Exemples of DFT calculations — and limitations

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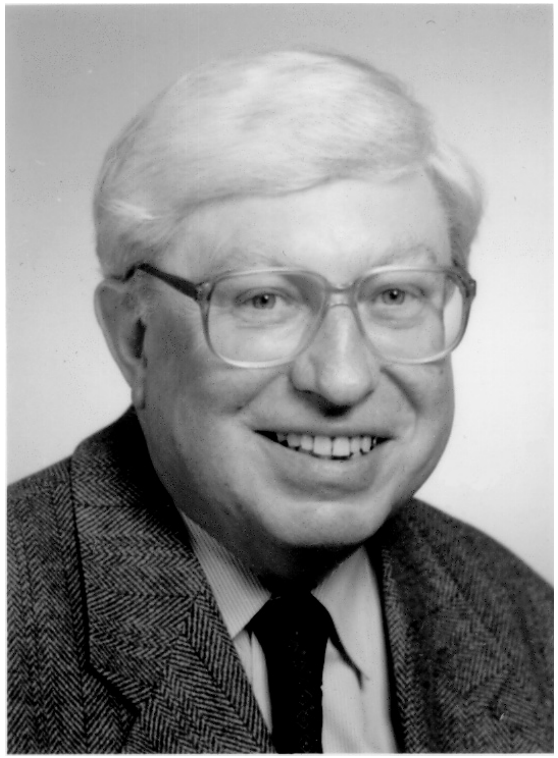
École de Sidi-BelAbbès de Nanomateriaux // Octobre 8-12, 2016

Summary

Surface science

Happy Birthday,
Herr Prof Dr Dr *h c* mult Ertl

Gerhard Ertl



Oxidation of CO on transition metal surfaces

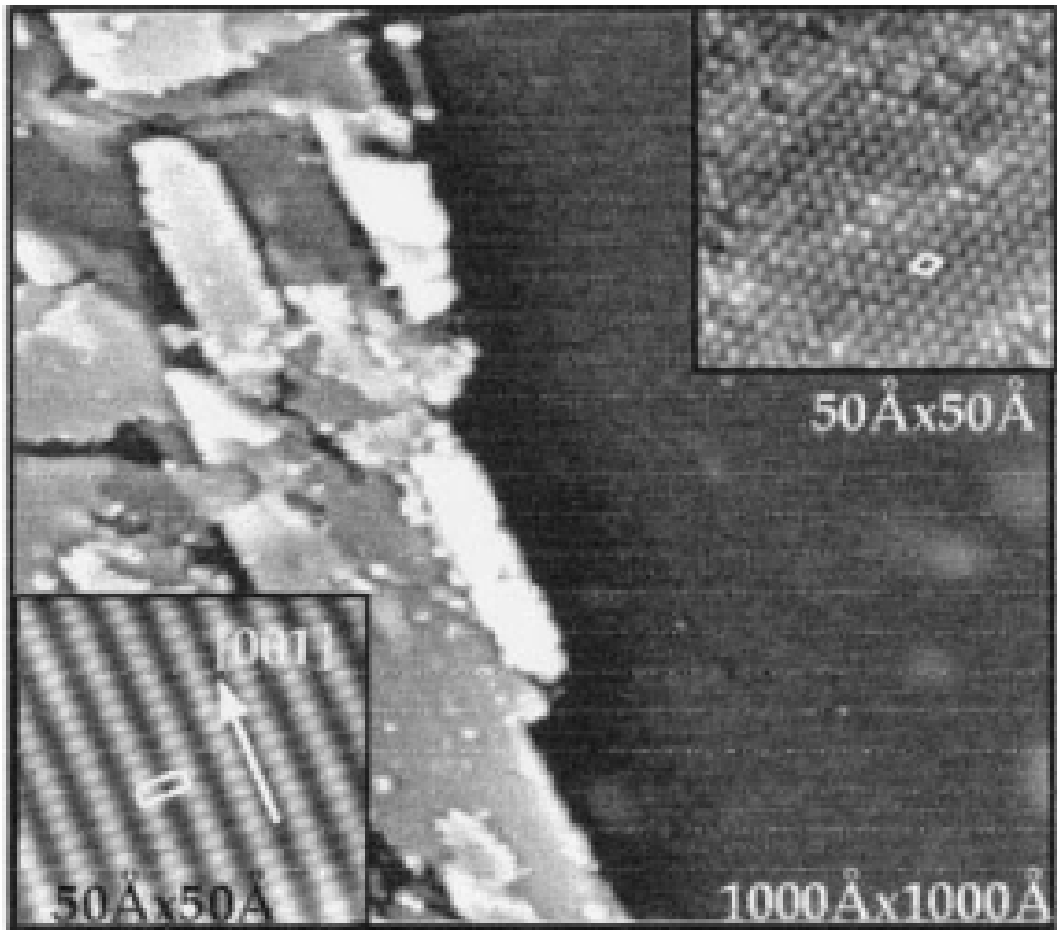
- Ru very bad catalyst at low O_2 pressure, excellent at high $p(O_2)$

REPORTS

Atomic-Scale Structure and Catalytic Reactivity of the $RuO_2(110)$ Surface

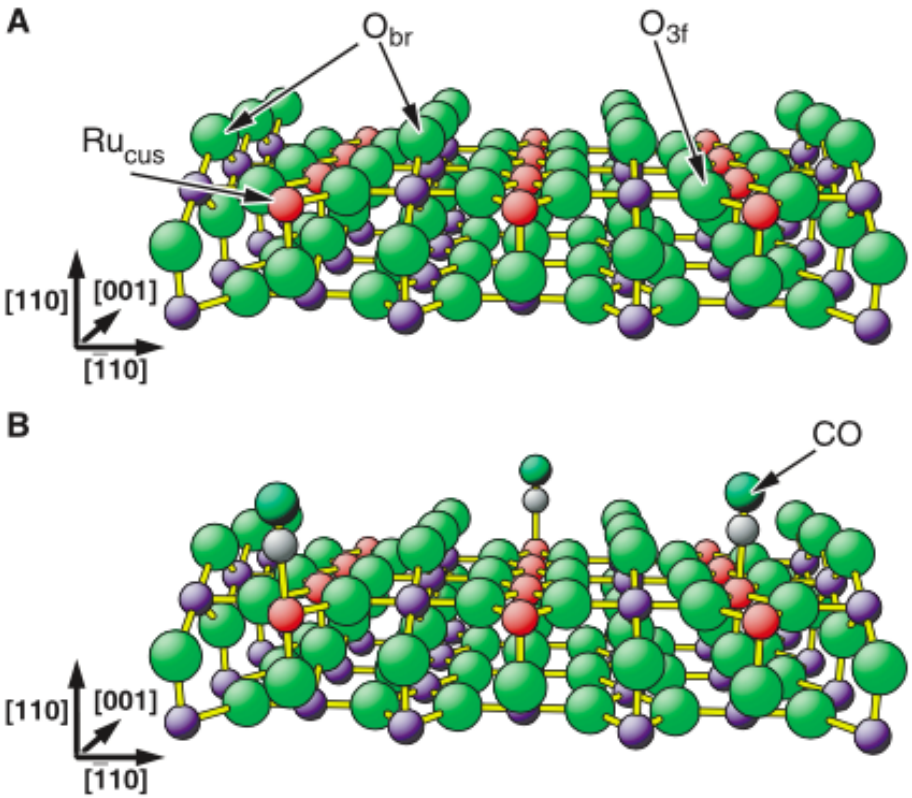
H. Over,[1*] Y. D. Kim,[1] A. P. Seitsonen,[1,2] S. Wendt,[1]
E. Lundgren,[3] M. Schmid,[3] P. Varga,[3] A. Morgante,[4] G. Ertl[1]

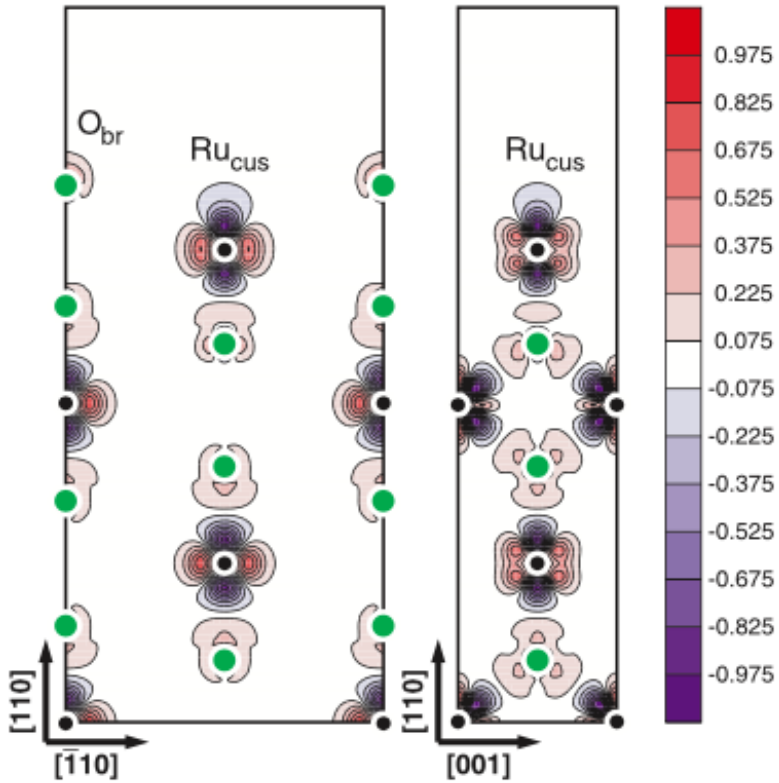
25 FEBRUARY 2000 VOL 287 SCIENCE www.sciencemag.org



(616 citations)

Ru(0001) under O_2 pressure

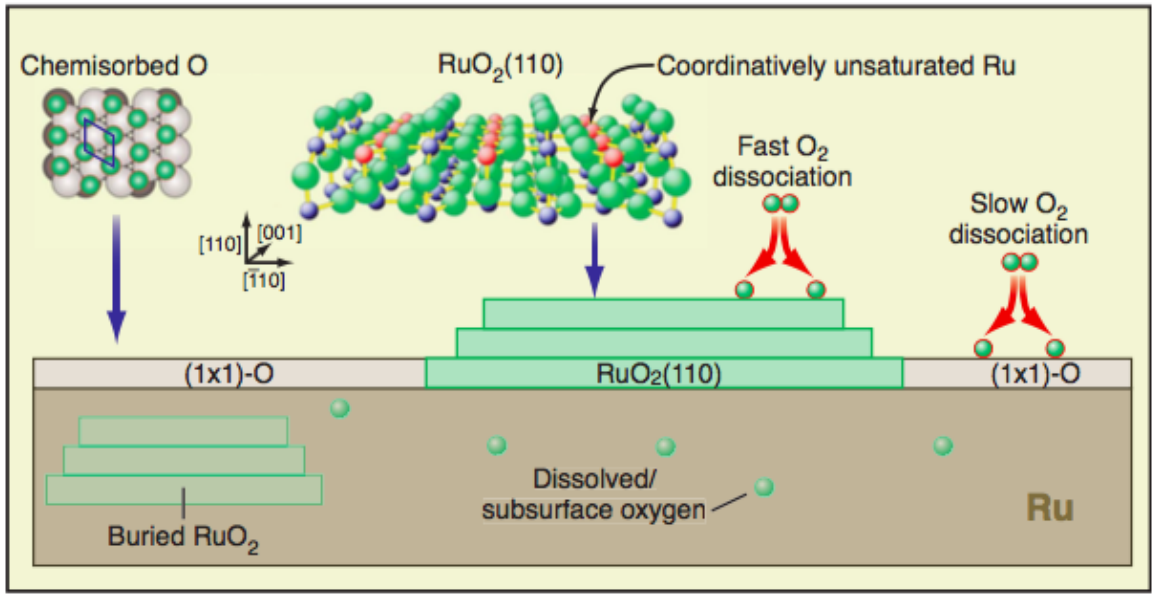




PERSPECTIVES: SURFACE CHEMISTRY

Oxidation of Metal Surfaces

H. Over and A. P. Seitsonen

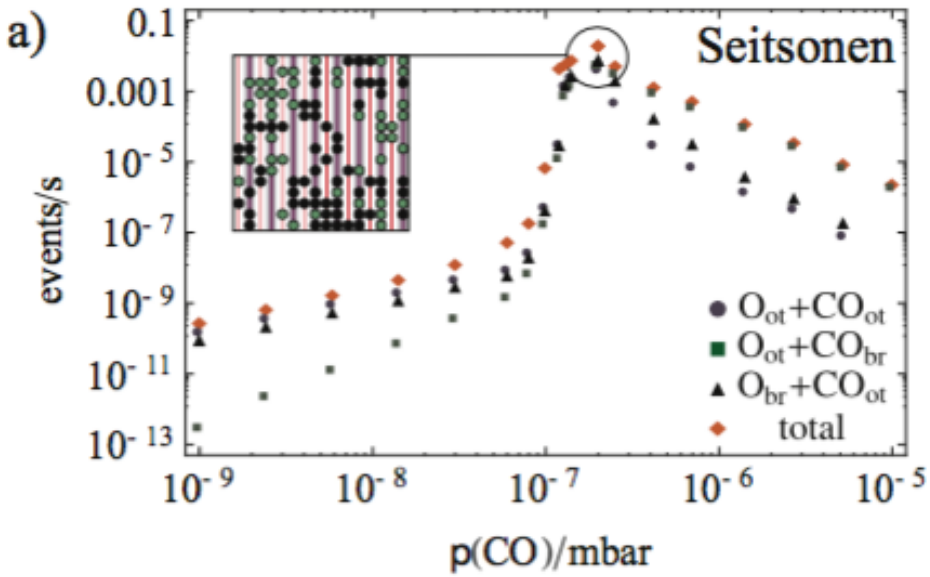


The rich oxygen chemistry of ruthenium (0001). The oxidation of Ru(0001) is one of the best studied systems in the literature (*10–12*). Chemisorbed oxygen, surface oxide, buried oxides, and subsurface oxygen may coexist in the near-surface region. This complexity is characteristic of the oxygen chemistry of many transition metal surfaces.

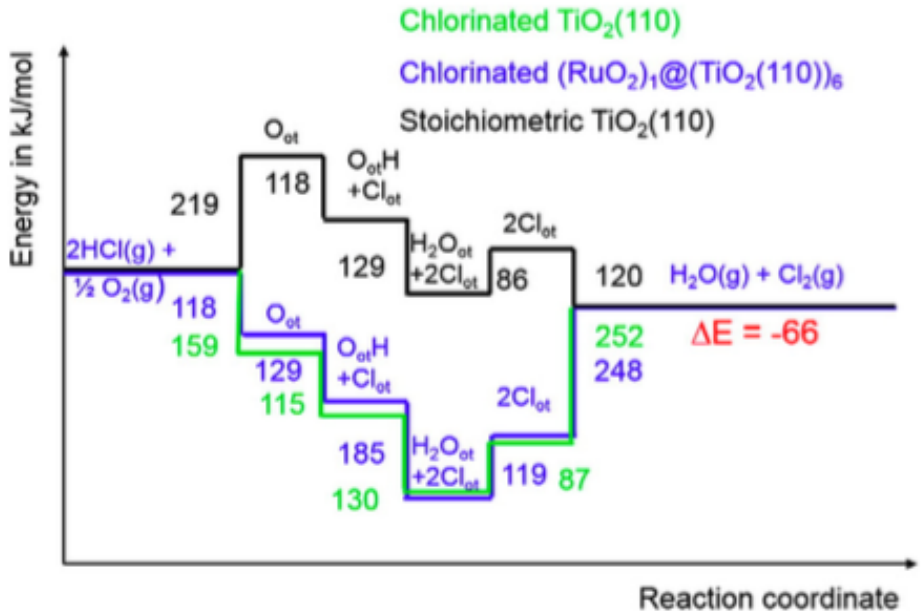
ncemag.org SCIENCE VOL 297 20 SEPTEMBER 2002 **2003**

Further applications of DFT energetics

kinetic Monte Carlo



Oxidation of HCl



Happy Birthday, Herr Prof Dr Dr *h c* mult Ertl

. . . in 2007:

10 October 2007

KUNGL. VETENSKAPSAKADEMIEN
THE ROYAL SWEDISH ACADEMY OF SCIENCES

Scientific Background on the Nobel Prize in Chemistry 2007

Chemical Processes on Solid Surfaces

Summary

Graphene

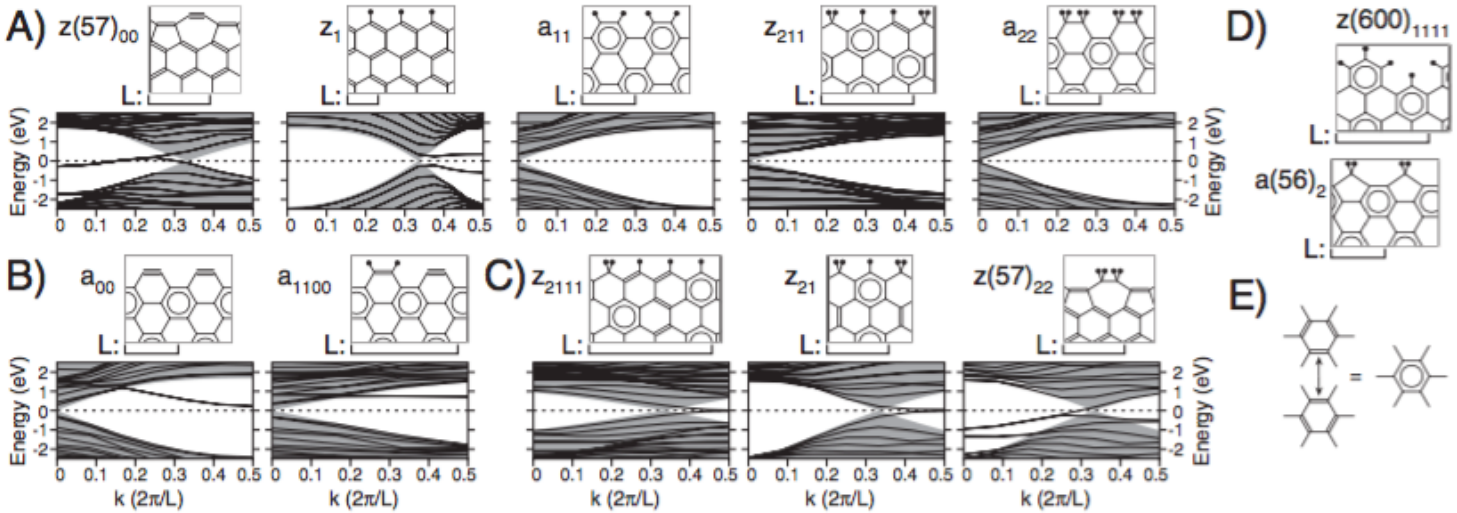
- Some unique properties, huge (technological) interest
- No band gap — would be needed in some applications
- Opening of gap via confinement

Graphene nano-ribbon

PRL 101, 096402 (2008) PHYSICAL REVIEW LETTERS week ending 29 AUGUST 2008

Structure, Stability, Edge States, and Aromaticity of Graphene Ribbons

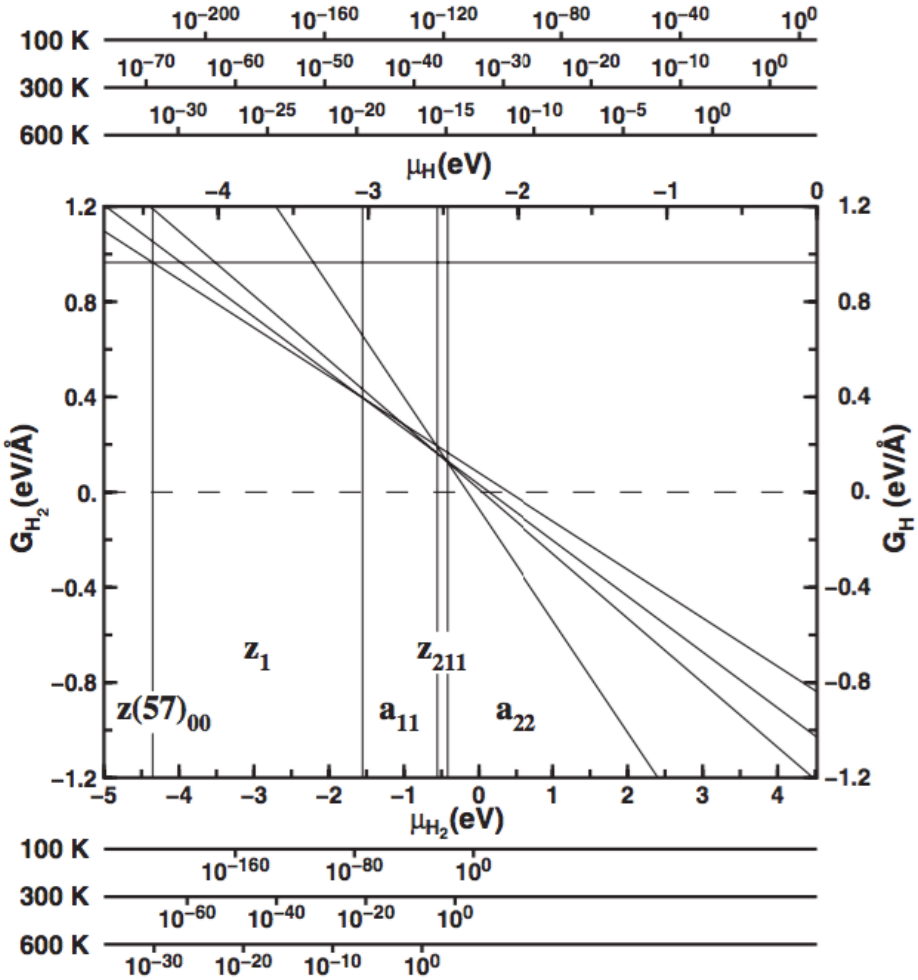
Tobias Wassmann, Ari P. Seitsonen, A. Marco Saitta, Michele Lazzeri, and Francesco Mauri
IMPMC, Université Paris 6 et 7, CNRS, IPGP, 140 rue de Lourmel, 75015 Paris, France
(Received 23 May 2008; published 27 August 2008)



GNR: Energetics

$$\mathcal{E}_{H_2} = \frac{1}{2L}\left(E^{\text{ribb}} - N_C E^{\text{blk}} - \frac{N_H}{2} E_{H_2}\right),$$

$$\mu_{H_2} = H^\circ(T) - H^\circ(0) - TS^\circ(T) + k_B T \ln\left(\frac{P}{P^\circ}\right),$$

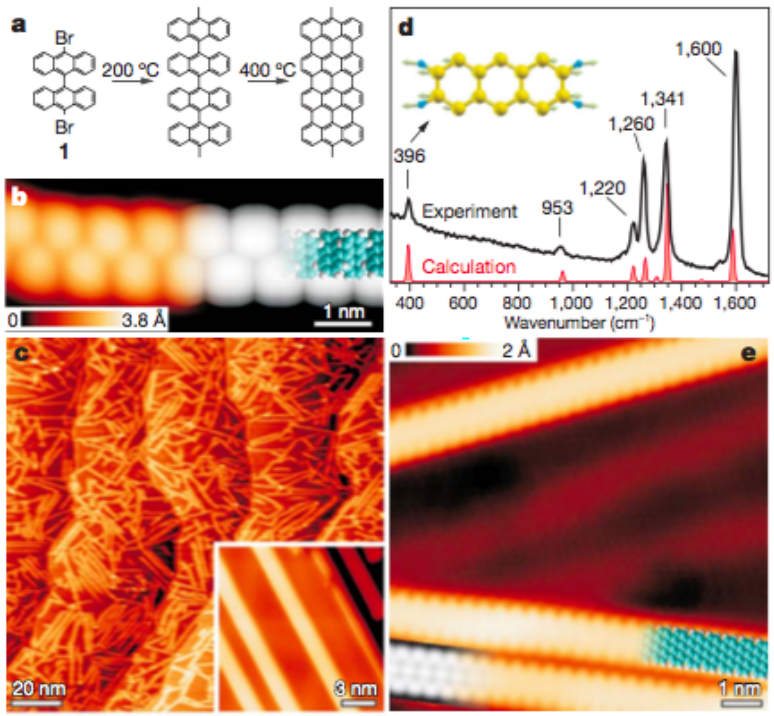


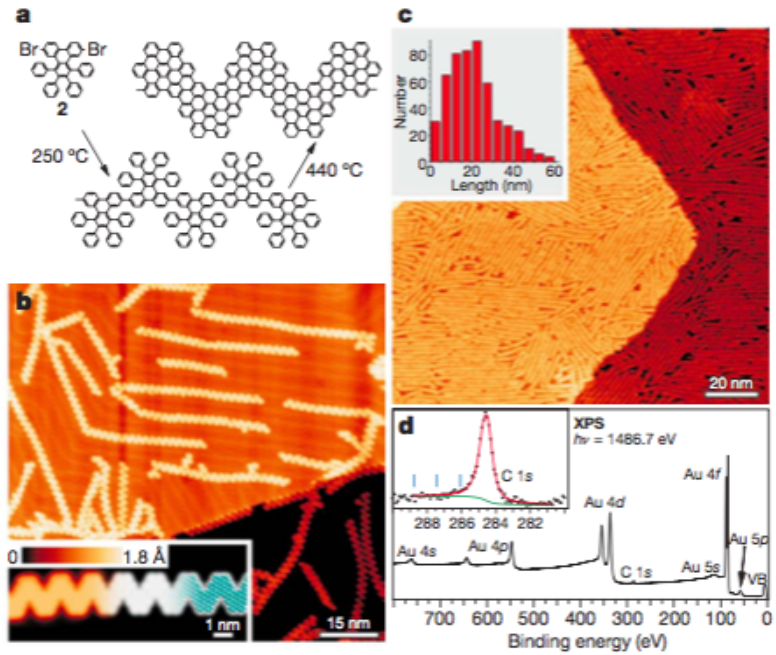
nature Vol 466|22 July 2010|doi:10.1038/nature09211

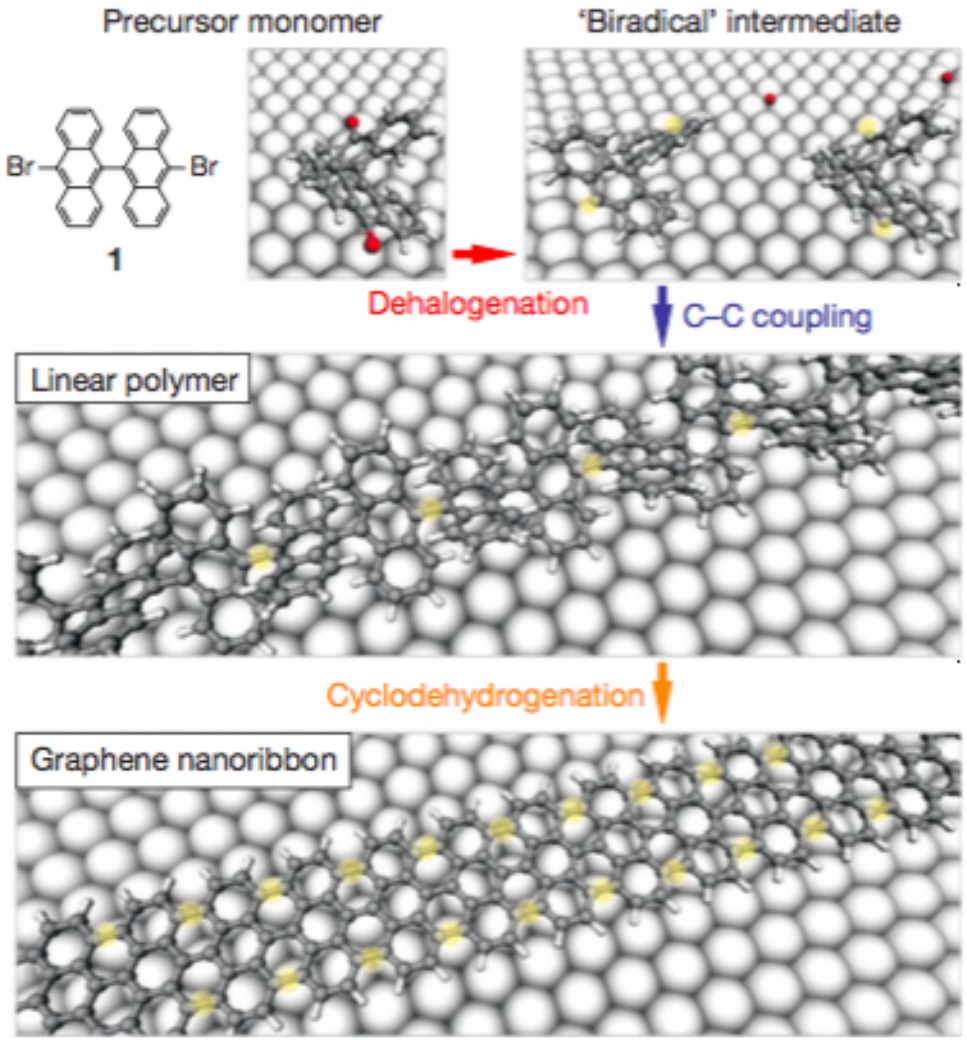
LETTERS

Atomically precise bottom-up fabrication of graphene nanoribbons

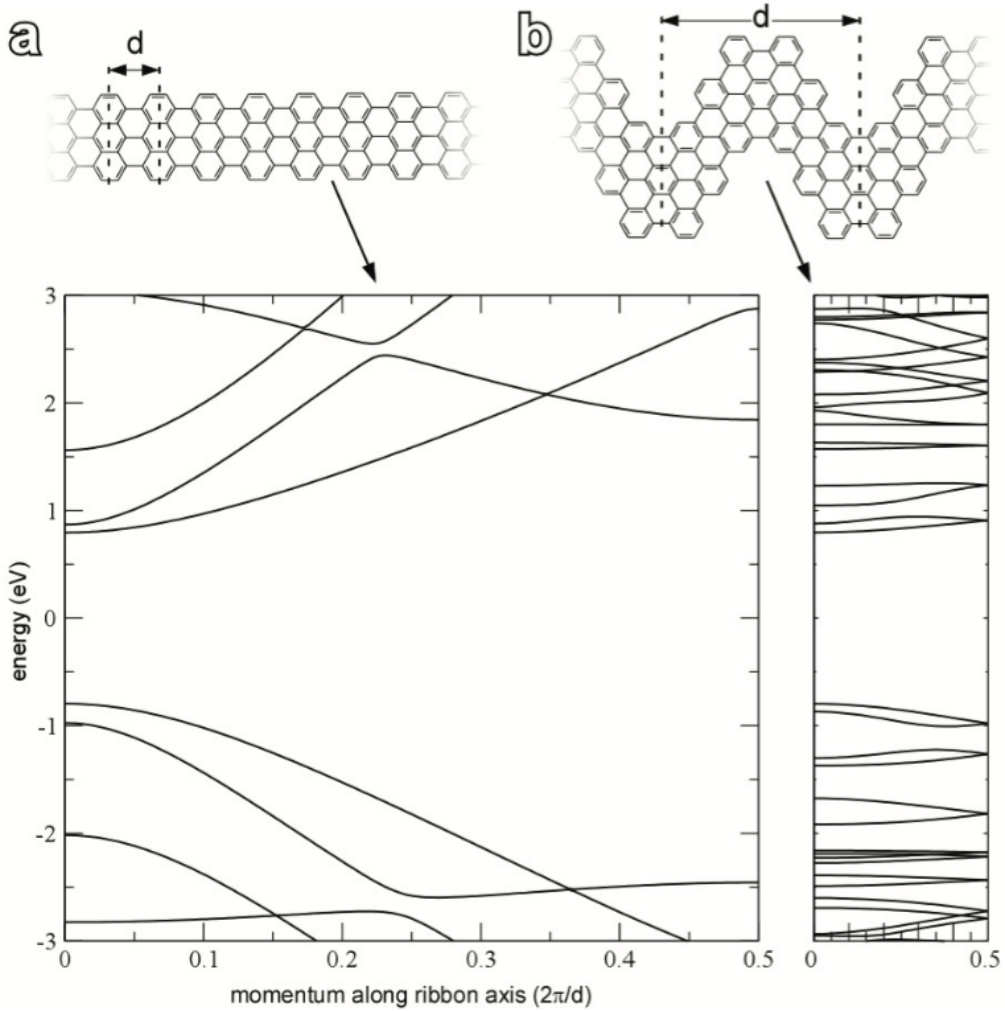
Jinming Cai[1]*, Pascal Ruffieux[1]*, Rached Jaafar[1], Marco Bieri[1], Thomas Braun[1], Stephan Blankenburg[1], Matthias Muoth[2], Ari P. Seitsonen[3,4], Moussa Saleh[5], Xinliang Feng[5], Klaus Müllen[5] & Roman Fasel[1,6]






Precursor monomer
'Biradical' intermediate
Br
Br
1
Dehalogenation
C–C coupling
Linear polymer
Cyclodehydrogenation
Graphene nanoribbon

GNR: Band structure



Summary

Molecular dynamics

Real-time dynamics of ions according to Newton's equation of motion:

$$\mathbf{F}_I = M_I \, \mathbf{a}_I$$

- Propagation of ionic positions
  - Verlet algorithm, velocity Verlet algorithm
  - $\mathbf{R}_I$, $\mathbf{v}_I$, $\mathbf{F}_I$
  - Needed: Initial values, forces
  - DFT: Evaluation of forces $\mathbf{F}_I$
  - Time step: $\delta t \approx 0.5$ fs
  - Simulation time: $t_{\mathrm{simulation}} = N_{\mathrm{step}} \times \delta t$
- $t_{\mathrm{simulation}} \approx 100$ ps $-$ 1 ns

Summary

Parametrisation of force fields based on DFTb-MD

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Geochimica et Cosmochimica Acta 141 (2014) 547–566

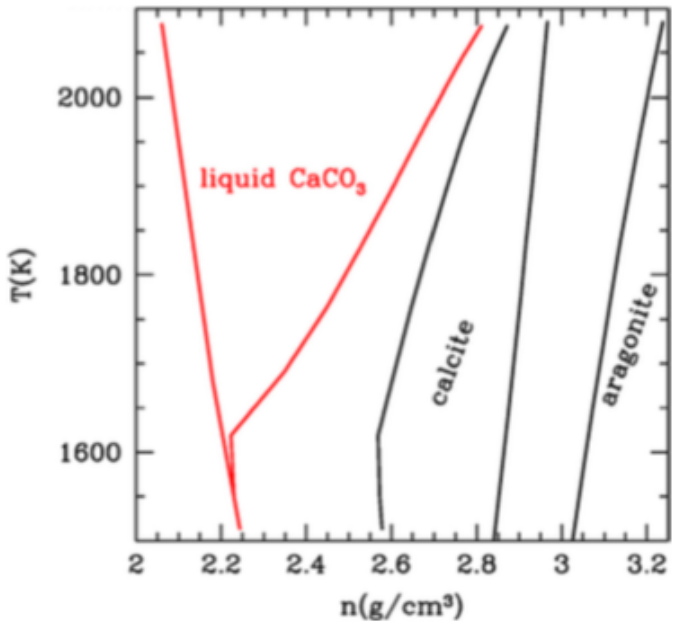
Geochimica et Cosmochimica Acta

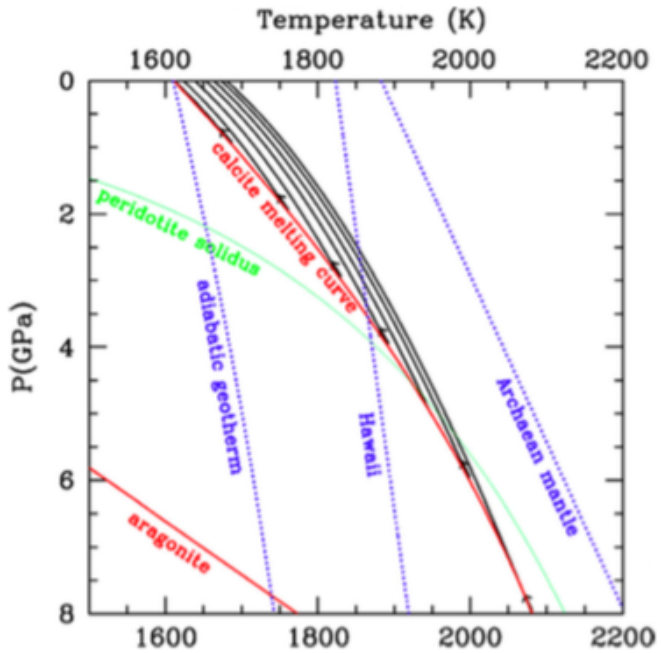
www.elsevier.com/locate/gca

Structure, equation of state and transport properties of molten calcium carbonate ($CaCO_3$) by atomistic simulations

Rodolphe Vuilleumier [a], Ari Seitsonen [b], Nicolas Sator [c,d], Bertrand Guillot [c,d,*]

[a] Laboratoire PASTEUR, UMR 8640 ENS-CNRS-UPMC Paris 6, Département de Chimie, Ecole Normale Supérieure, 75005 Paris, France
[b] Physikalisch-Chemiches Institut, Universität Zürich, CH-8057 Zürich, Switzerland
[c] Sorbonne Universités, UPMC Univ Paris 06, UMR 7600, LPTMC, F 75005 Paris, France
[d] CNRS, UMR 7600, LPTMC, F 75005 Paris, France





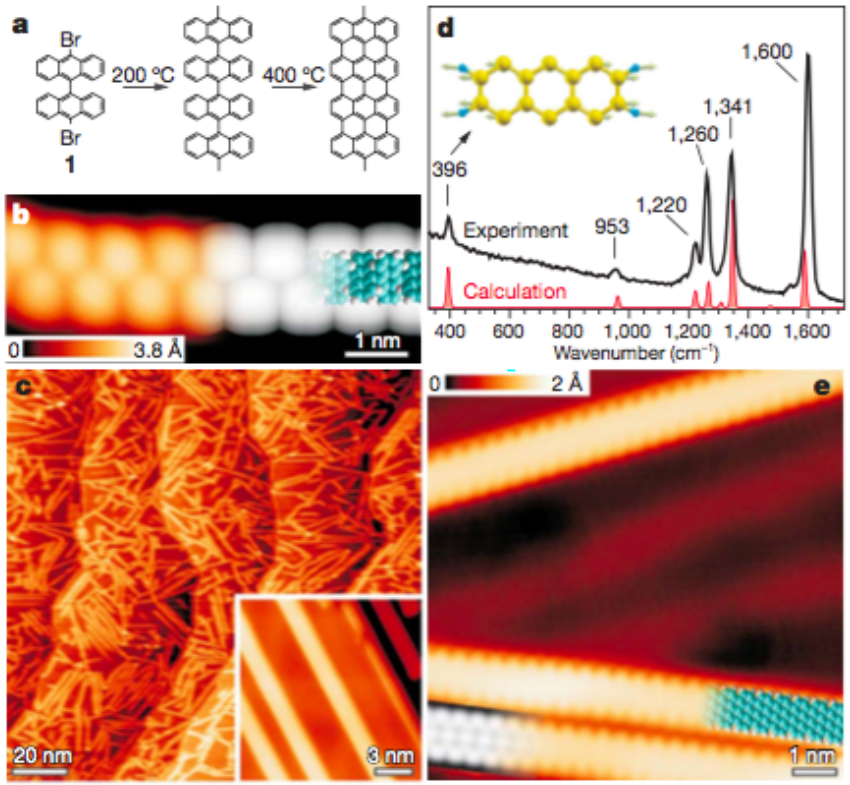
Calculation of infra-red, Raman vibrational spectra

Sunday, Prof Krim: Infra-red $\propto D$ (dipole), Raman $\propto \alpha$ (polarisability)

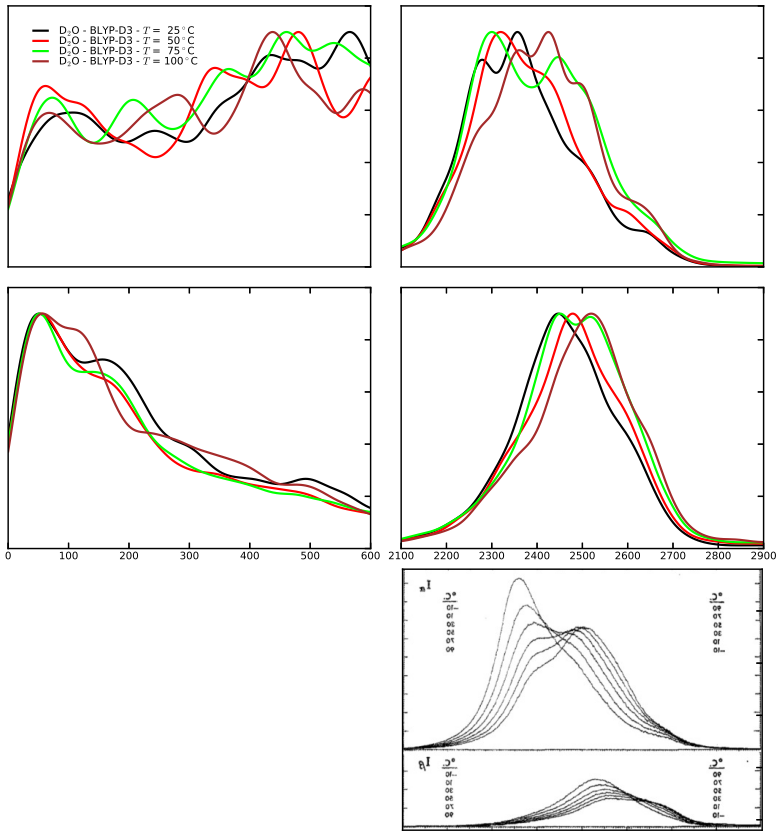
- Static calculation: $D(\mathbf{R}_\nu)$, $\alpha(\mathbf{R}_\nu)$
- Dynamic simulation: FT$[D(t)]$, FT$[\alpha(\mathbf{R}_\nu)]$

Calculation of infra-red, Raman vibrational spectra: Examples

Static calculation: $\alpha(\mathbf{R}_\nu)$



Dynamic simulation: FT$[\alpha(\mathbf{R}_\nu)]$



Band structure, comparison with ARPES: $\varepsilon_{E,\mathbf{k}} \approx \varepsilon^{\mathrm{KS}}_{i\mathbf{k}}$

Surface Science 643 (2016) 150–155

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Electronic structure of reconstructed Au(111) studied with density functional theory

Ari Paavo Seitsonen

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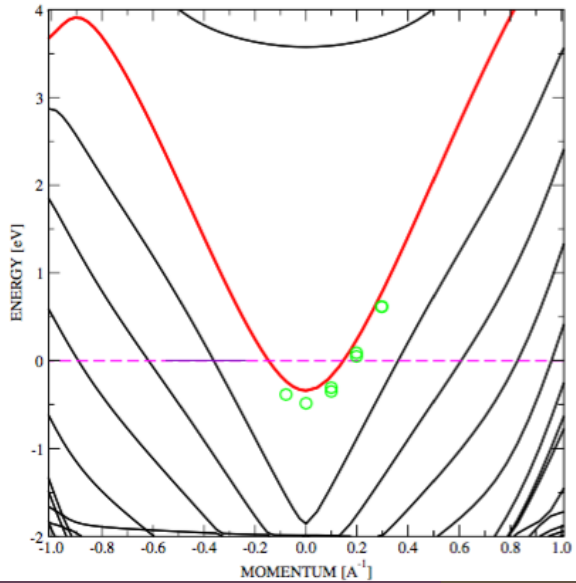
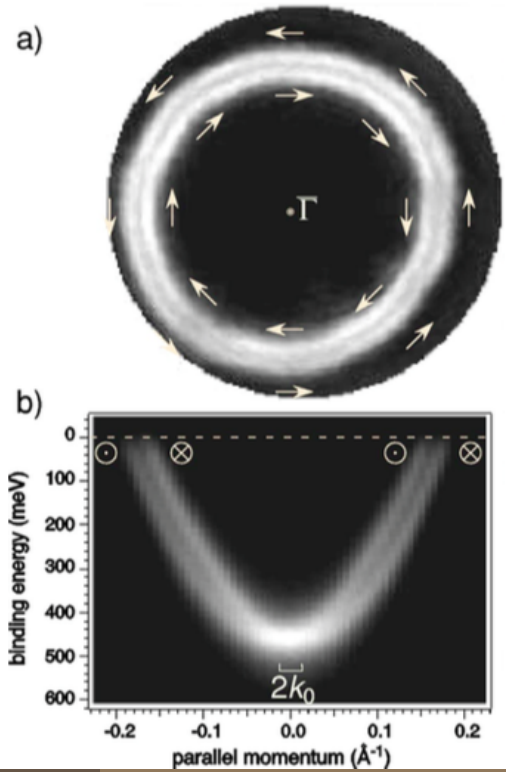
Département de Chimie, École Normale Supérieure, 24 rue Lhomond, F-75005, Paris, France



PHYSICAL REVIEW B **69**, 241401(R) (2004)

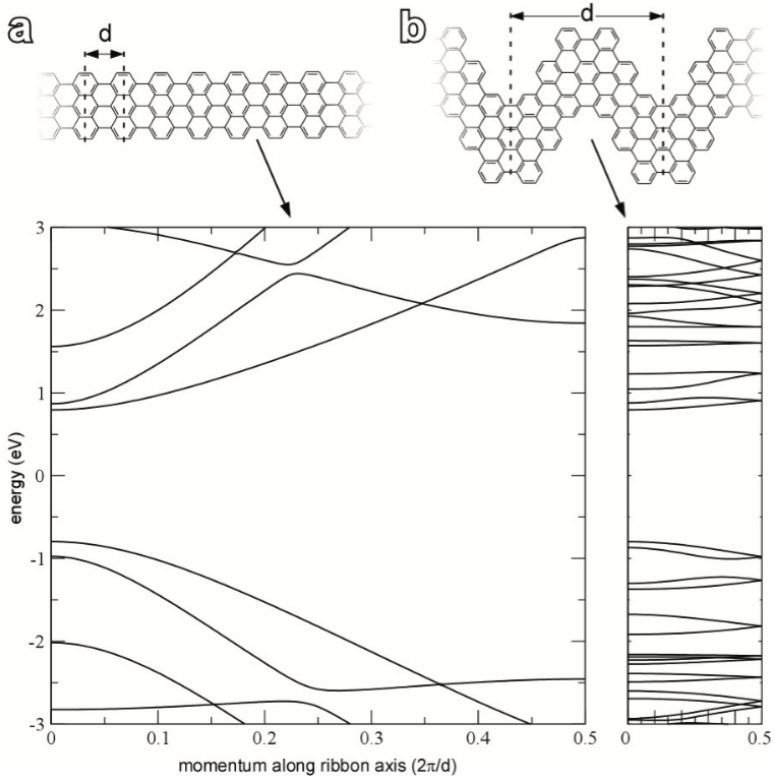
Spin structure of the Shockley surface state on Au(111)

M. Hoesch,[1,2] M. Muntwiler,[1] V. N. Petrov,[3] M. Hengsberger,[1] L. Patthey,[2] M. Shi,[2] M. Falub,[2] T. Greber,[1] and J. Osterwalder[1]
[1]*Physik-Institut, Universität Zürich-Irchel, 8057 Zürich, Switzerland*
[2]*Synchrotron Radiation Research Department, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland*
[3]*St. Petersburg Technical University, 195251 St. Petersburg, Russia*



Band structure

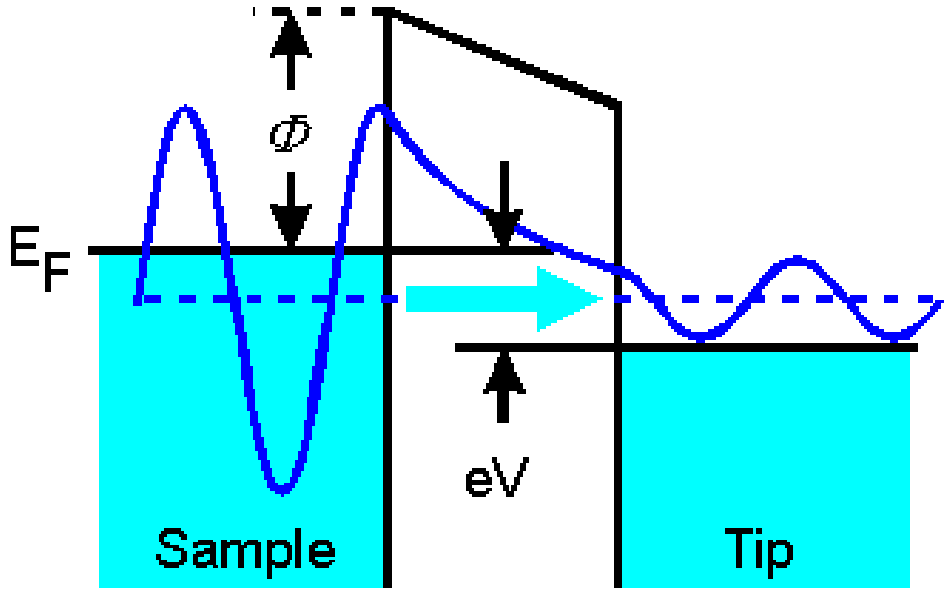
$$\varepsilon_{E,\mathbf{k}} \approx \varepsilon^{\mathrm{KS}}_{i\mathbf{k}}$$



"Band gap problem": LDA, GGA, ... underestimate band gaps

Scanning tunnelling microscope: DFT modelling

- Tersoff-Hamann model: $I(E) \propto \int_{\varepsilon}^{\varepsilon+eV_{\mathrm{bias}}} |\psi_{\varepsilon}(\mathbf{r})|^2 \, \delta(\varepsilon - \varepsilon_E) \, d\varepsilon$
- Bardeen model: Electronic structure of tip included non-self-consistently

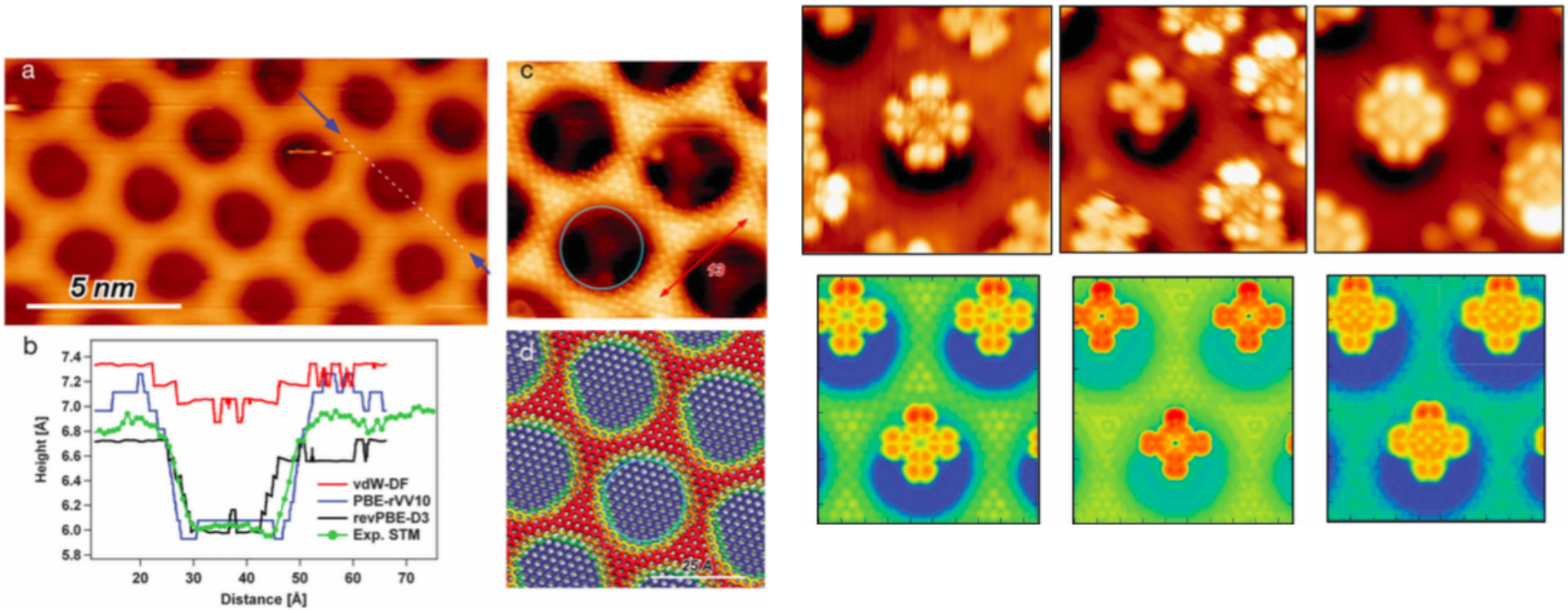


Scanning tunnelling microscope: DFT modelling

Cite this: *Phys. Chem. Chem. Phys.*, 2014, 16, 12374

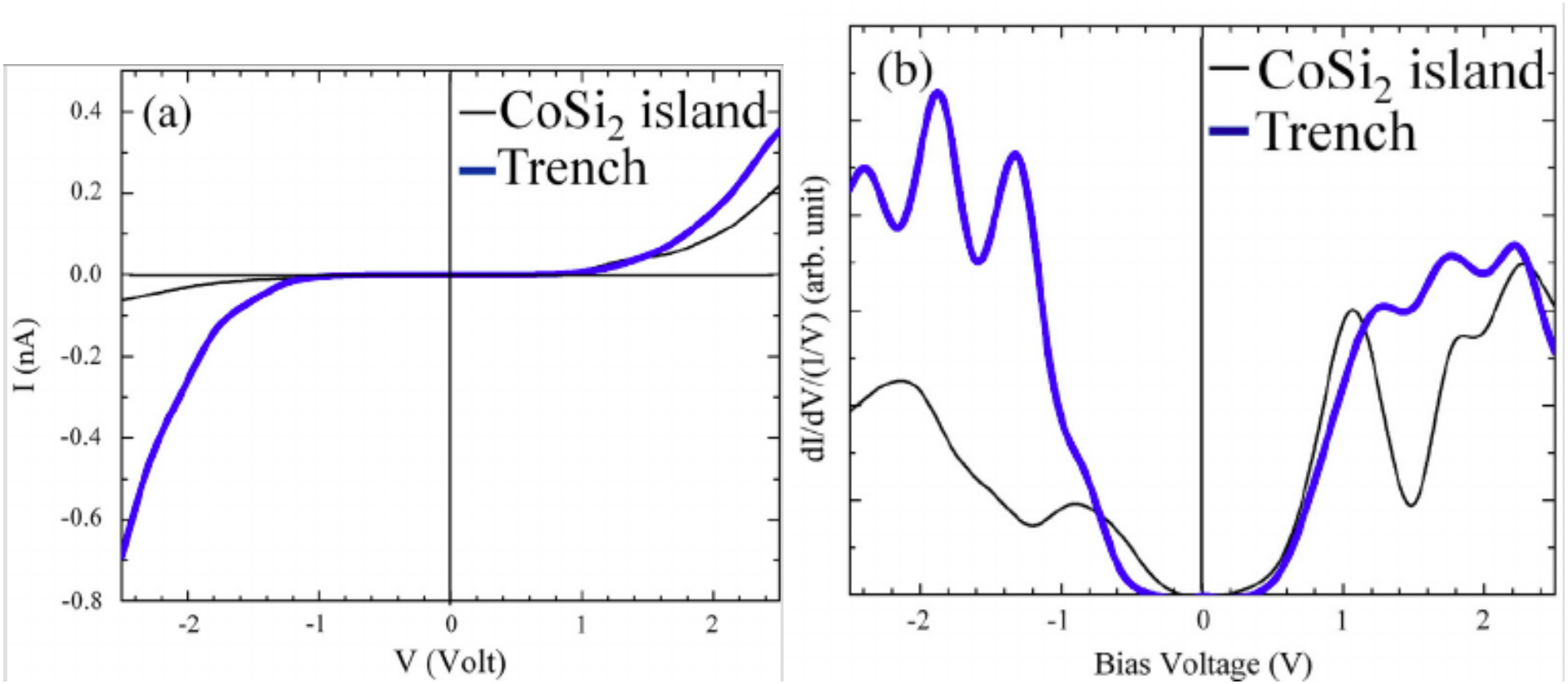
Site-selective adsorption of phthalocyanine on h-BN/Rh(111) nanomesh†

Marcella Iannuzzi,*[a] Fabien Tran,[b] Roland Widmer,[c] Thomas Dienel,[c] Kevin Radican,[c] Yun Ding,[a] Jürg Hutter[a] and Oliver Gröning[c]



Scanning tunnelling spectroscopy: DFT modelling

- Signal $\propto dI/dV$
- Tersoff-Hamann model: $dI/dV(E) \approx |\psi_E(\mathbf{r})|^2\, \delta(E - \varepsilon_E)\, dE$

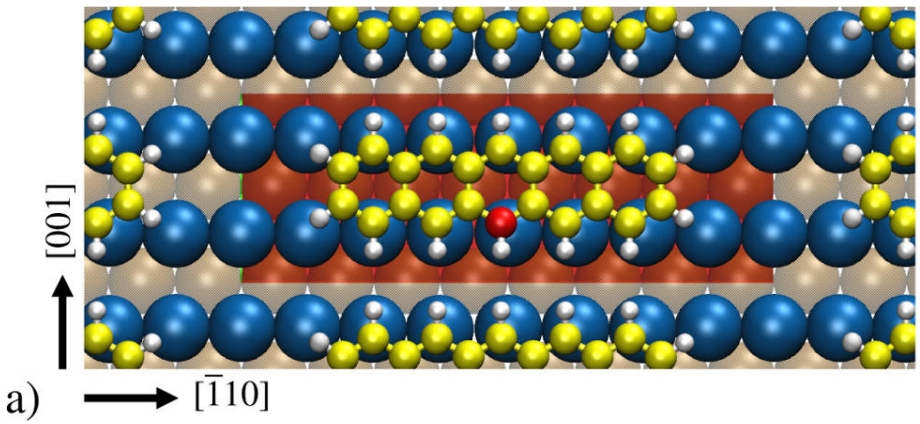


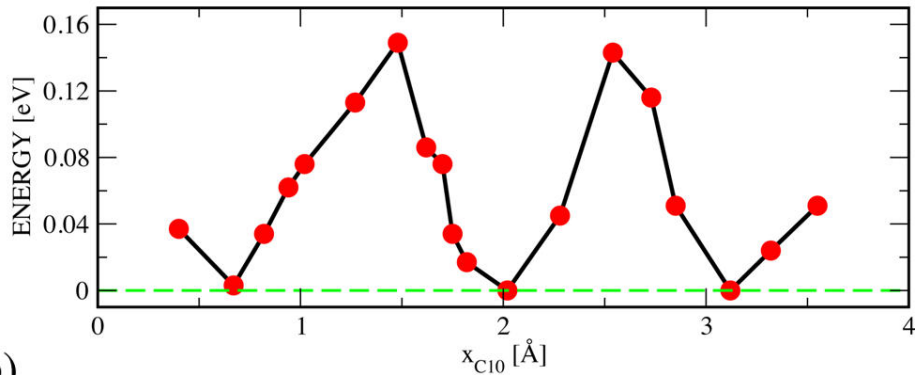
Orbital overlap: Example pentacene/Cu(110)

Electronic Structure of an Organic/Metal Interface: Pentacene/ Cu(110)

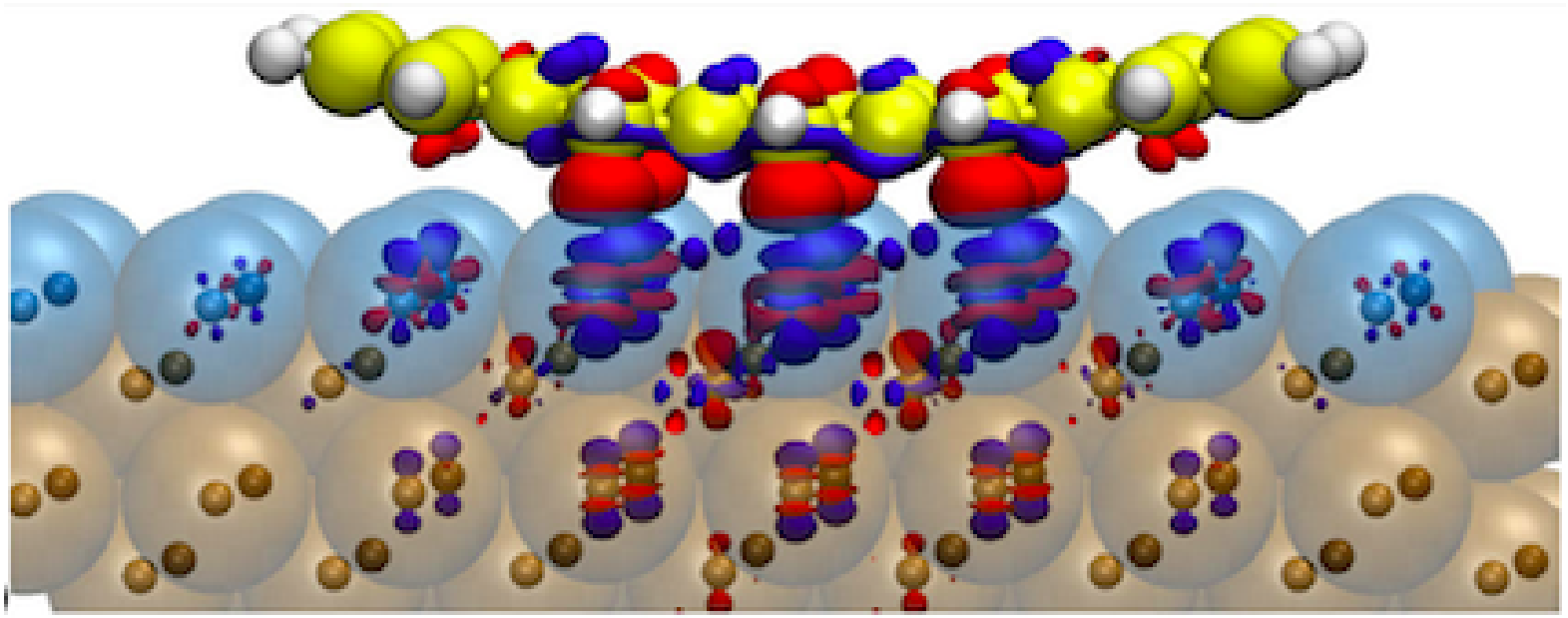
Kathrin Müller,[†,⊥] Ari P. Seitsonen,[‡] Thomas Brugger,[§] James Westover,[∥] Thomas Greber,[§] Thomas Jung,[†] and Abdelkader Kara*[,∥]

dx.doi.org/10.1021/jp308058u | J. Phys. Chem. C 2012, 116, 23465−23471

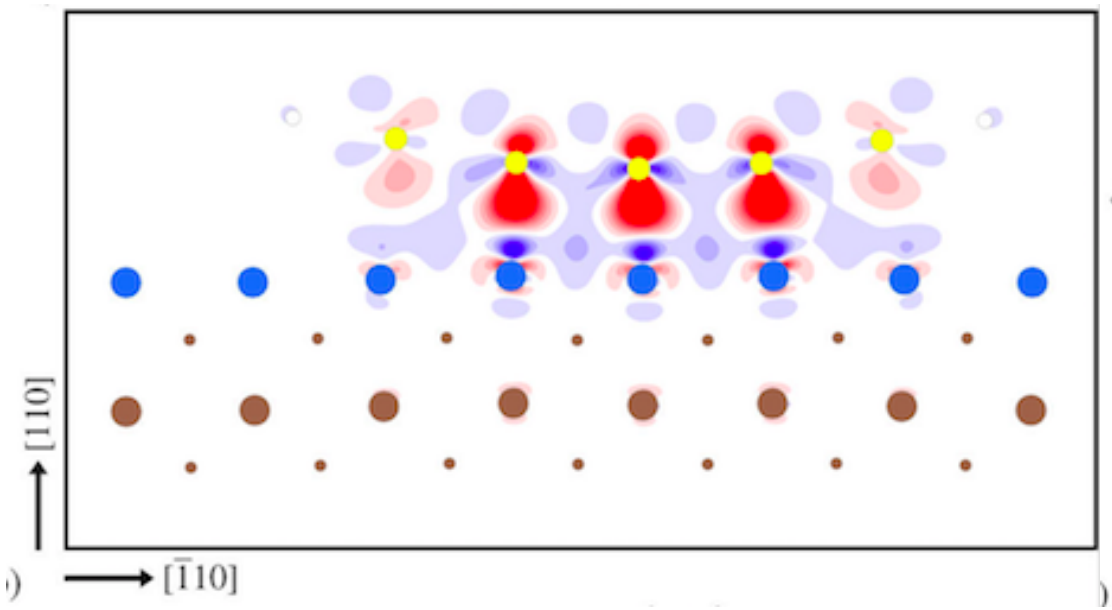


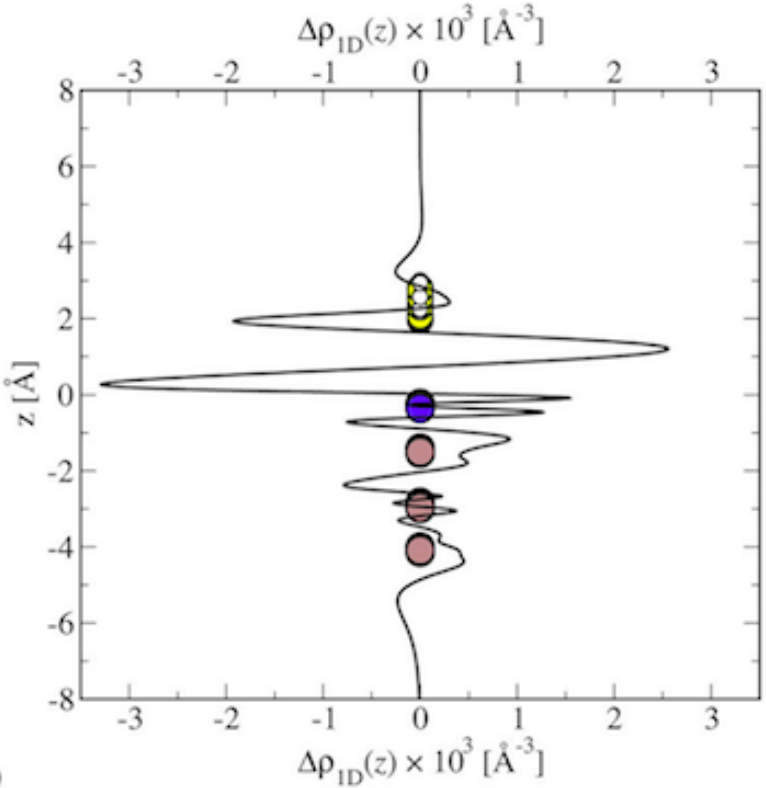


Density difference: Example pentacene/Cu(110)



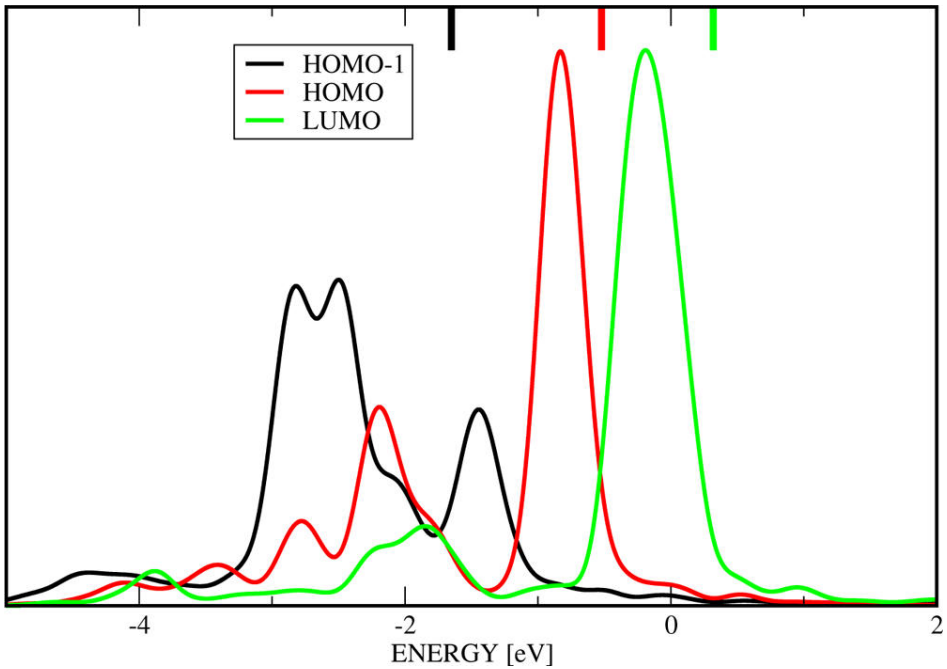
Density difference: Example pentacene/Cu(110)

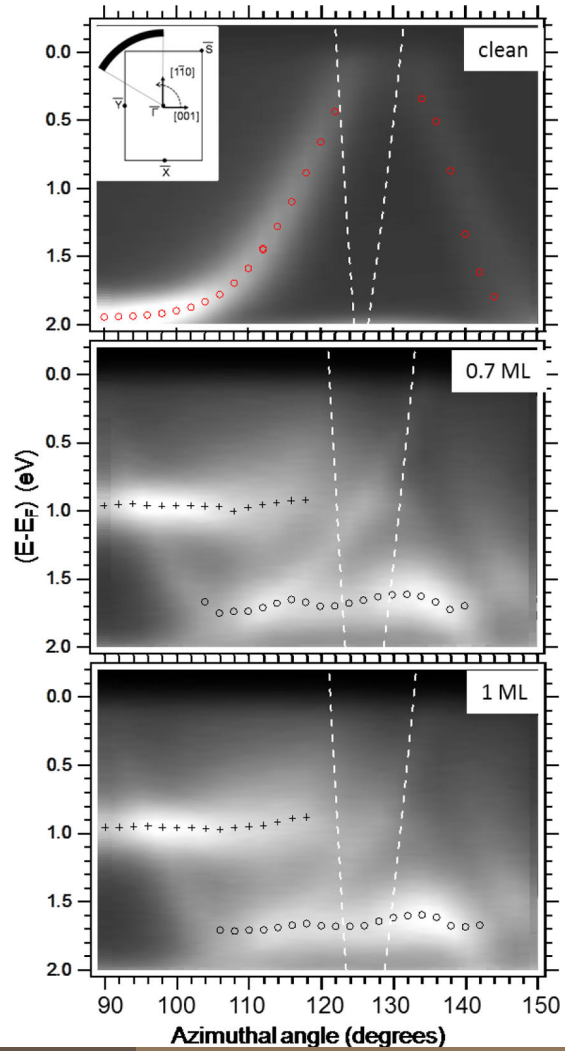




Orbital overlap: Example pentacene/Cu(110)

$$O_{j\mathbf{k}}(E) = \sum_{i\mathbf{k}} w_{\mathbf{k}} \, |\langle \phi_{j\mathbf{k}} | \psi_{i\mathbf{k}} \rangle|^2 \delta(E - E_{i\mathbf{k}})$$





DFT: Other observable quantities

- Sum-frequency generation
- NMR, EPR: Chemical shifts, g tensors, hyper-fine interactions, ...
- XPS: Core-level binding energies

Summary

Example machines

Summary

DFT in practise — Limitations

DFT *is* exact . . .

. . . yet

- Self-interaction
  - Ionisation, affinity energies; level alignment
  - Band gaps(?)
  - TD-DFT: Wrong asymptotic potential & charge transfer-excitations
- Overall accuracy: Reaction barriers *etc*

DFT in practise — Limitations

DFT computational load

- 10-10^2 (PC), 10^3-10^{5-6} (HPC) atoms
- 1 ns