Procesos Físico-Químicos elementales en interfases y nanoestructuras a partir de “primeros principios”

H. Fabio Busnengo

Group of Physical-Chemistry
at Interfaces and Nanostructures
http://meteoro.fceia.unr.edu.ar/Gas-Surface
Instituto de Física Rosario (IFIR)

1er Encuentro
Red Compumat
CAC - 23/05/2013

Fabio
Busnengo

Alejandra
Martínez

Paula
Abufager

Pablo
Lustemberg

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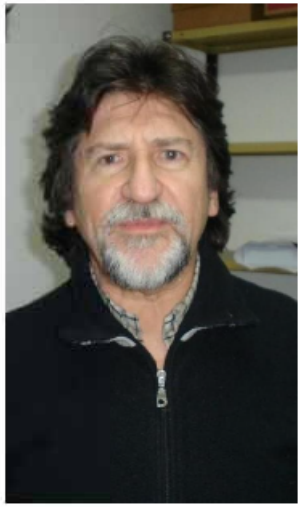
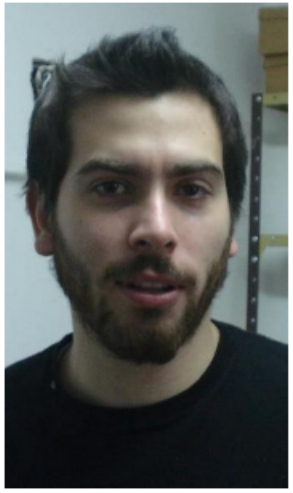


César
Ramirez

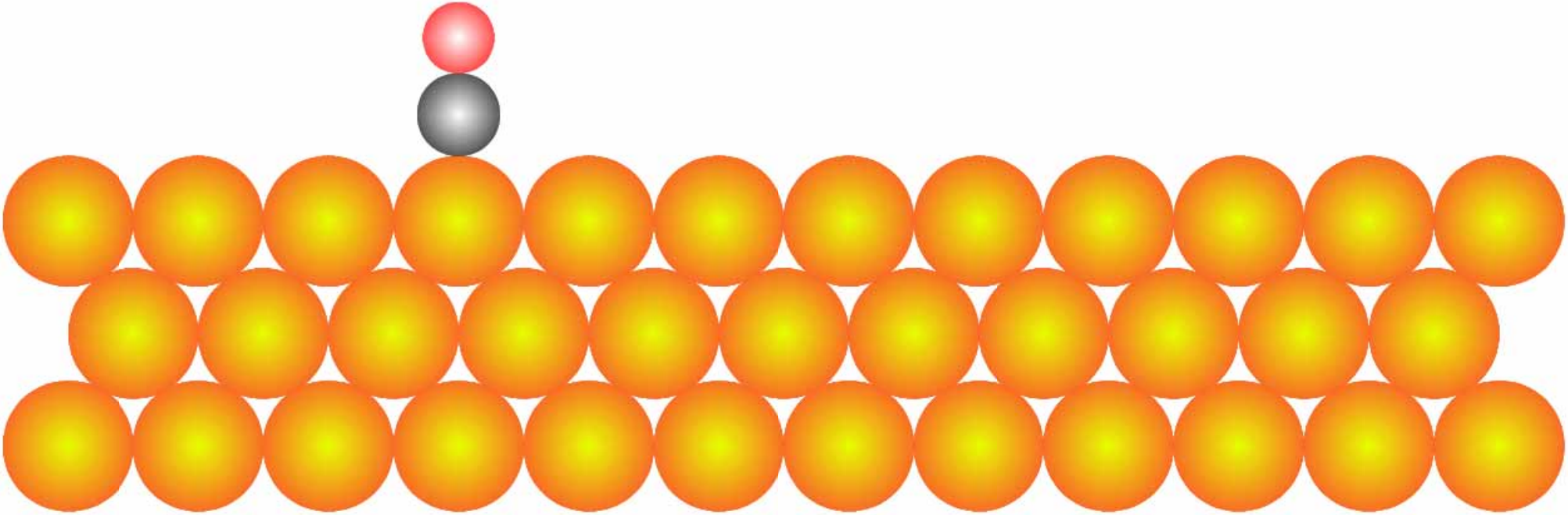


Ariel
Lozano

Raquel
Moiraghi

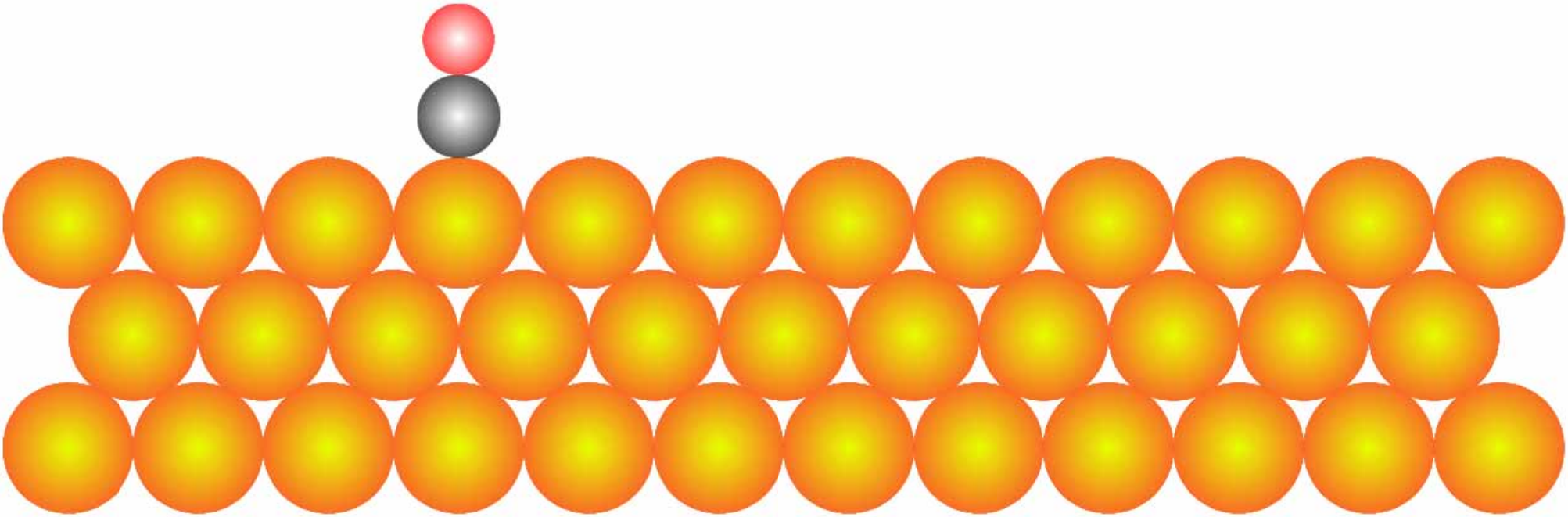
Maximiliano
Ramos

What do you see in this picture ?



What do you see in this picture ?

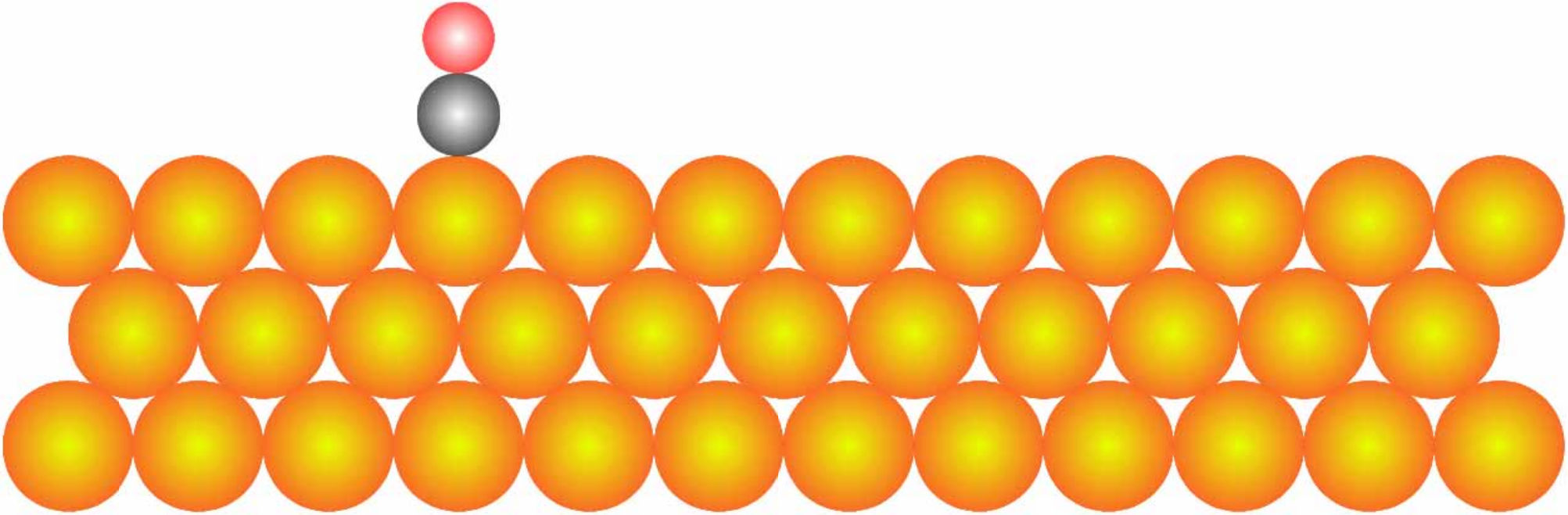
Solid State Physicists: Crystal surface with an impurity



What do you see in this picture ?

Solid State Physicists: Crystal surface with an impurity

Chemists: Molecule in contact with a thermal bath

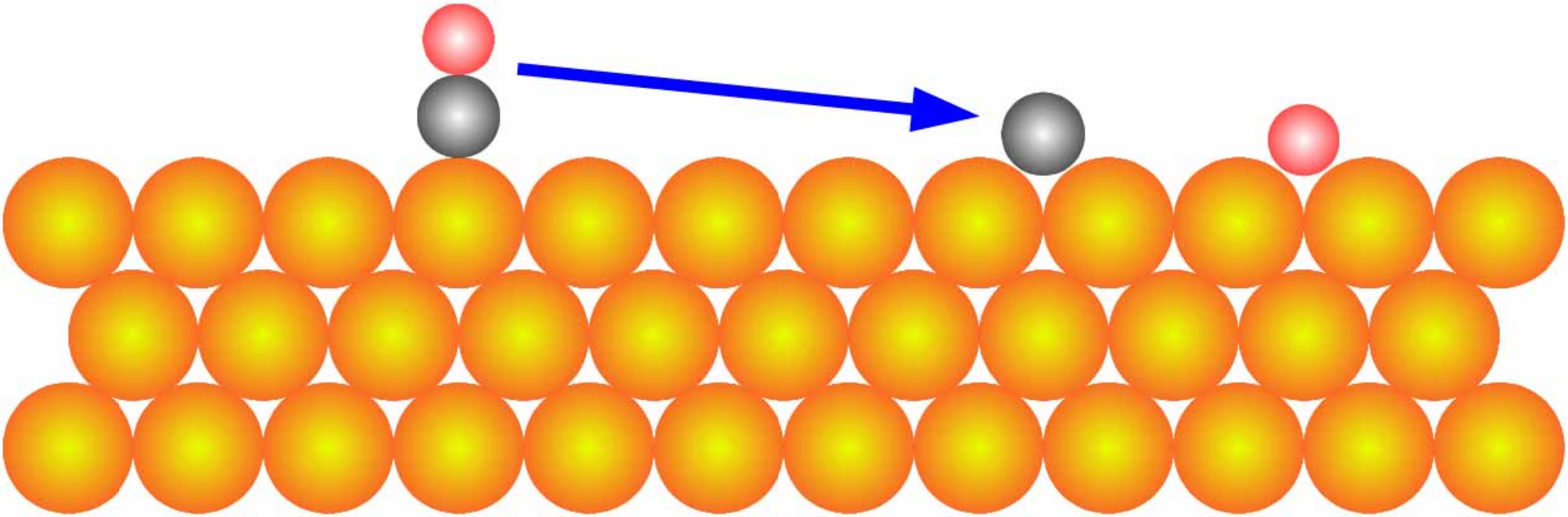


Reactive processes at surfaces

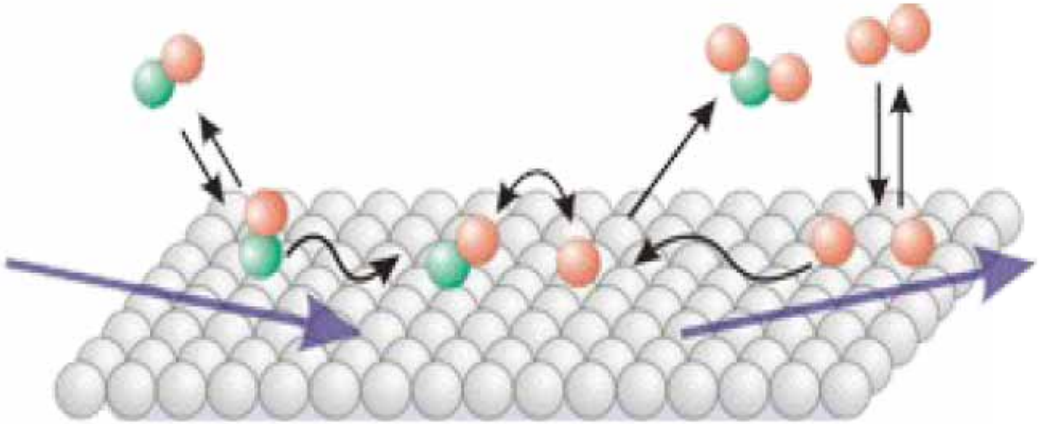
Solid State Physicists: Crystal surface with an impurity

Surface Physical-Chemists

Chemists: Molecule in contact with a thermal bath



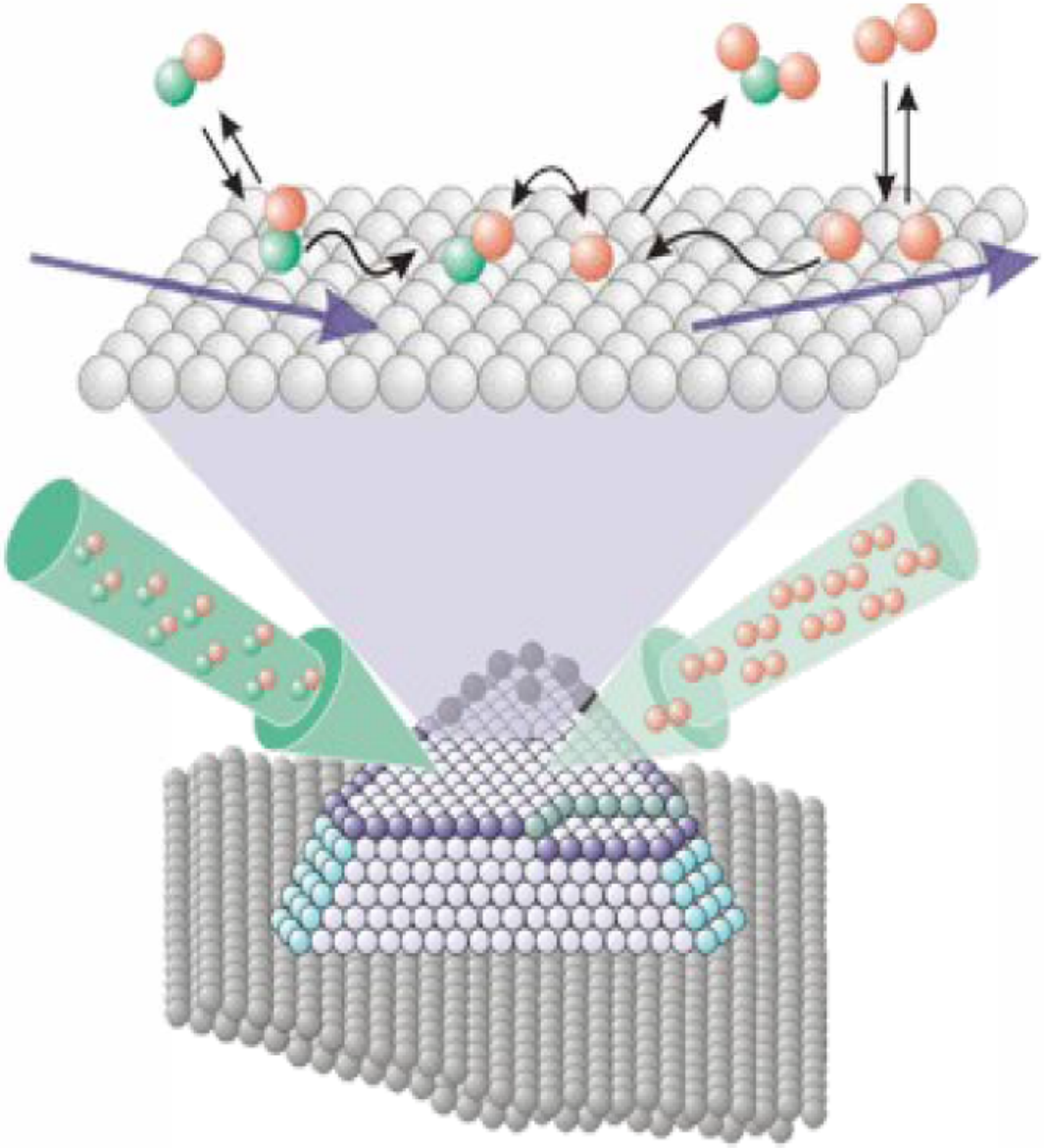
Reactive processes at surfaces



Surface Physical-Chemistry

Picture taken from http://www.fhi-berlin.mpg.de/cp/mbg/

Reactive processes at surfaces



Surface Physical-Chemistry

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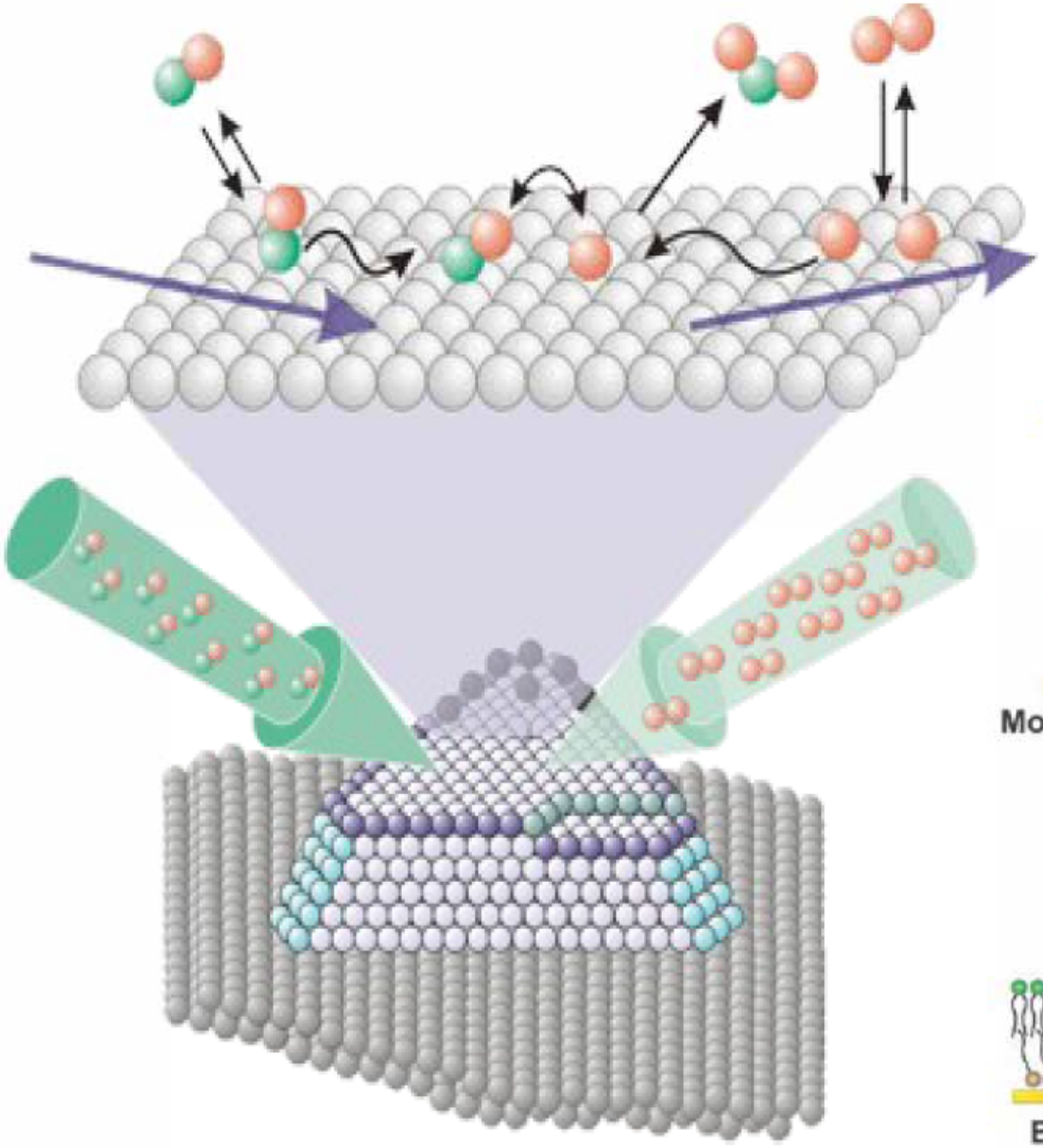
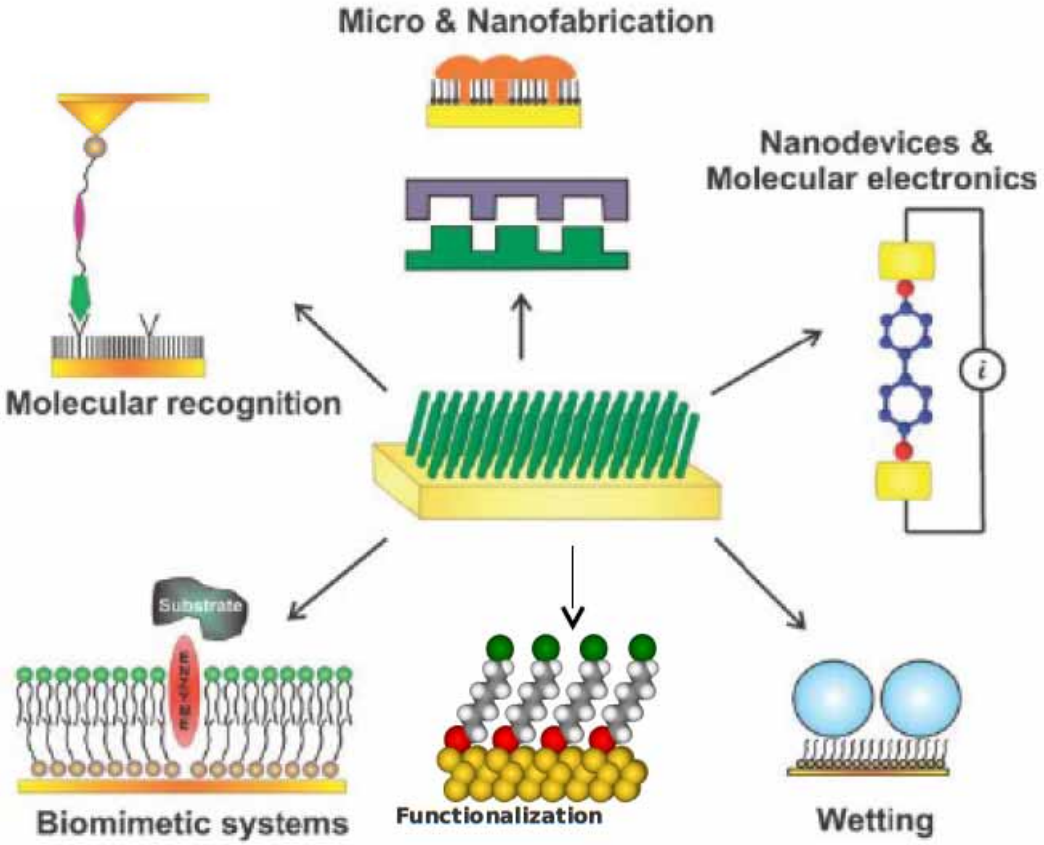


Surface Physical-Chemistry

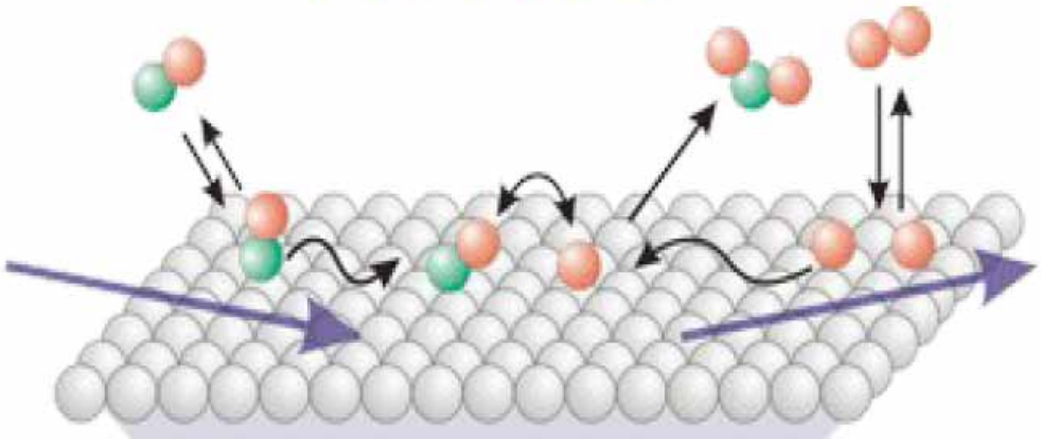


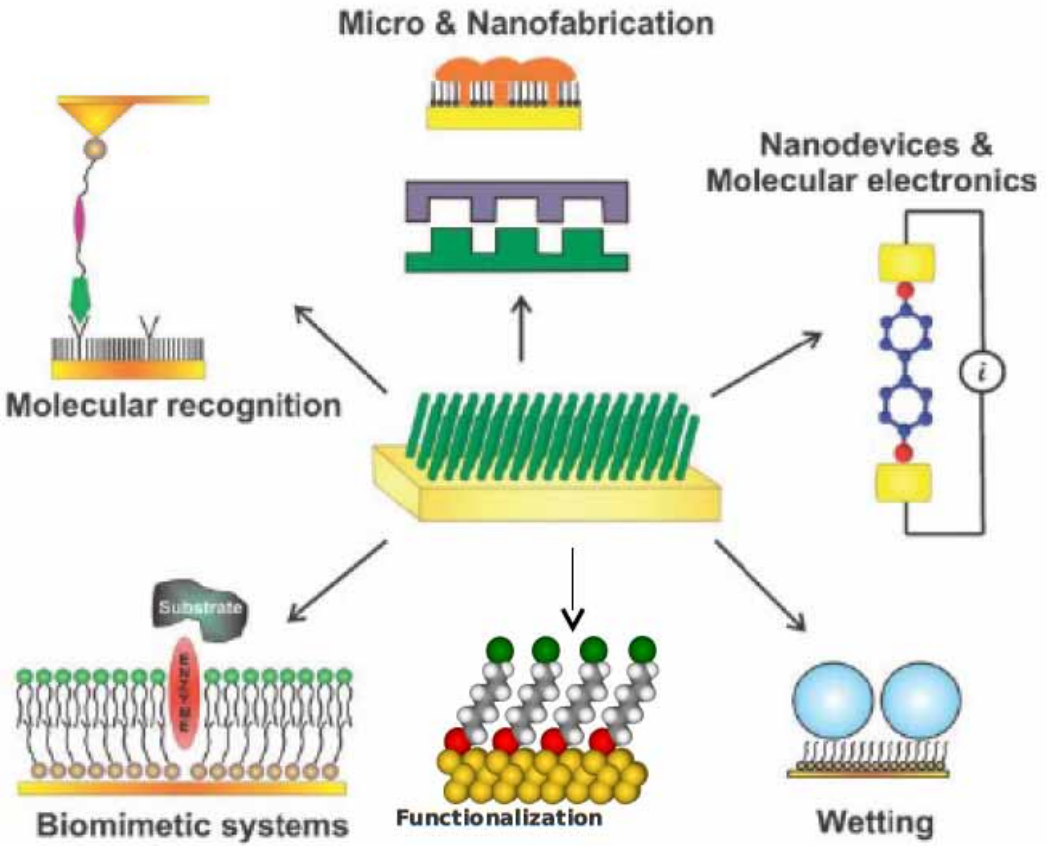
Picture taken from http://www.fhi-berlin.mpg.de/cp/mbg/

Taken from Vericat et al. (2010)

Reactive processes at surfaces

DFT-GGA (-D)
+
(R)FF
+
MD / MC





Reactive processes at surfaces

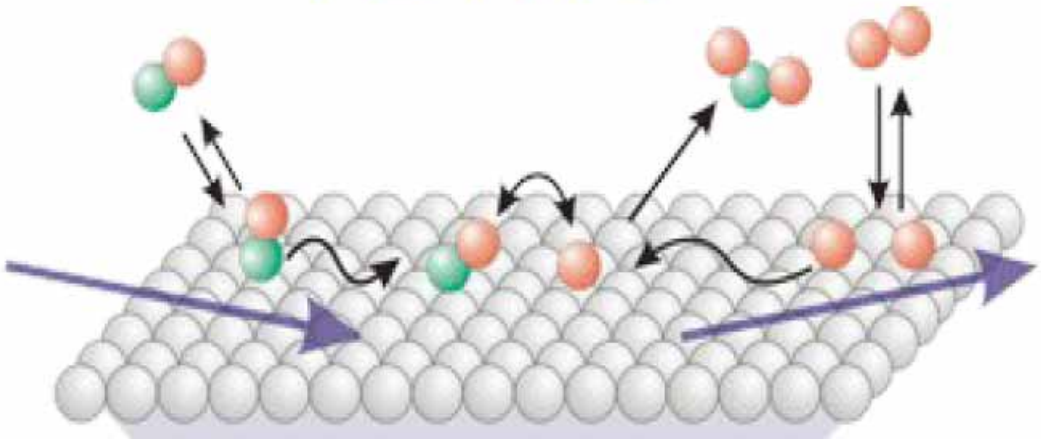
Solid State Physicists

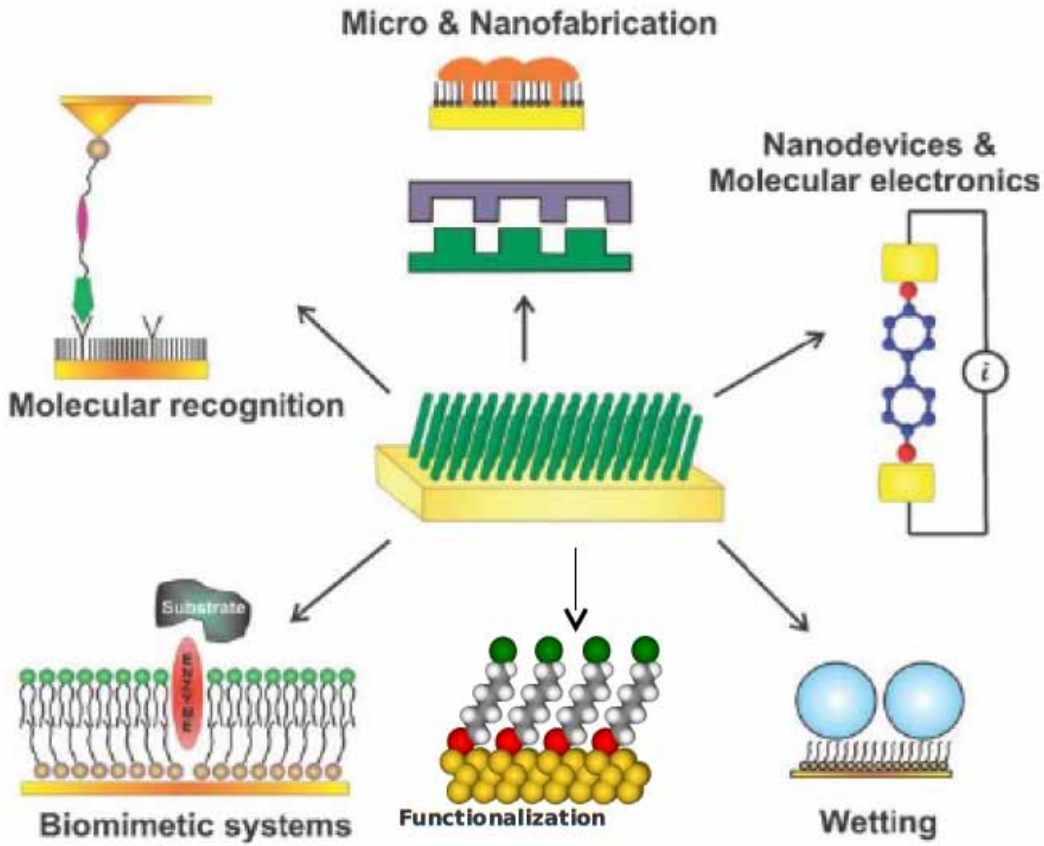
DFT-GGA is
too complex for
understanding !

Quantum Chemists

DFT-GGA is
too simple for
accuracy !

DFT-GGA (-D)
+
(R)FF
+
MD / MC





Reactive processes at surfaces

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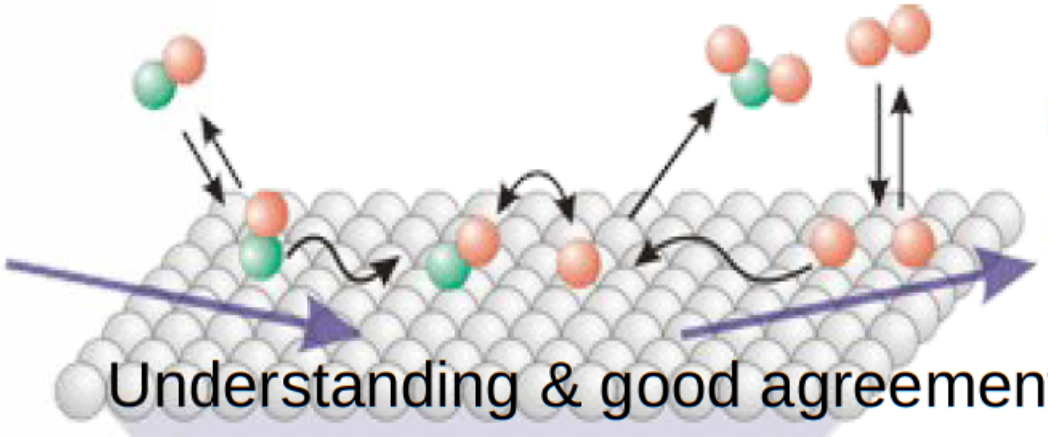
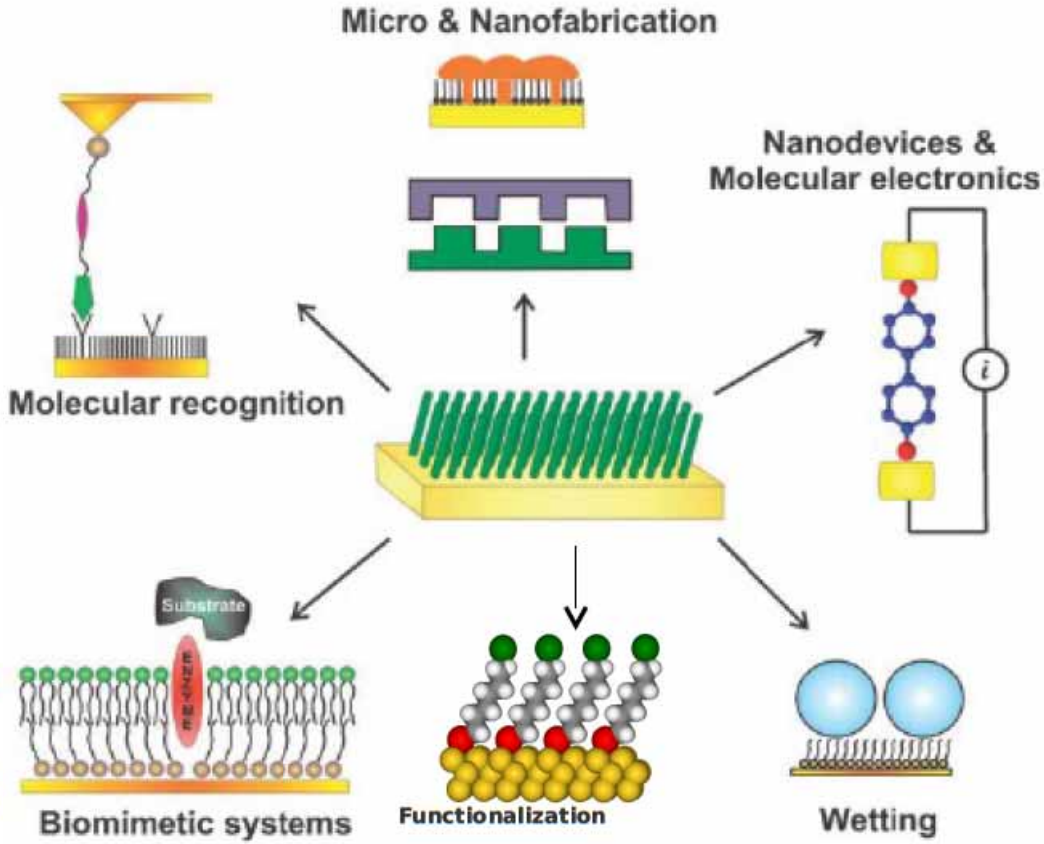
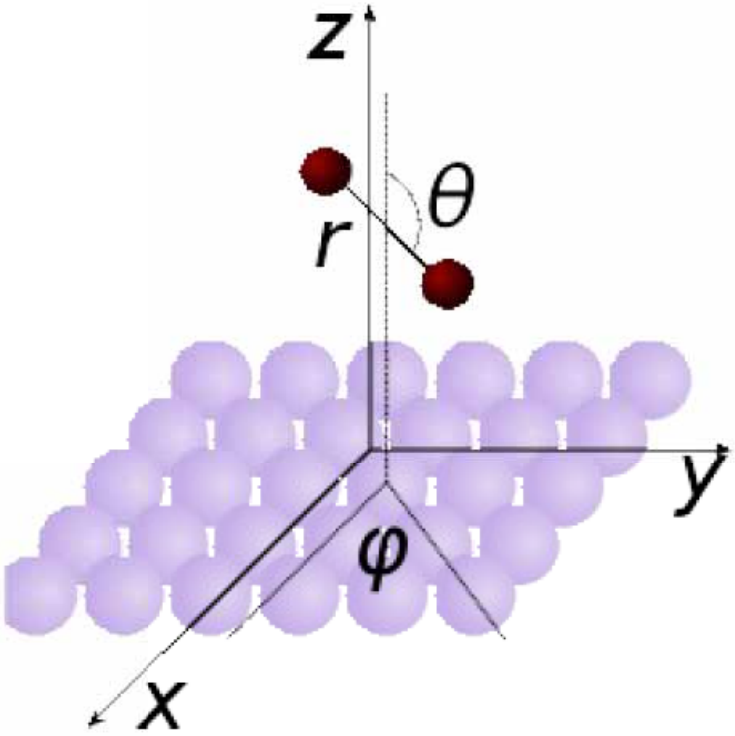


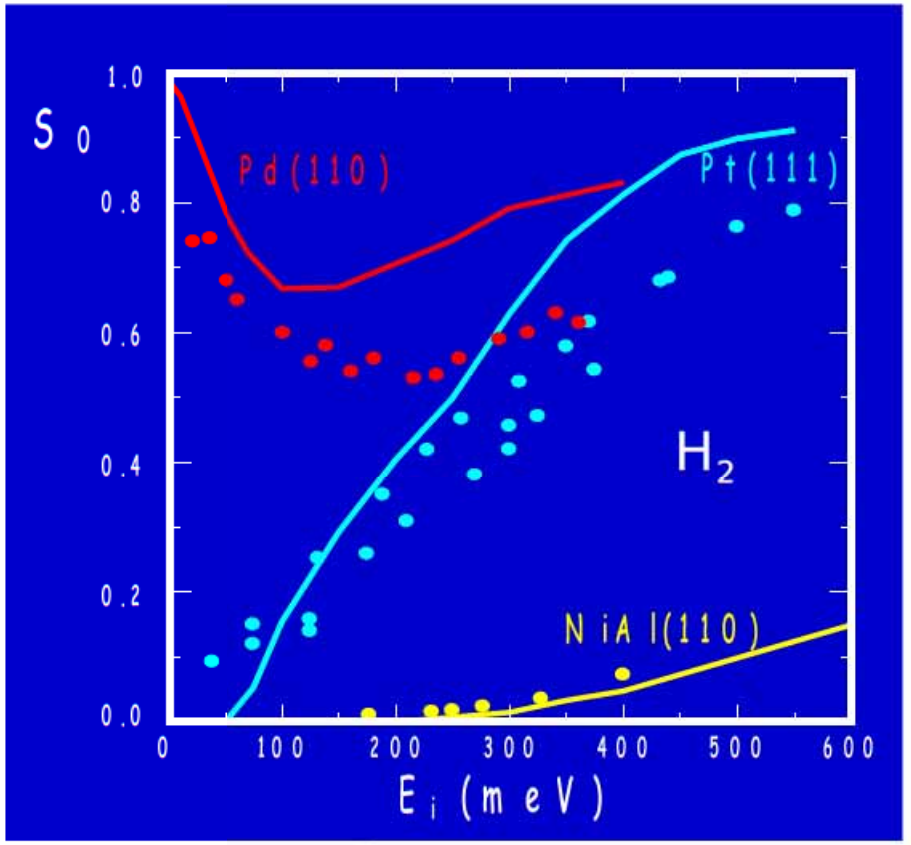


Understanding & good agreement with experiments … “sometimes”

What do we study ?



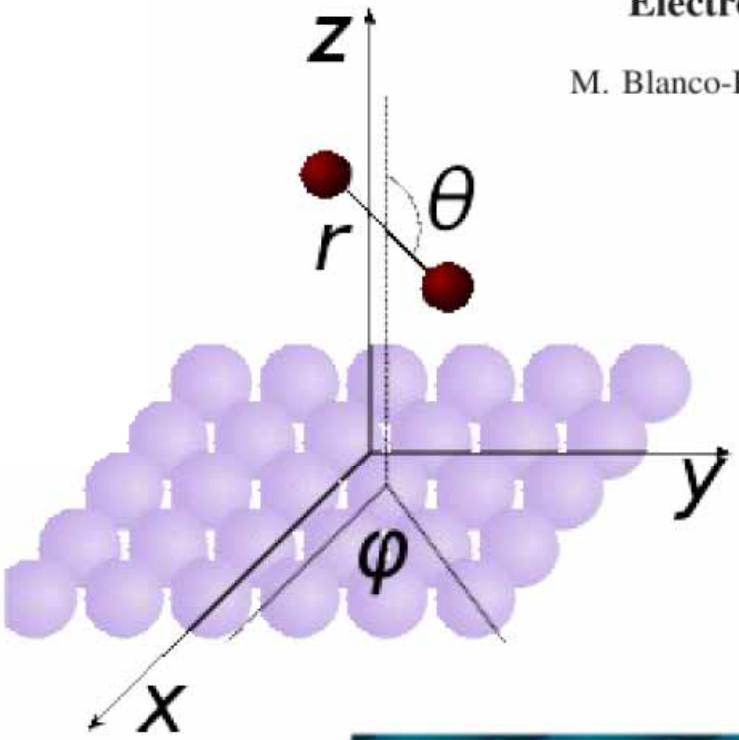
What do we mean by good agreement with experiments ?



Chemically Accurate Simulation of a Prototypical Surface Reaction: H_2 Dissociation on Cu(111)

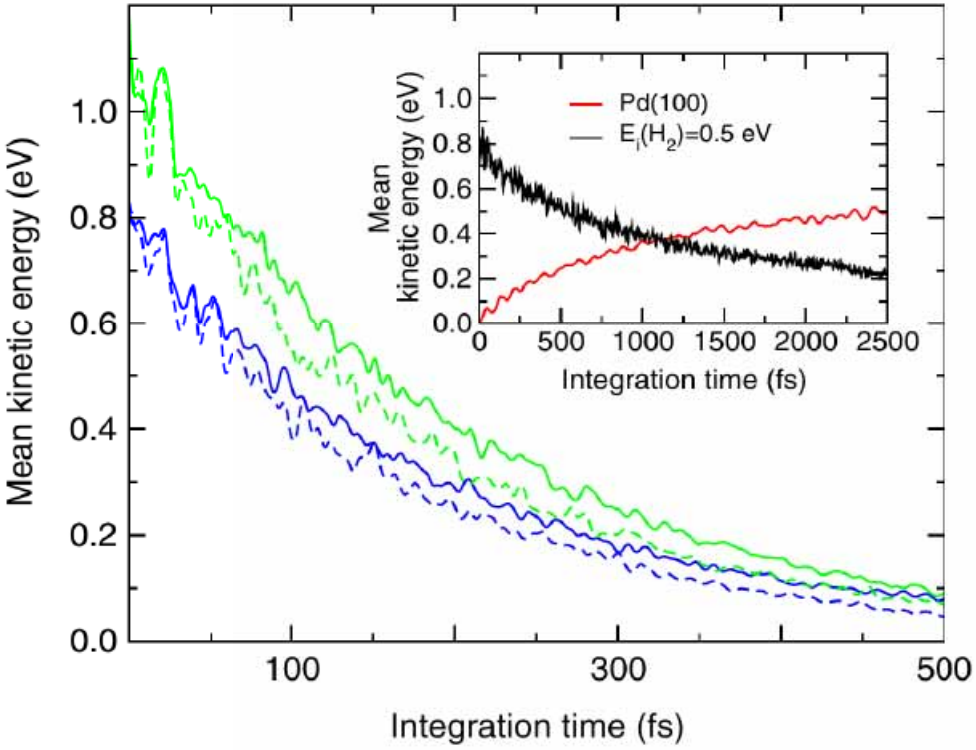
C. Díaz,[1*] E. Pijper,[1] R. A. Olsen,[1†] H. F. Busnengo,[2] D. J. Auerbach,[3,4] G. J. Kroes[1‡]

What do we study ?



Electronic Friction Dominates Hydrogen Hot-Atom Relaxation on Pd(100)

M. Blanco-Rey,[1,2] J. I. Juaristi,[1,3,2] R. Díez Muiño,[3,2] H. F. Busnengo,[4] G. J. Kroes,[5] and M. Alducin[3,2]



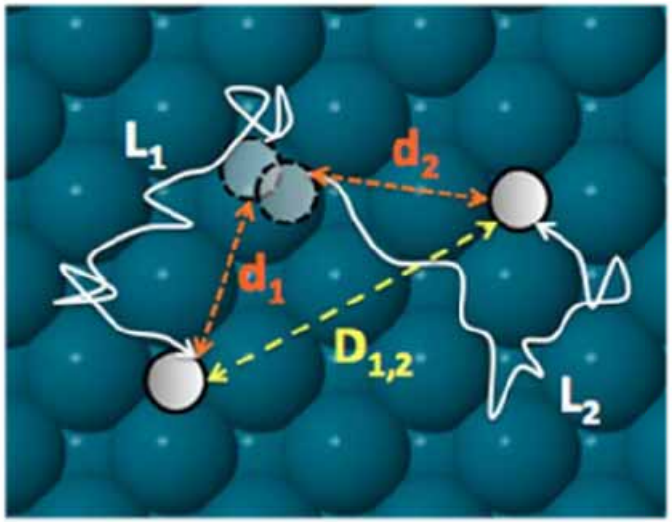


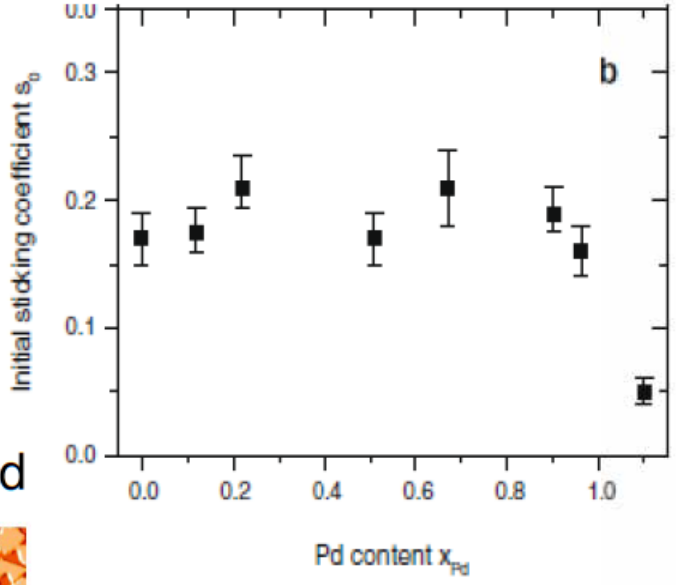
FIG. 1 (color online). Main panel: mean H_2 kinetic kinetic energy as a function of time. Blue (green) lines correspond to molecules impinging with $E_i = 0.5(1.0)$ eV. Solid (dashed) lines represent the AIMDEF results obtained in the FS (NFS) approach. Inset: kinetic energy in the absence of electronic friction as a function of time. The energy lost by H_2 (black line) is transferred into Pd atom motion (red line).

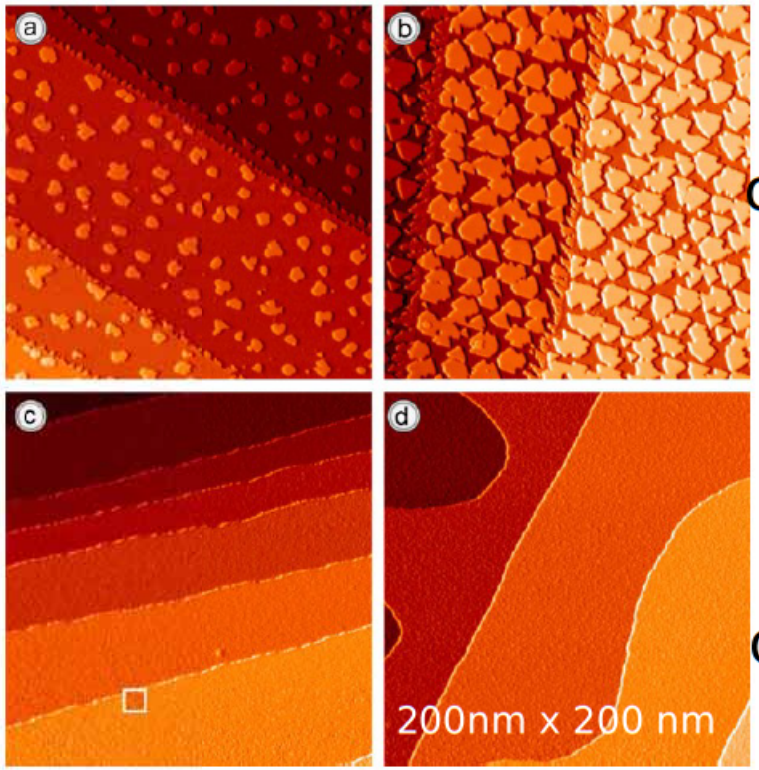
Surface alloys: Pd_xRu_{1-x}/Ru(0001)

Pd on Ru(0001) @ RT

Pd coverage

0.14 ML Pd → 0.53 ML Pd

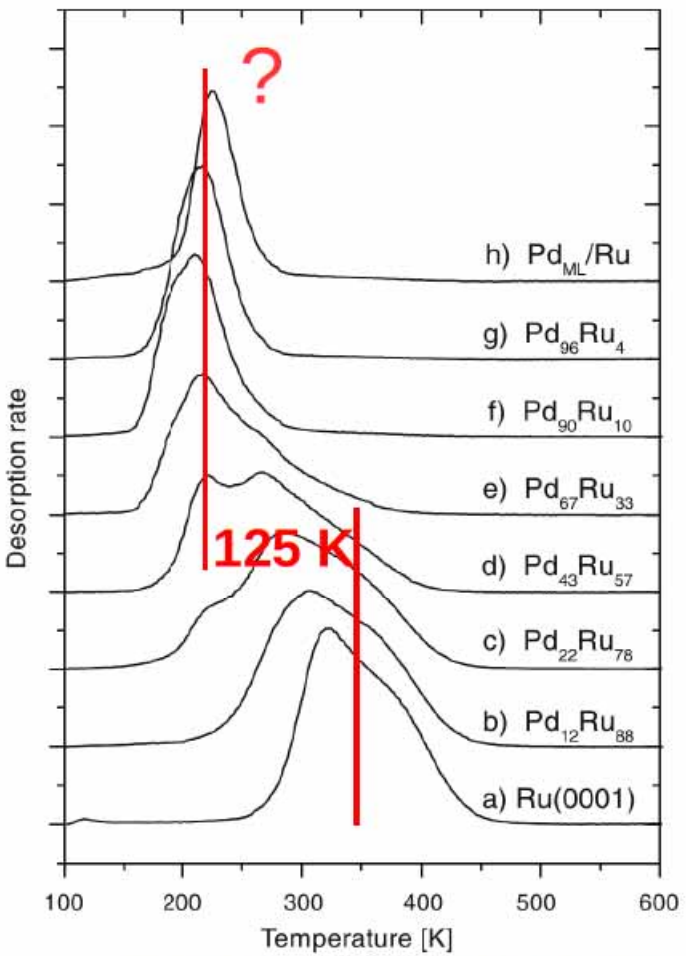




Pd islands on Ru(0001)

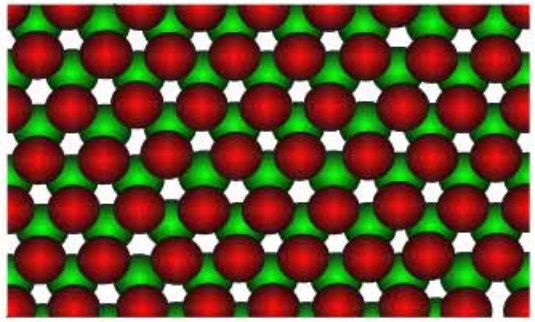
Annealing to T_s=1150 K

Pd_xRu_{1-x} SA on Ru(0001)



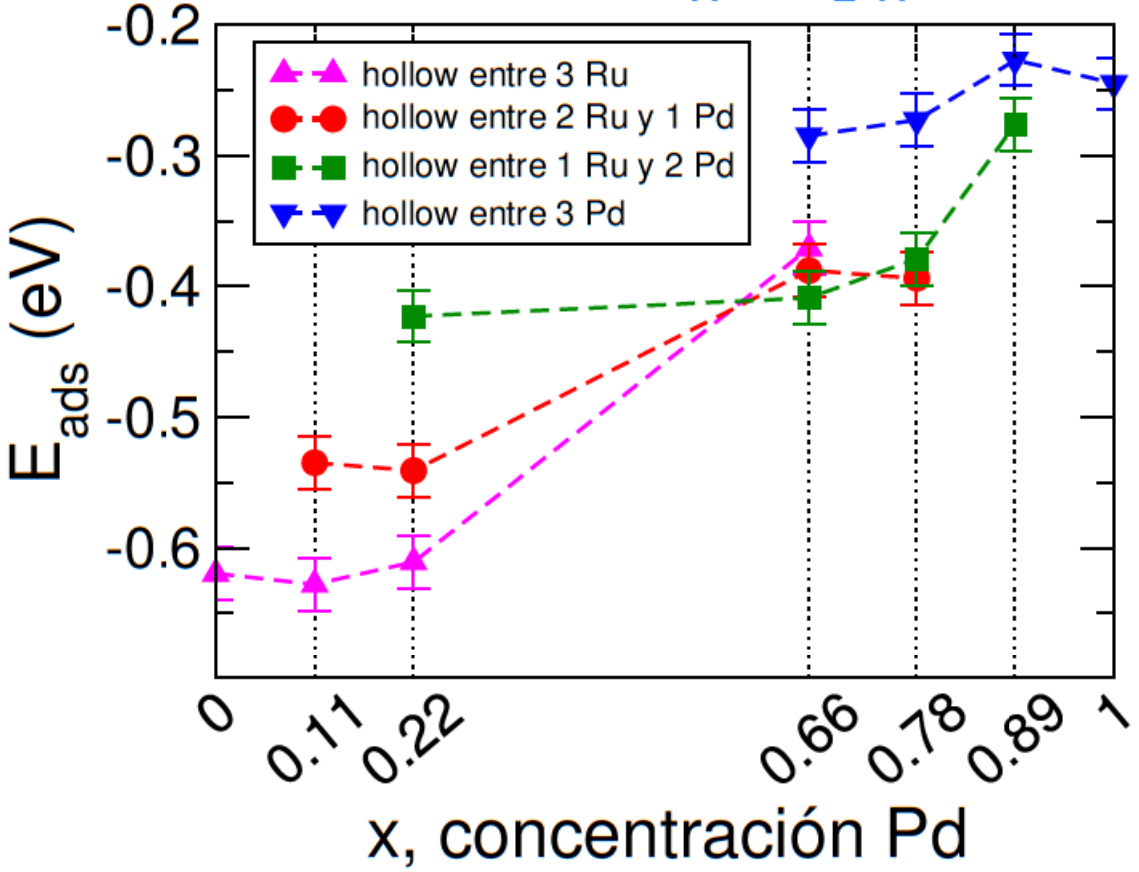
x ~ 1

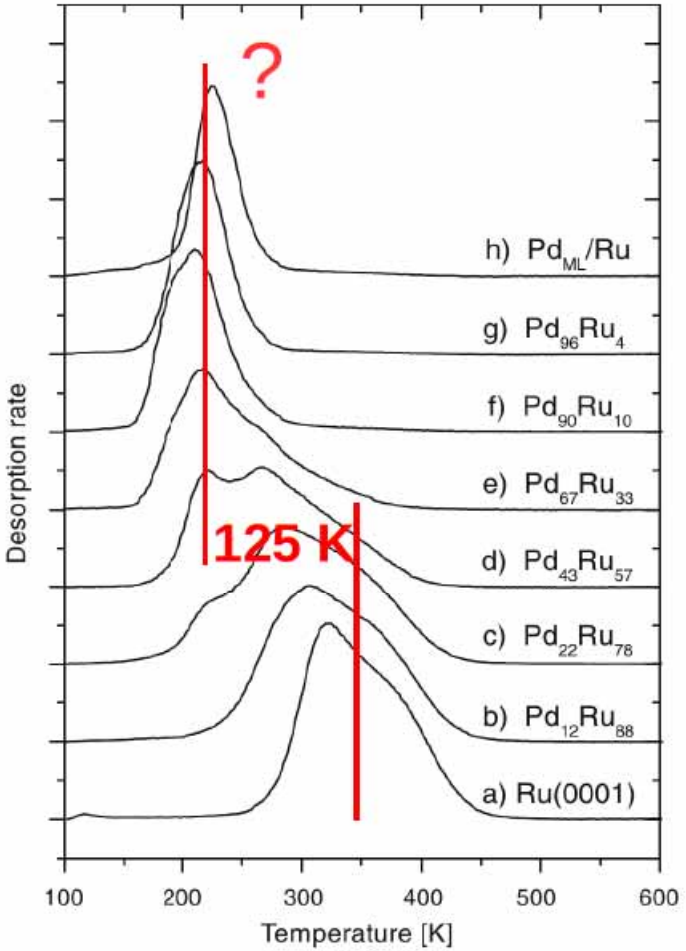
Pd_{ML}/Ru(0001)

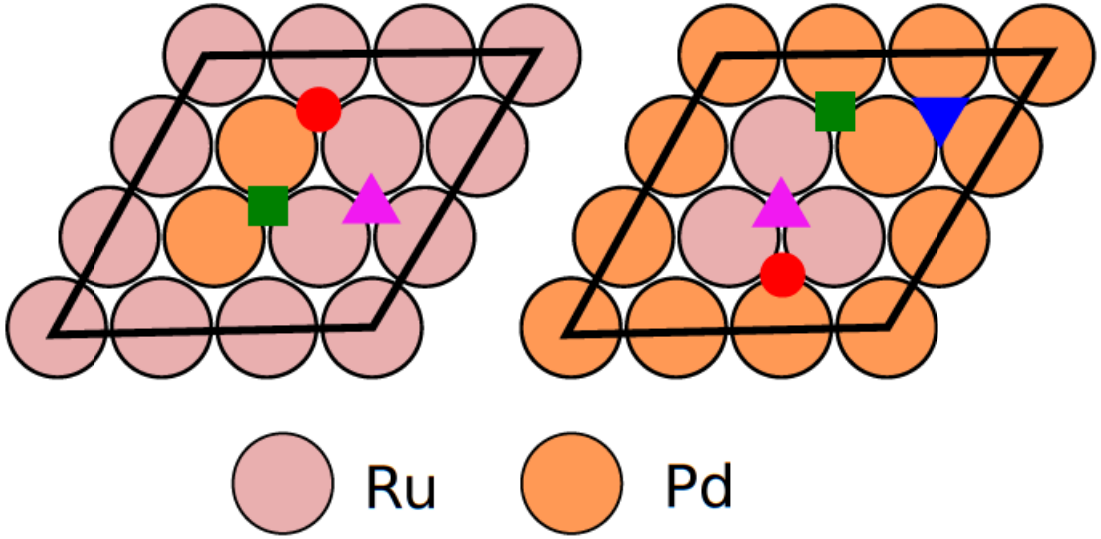


Hartmann etal. Surf. Sci. 2009

$Pd_xRu_{1-x}/Ru(0001)$







PCCP

$Pd_xRu_{1-x}/Ru(0001)$

RSC Publishing

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Environment-driven reactivity of H_2 on PdRu surface alloys†

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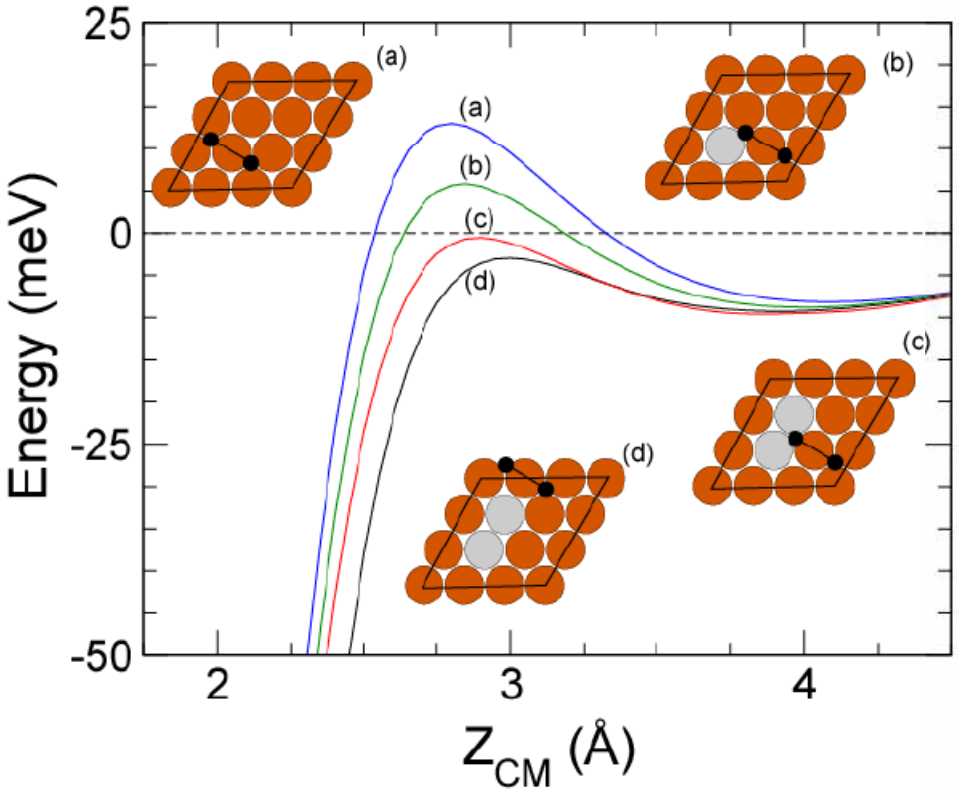
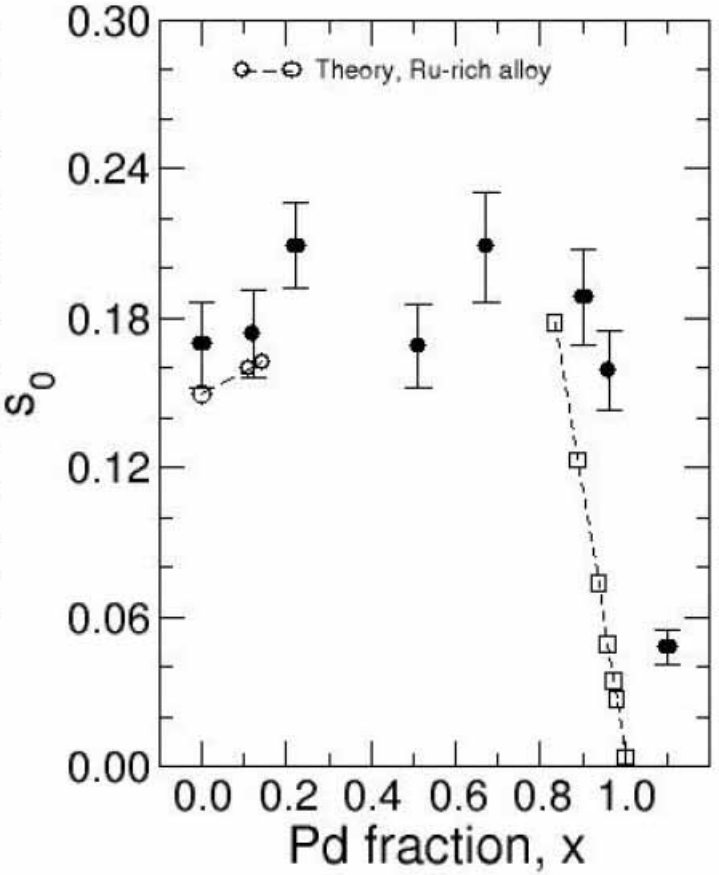
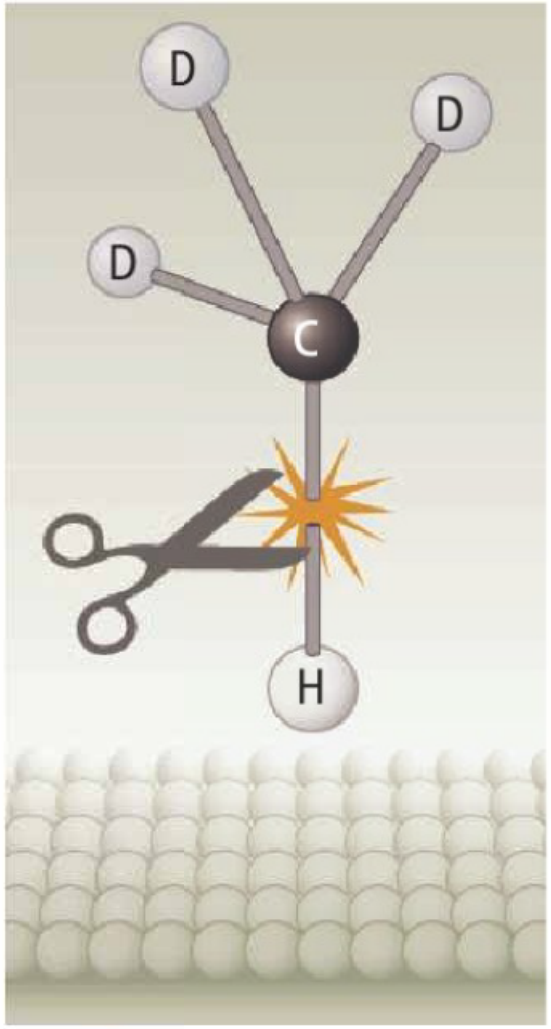
M. Ramos,[a] M. Minniti,[b] C. Díaz,[c] D. Farías,[b] R. Miranda,[bd] F. Martín,[cd] A. E. Martínez[a] and H. F. Busnengo*[a]

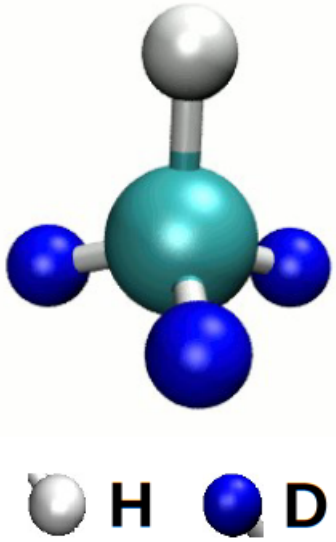


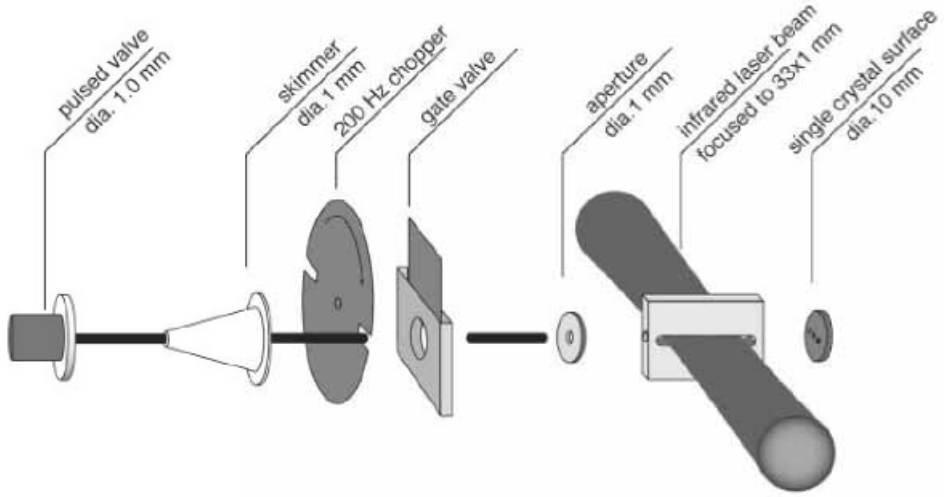


Bond selectivity



Deuterated isotopologues of Methane





Faraday Discuss., 2012, **157**, 285–295

Vibrationally bond-selected chemisorption of methane isotopologues on Pt(111) studied by reflection absorption infrared spectroscopy†

Li Chen,[a] Hirokazu Ueta,[a] Régis Bisson[b] and Rainer D. Beck*[a]

8 FEBRUARY 2008 VOL 319 SCIENCE

Bond-Selective Control of a Heterogeneously Catalyzed Reaction

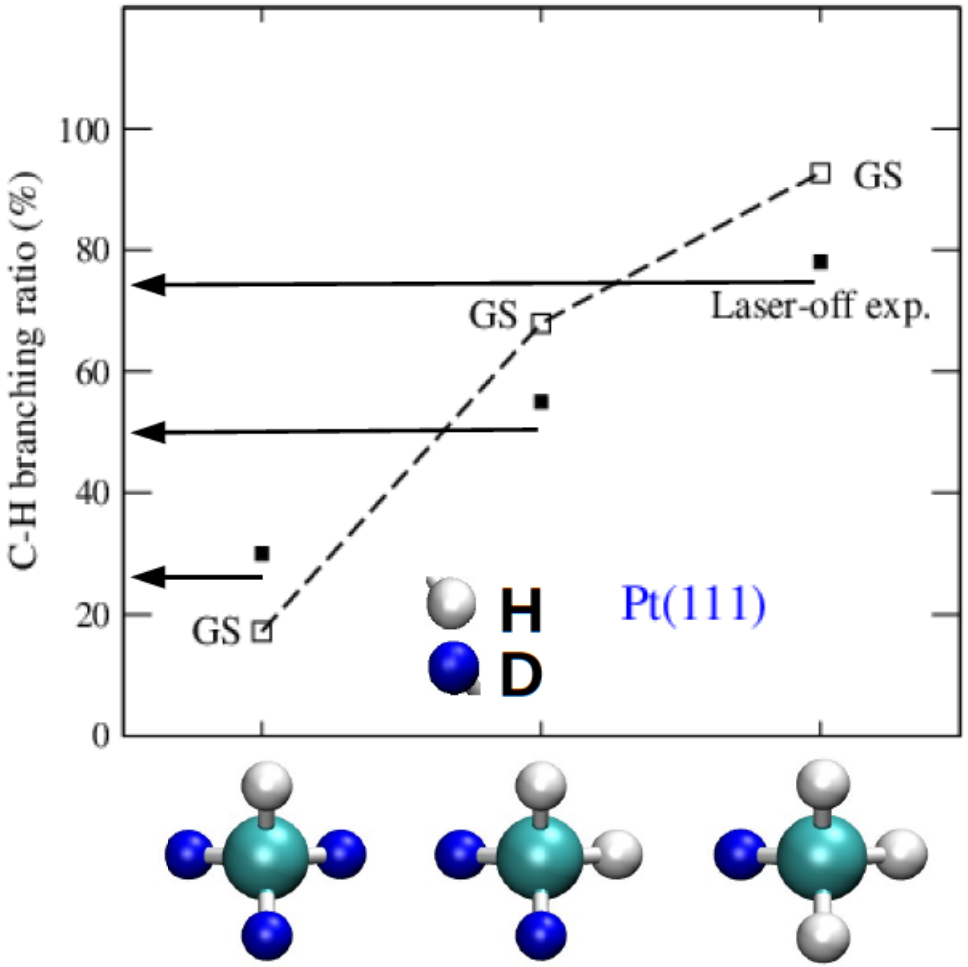
Daniel R. Killelea,* Victoria L. Campbell, Nicholas S. Shuman,† Arthur L. Utz‡

CHD_3/Ni(111)

QCMD, bond selectivity

Towards Bond Selective Chemistry from First Principles: Methane on Metal Surfaces

X. J. Shen,[1,2] A. Lozano,[3] W. Dong,[1,*] H. F. Busnengo,[3,†] and X. H. Yan[2]



QCMD, bond selectivity

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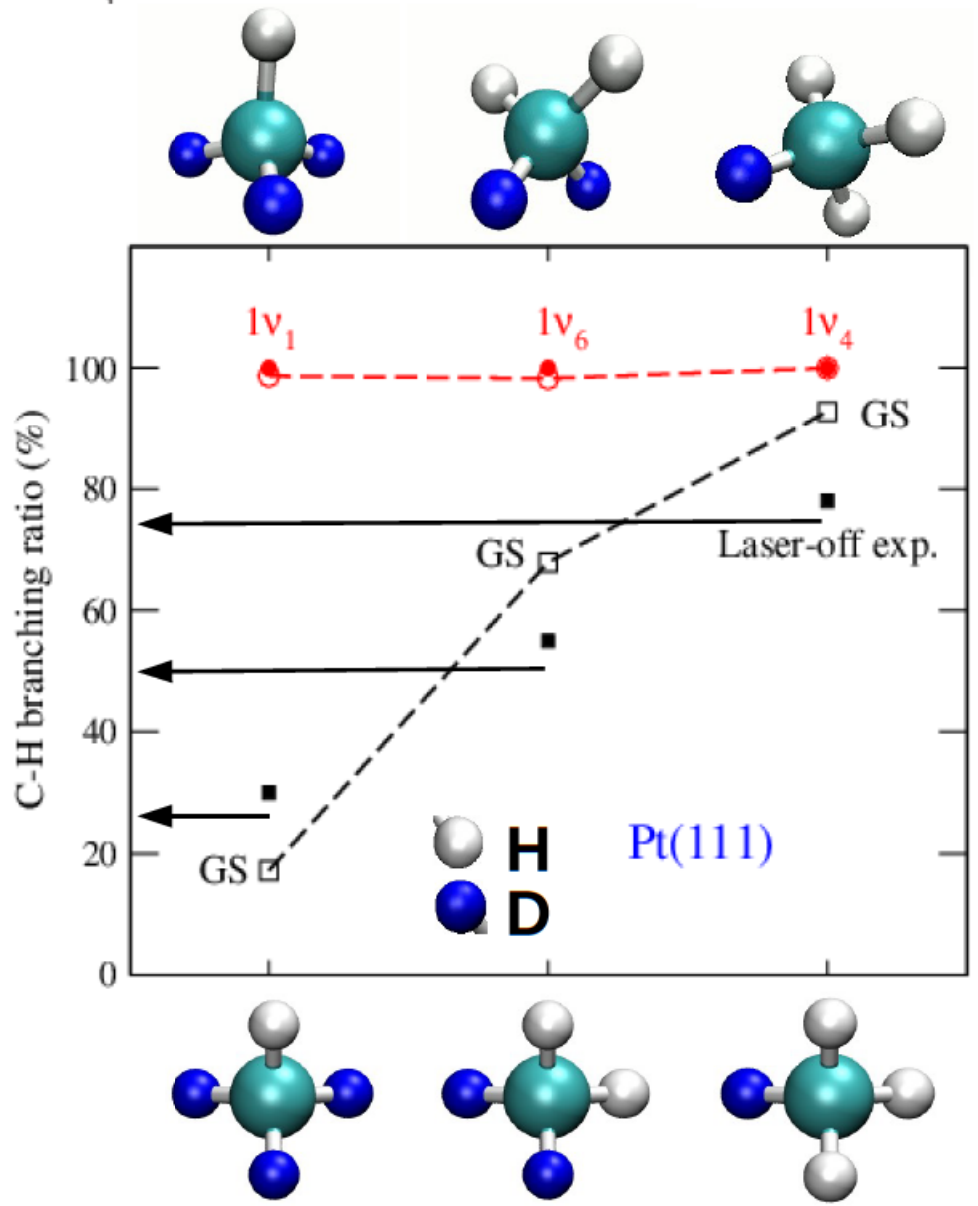
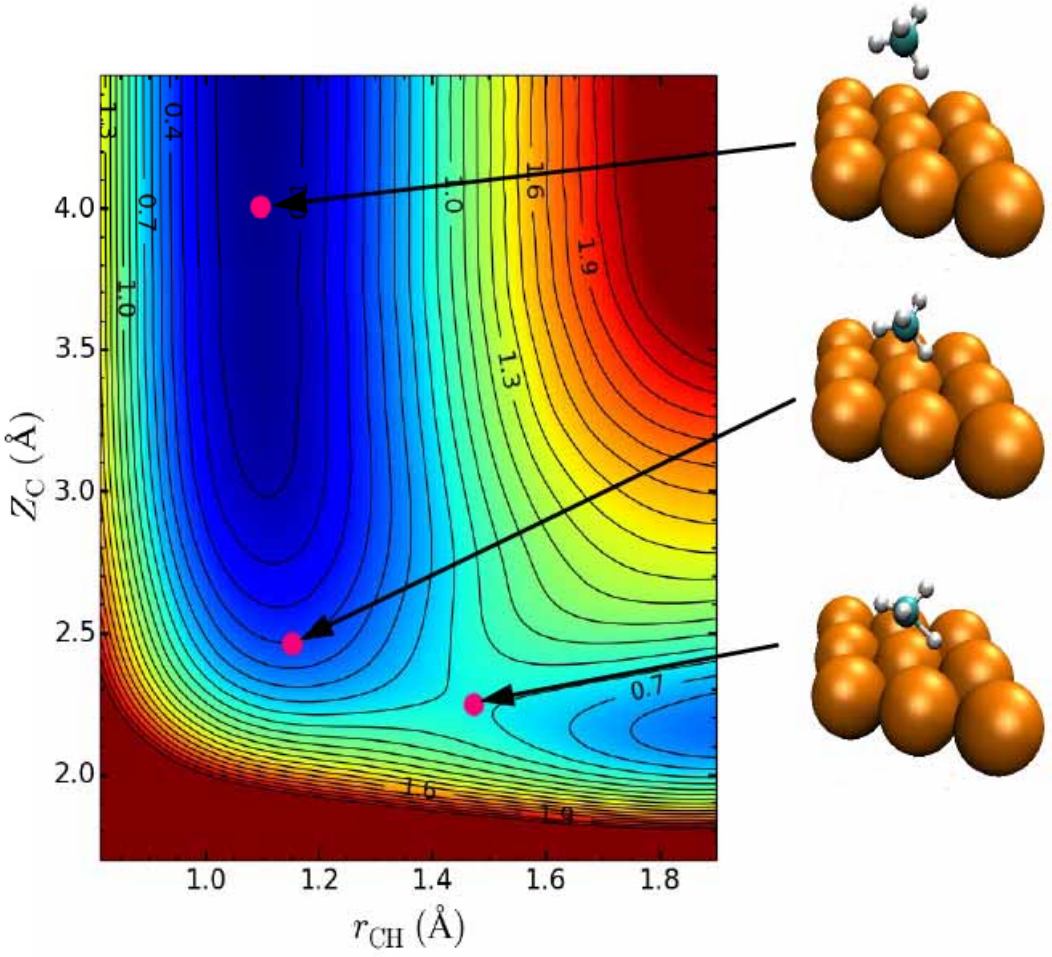
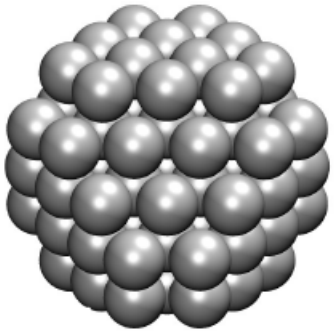
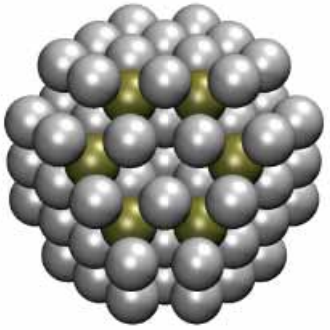




Reactivity of Pd NP (+C)

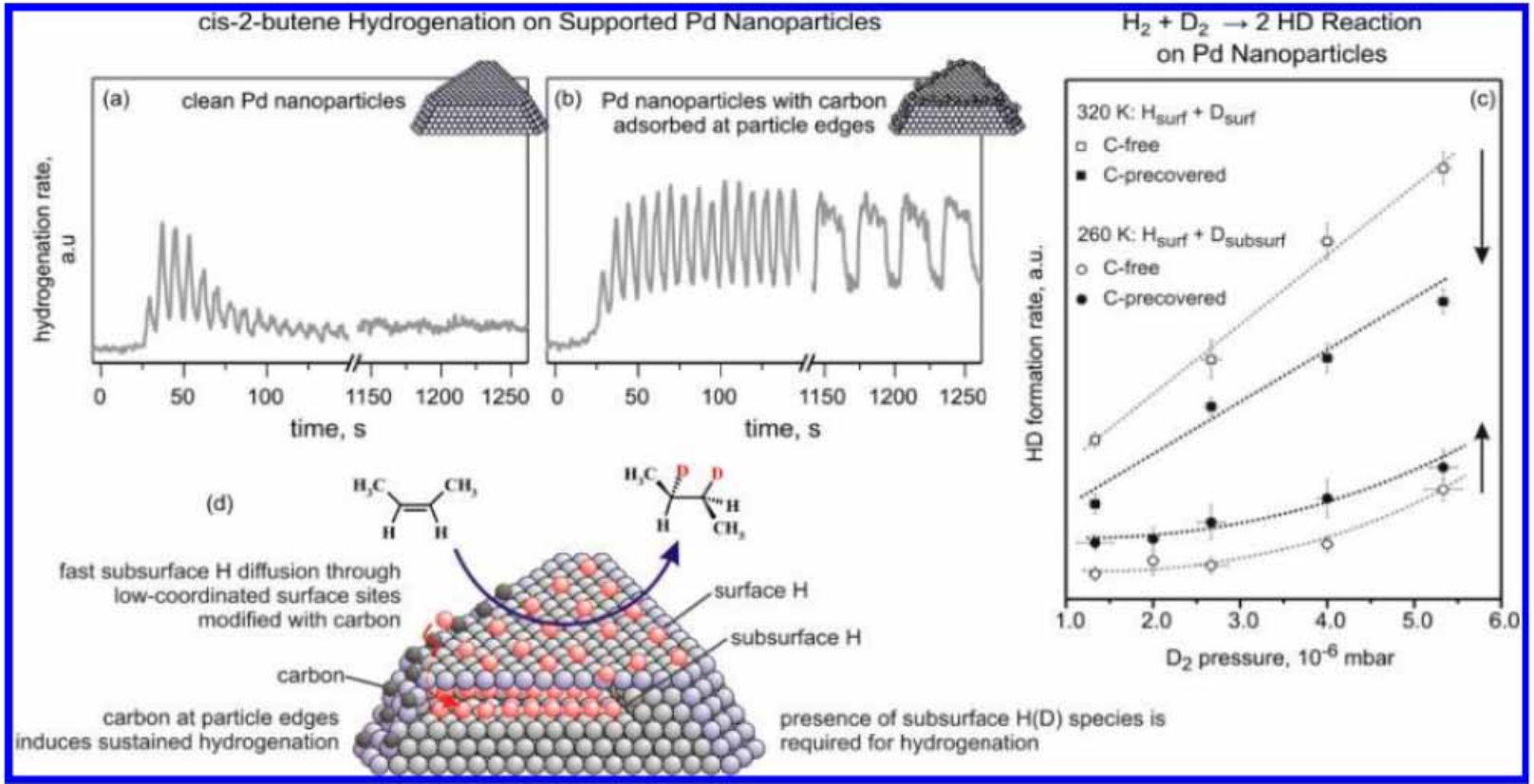




In collaboration with Dr. E. Bringa

Nanoparticles for Heterogeneous Catalysis: New Mechanistic Insights

SWETLANA SCHAUERMANN, NIKLAS NILIUS,
SHAMIL SHAIKHUTDINOV, AND HANS-JOACHIM FREUND*



Reactivity of oxides: CeO_2 (Dr. P. Lustemberg)

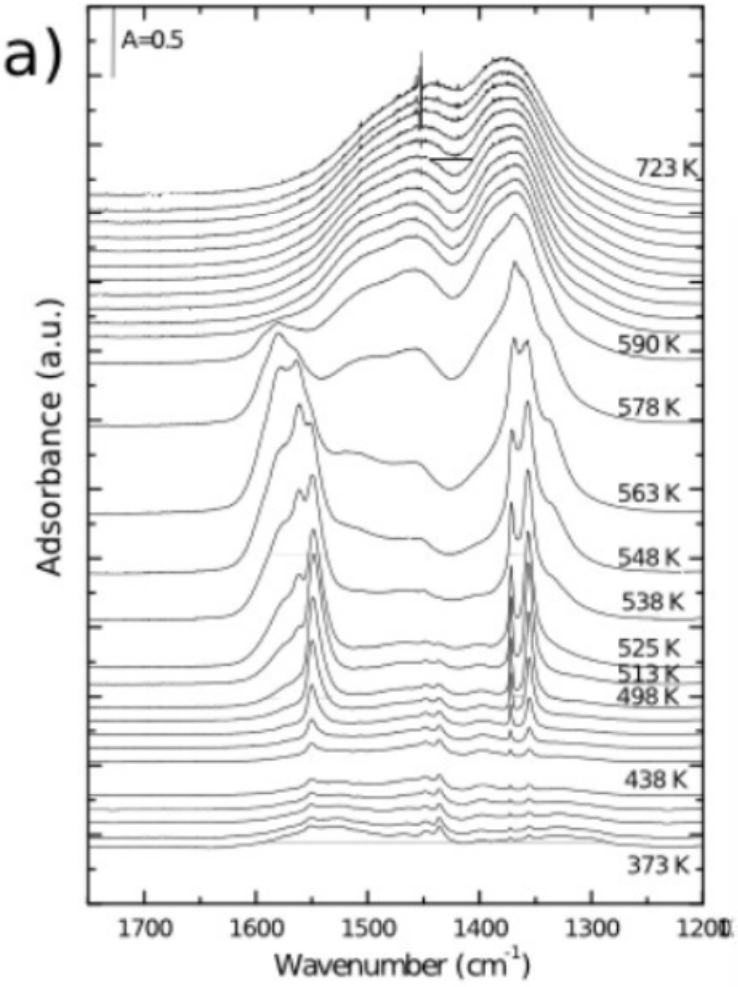
$$n\,CO(g) + \frac{k}{2}\,H_2 + \frac{l}{2}\,O_2(g) + CeO_2 \rightarrow [n\,HCOO + (k-n)\,H + (l-n)\,O]/CeO_2$$

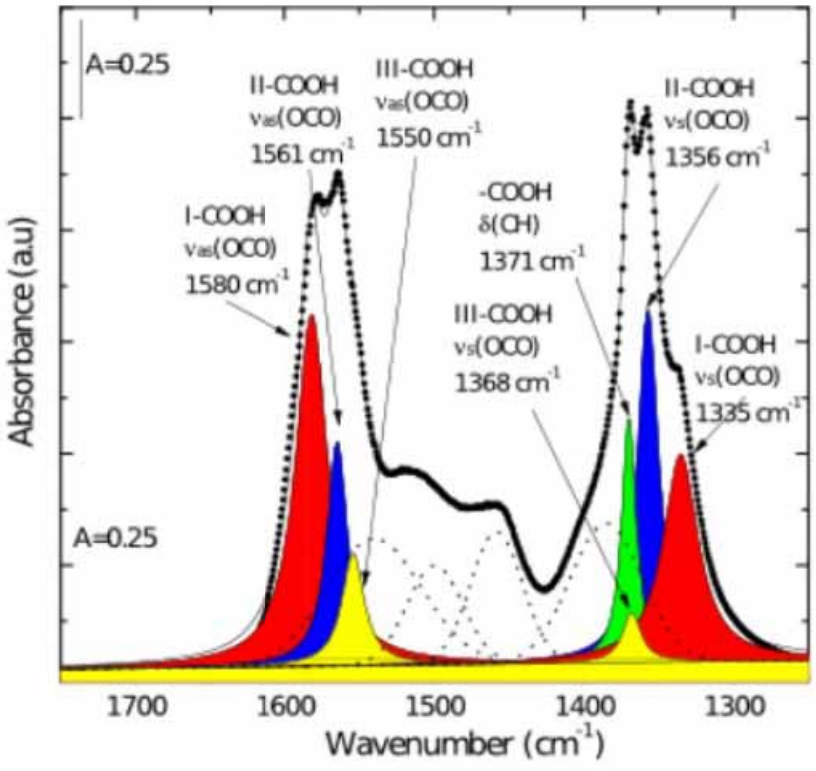
$$n\,HCOOH(g) + \frac{k}{2}\,H_2 + \frac{l}{2}\,O_2(g) + CeO_2 \rightarrow [n\,HCOO + (k+n)\,H + l\,O]/CeO_2$$

$$n\,H_3COH(g) + \frac{k}{2}\,H_2 + \frac{l}{2}\,O_2(g) + CeO_2 \rightarrow [n\,HCOO + (k+3n)\,H + (l-n)\,O]/CeO_2$$

IR data

In collaboration with Dr. A. Bonivardi (INTEC)





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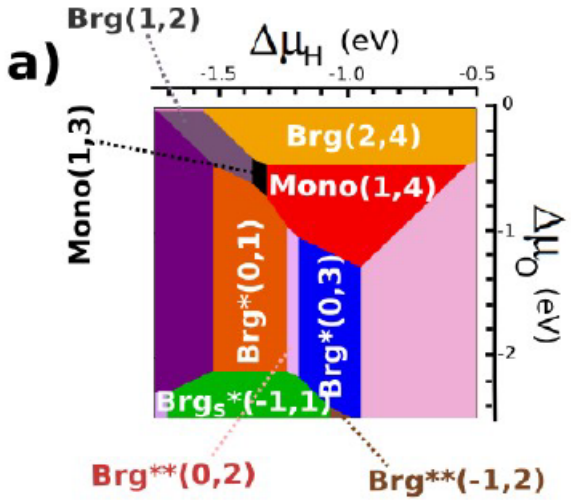
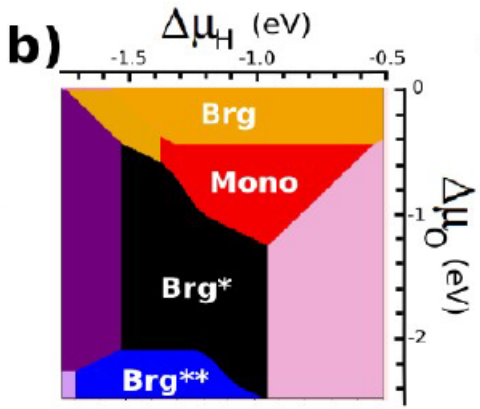
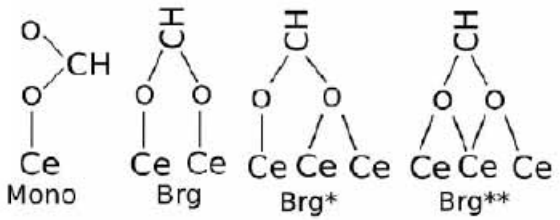
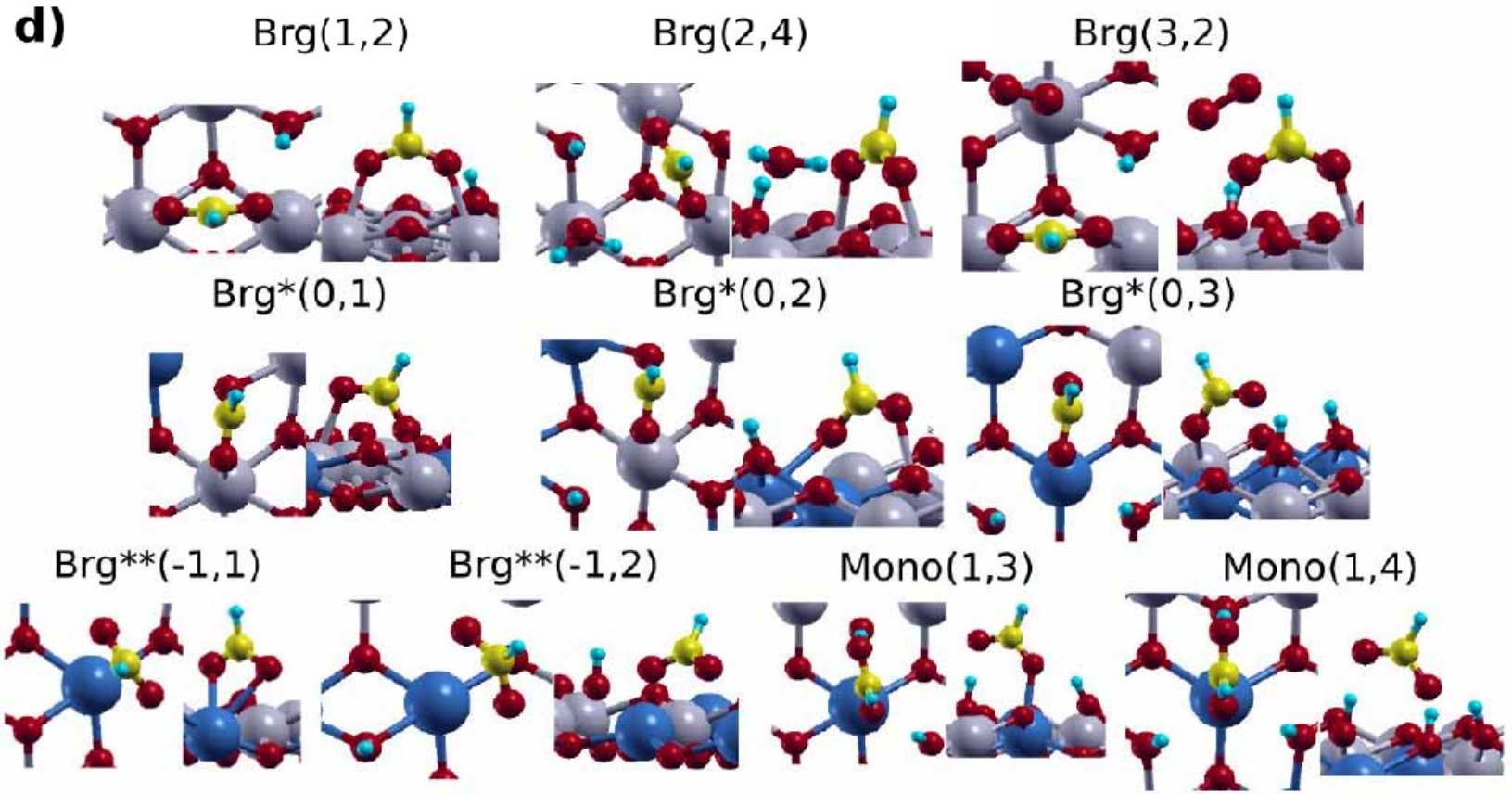






In collaboration with
Dr. V. Ganduglia-Pirovano

LDA+U

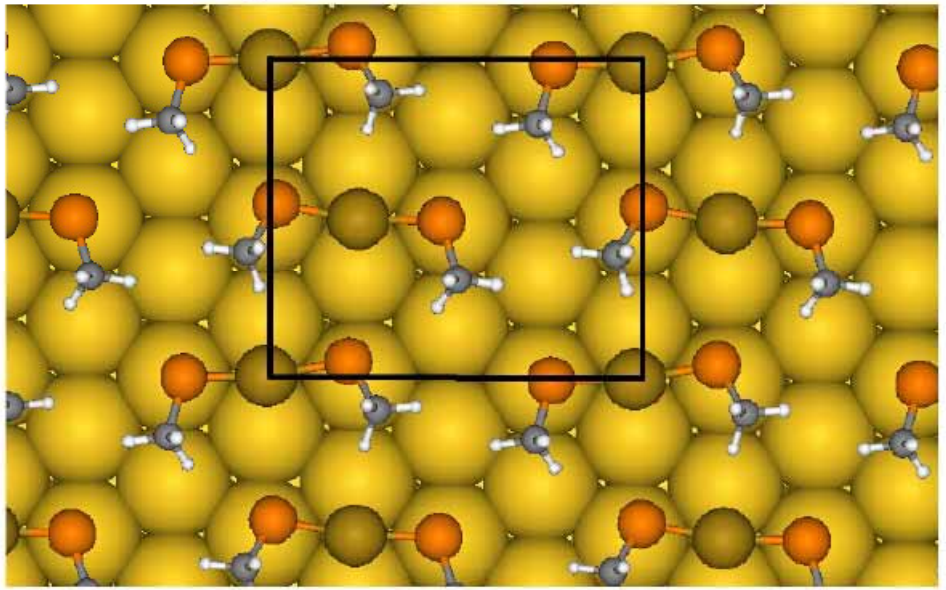


SAMs of alkanethiols

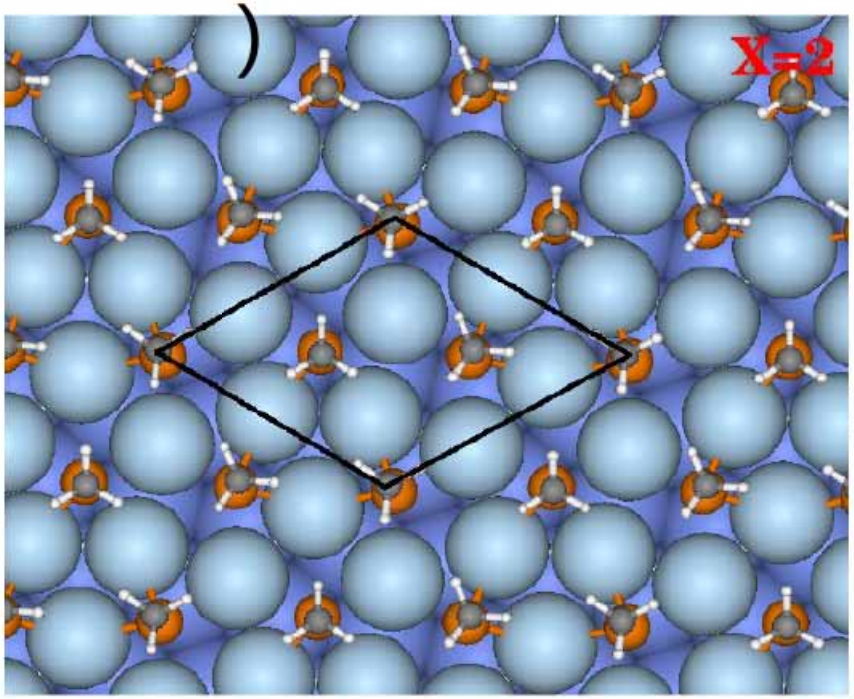
Theoretical study of the structure of self-assembled monolayers of short alkylthiolates on Au(111) and Ag(111): the role of induced substrate reconstruction and chain–chain interactions

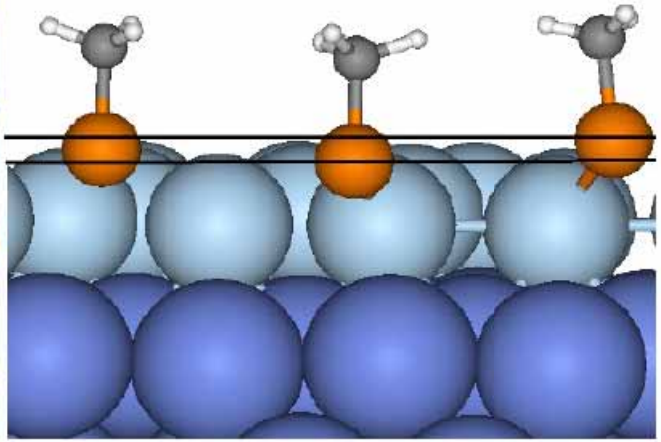
P. N. Abufager,[a] J. G. Solano Canchaya,[a] Y. Wang,[b] M. Alcamí,[b] F. Martín,[bc] L. Alvarez Soria,[d] M. L. Martiarena,[d] K. Reuter[e] and H. F. Busnengo*[a]

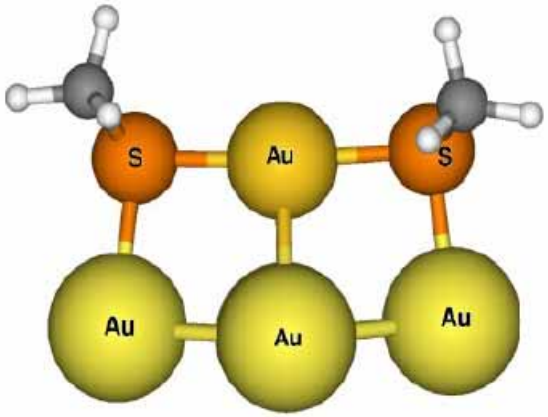
Au(111)



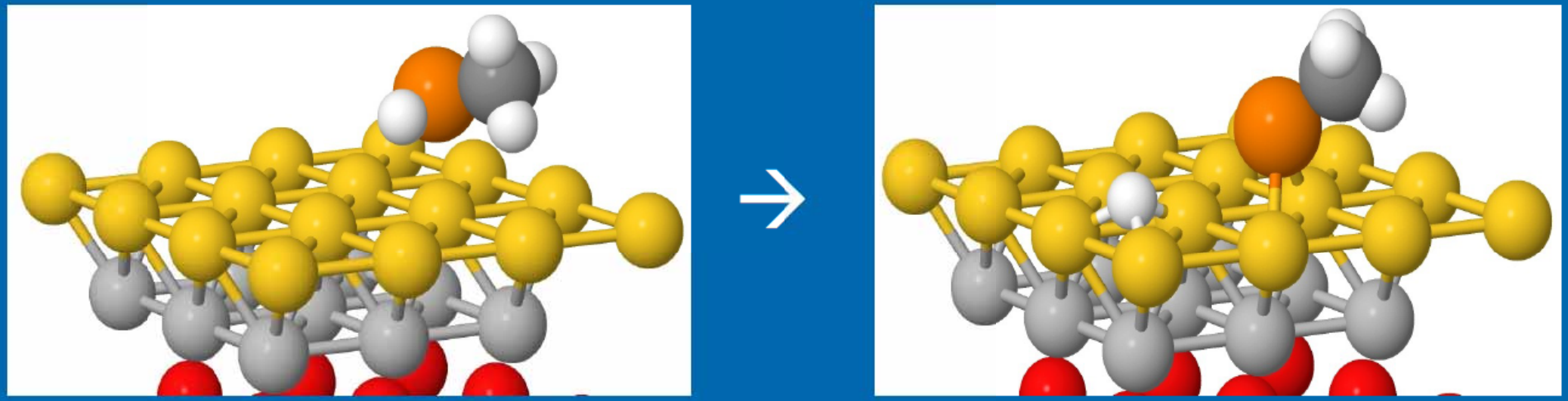
Ag(111)



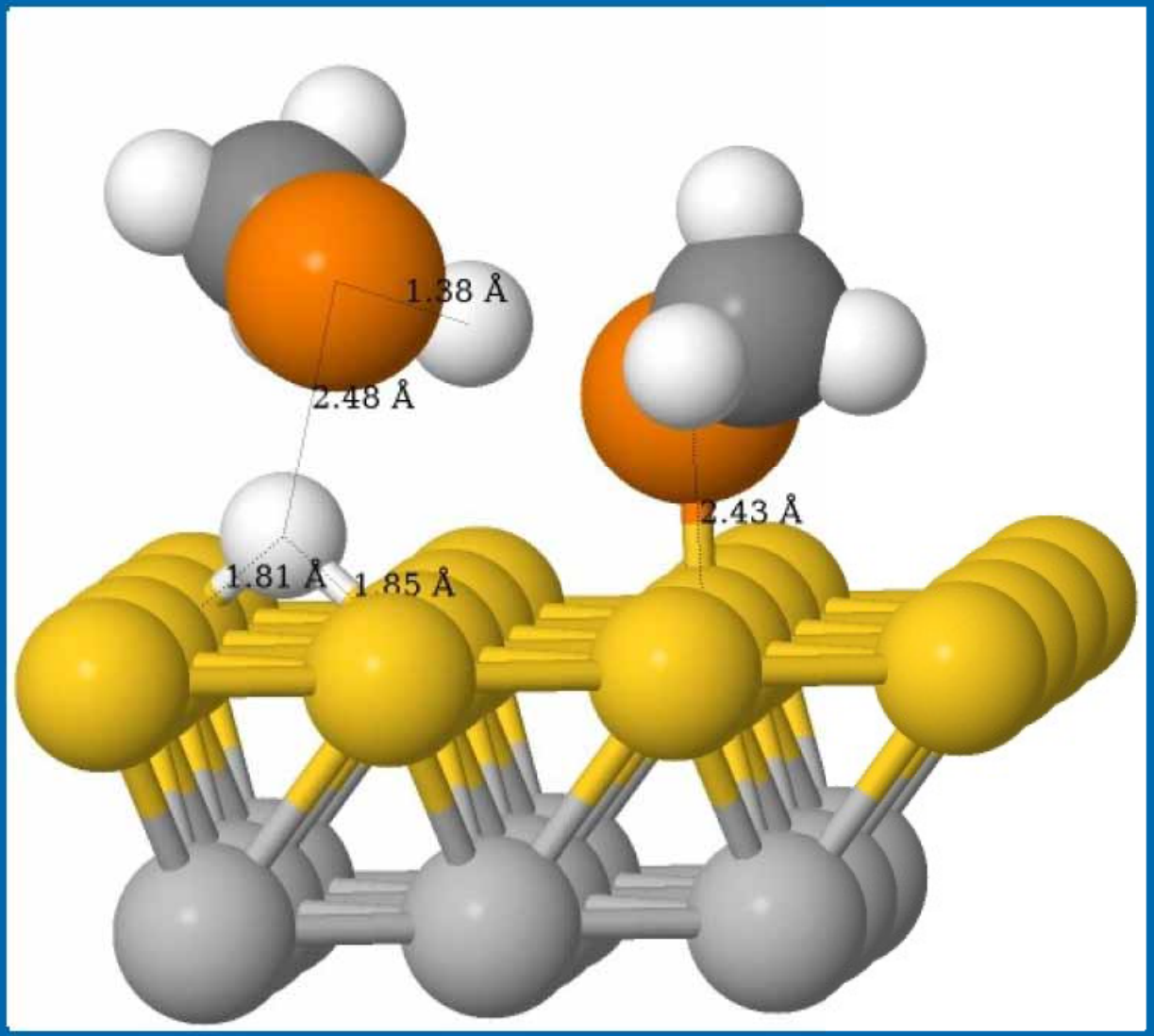




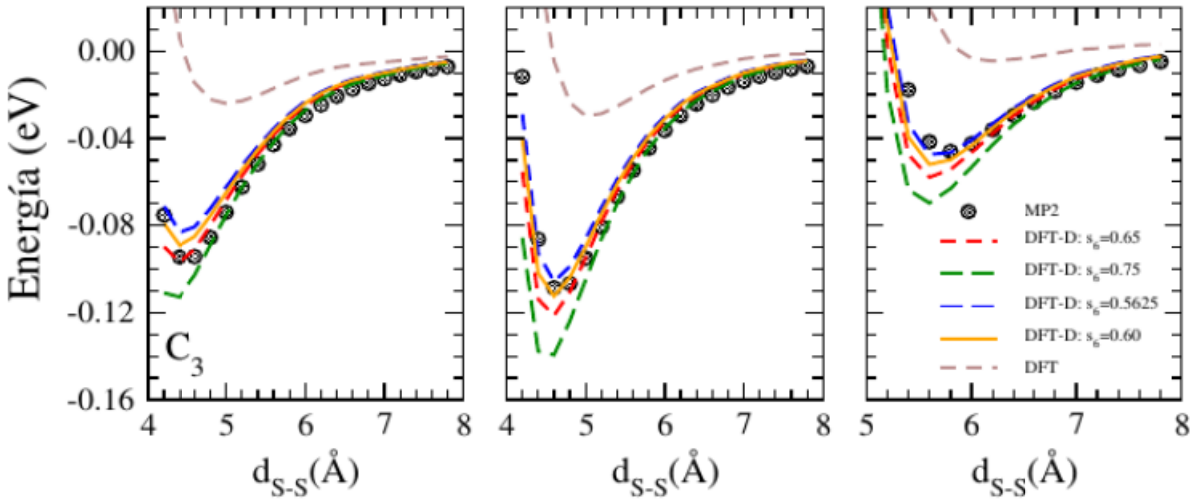
S-H dissociation mechanism ?



Cooperative H-transfer pathway for $HSCH_3$

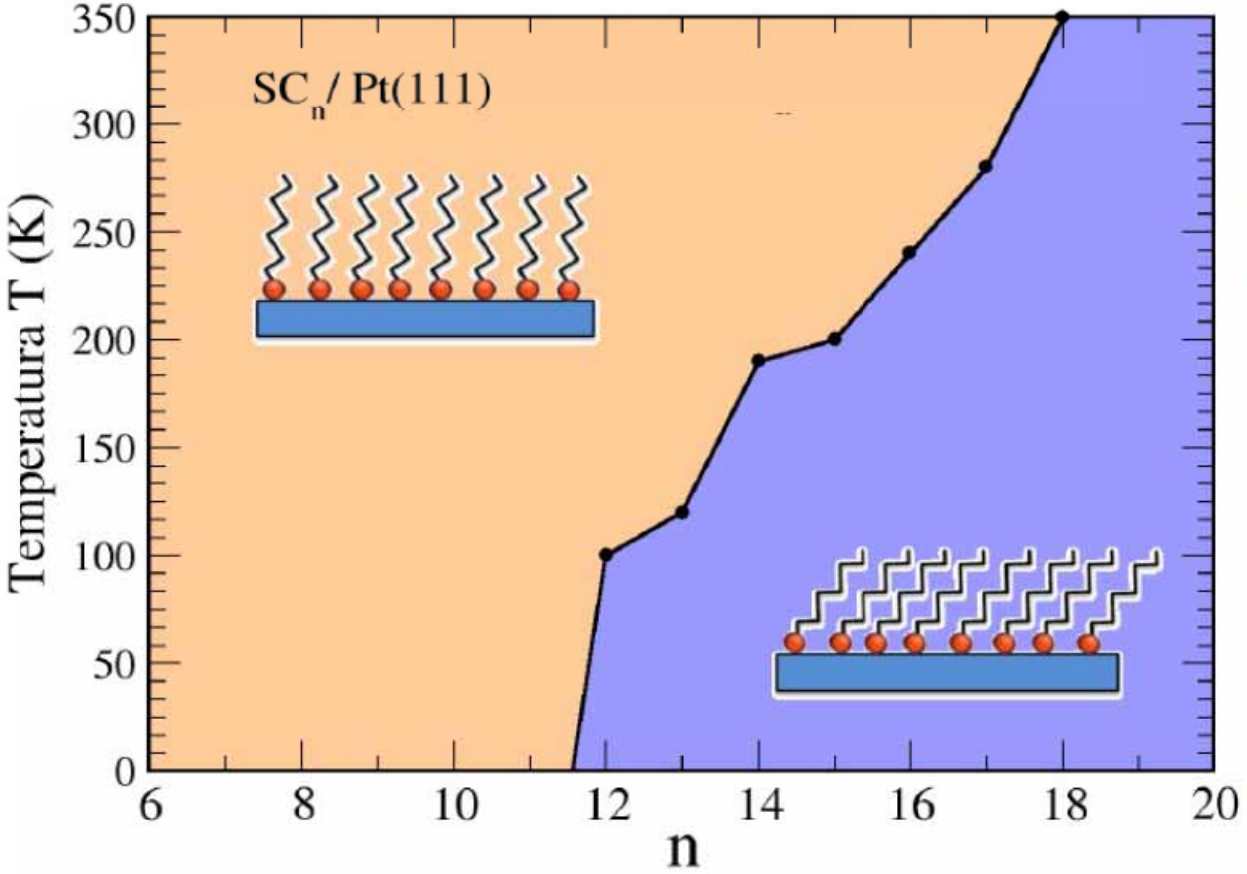


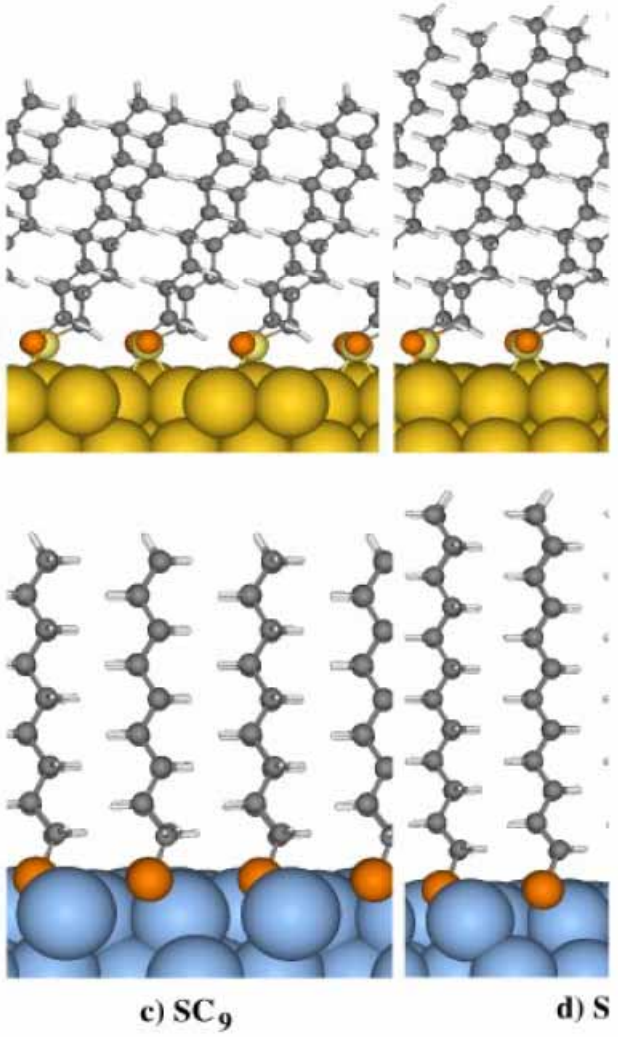
SAMs of “long chain” alkanethiols



MP2

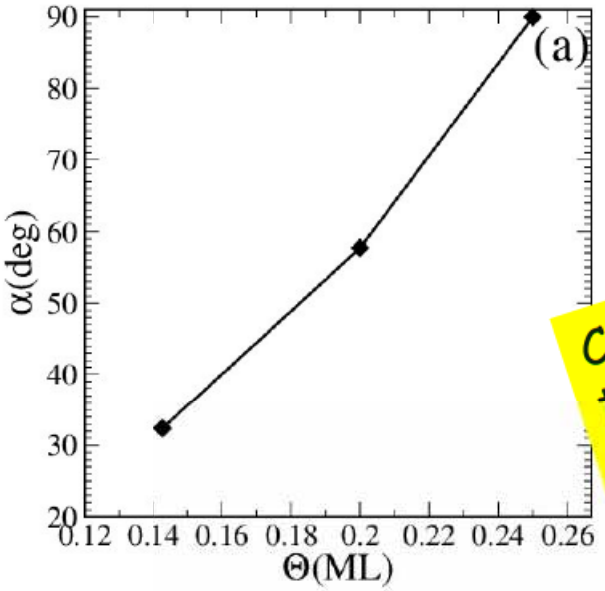
DFT-D

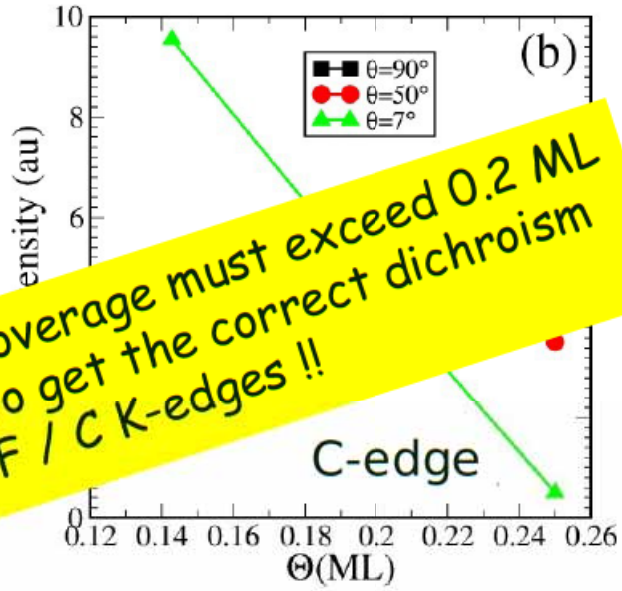




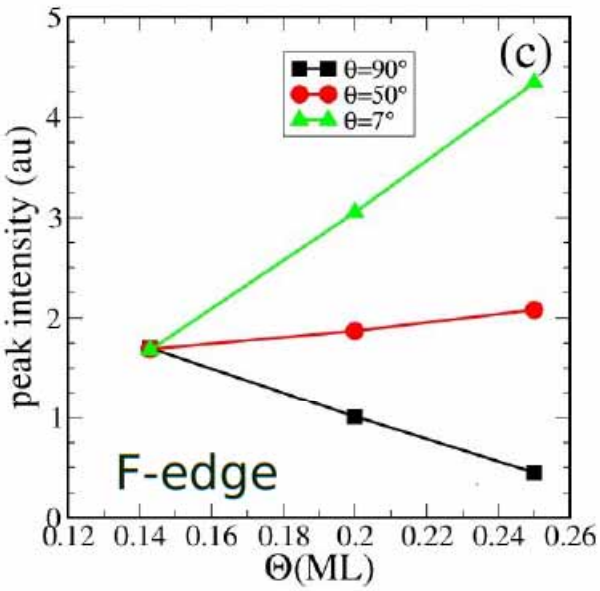
NEXAFS simulation from first principles (Dr. P. Abufager)

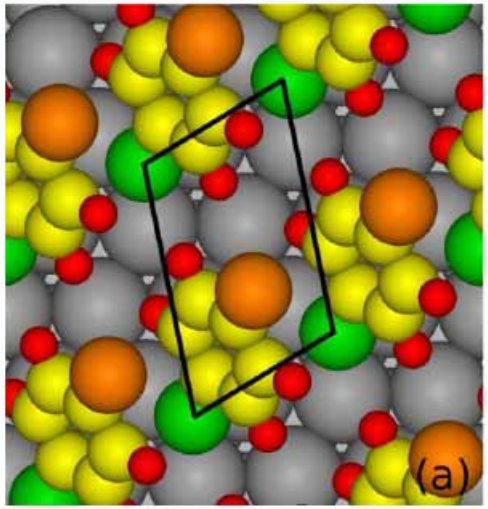
Can we use the inverse dichroism between F and C to resolve the molecular orientation and the coverage of the monolayer?

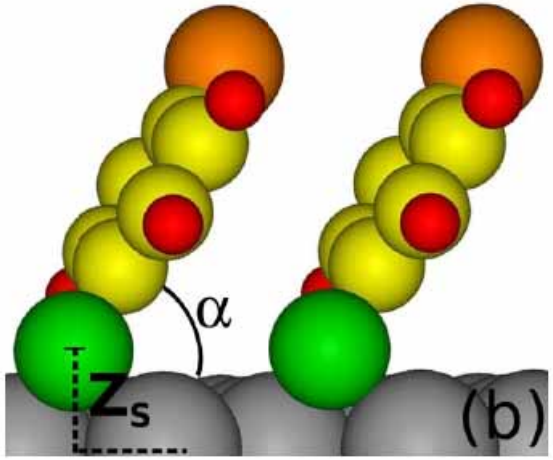




Coverage must exceed 0.2 ML to get the correct dichroism F / C K-edges !!







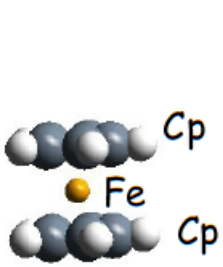
Possible structure
Θ=0.2 α=58°
α_{exp}=60° from C-K edge

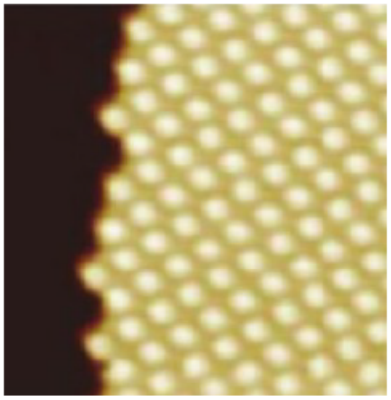
work function change
Theory $\Delta\Phi$=-0.49eV
Exp. $\Delta\Phi$=-0.58eV

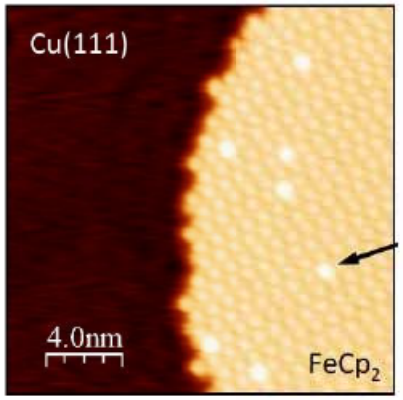
Paper in preparation

Magnetic properties and electronic transport in molecular-metal interfaces (Dr. P. Abufager)

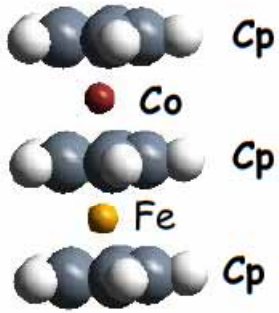
in collaboration with R.Robles, N. Lorente, L. Limot (exp.)







CoFeCp3



FeCp2/Cu(111)

NO magnetism

CoFeCp3/Cu(111)

Magnetic properties appear

Co deposition by STM

Theoretical work

- Magnetic properties molecule-surface interface: DFT calculations (VASP/SIESTA).
- Kondo effect by means of an Anderson Hamiltonian based on DFT data
- Transport properties DFT+NEGF formalism :TRANSIESTA Code

Thanks for your attention !