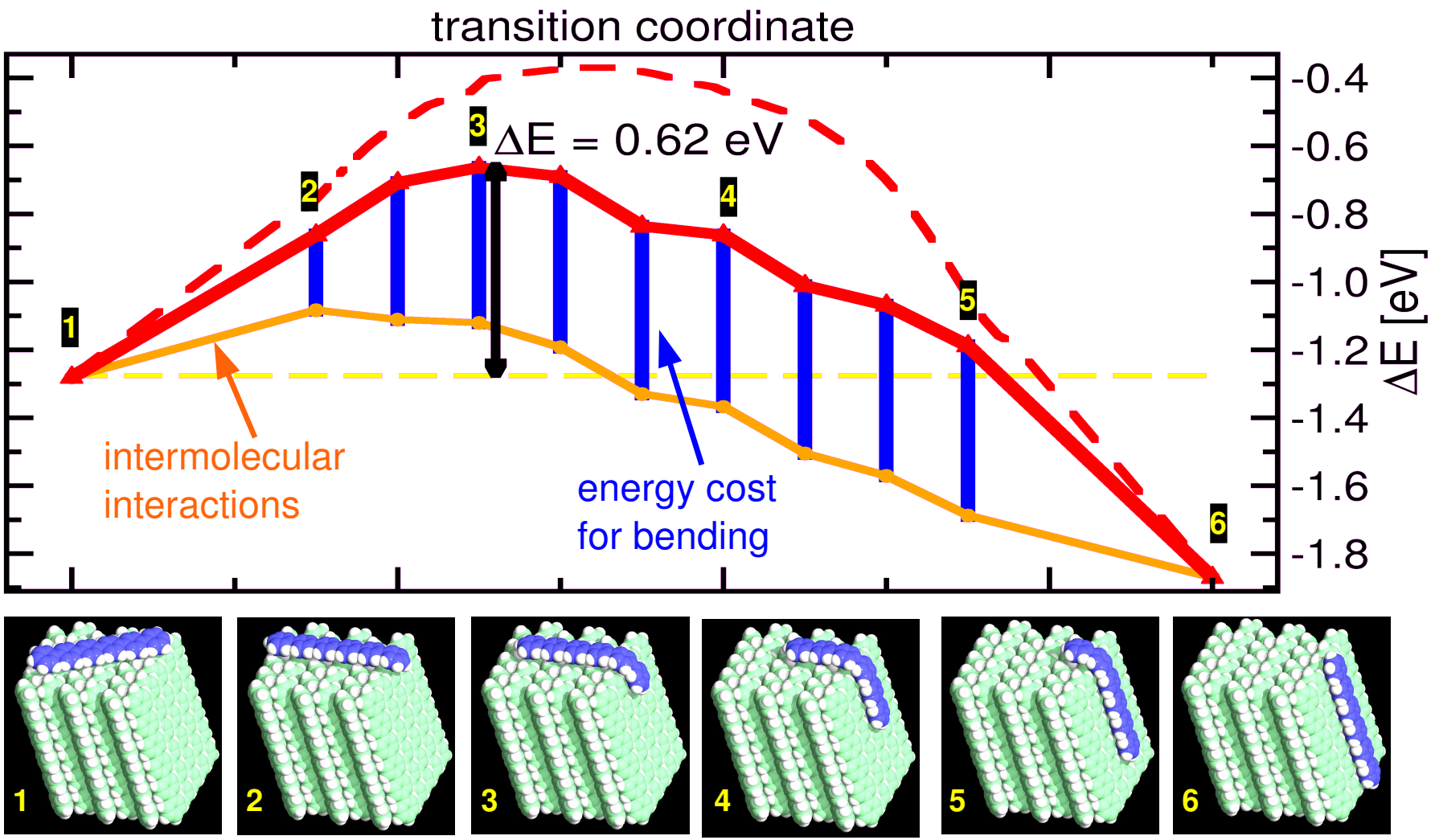
$$\omega = \frac{\tau}{(\Delta t)^2} = \frac{\text{residence time}}{(\text{deposition time})^2}$$

2nd layer nucleation rate

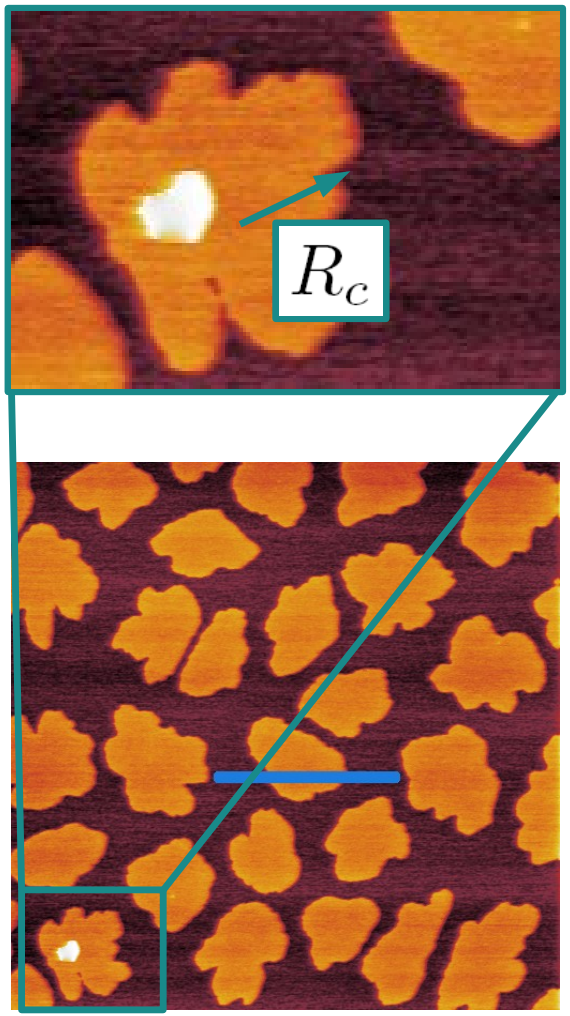
Step-Edge Barrier



Step-Edge Barrier



Layer-Dependent ESB



AFM image: Film thickness = 1nm

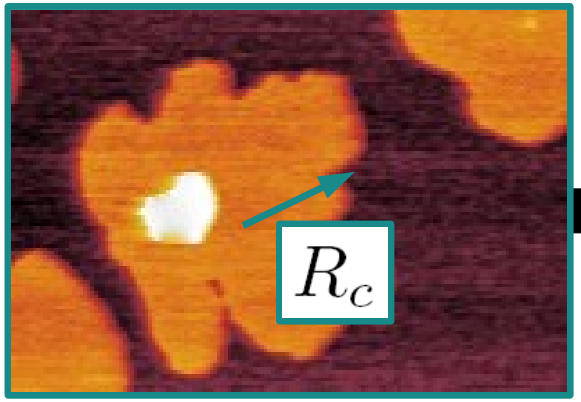
ESB = 0.26 eV

$$R_c \propto \left(\frac{\nu'}{NF}\right)^{1/7} \approx 400nm$$

$$\omega = \frac{\tau}{(\Delta t)^2} = \frac{\text{residence time}}{(\text{deposition time})^2}$$

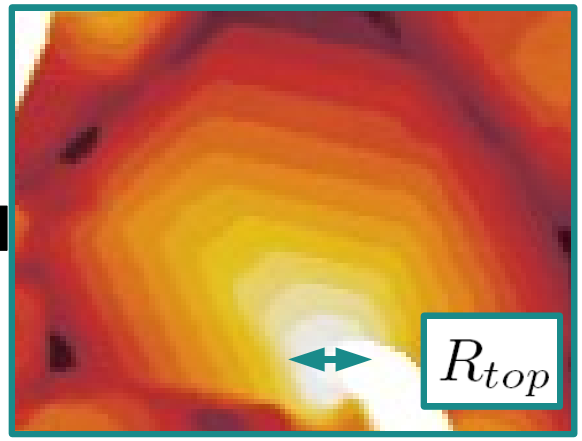
2nd layer nucleation rate

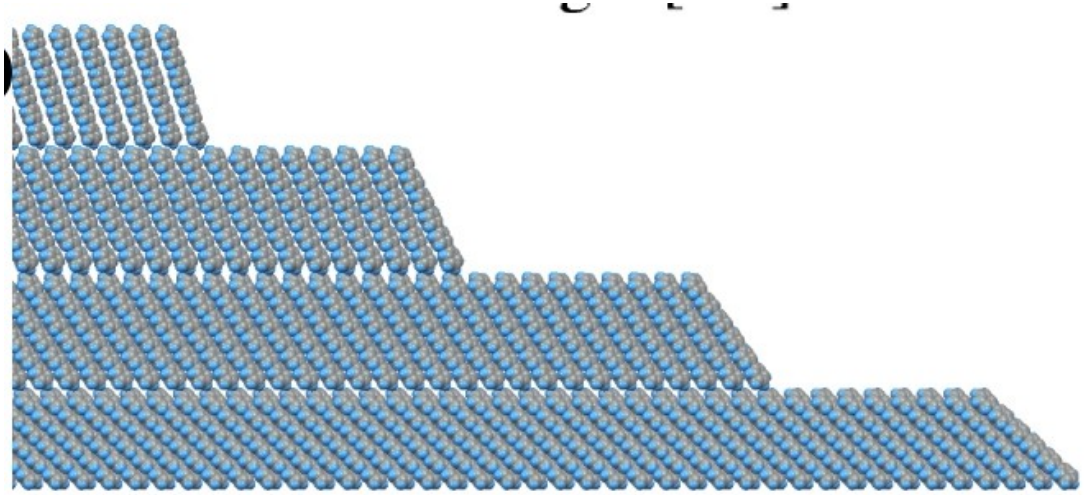
Layer-Dependent ESB



ESB

0.26 vs. 0.67





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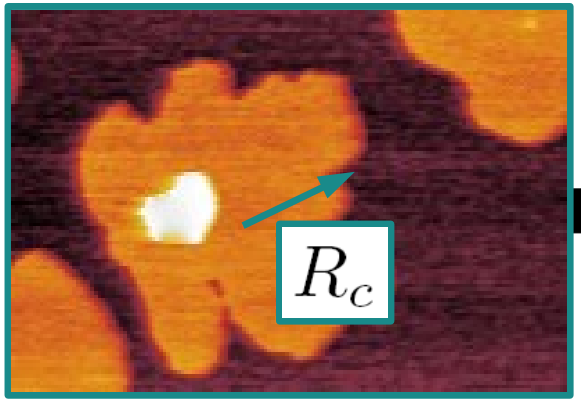
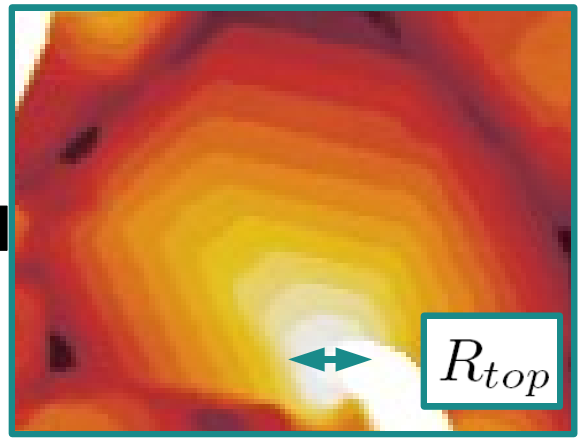
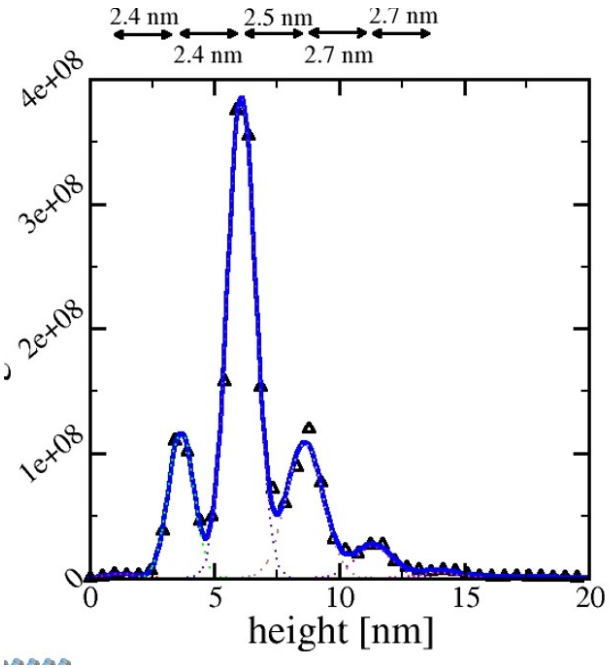
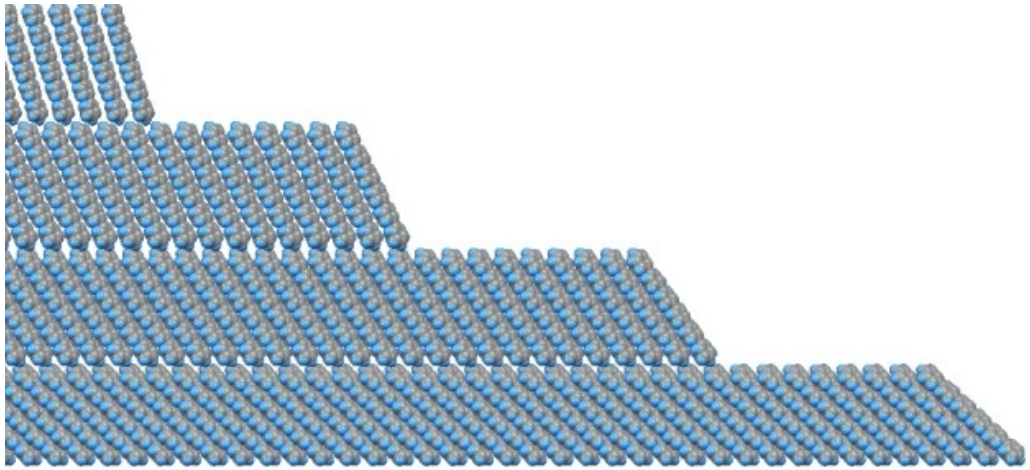


ESB

0.26 vs. 0.67







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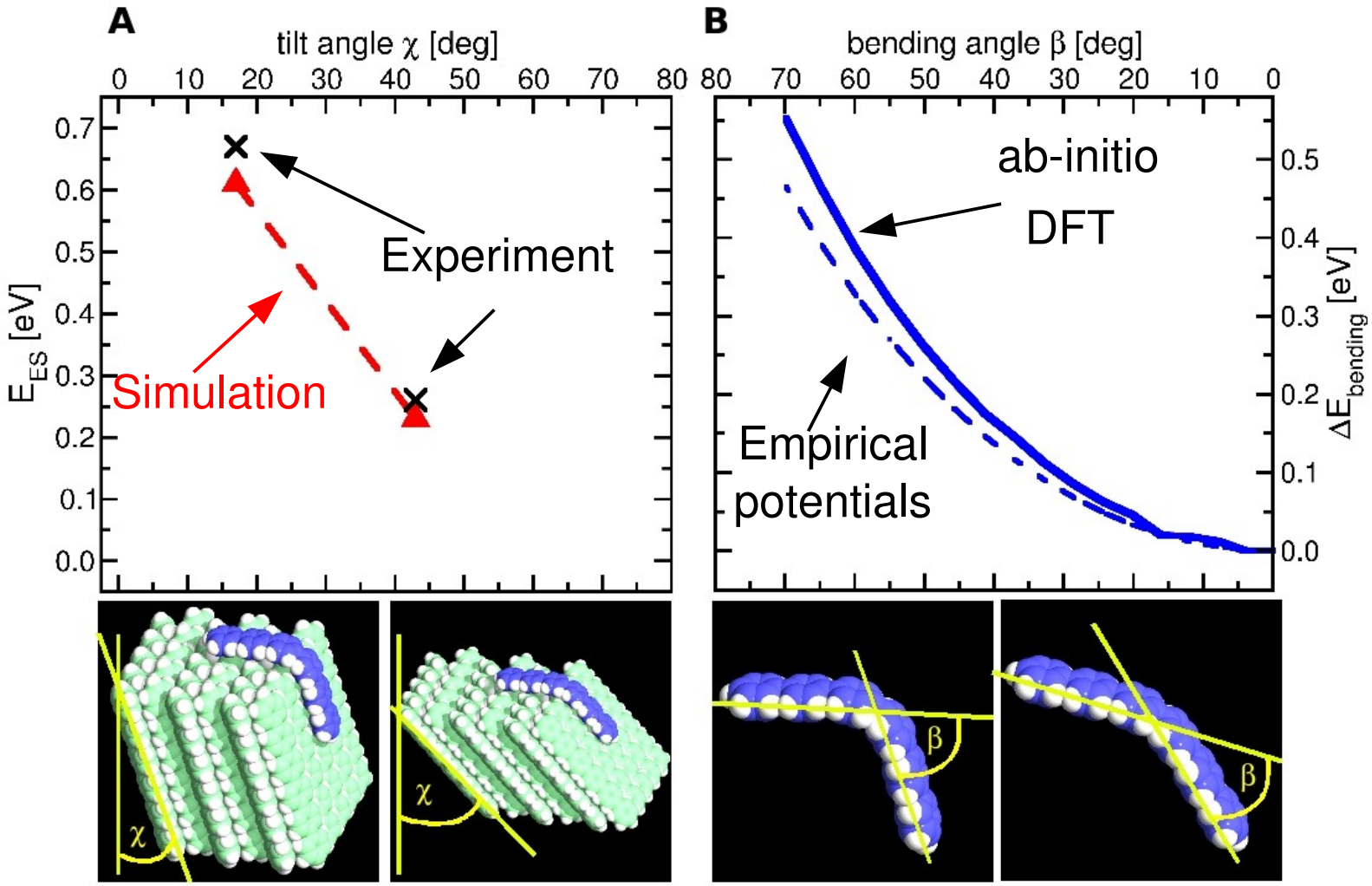
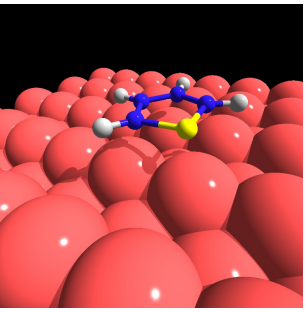


G. Hlawacek et al., *Science* ***321****, 108 (2008).*

Overview



Van der Waals Interactions within DFT

Organic / organic works fine; organic / metal interactions still problematic

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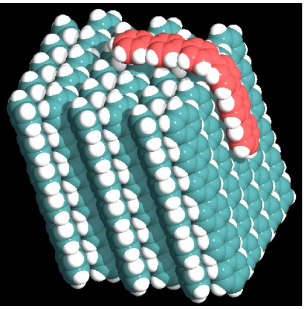
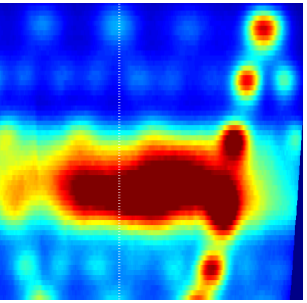
Sony et al., *PRL.* **99**, 176401 (2007).
Romaner et al., *NJP* **11**, 053010 (2009).



Organic Thin Film Growth

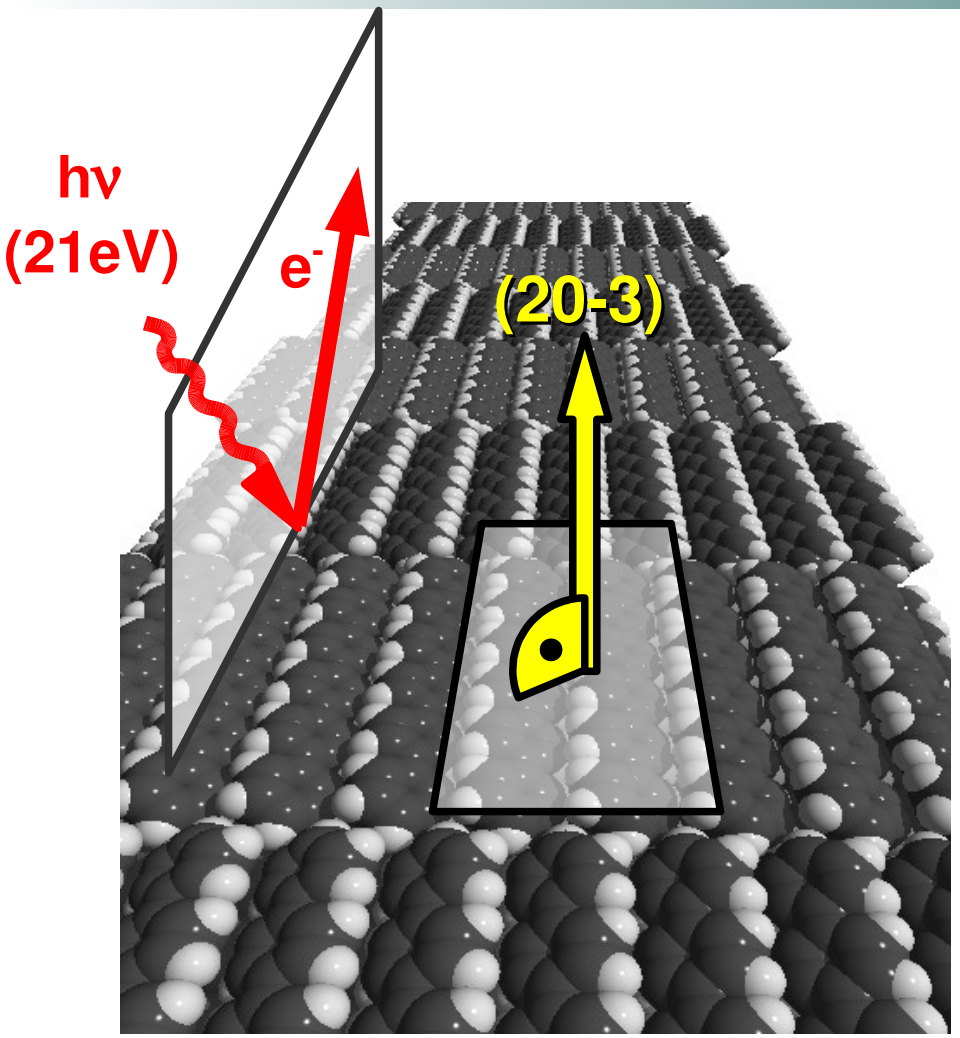
Some success in understanding certain kinetic barrieres,
but still a lot of work to do ...

G. Hlawacek et al., *Science* **321**, 108 (2008).
See also: Goose et al., *PRB* **81**, 205310 (2010).



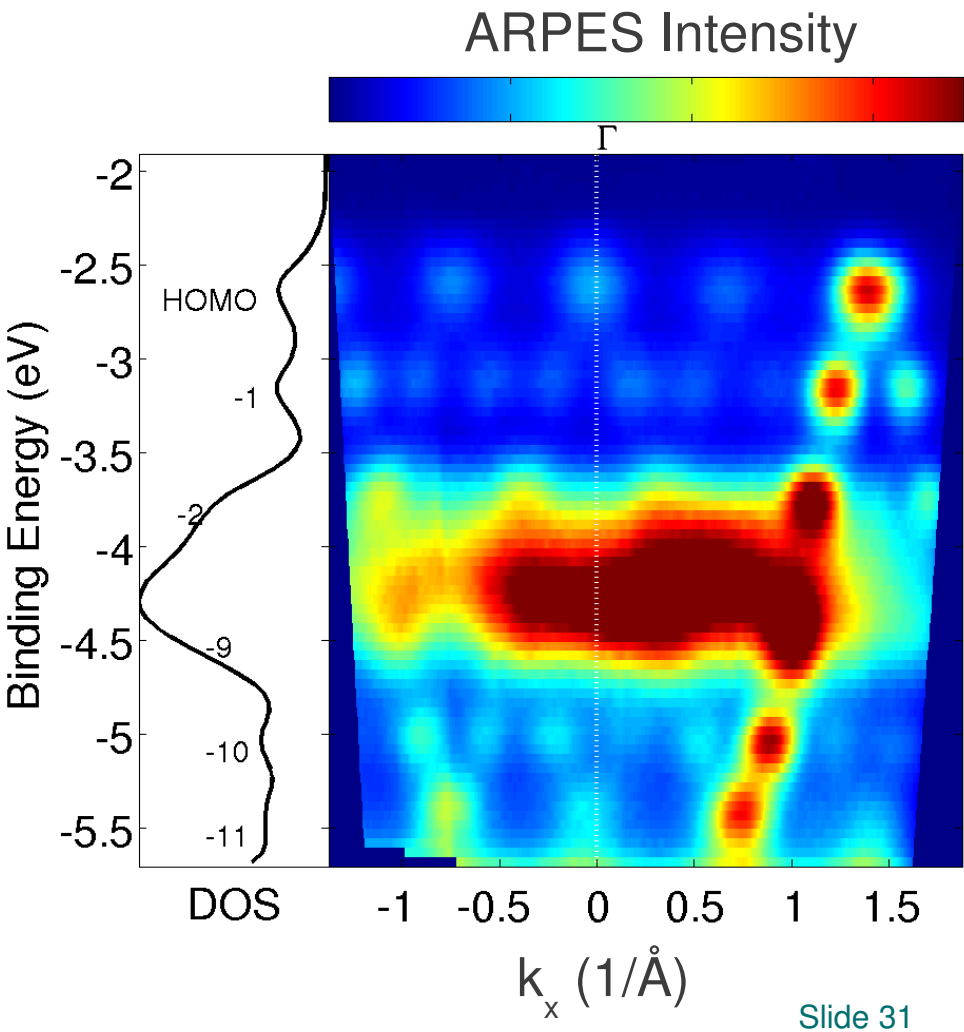
III. Electronic Structure

Uniaxially Aligned Sexiphenyl

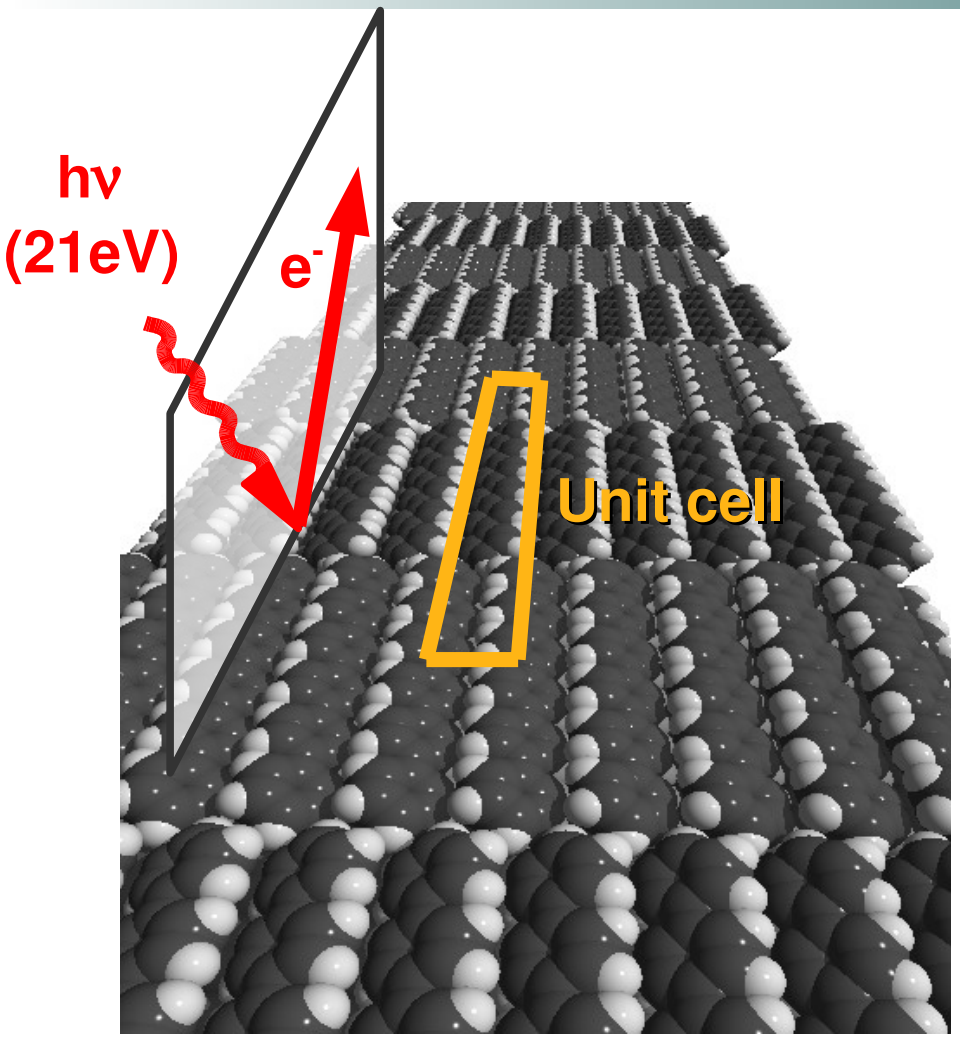


Uniaxially ordered para-sexiphenyl film
on Cu(110)_(2x1)O

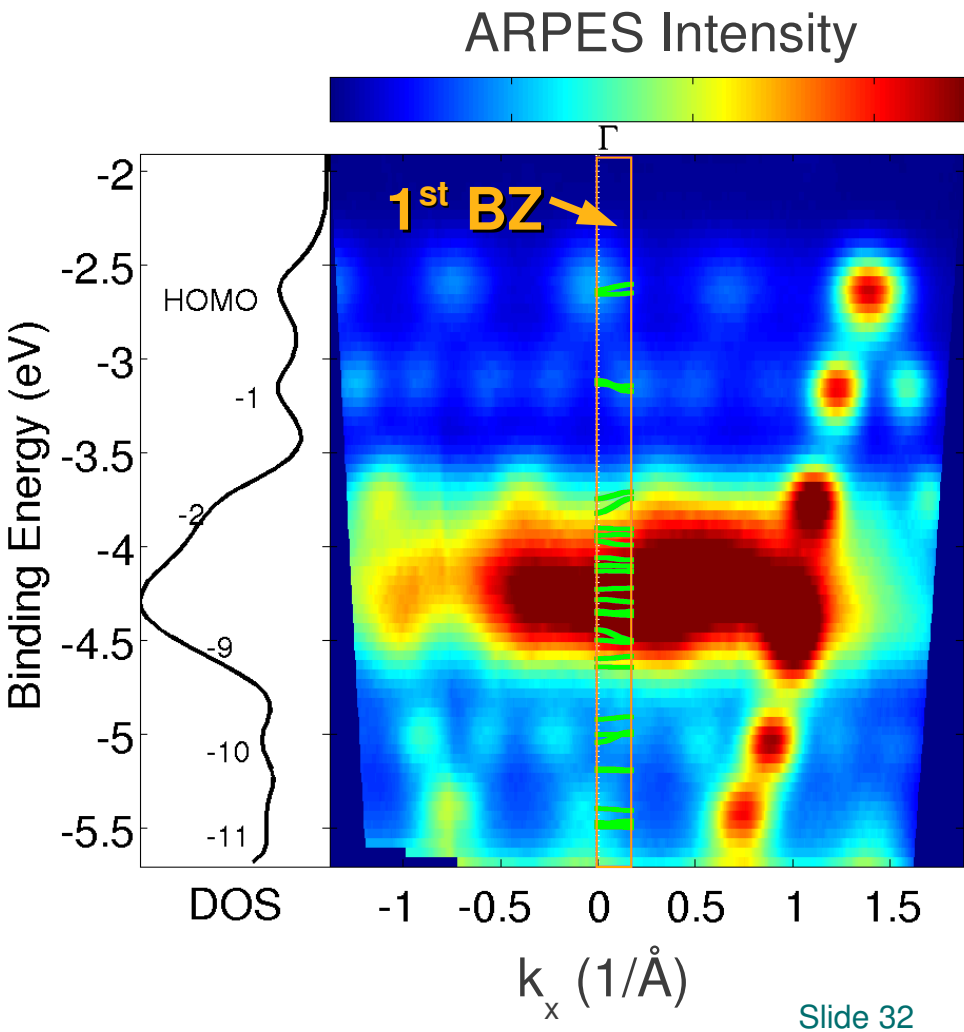
ARPES data from Stephen Berkebile



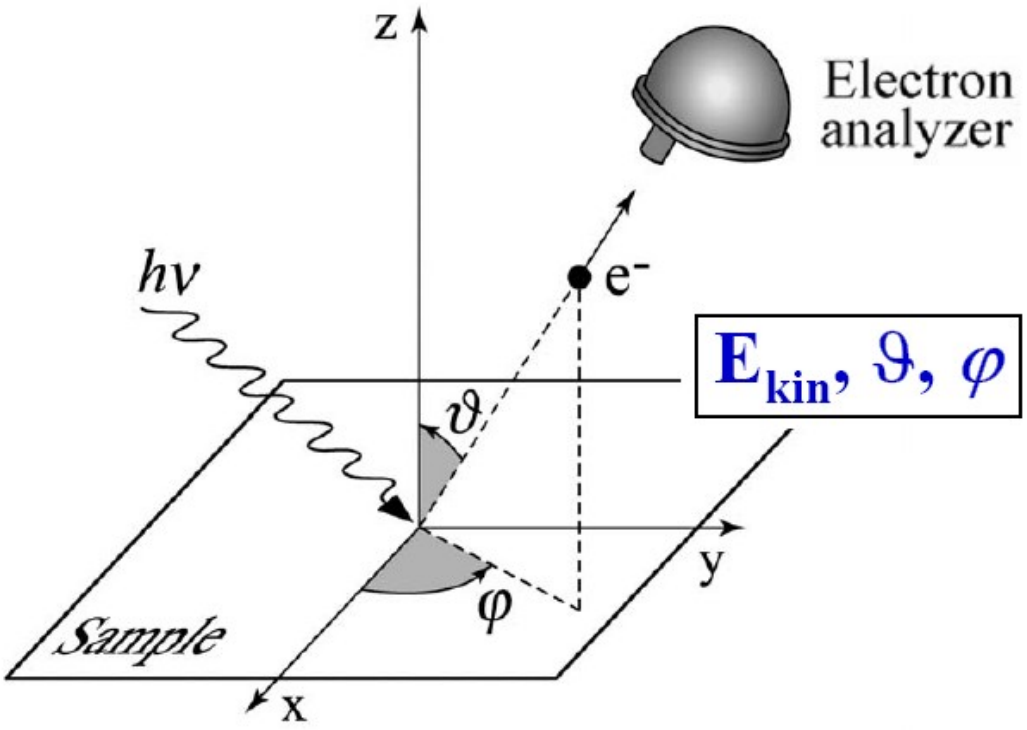
Uniaxially Aligned Sexiphenyl



Band structure from:
Puschnig et al., *PRB* **60**, 7891 (1999).



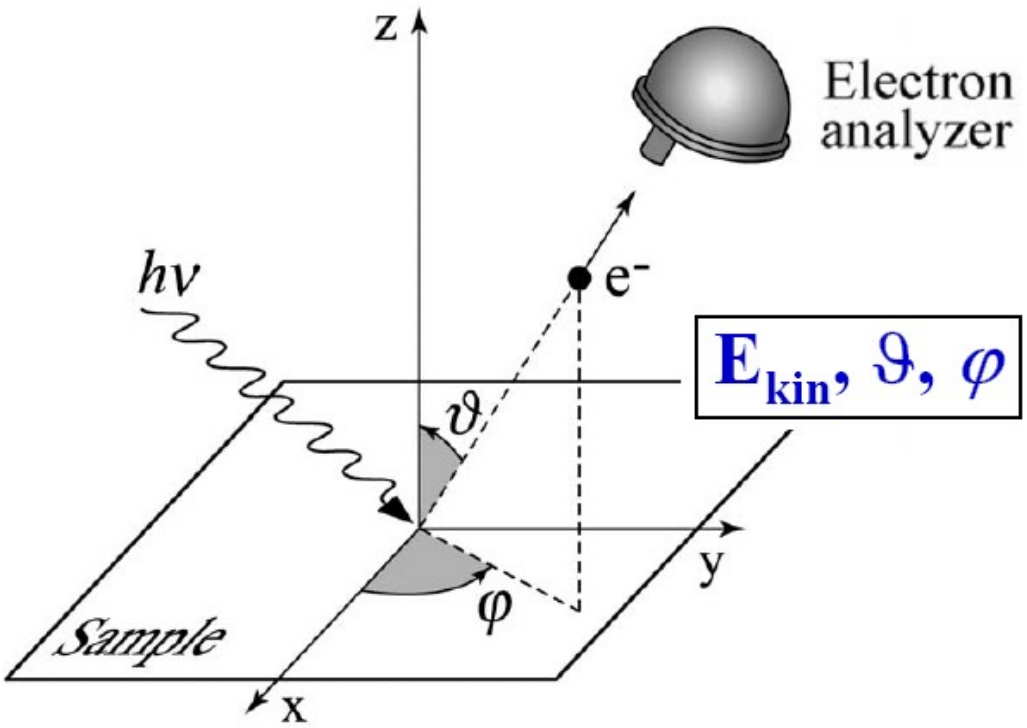
Angle-Resolved Photoemission



Photoemission Intensity

One Step Model

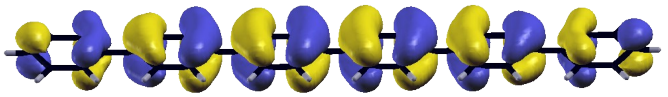
$$I(\theta, \phi; E_{\mathrm{kin}}) \propto \sum_i \left| \langle \psi_f^*(\theta, \phi; E_{\mathrm{kin}}) | \mathbf{A} \cdot \mathbf{p} | \psi_i \rangle \right|^2 \times \delta\left(E_i + \Phi + E_{\mathrm{kin}} - \hbar\omega\right)$$



Photoemission Intensity

One Step Model

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

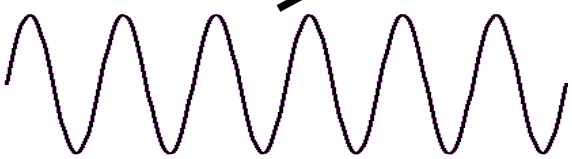


molecular orbital

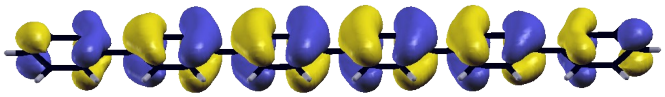
Photoemission Intensity

One Step Model

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



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



molecular orbital

Approximation: final state = plane wave

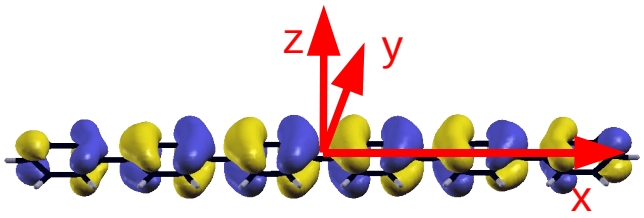
$$I_i(\theta, \phi) \propto \left|(\mathbf{A} \cdot \mathbf{k})\right|^2 \times \left|\tilde{\psi}_i(\mathbf{k})\right|^2$$

Fourier Transform of Initial State Orbital

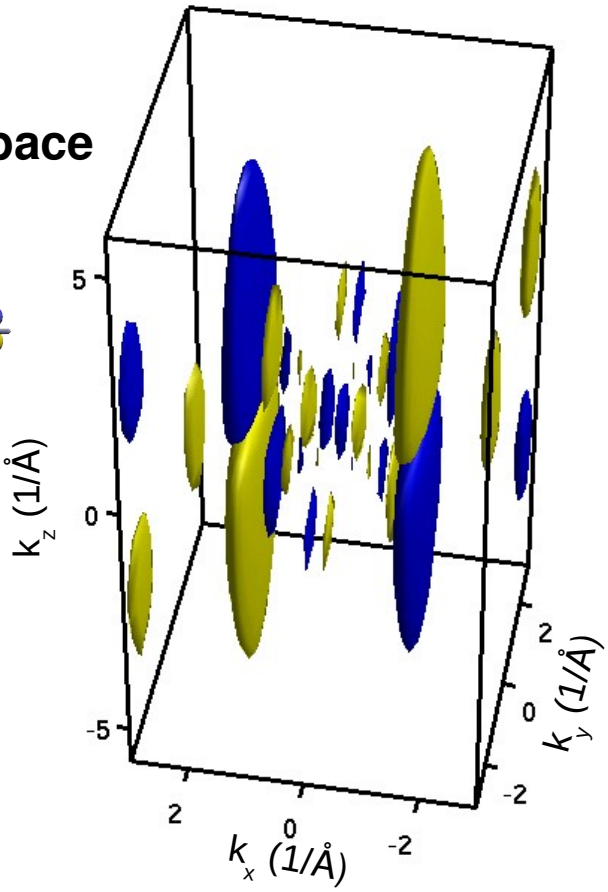
[Feibelman and Eastman, *Phys. Rev. B* **10**, 4932 (1974).]

Comparison with DFT

Molecular Orbital in Real Space

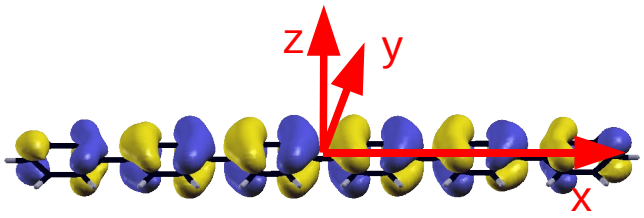


Calculation of the Fourier Transform

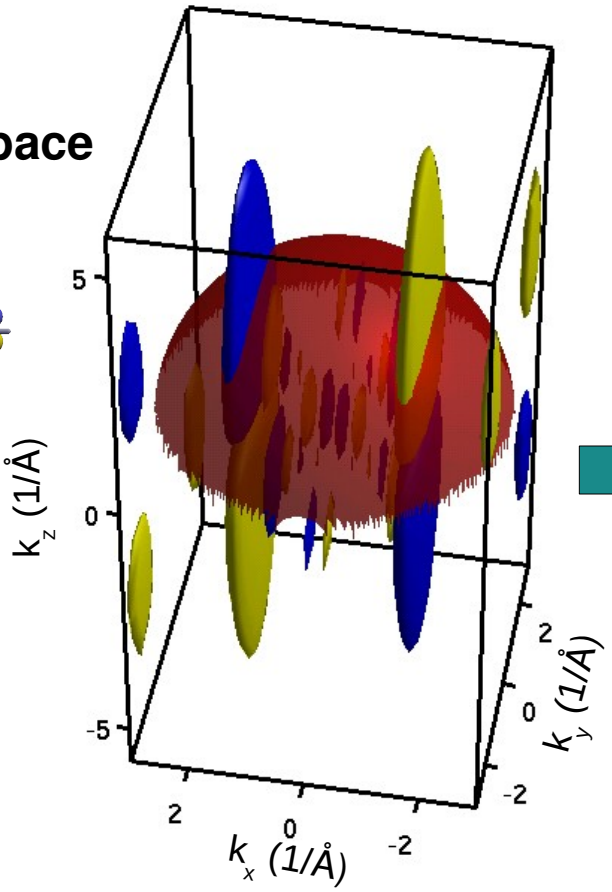


Comparison with DFT

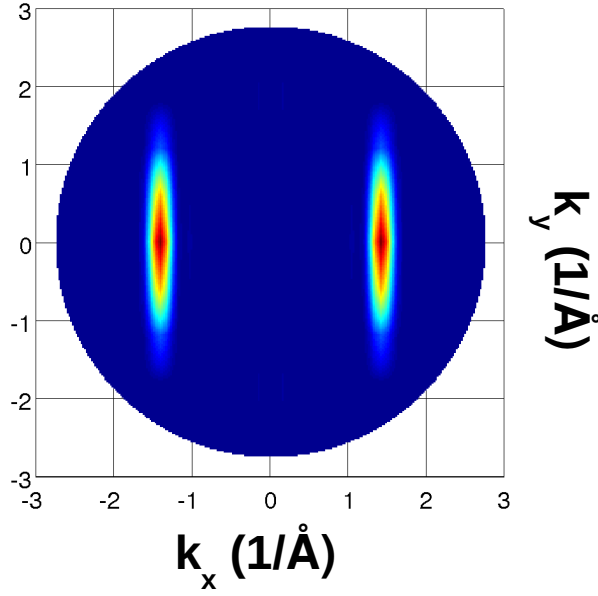
Molecular Orbital in Real Space



Calculation of the Fourier Transform

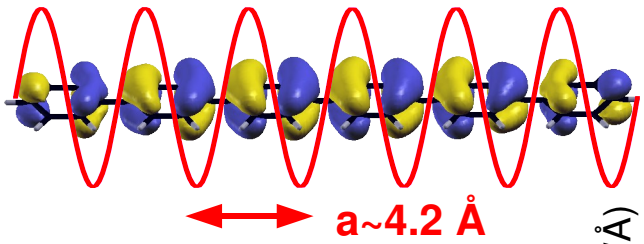


Hemispherical Cut Through 3D Fourier Transform

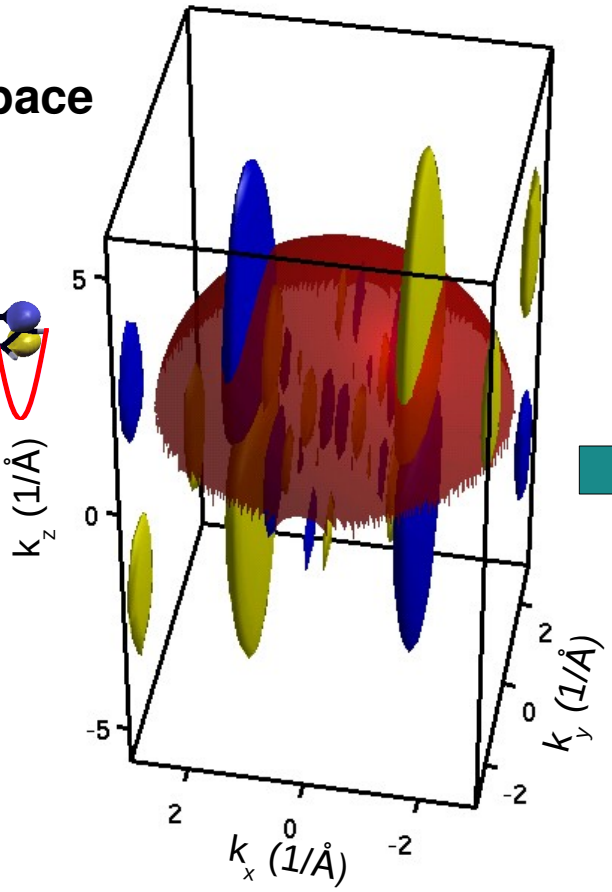


Comparison with DFT

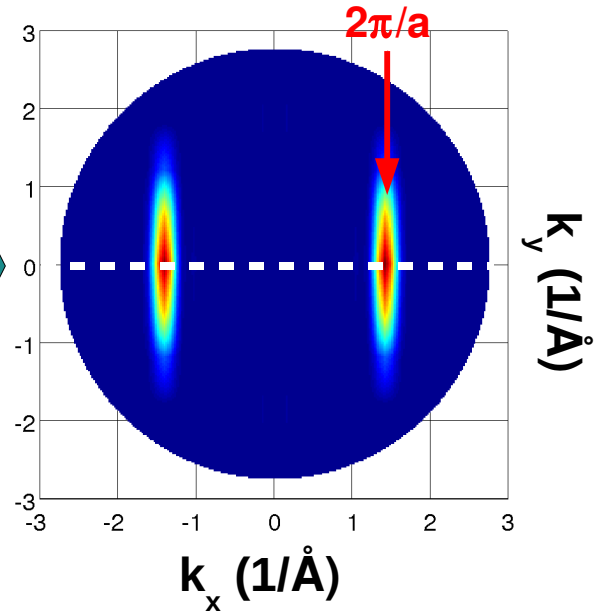
Molecular Orbital in Real Space



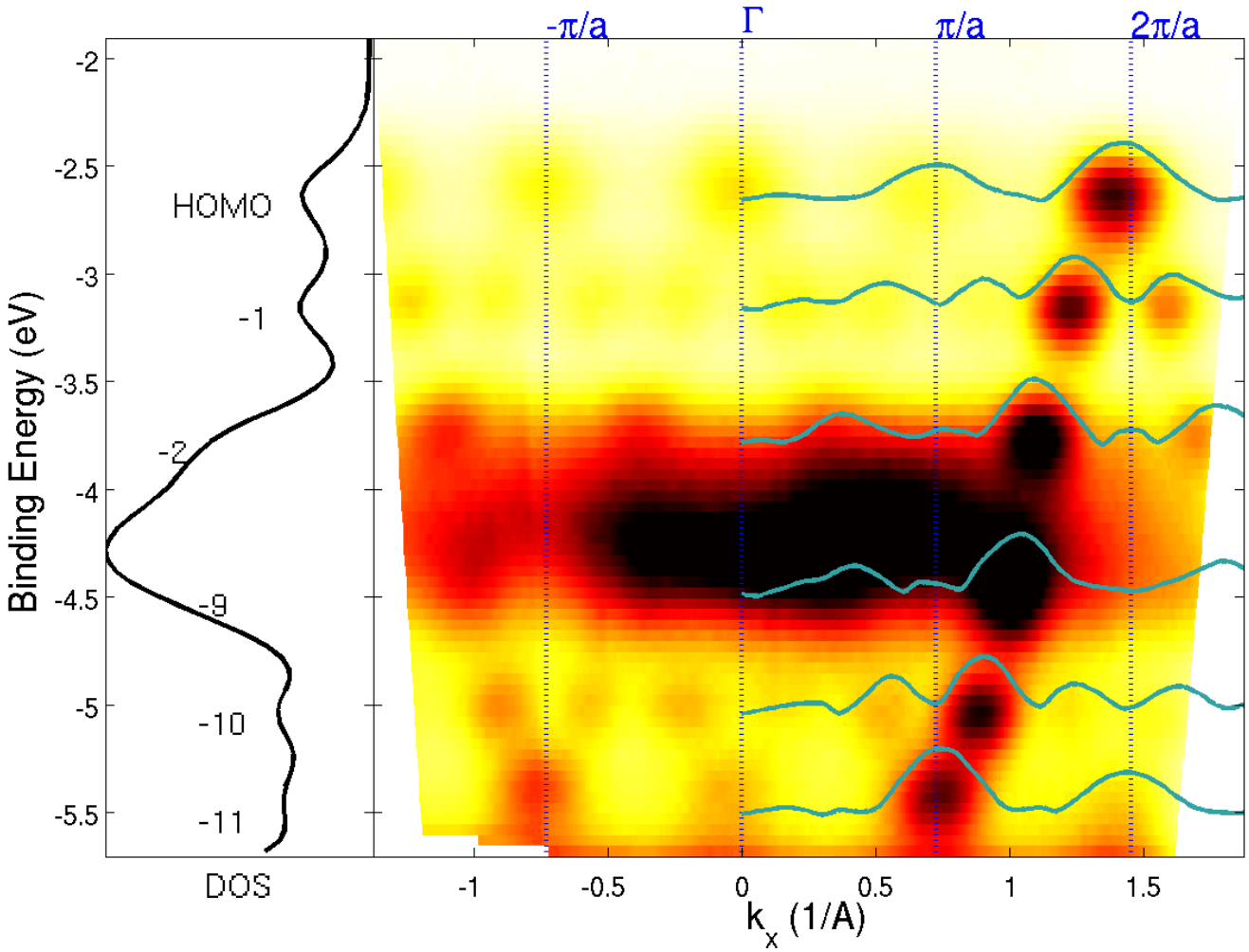
Calculation of the Fourier Transform

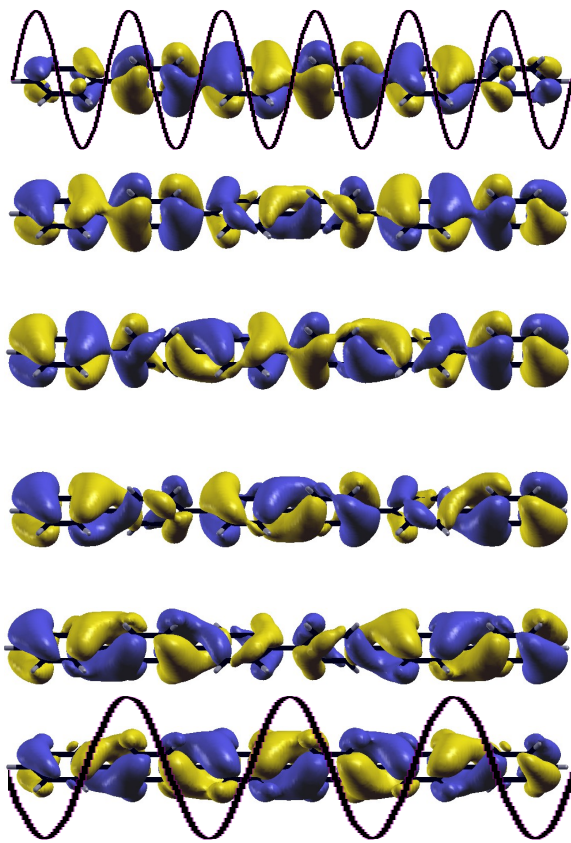


Hemispherical Cut Through 3D Fourier Transform



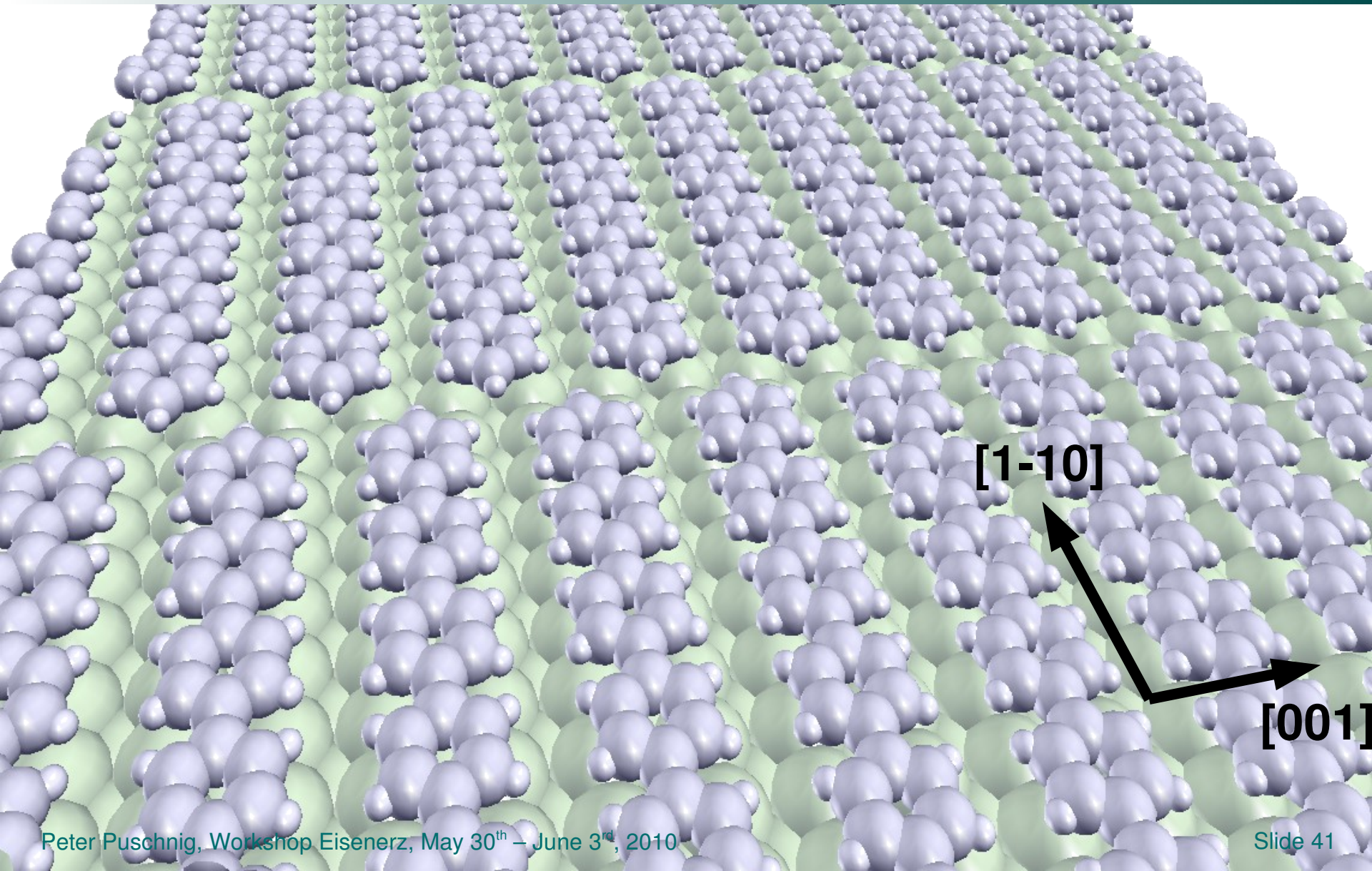
Sexiphenyl Orbitals



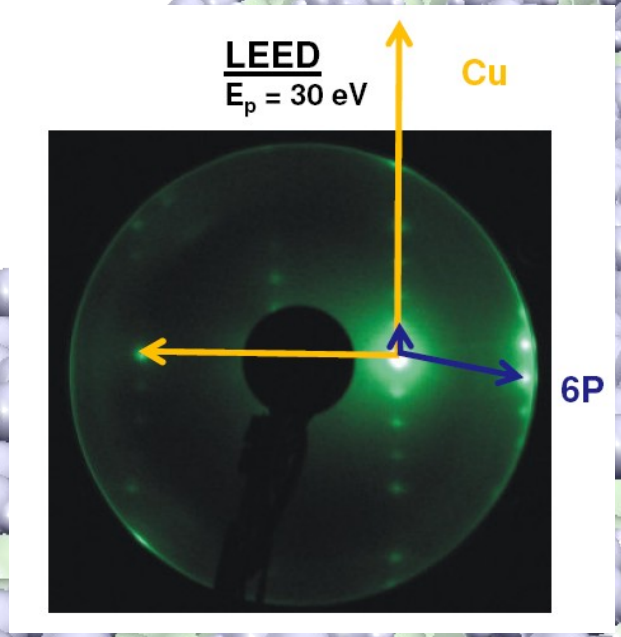


G. Koller et al., *Science* ***317****, 351 (2007).*

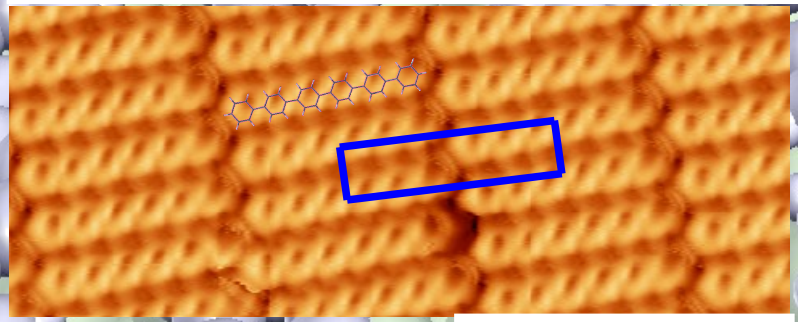
Sexiphenyl Monolayer on Cu(110)



Sexiphenyl Monolayer on Cu(110)



Low-T STM by courtesy of Stephen Berkebile



-130 mV / 0.38 nA

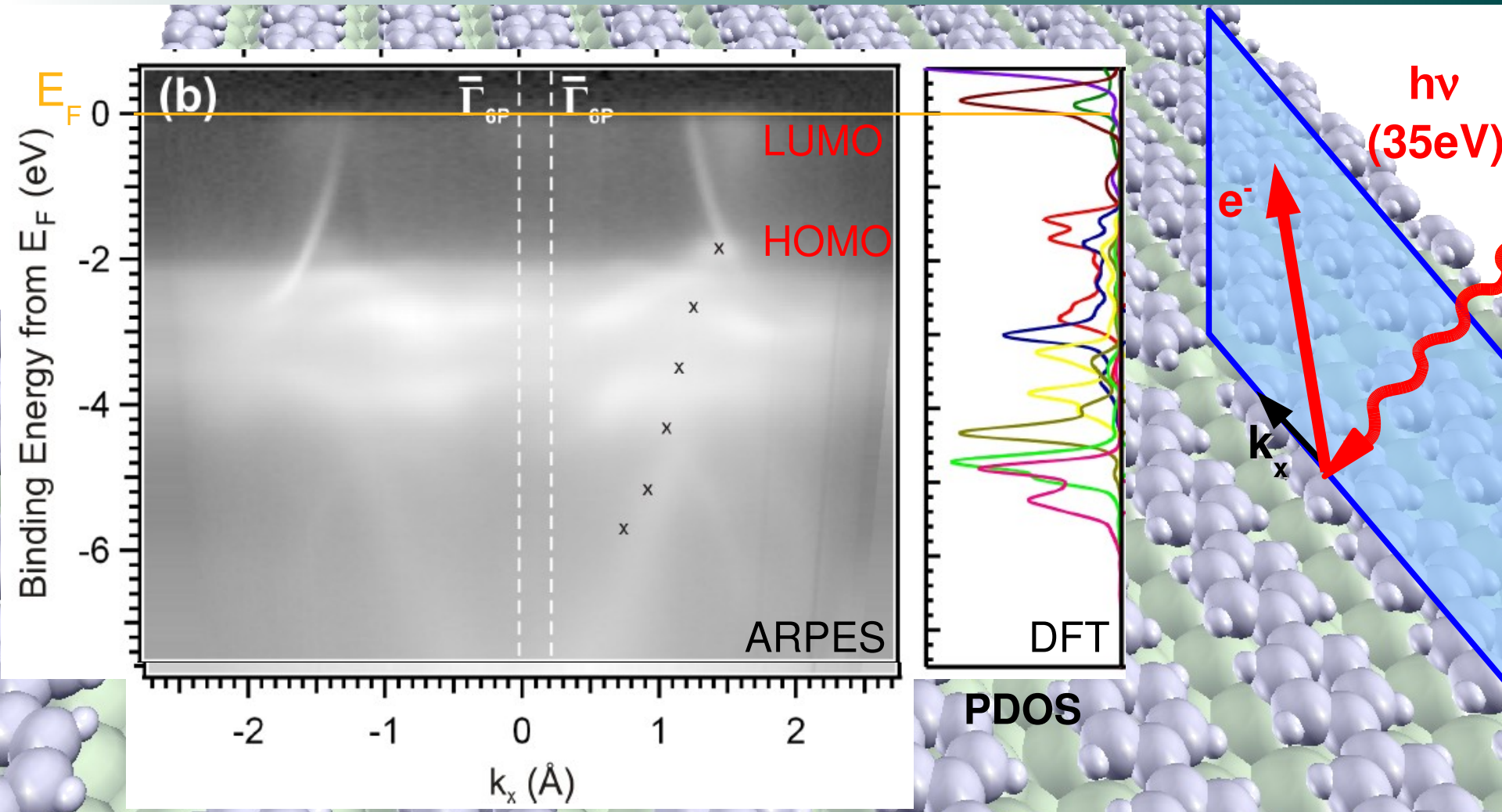
$11\ a_{Cu}$ / sqrt(2)

$2\ a_{Cu}$

[1-10]

[001]

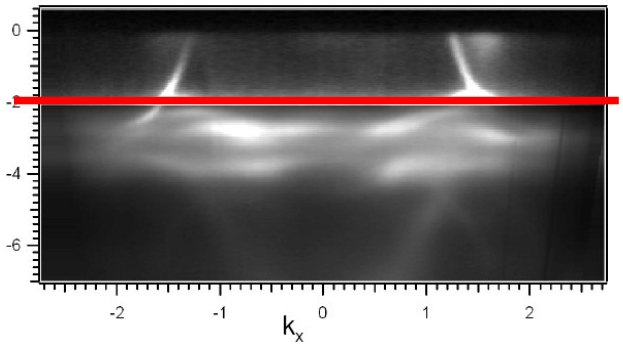
Sexiphenyl Monolayer on Cu(110)

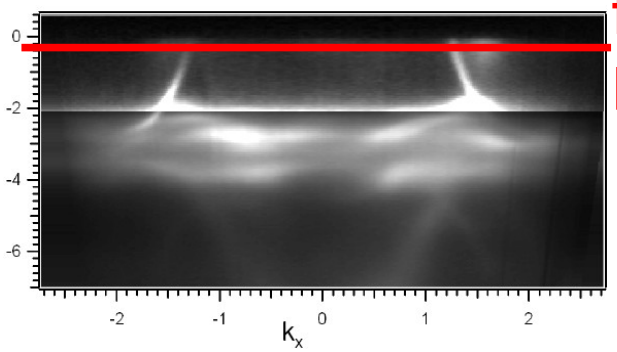


Berkebile et al. (submitted to PNAS)

2D-Momentum Maps

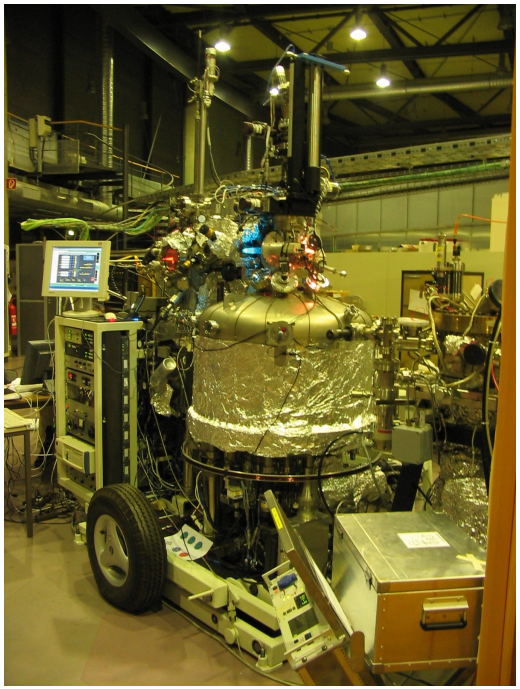
HOMO

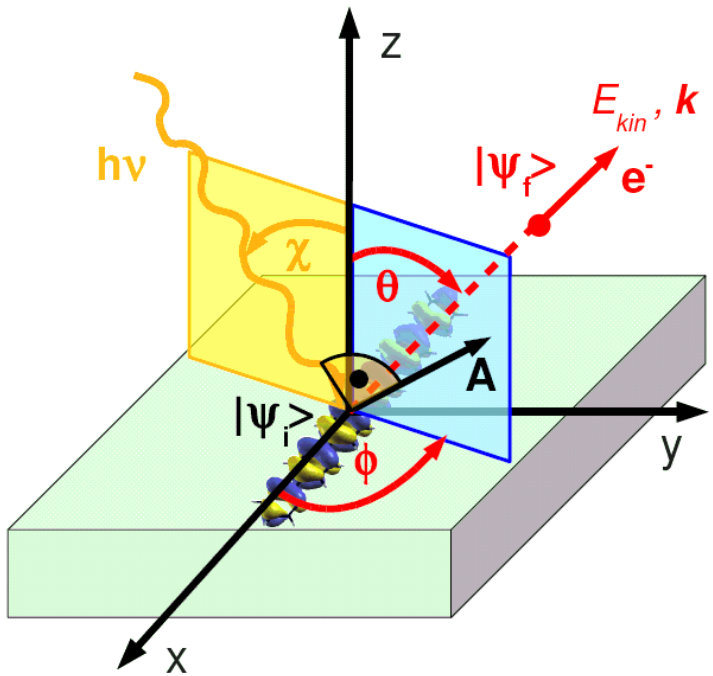




filled LUMO

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

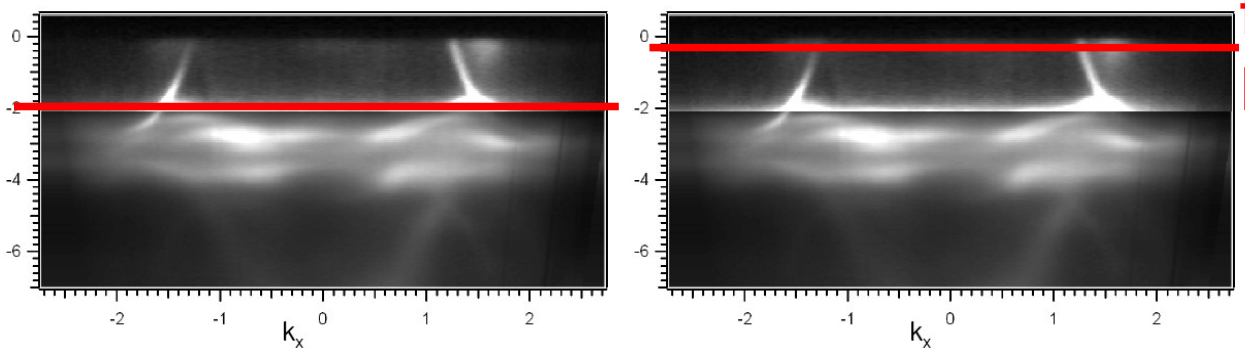




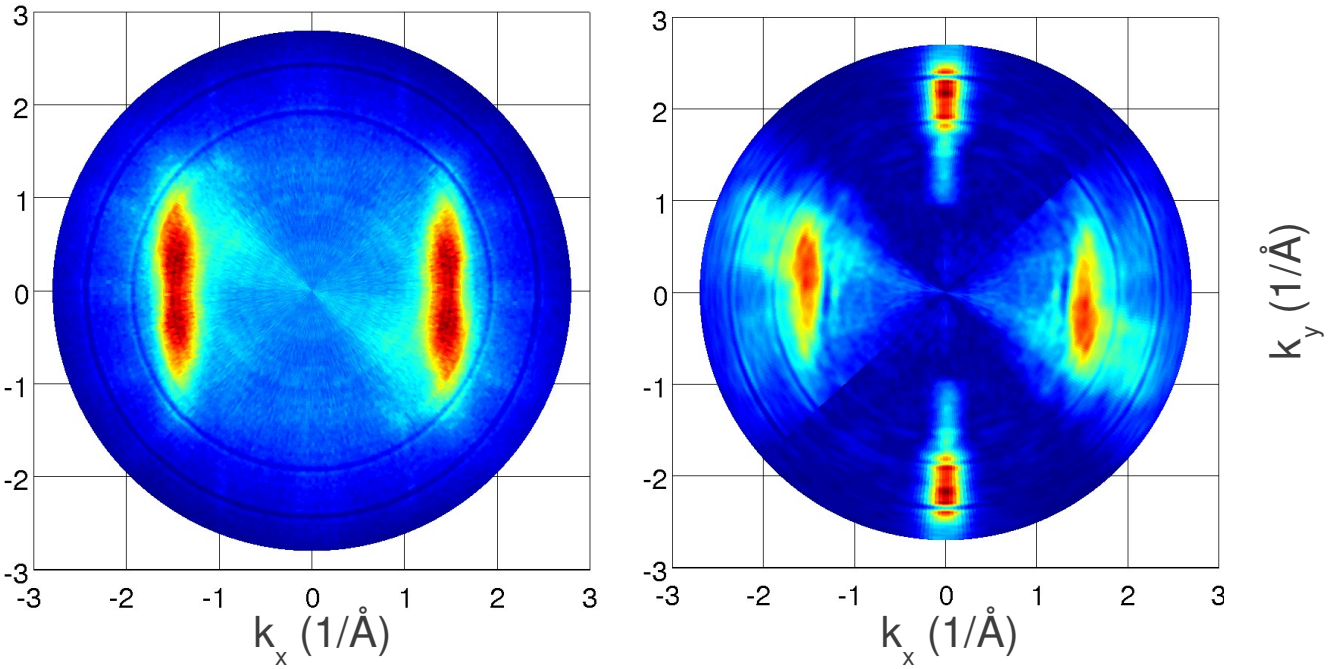
2D-Momentum Maps

HOMO

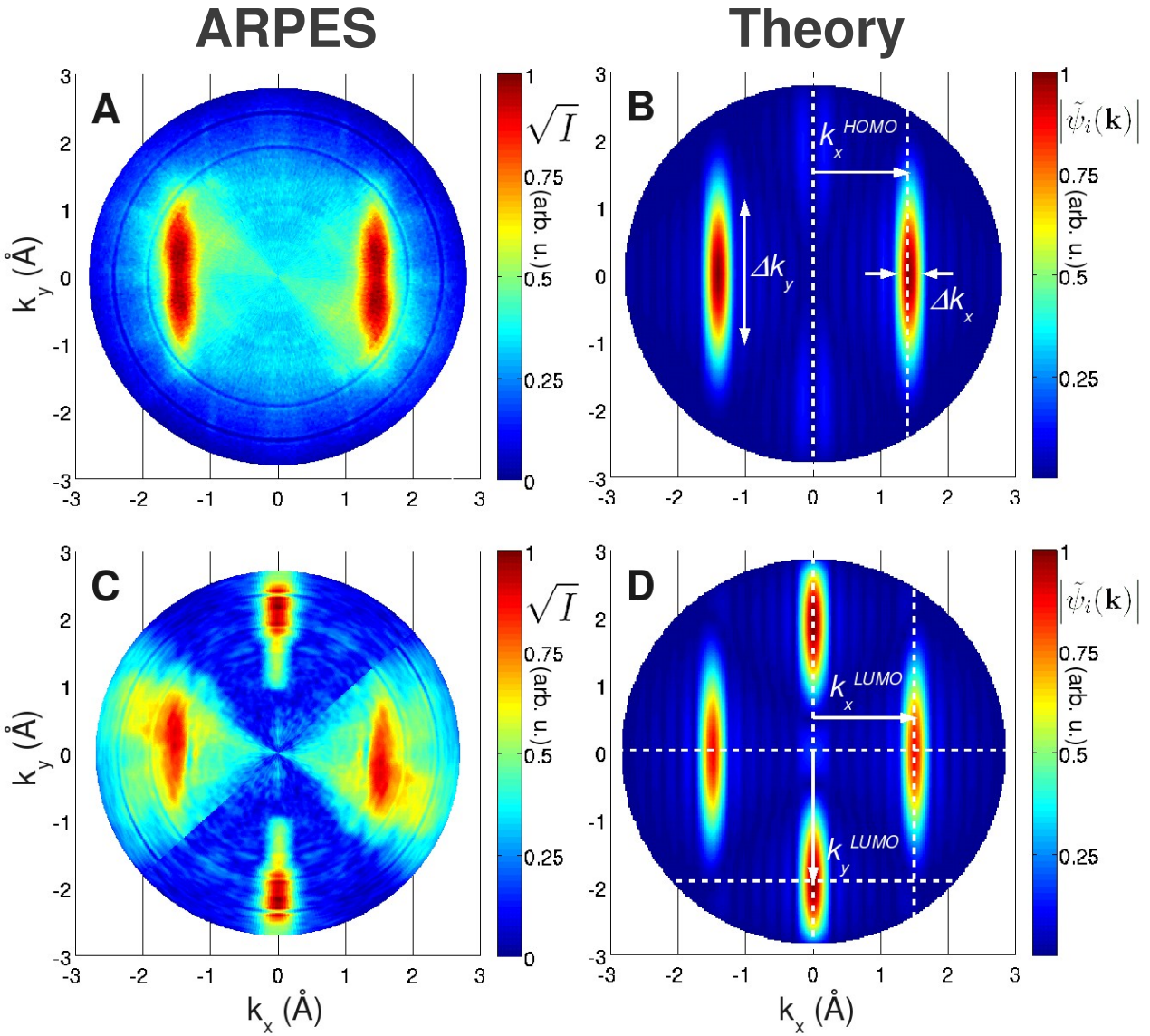
filled LUMO



ARPES data for a monolayer of 6P / Cu(110)



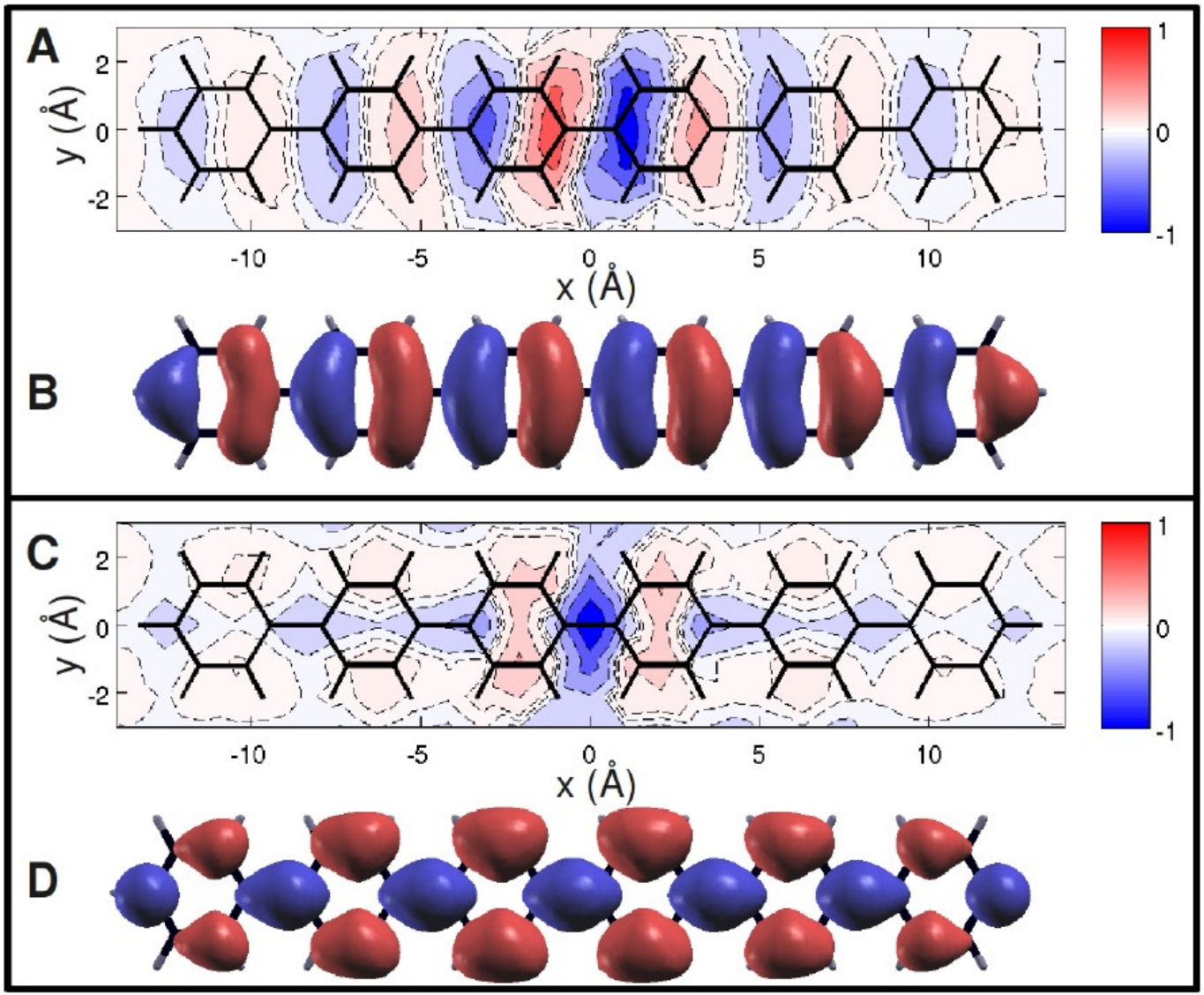
2D-Momentum Maps



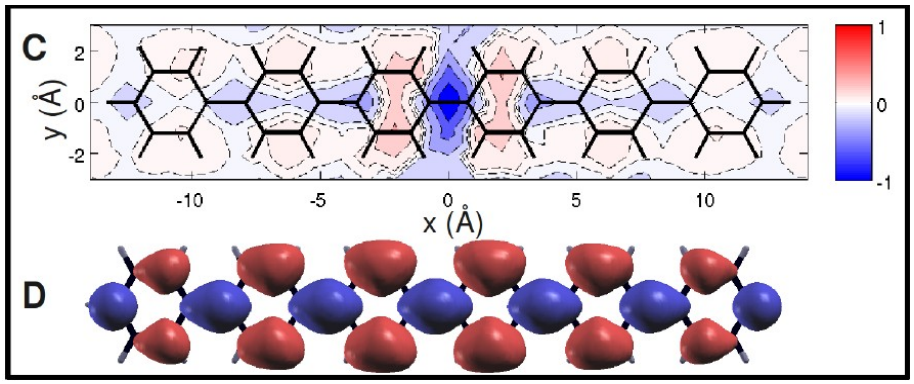
Reconstruction of Orbitals

HOMO

Filled LUMO

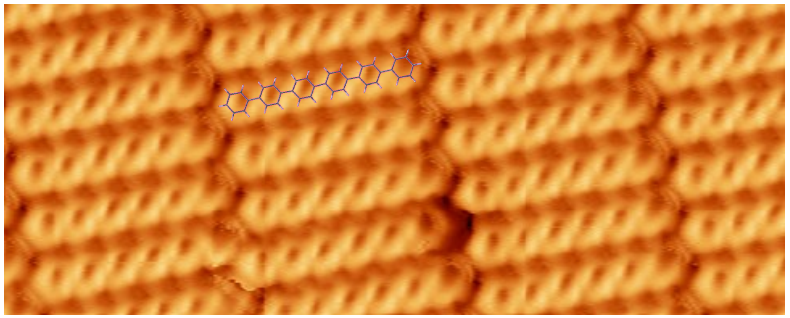


Low-T STM Images



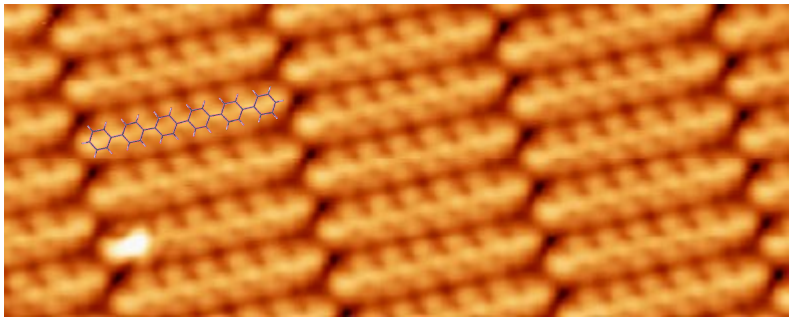
Filled LUMO

Low-T STM images
by courtesy of Stephen Berkebile

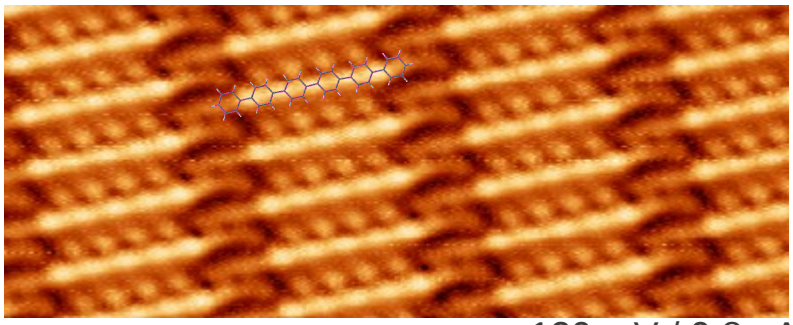


-130 mV / 0.38 nA

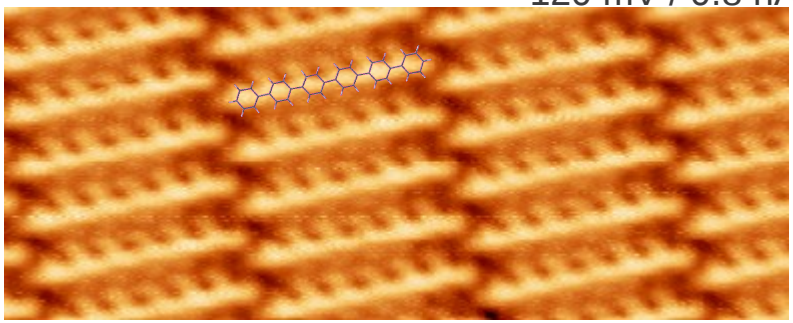
100x40 Å^2



170 mV / 1 nA

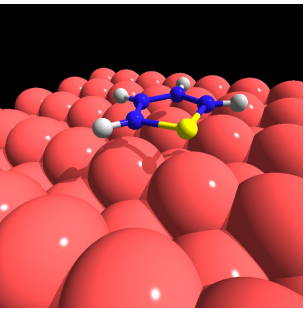


120 mV / 0.8 nA



-120 mV / 0.8 nA

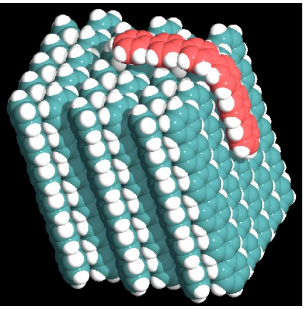
Summary



Van der Waals Interactions within DFT

Organic / organic works fine; organic / metal interactions still problematic

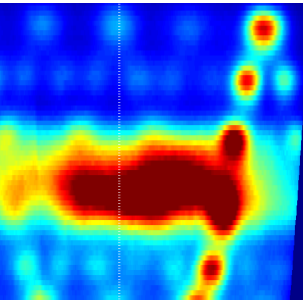
Nabok et al., *PRB* **77**, 245316 (2008).
Sony et al., *PRL.* **99**, 176401 (2007).
Romaner et al., *NJP* **11**, 053010 (2009).



Organic Thin Film Growth

Some success in understanding certain kinetic barrieres,
but still a lot of work to do ...

G. Hlawacek et al., *Science* **321**, 108 (2008).
See also: Goose et al., *PRB* **81**, 205310 (2010).

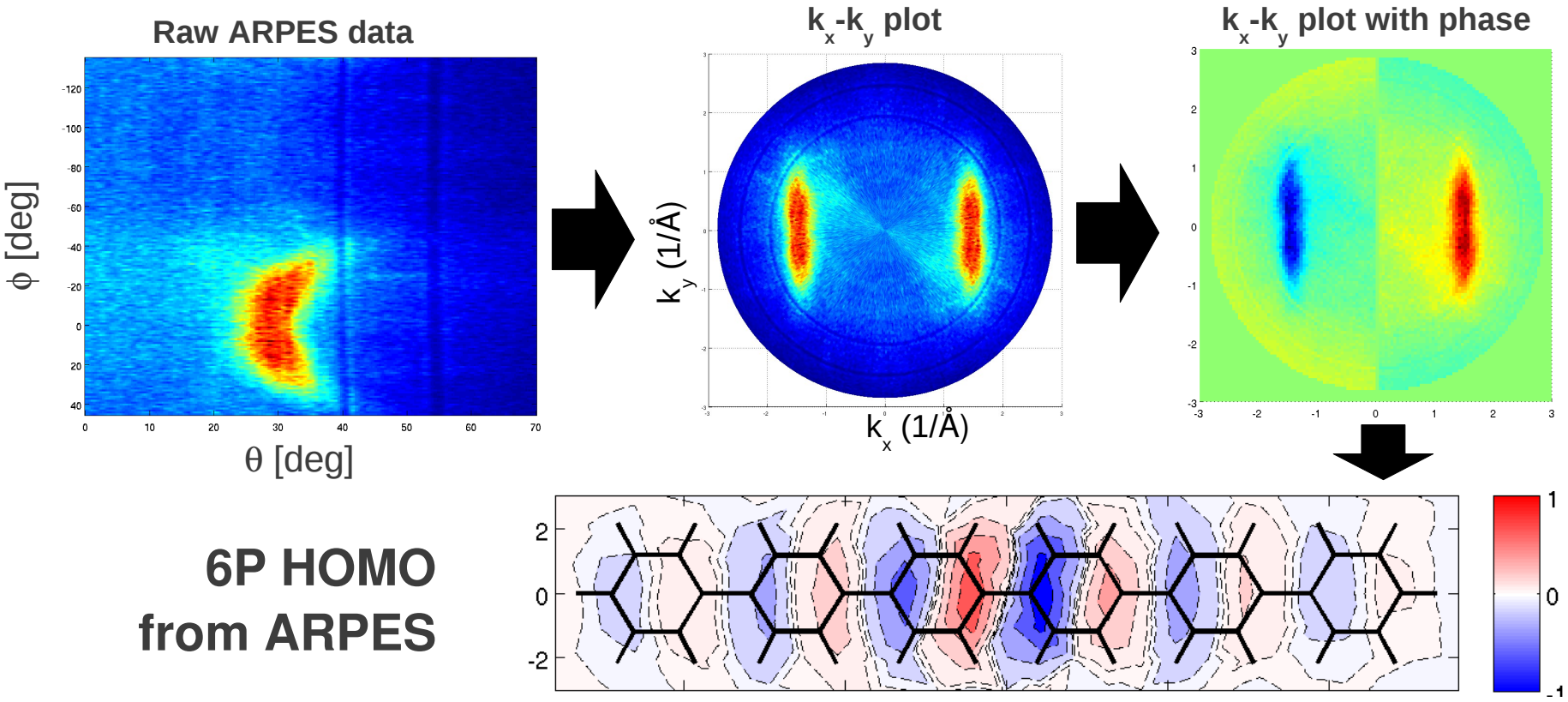


Real Space Orbital Information from ARPES

Proof of principle done, future prospects: 3D images, complement STM, ..

Koller et al., *Science **317**, 351 (2007);* Berkebile et al., *PRB* **77**, 115312 (2008).
Puschnig et al., *Science* **326**, 702 (2009).
Ziroff et al., *PRL* (June, 2010).

Reconstruction of Orbitals



6P HOMO from ARPES

Puschnig et al., *Science* **326**, 702 (2009).