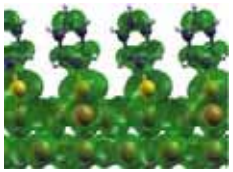
Metal/Organic Interfaces



from *first-principles*

Georg Heimel

Institut für Physik, Humboldt-Universität zu Berlin

Outline

- Investigated Systems / Motivation
- Methods
- Overview over recent and current research
  - *Self-assembled monolayers on metals*
  - *Metal/molecule charge-transfer systems*
  - *Stretching/breaking single-molecule junctions*
  - *Doping in single-molecule junctions*
- Outlook
- Summary and Conclusions

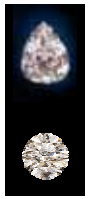
The Early Days ...

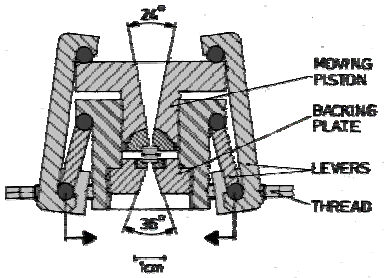
Graz, Austria

Institute of Solid State Physics
Graz University of Technology

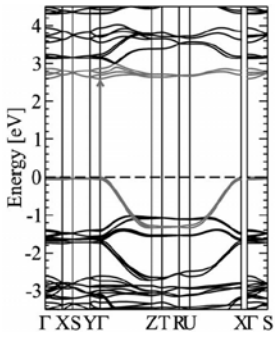
Research Topics:

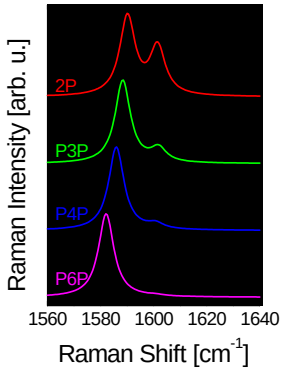
Structural, **Electronic**, and **Optical** Material Properties of ***Organic Semiconductors*** (**Experiment** and **Theory**)



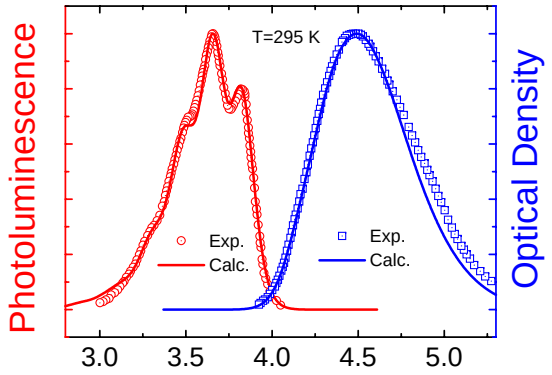


X-ray and Raman under high pressure





Bandstructure and Quantum Chemistry



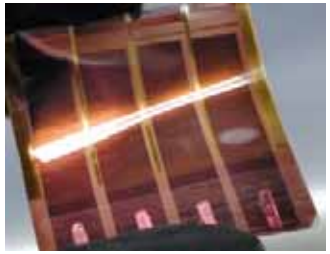
Optical Spectroscopy

Hybrid Organic / Inorganic Devices

Organic Electronics:

Lighting
OSRAM, 7.4.2008

Display
available from SONY

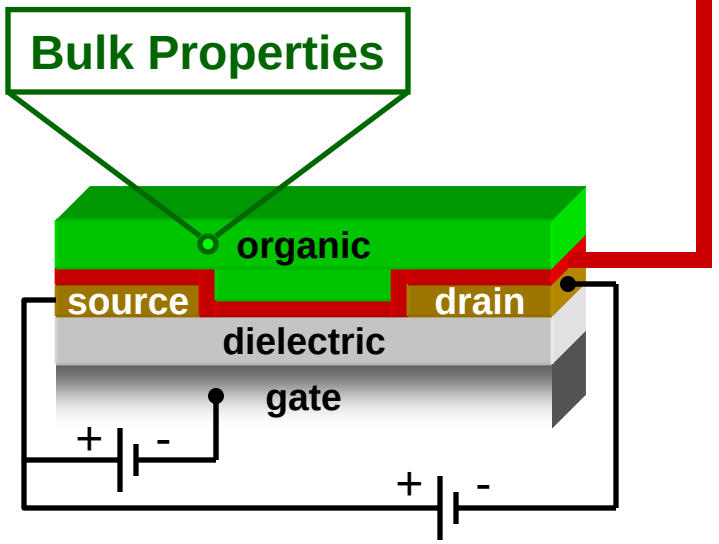


Photovoltaics
Fraunhofer ISE Freiburg, 1.2.2008

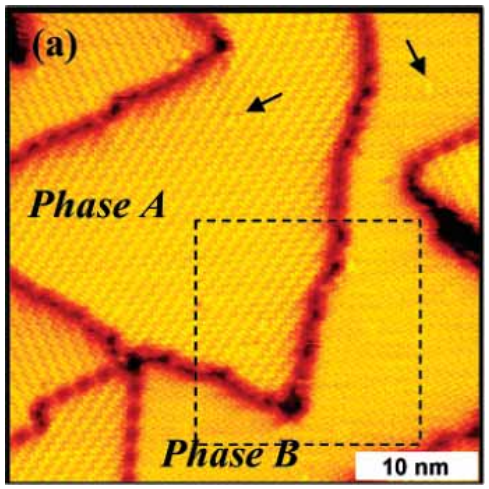
RFID and FET
Holst Center, 6.2.2008

Interface Properties:

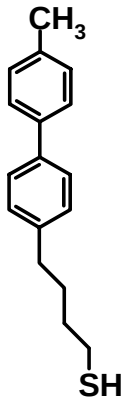
- Charge-injection barriers
- Morphology control
- Charge-carrier traps
- ...

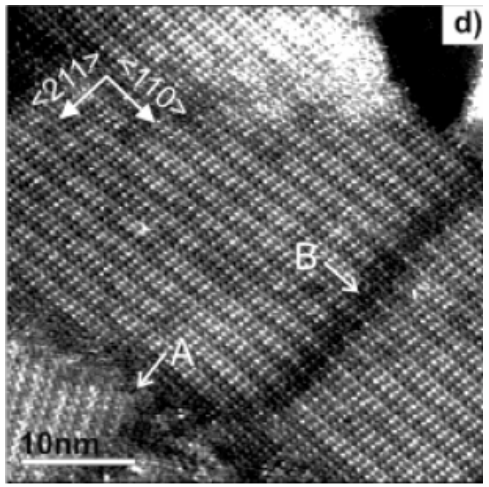


DFT studies of SAMs on Metals

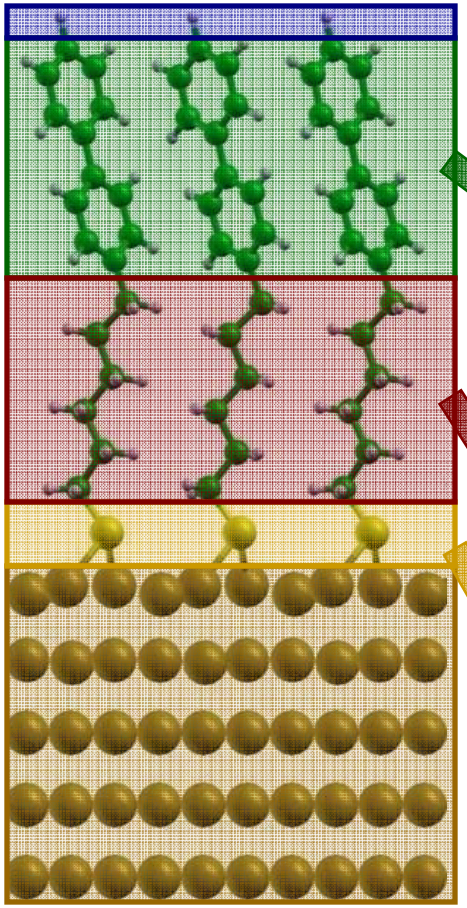


D. Riposan *et al.*, *J. Phys. Chem. B* **110**, 23926 (2006).





P.Cyganic *et al.*, *J. Phys. Chem. B* **108**, 4989 (2004).



head group:
-NH_2, -CN, -NO_2,
-F, -OH, *etc.*

π-core:
phenyls
ethylenes
ethinylenes
acenes

spacer:
alkanes

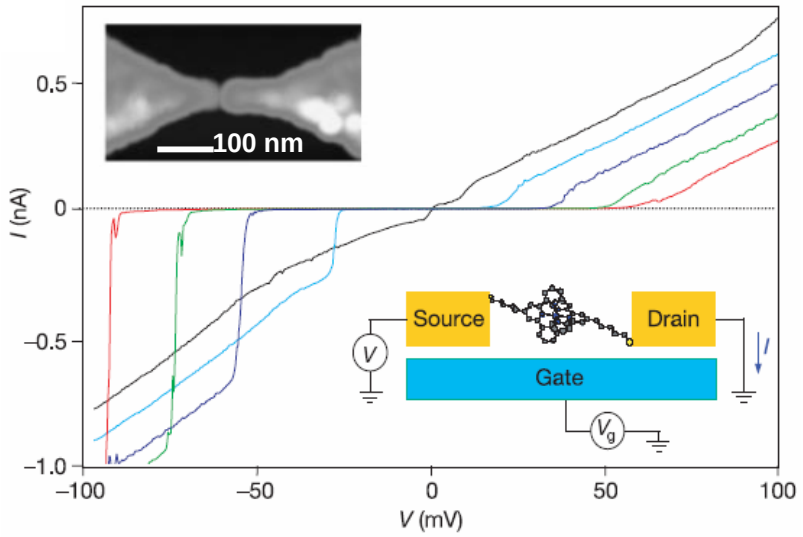
docking group:
-SH
-CN
-NC
-pyridine

metal (111):
Au, Ag, Cu, Pt

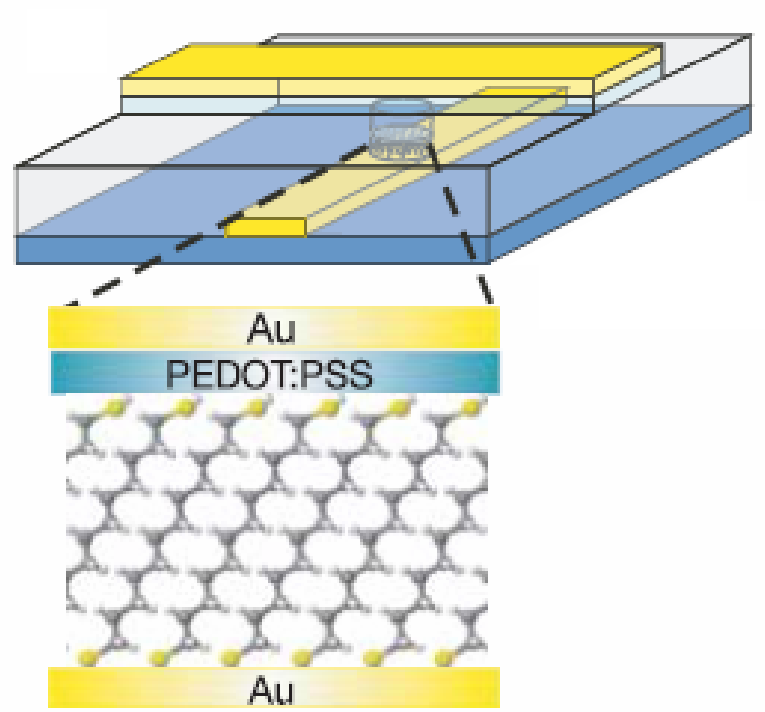
Interest in and Application of SAMs

- *Hydrophopic/philic surfaces*
- *Nanolithography*
- *Chemical sensing*
- **Organic electronics**
- **Molecular electronics**
- …

- *Corrosion protection*
- *Biocompatible Surfaces*
- *Functional surfaces*



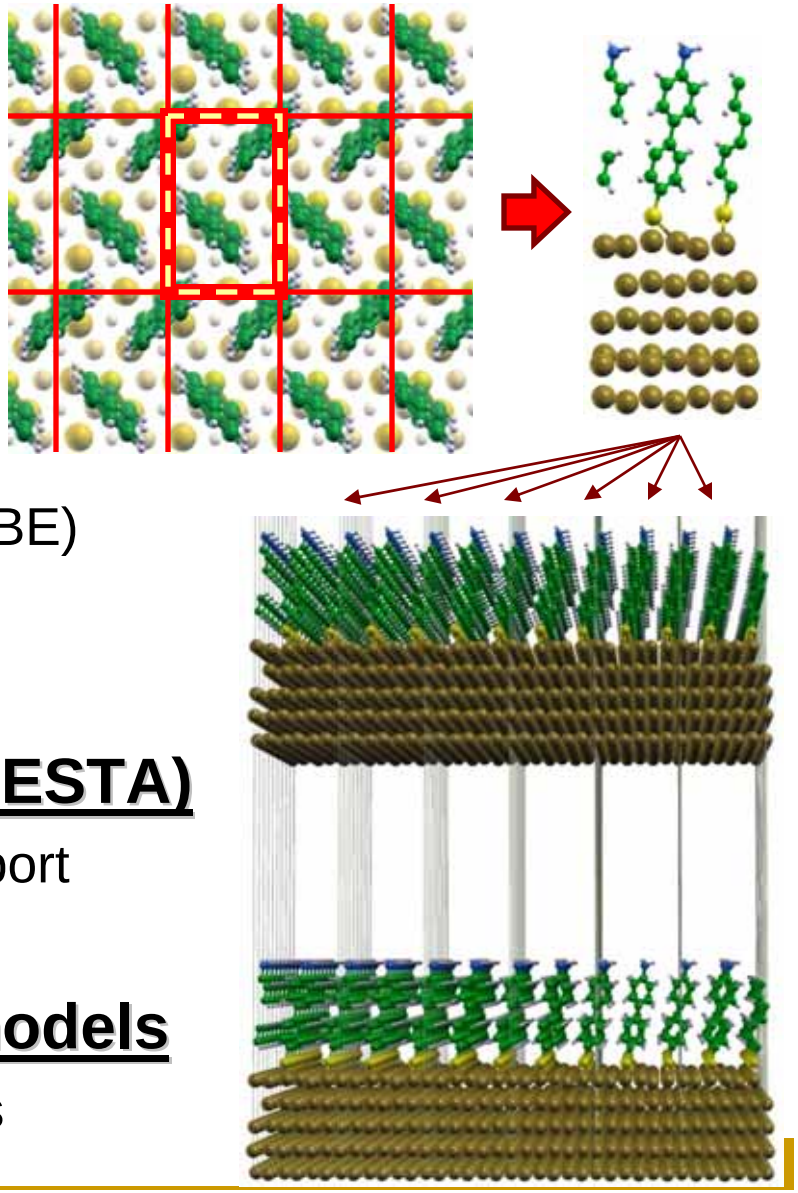
J. Park *et al.*, Nature **417**, 722 (2002).



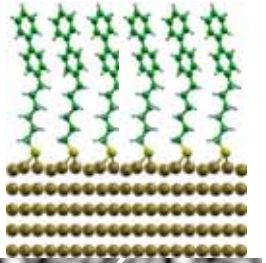
H. Akkerman *et al.*, Nature **441**, 69 (2006).

Methodology

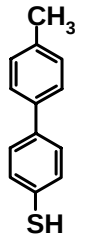
- **DFT bandstructure**
  - VASP, SIESTA
  - PAWs, norm-conserving Troullier-Martins Pseudo-Potentials
  - Plane-waves or LCAO basis set
  - Standard GGA functionals (PW91, PBE)
- **Quantum chemistry**
  - Gaussian03
- **Implementation and Coding (SIESTA)**
  - Surface Green's functions and transport
  - COOP, fragment orbitals, ...
- **Data analysis & electrostatic models**
  - Mathematica, Fortran90, shell-scripts

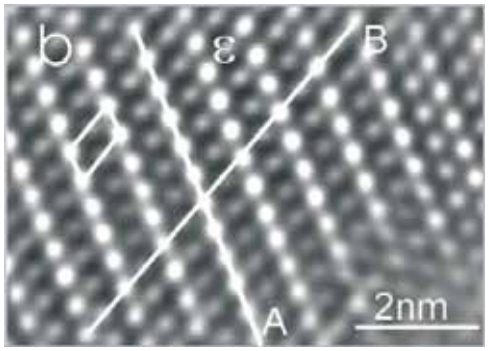


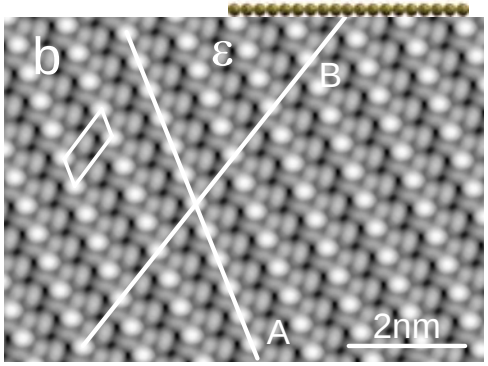
Establish Links to Experiment



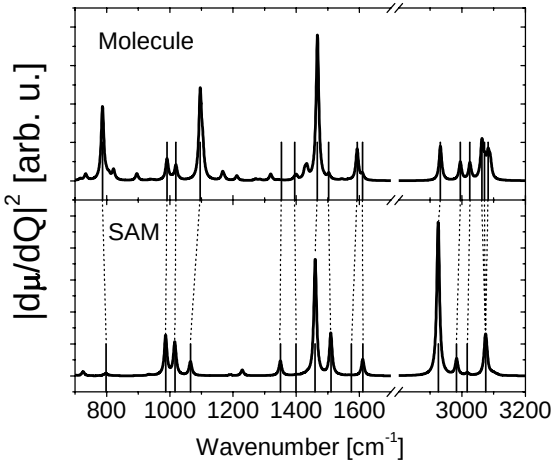
- Adsorption/Desorption energies
- STM images
- Structure
- Core-level shifts
- Infrared spectra



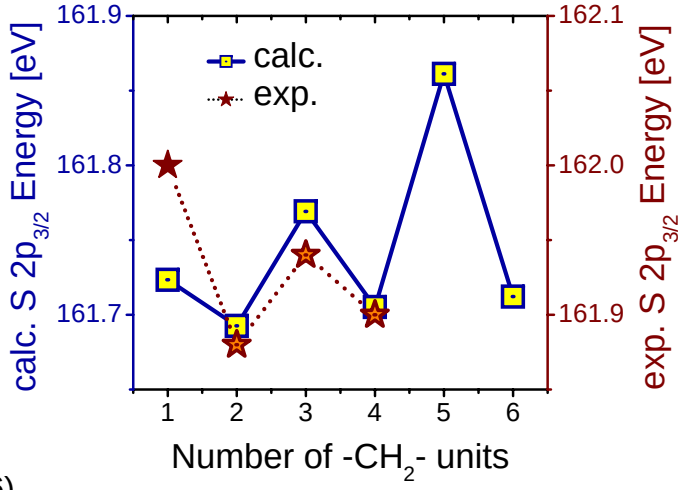


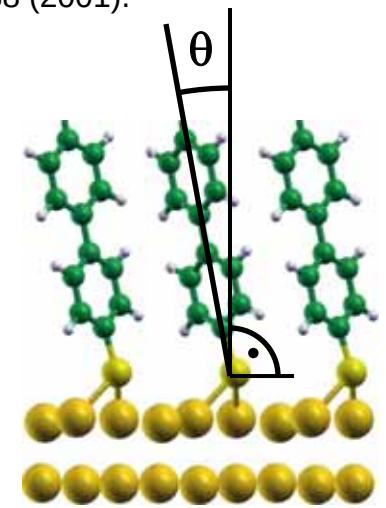


W. Azzam *et al.*, *Langmuir* **19**, 4958 (2003).
K. Heister *et al.*, J. Phys. Chem. B **105**, 6888 (2001).

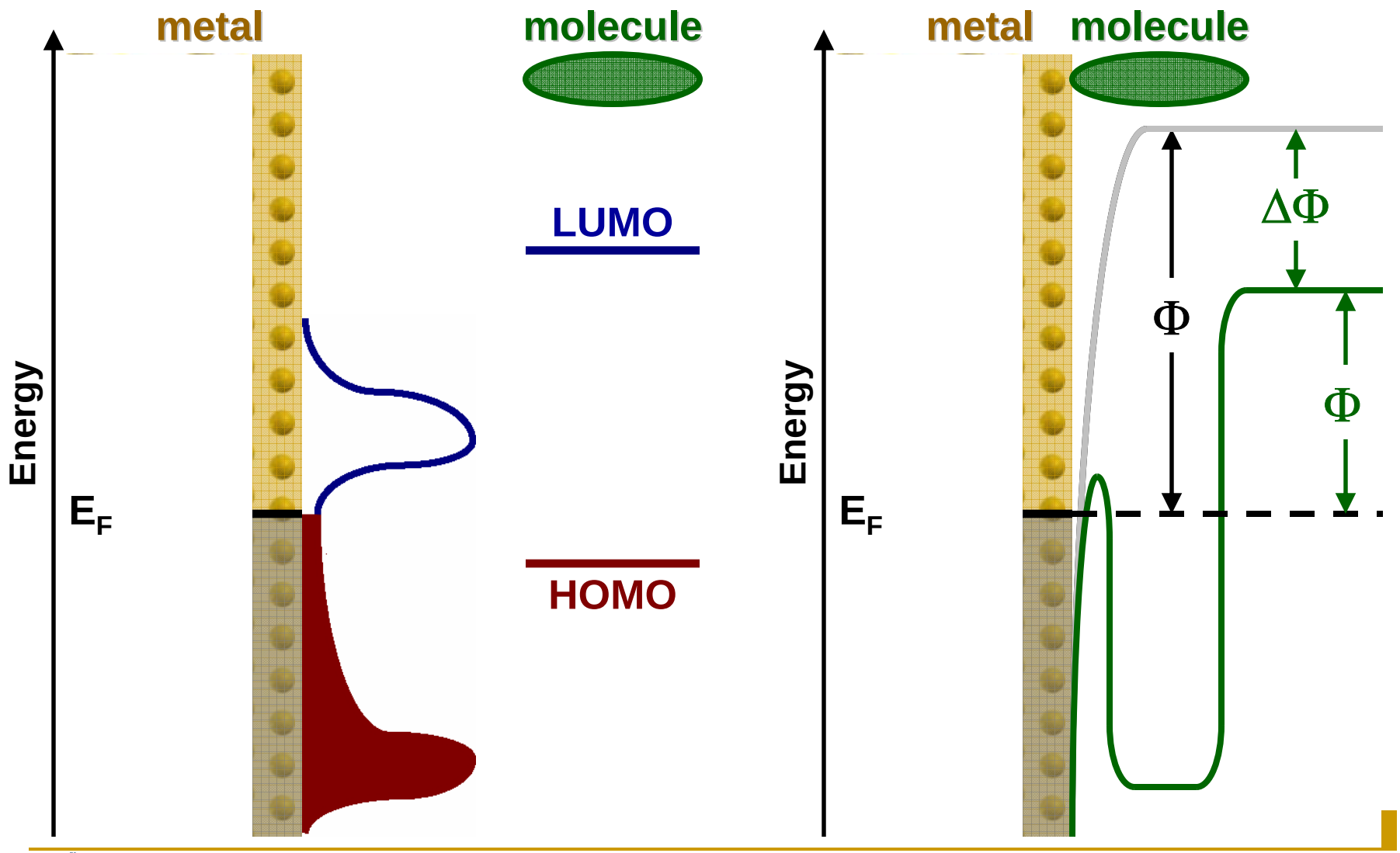


G. Heimel *et al.*, Surf. Sci. **600**, 4548 (2006).



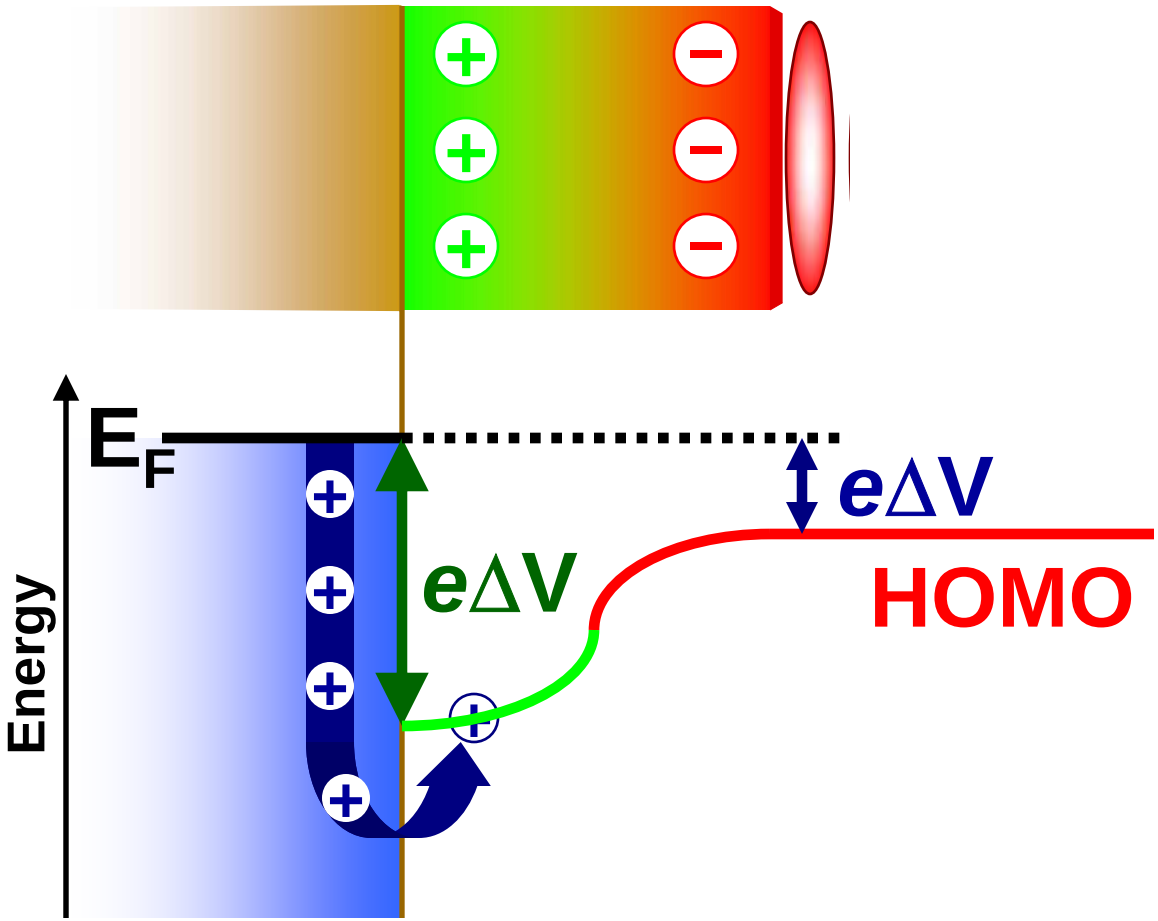


Workfunction and Level Alignment



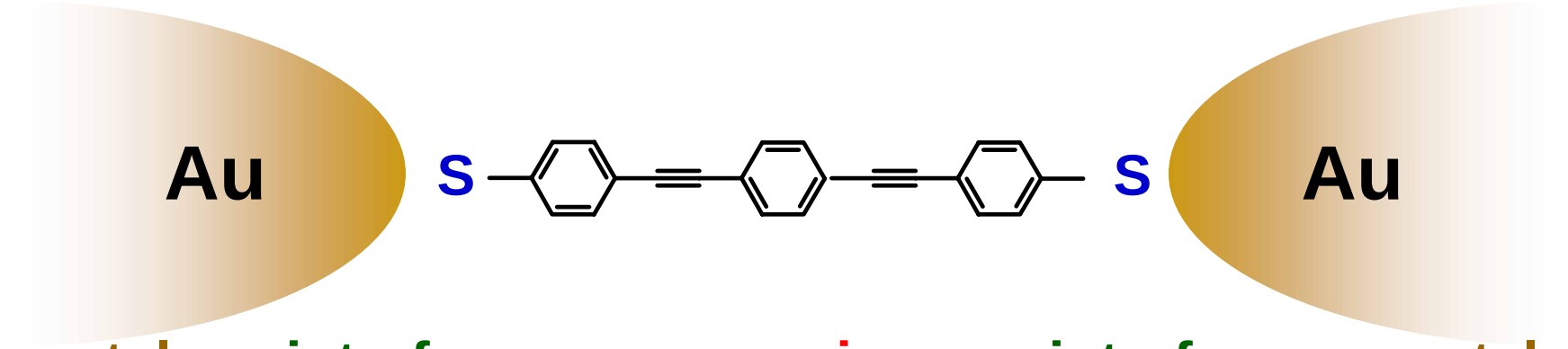
Charge-Injection Barriers

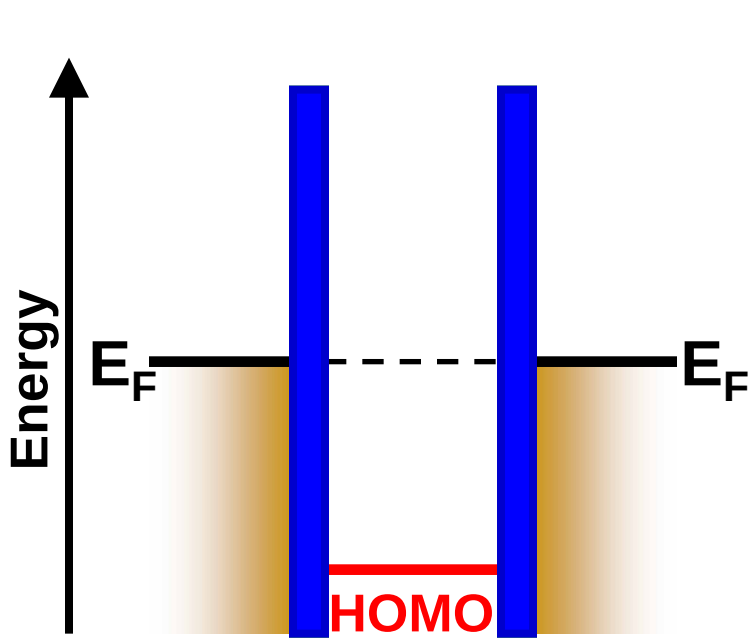
metal interface organic

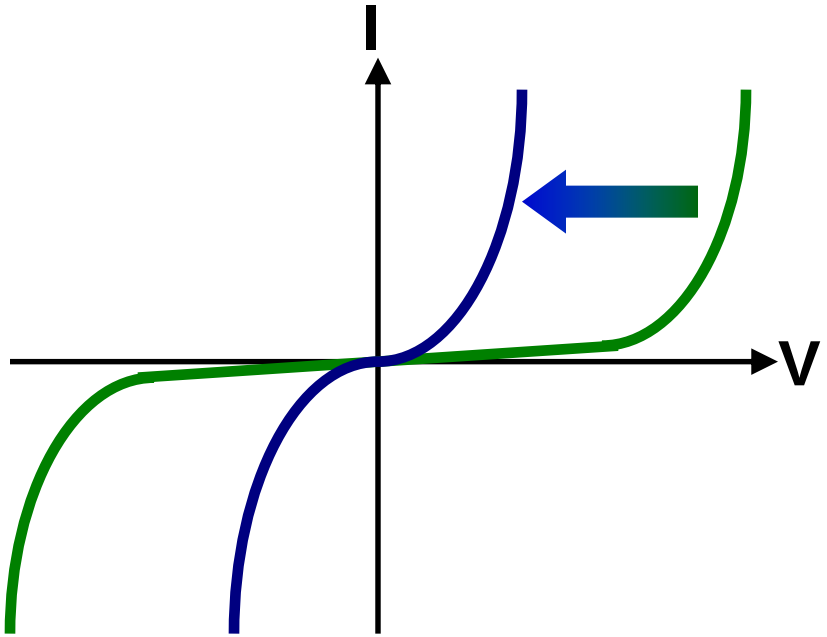


$$j \propto exp\left(-\frac{e\Delta V}{k_B T}\right)$$

Interfaces in Molecular Electronics



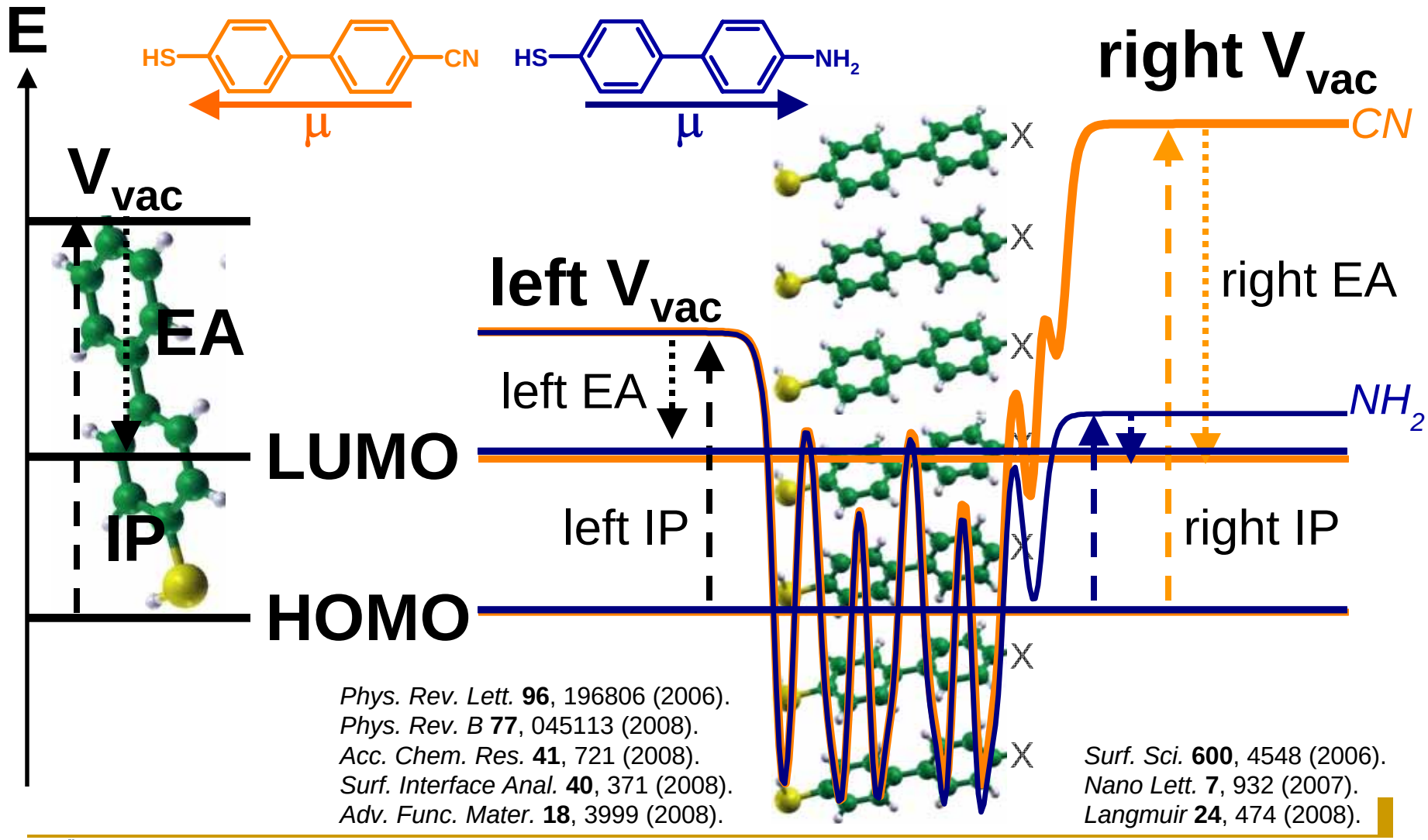




Outline

- Investigated Systems / Motivation
- Methods
- Overview over recent and current research
  - *Self-assembled monolayers on metals*
  - *Metal/molecule charge-transfer systems*
  - *Stretching/breaking single-molecule junctions*
  - *Doping in single-molecule junctions*
- Outlook
- Summary and Conclusions

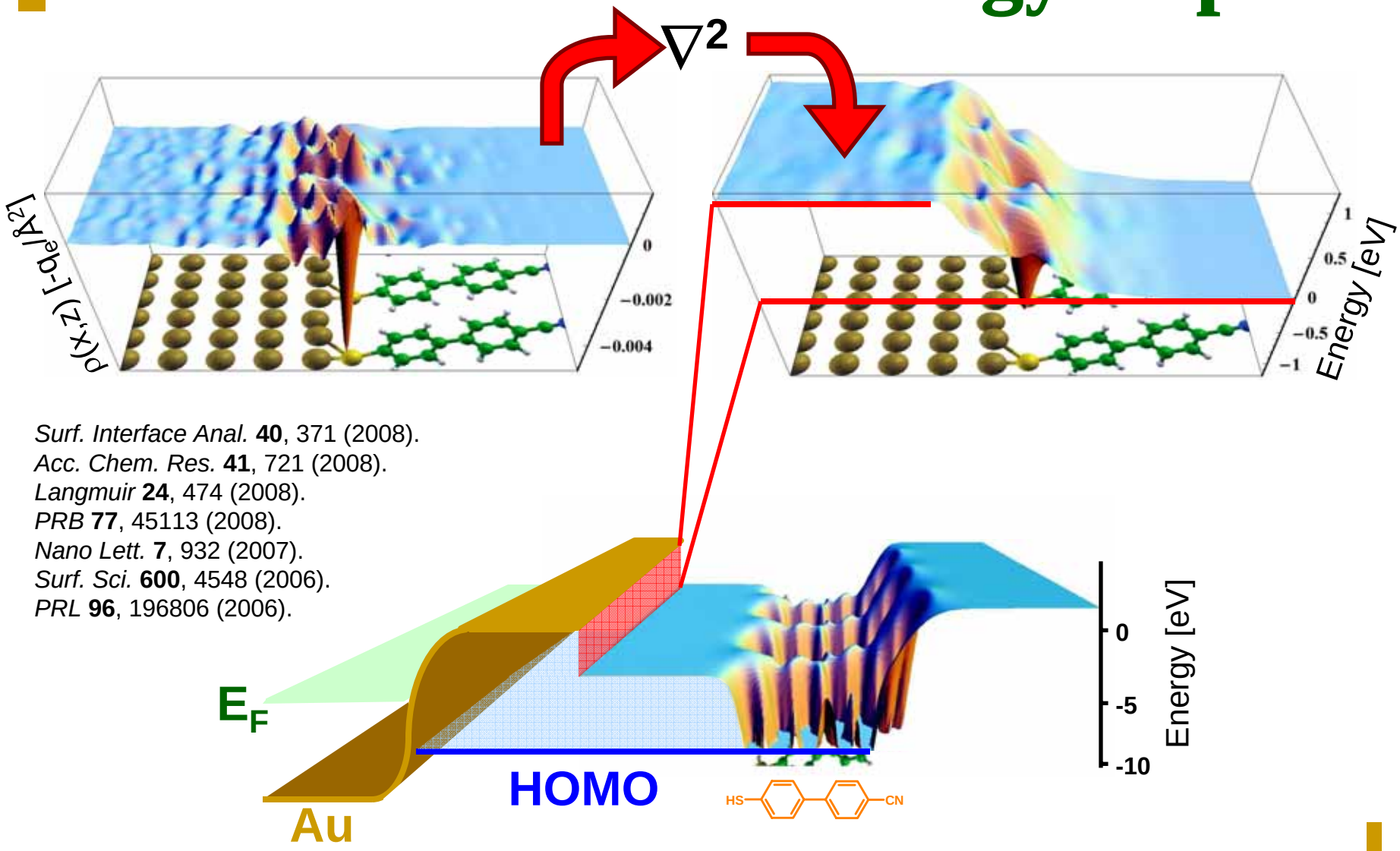
The SAM as a Dipole Layer



Phys. Rev. Lett. **96**, 196806 (2006).
Phys. Rev. B **77**, 045113 (2008).
Acc. Chem. Res. **41**, 721 (2008).
Surf. Interface Anal. **40**, 371 (2008).
Adv. Func. Mater. **18**, 3999 (2008).

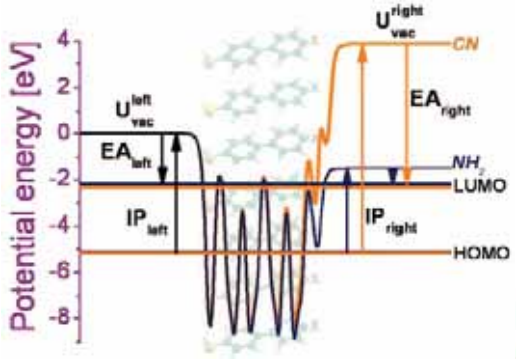
Surf. Sci. **600**, 4548 (2006).
Nano Lett. **7**, 932 (2007).
Langmuir **24**, 474 (2008).

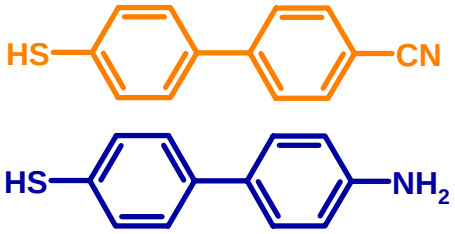
Interfacial Potential-Energy Steps

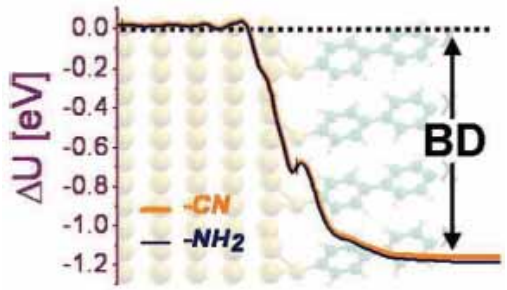


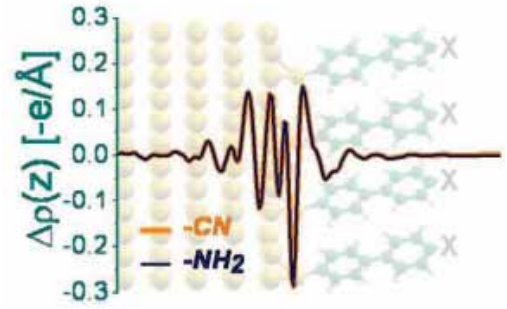
Surf. Interface Anal. **40**, 371 (2008).
Acc. Chem. Res. **41**, 721 (2008).
Langmuir **24**, 474 (2008).
PRB **77**, 45113 (2008).
Nano Lett. **7**, 932 (2007).
Surf. Sci. **600**, 4548 (2006).
PRL **96**, 196806 (2006).

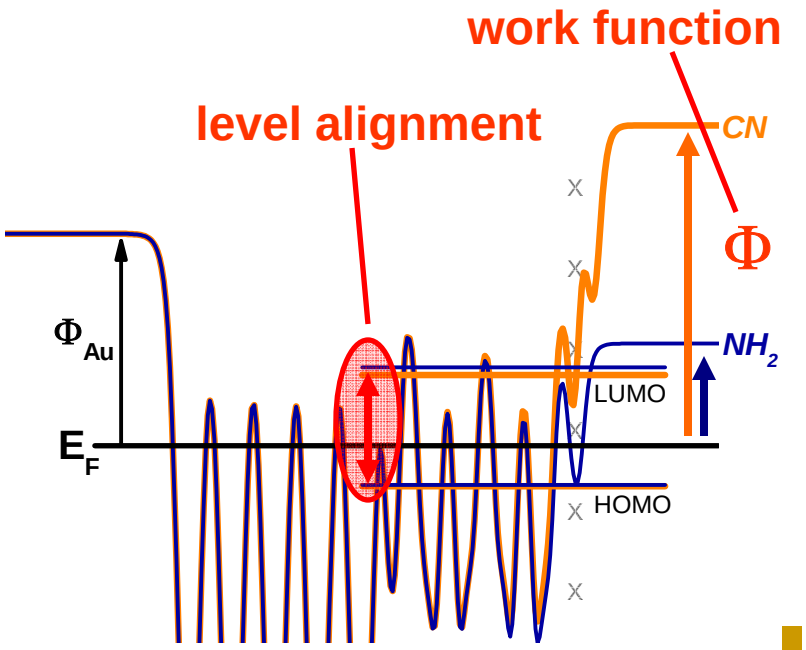
The Final Picture





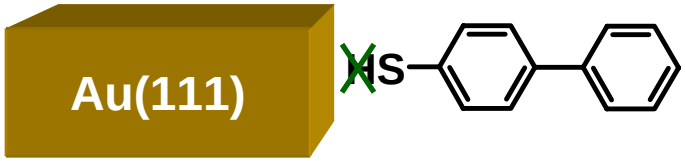




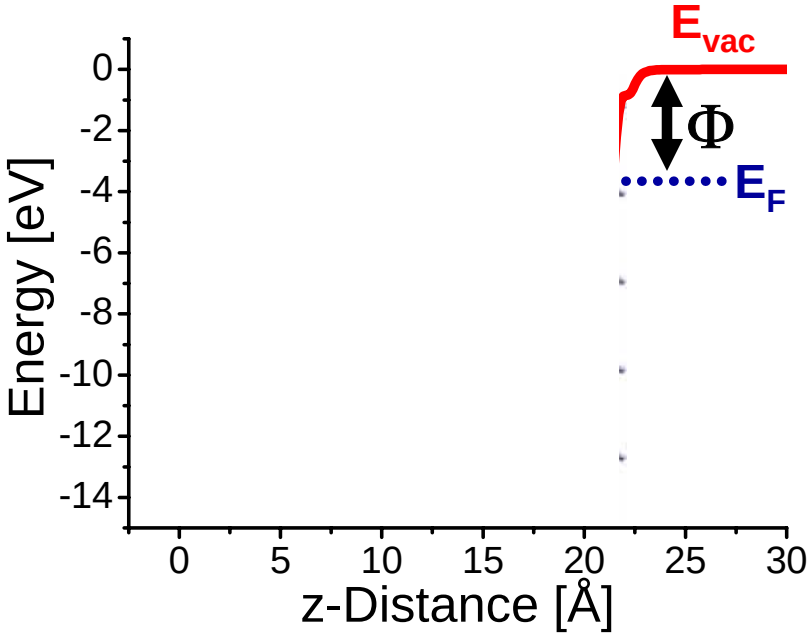


Surf. Sci. **600**, 4548 (2006).
Nano Lett. **7**, 932 (2007).
Langmuir **24**, 474 (2008).
Phys. Rev. Lett. **96**, 196806 (2006).
Phys. Rev. B **77**, 045113 (2008).
Acc. Chem. Res. **41**, 721 (2008).
Surf. Interface Anal. **40**, 371 (2008).
Adv. Func. Mater. **18**, 3999 (2008).

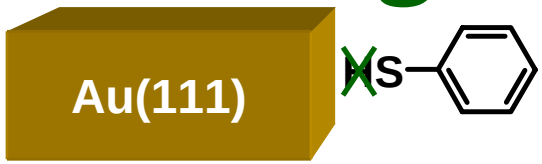
Workfunction and Level Alignment

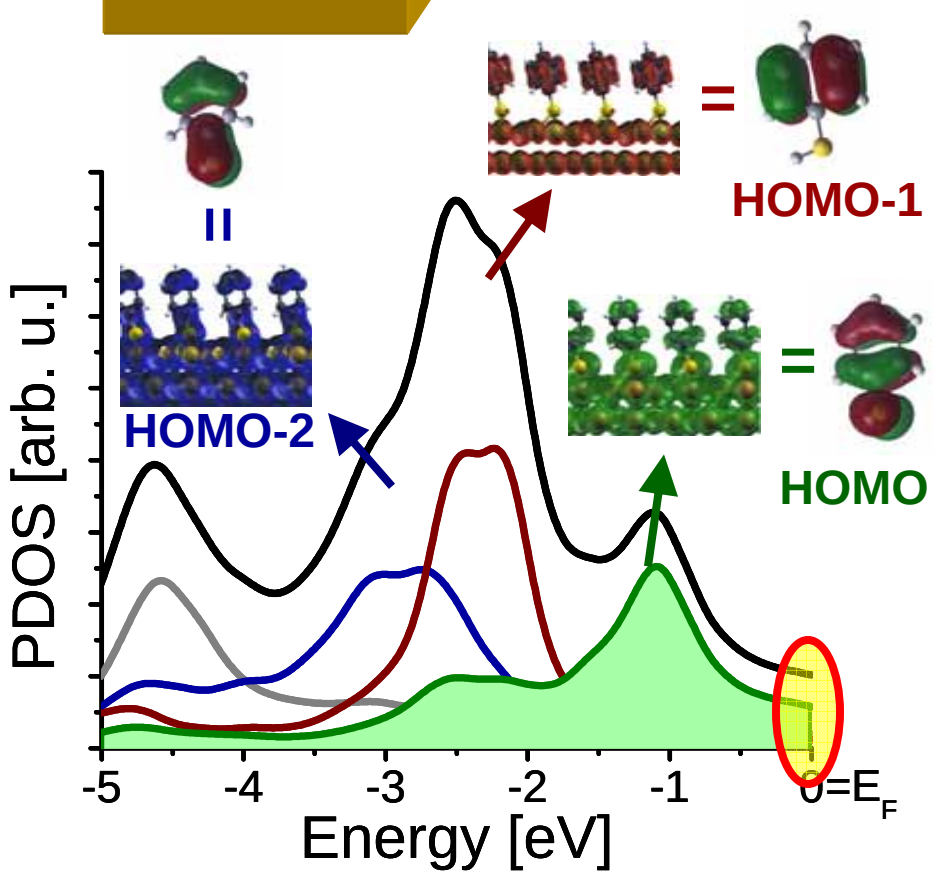


$\Delta\Phi_{calc}$ = -1.5 eV



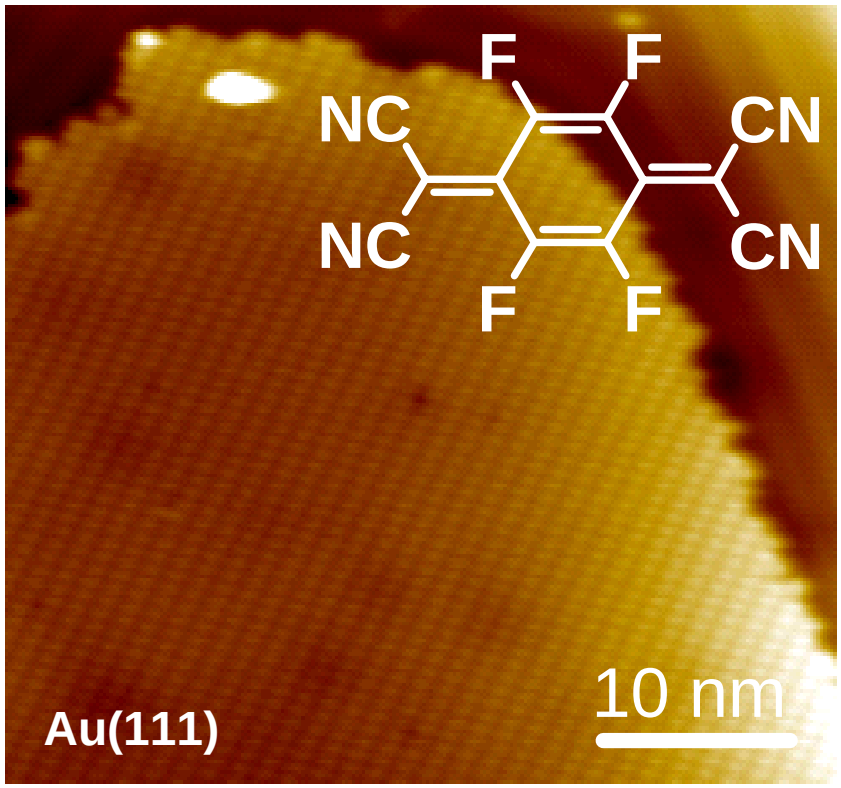
G. Heimel *et al.*, Phys. Rev. Lett. **96**, 196806, (2006).
G. Heimel *et al.*, Nano Lett. **7**, 932 (2007).
G. Heimel *et al.*, Acc. Chem. Res. **41**, 721 (2008).



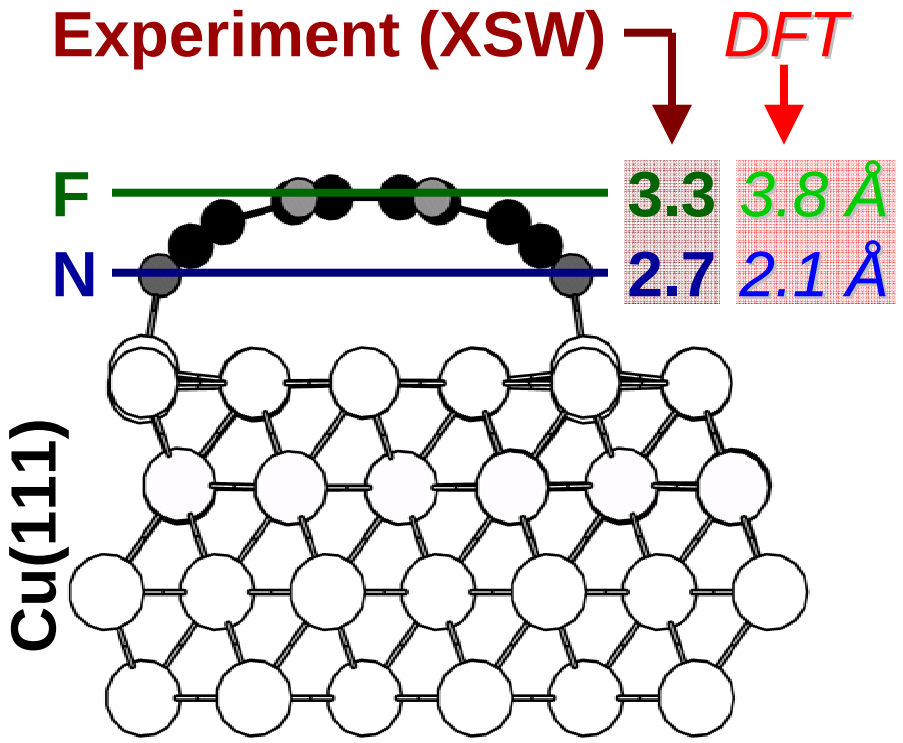


L. Romaner *et al.*, Small **2**, 1468 (2006).
G. Rangger *et al.*, Surf. Interface Anal. **40**, 371 (2008).
L. Romaner *et al.*, Phys. Rev. Lett. **99**, 256801 (2007).

F4TCNQ on Coinage Metals



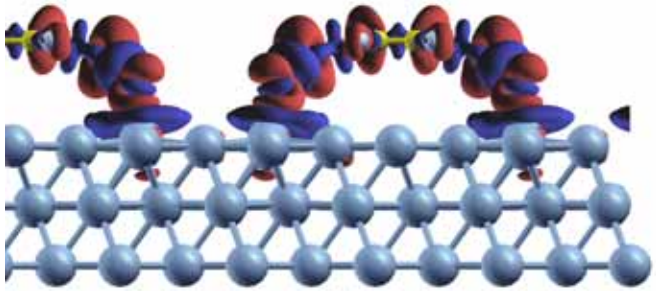
F. Jäckel *et al.*, Phys. Rev. Lett. **100**, 126102 (2008).



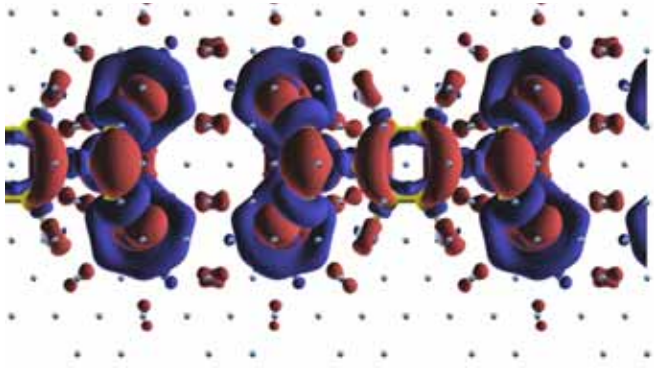
L. Romaner *et al.*, Phys. Rev. Lett. **99**, 256801 (2007).
G. Rangger *et al.*, submitted.

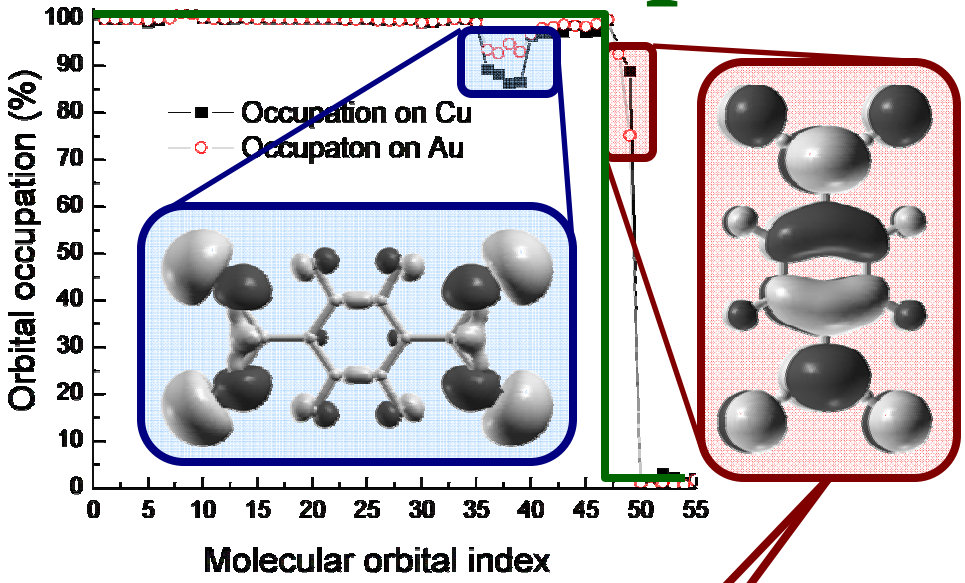
Charge Flow *vs.* Orbital Occupation

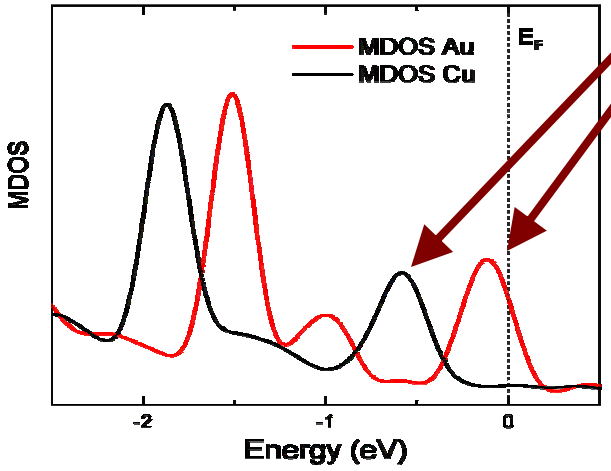
$$\Delta q_e = q_e^{combined} - \left(q_e^{slab} + q_e^{monolayer}\right)$$



electron accumulation
electron depletion







Reminiscent of ***CO*** on ***Ni(100)***:

σ → metal
metal → π*

N. Koch *et al.*, Phys. Rev. Lett. **95**, 237601 (2005).
L. Romaner *et al.*, Phys. Rev. Lett. **99**, 256801 (2007).
L. Romaner *et al.*, Small **2**, 1468 (2006).

R. Hoffmann, Rev. Mod. Phys. **60**, 601 (1988).

Outline

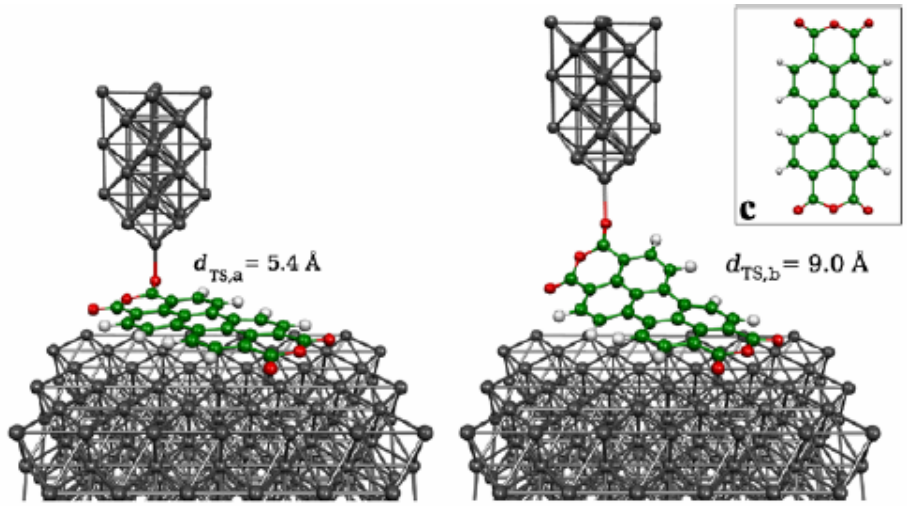
- Investigated Systems / Motivation
- Methods
- Overview over recent and current research
  - *Self-assembled monolayers on metals*
  - *Metal/molecule charge-transfer systems*
  - *Stretching/breaking single molecule junctions*
  - *Doping in single-molecule junctions*
- Outlook
- Summary and Conclusions

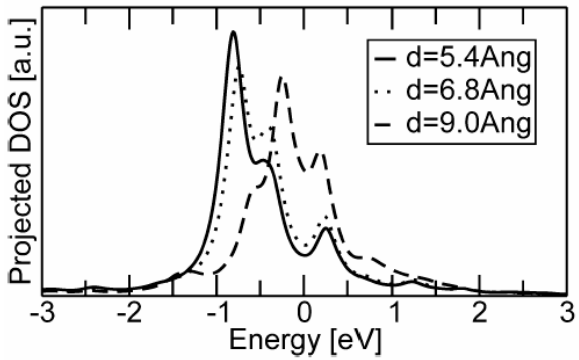
Stretching Molecular Junctions I

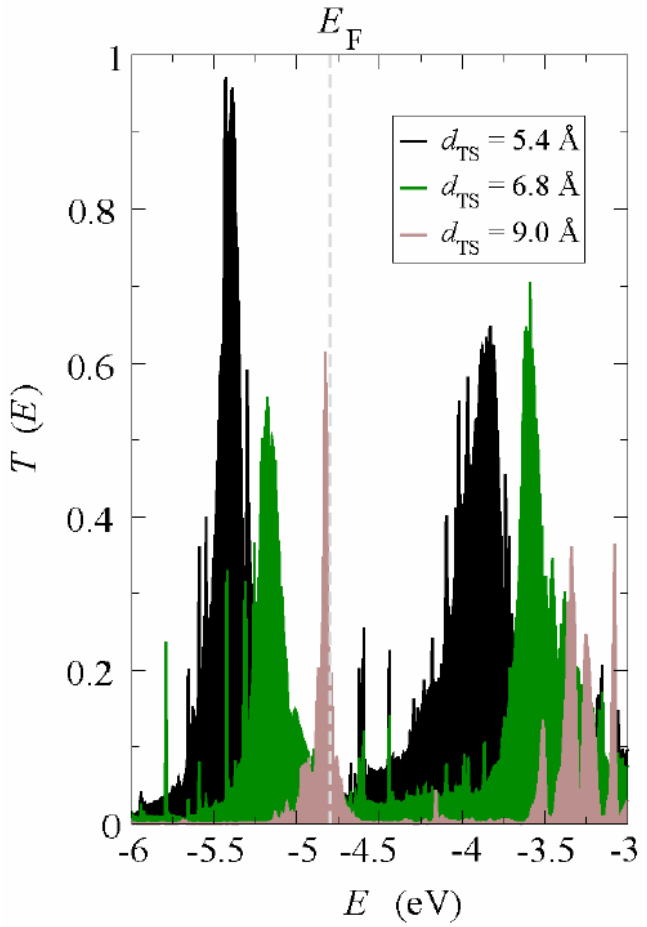
Quantum transport through STM-lifted single PTCDA molecules

Florian Pump · Ruslan Temirov · Olga Neucheva · Serguei Soubatch · Stefan Tautz · Michael Rohlfing · Gianaurelio Cuniberti

Appl Phys A (2008) 93: 335–343





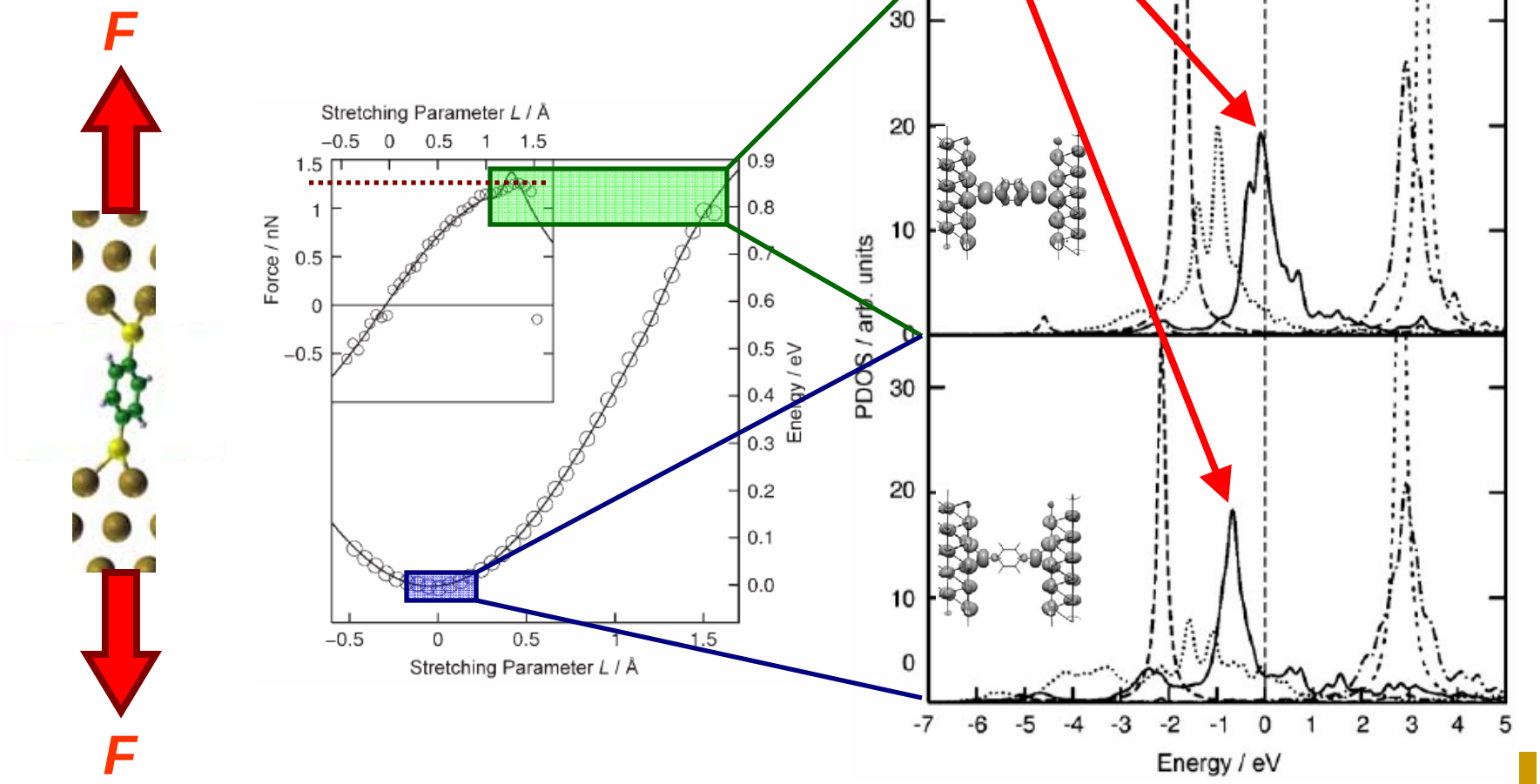


Stretching Molecular Junctions II

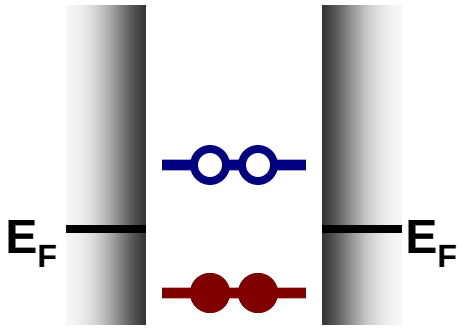
Stretching and Breaking of a Molecular Junction

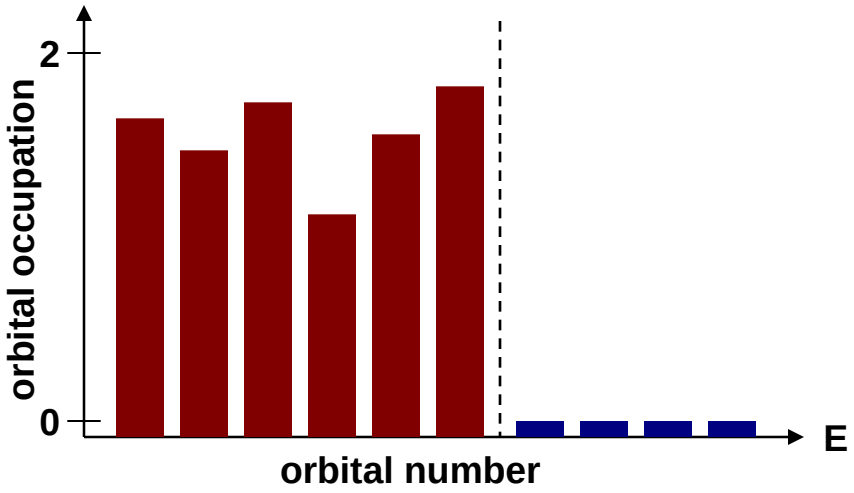
*Lorenz Romaner, Georg Heimel, Mathis Gruber, Jean-Luc Brédas, and Egbert Zojer**

small 2006, 2, No. 12, 1468 – 1475

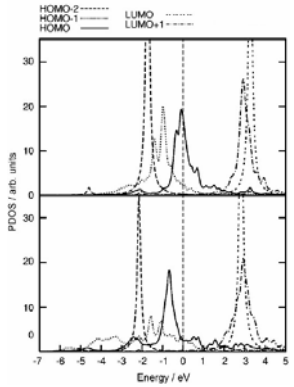


Orbital Occupation and Stretching

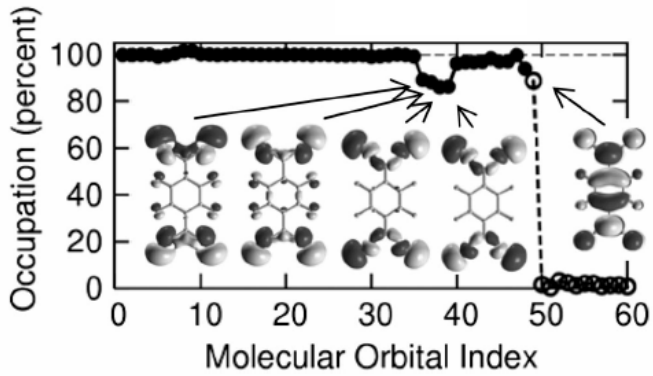




molecule remains *charge-neutral* through stretching process!

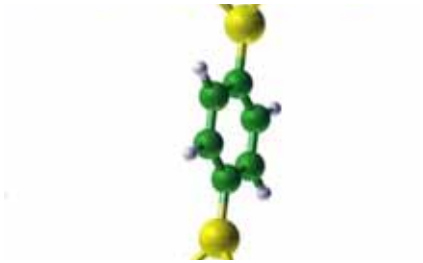


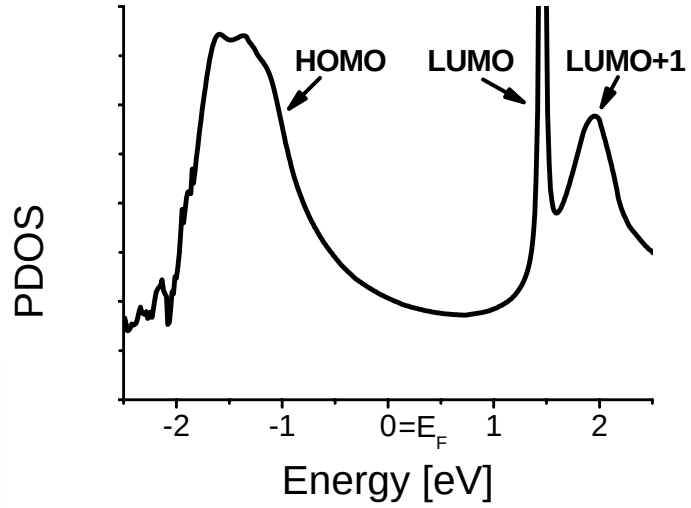
L. Romaner *et al.*, Small **2**, 1468 (2006).

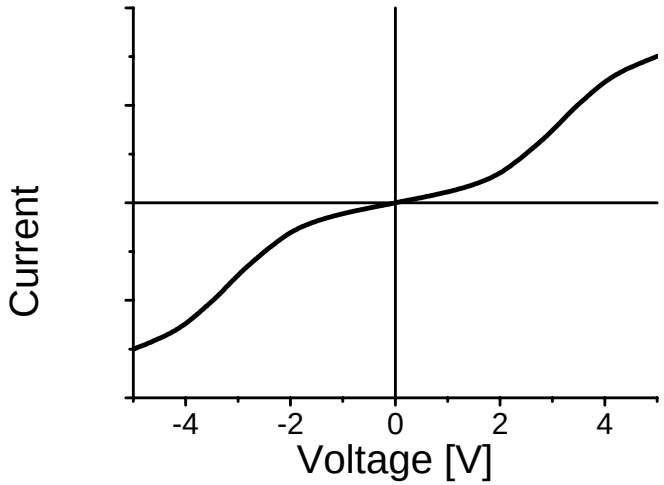


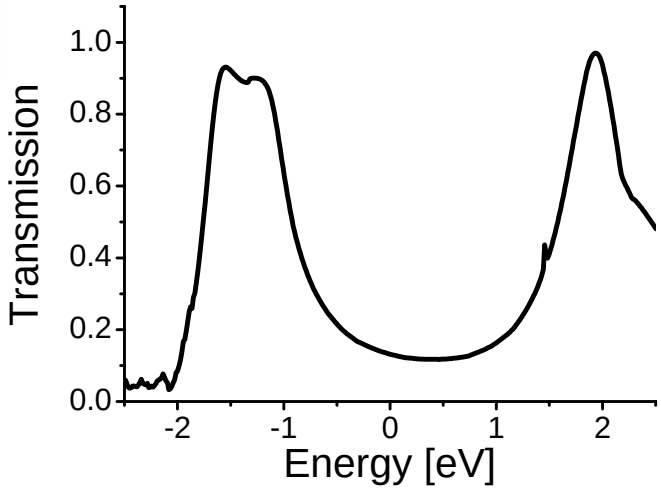
L. Romaner *et al.*, Phys. Rev. Lett. **99**, 256801 (2007).

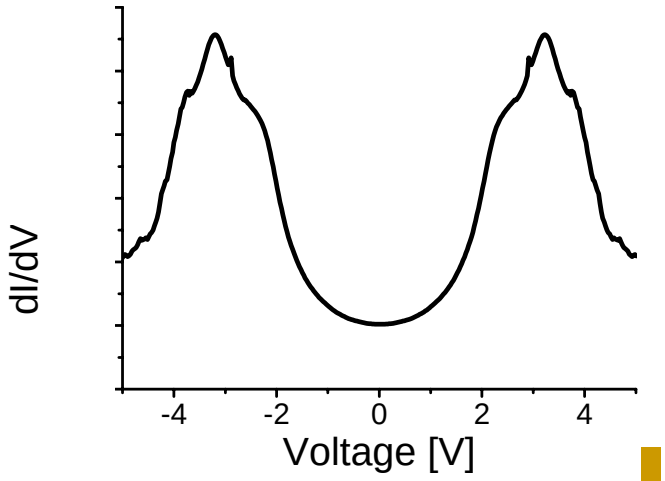
DFT-based Ballistic Transport







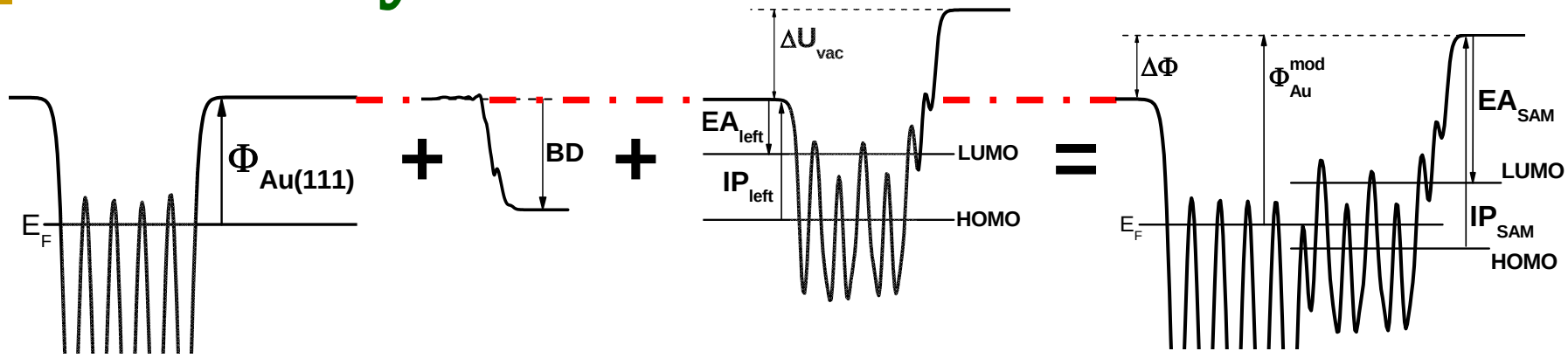




Outline

- Investigated Systems / Motivation
- Methods
- Overview over recent and current research
  - *Self-assembled monolayers on metals*
  - *Metal/molecule charge-transfer systems*
  - *Stretching/breaking single-molecule junctions*
  - *Doping in single-molecule junctions*
- Outlook
- Summary and Conclusions

Summary



- Interfaces in self-assembled monolayers
  - *Level-alignment and work function*
- Metal/molecule charge-transfer systems
  - *Molecular distortion and (back)donation*
- Fermi-level pinning in molecular junctions
  - *Break junctions and (neutral) radicals*

Acknowledgements

X-ray

Roland Resel (TUGraz)
Martin Oehzelt (JKU Linz)
Andreas Aichholzer (?)
Felix Porsch (HasyLab)
Manfred Kriechbaum (ÖAW)
Michael Winokur (Madison, WI)
Michael Hanfland (ESRF)

Raman

M. Chandrasekhar (Columbia, MO)
Chris Martin (?)
Suchi Guha (Columbia, MO)
Wilhelm Graupner (AVL Graz)
Dieter Somitsch (?)
Peter Knoll (KFU Graz)

Bandstructure

Peter Puschnig (MU Leoben)
Kerstin Hummer (Uni Wien)
C. Ambrosch-Draxl (MU Leoben)

UV/VIS

Maria Daghofer (Oak Ridge)

Surfaces & Clusters

Lorenz Romaner (MU Leoben)
Egbert Zojer (TUGraz)
Mathis Gruber (FHI Berlin)
Gerold Rangger (TUGraz)
Peter Pacher (TUGraz)
Jean-Luc Brédas (GaTech)
Georg Kresse (Uni Wien)
Chris Zangmeister (NIST)
Roger D. Van Zee (NIST)

Organics

N. Koch (HUB)
S. Duhm (Chiba)
I. Salzmann (HUB)
J. P. Rabe (HUB)
B. Bröker (HUB)
A. Vollmer (Bessy)
F. Schreiber (TÜB)
A. Gerlach (TÜB)

FWF Der Wissenschaftsfonds.

SIXTH FRAMEWORK PROGRAMME MARIE CURIE ACTIONS