



ESMoINa

European School on
Molecular Nanoscience

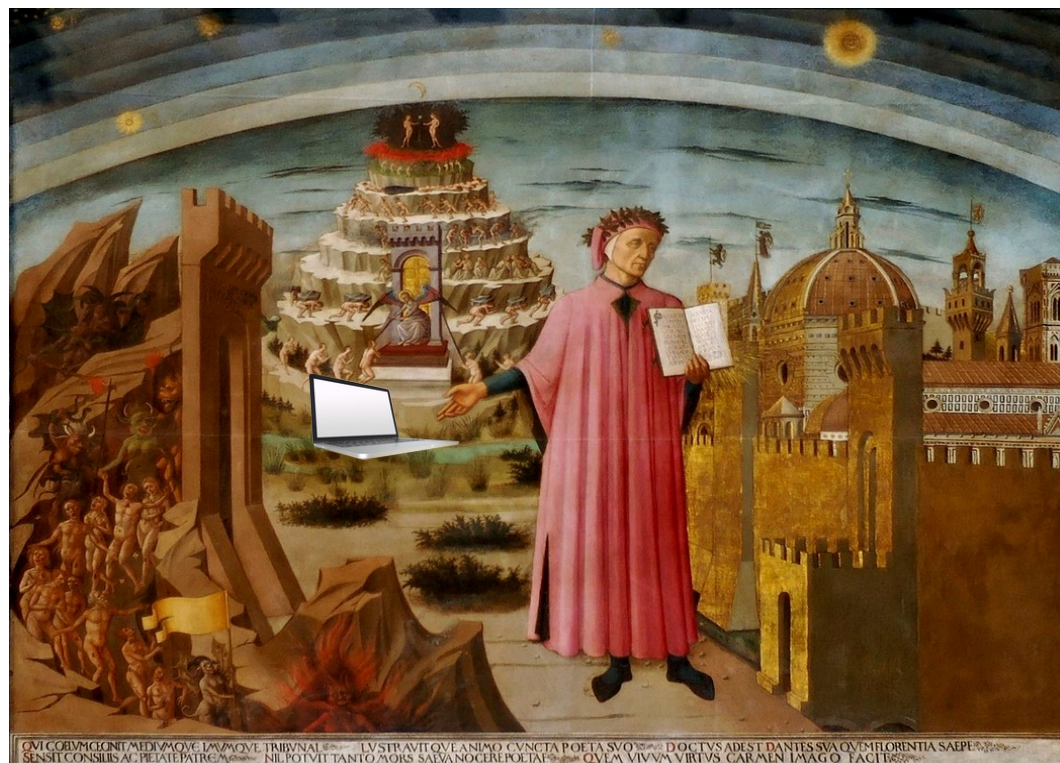
Molecular Magnets on Surface: a Dantesque Journey Through the *Ab Initio* Realm



UNIVERSITÀ
DEGLI STUDI
FIRENZE

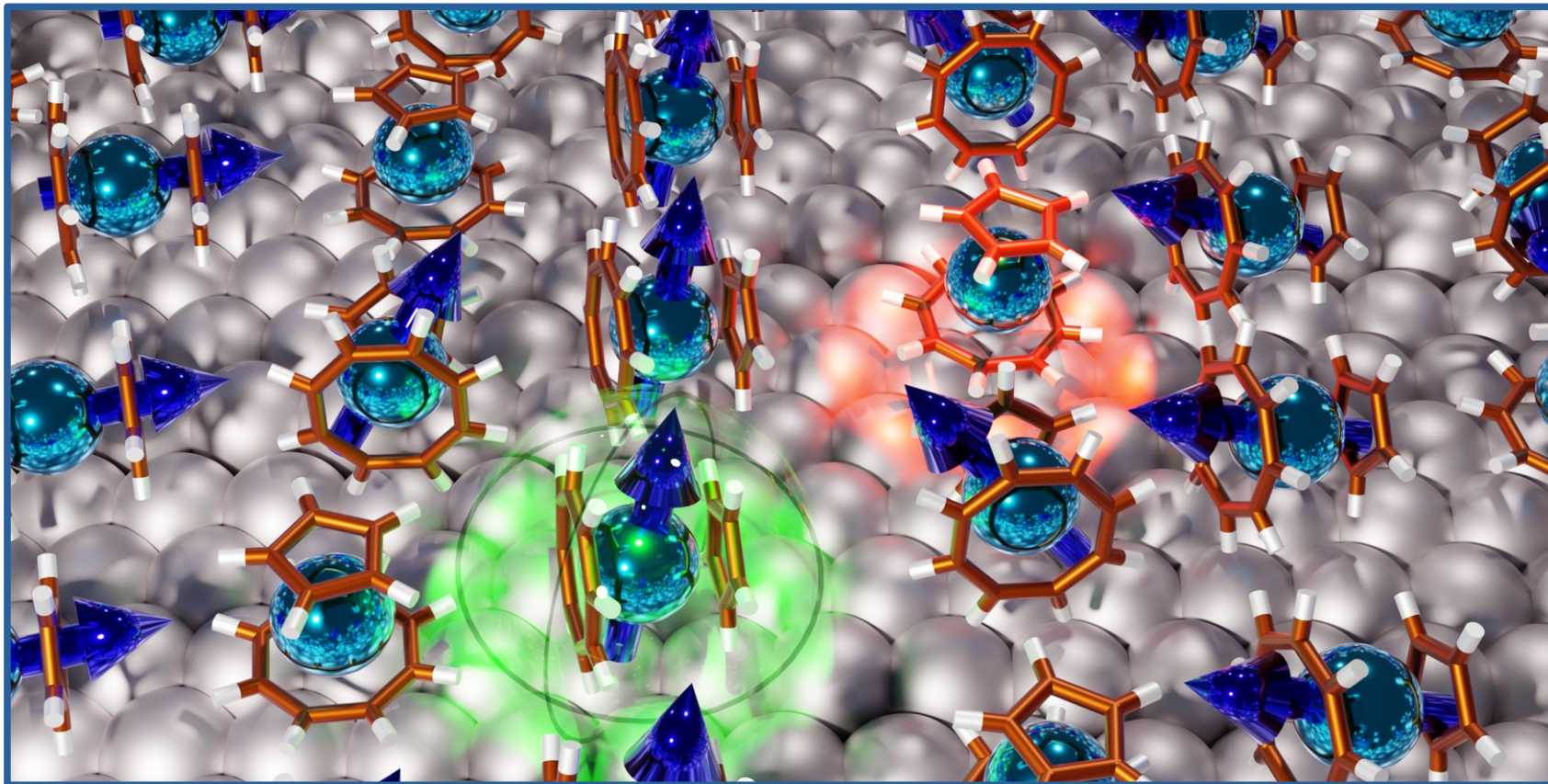


LAMM
Laboratorio di Magnetismo Molecolare



Why Molecules on Surface? Addressability!

Necessity of safe adsorption and organization on surface to access and control the single molecule and build the molecular equivalent of a printed circuit



Molecules on Surface: a No Man's Land

Chemist's
realm



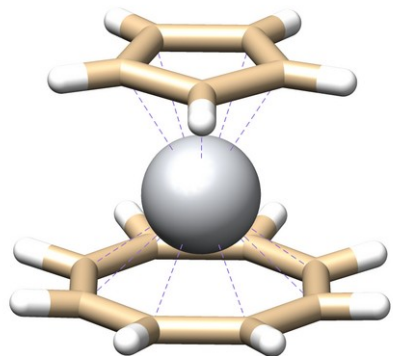
Gas, Solutions,
Molecular Crystals

"Middle Heart"

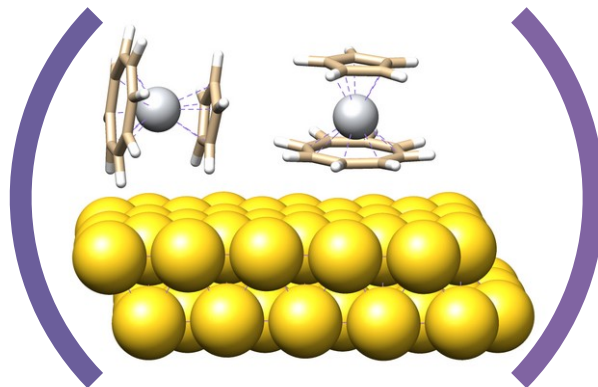
Solid State,
Bulk materials



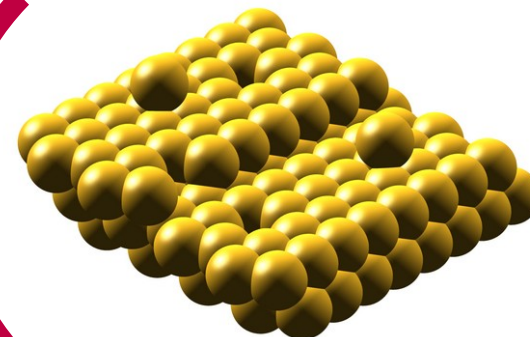
Physicist's
realm



Magnetic
Molecules



Molecules@Surface



Surfaces

Molecular
Geometry?

Magnetic
Properties?

Electronic
Structure?

A 'Dark Wood' of Experimental Techniques

Spectroscopies

- Electronic (UV/Vis)
- Vibrational (IR/Raman)
- Photoelectron (UPS/XPS)
- X-Ray (XAS/XMCD/XNLD)
- Magnetic (EPR, NMR)

Scanning Probe Microscopies

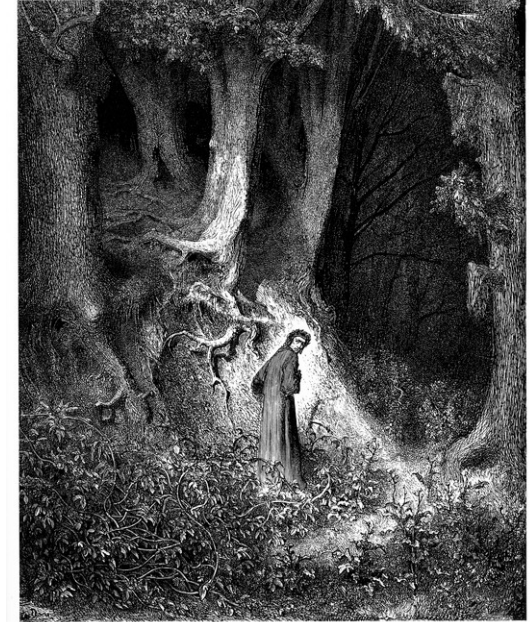
- Tunneling
- Atomic Force
- Magnetic Force

Electron Diffractions

- Low-Energy Electron (LEED)
- Transmission (TEM)



**Very Complex
electronic Structure
arising from electrons
in *d* and *f* orbitals**



*When I had journeyed half of our life's way,
I found myself within a shadowed forest,
for I had lost the path that does not stray.*

Divina Commedia, Inferno, Canto I

What do we want from theory?

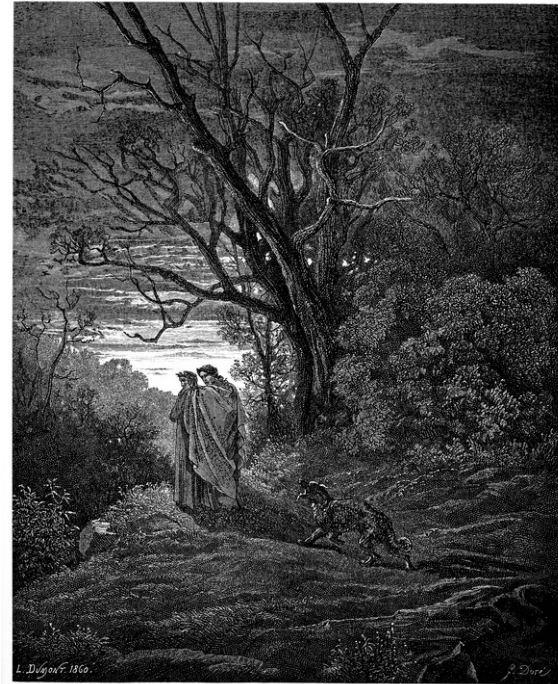
Theory as a 'Virgil', a guide
through the darkness

Interpretation of features and
trends in experimental data

Predictive tools, accurate
numbers, magneto-structural
correlation, *in silico* design

Qualitative and pictorial
Insights

Concepts, models

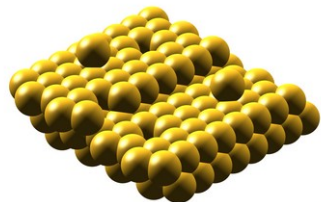


Entering the Chemical Hell

Circles of hell to face:

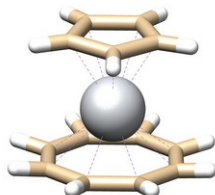
I Circle

The Surface



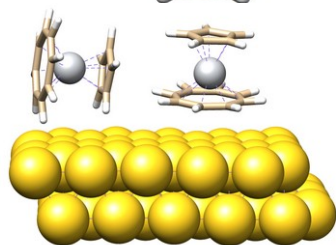
II Circle

The Molecular Magnet



III Circle

The Molecule/Surface Interaction



IV Circle

[CpTi(cot)]: a case study

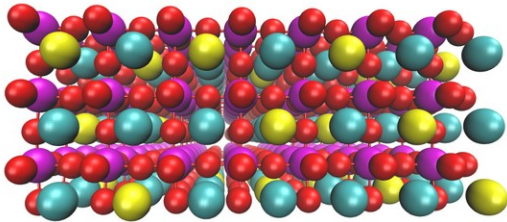
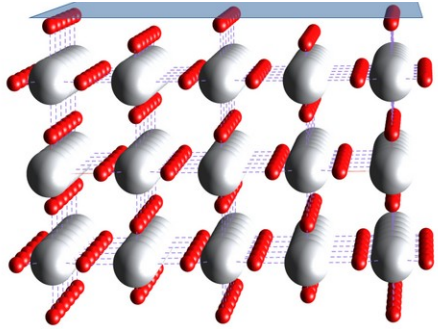
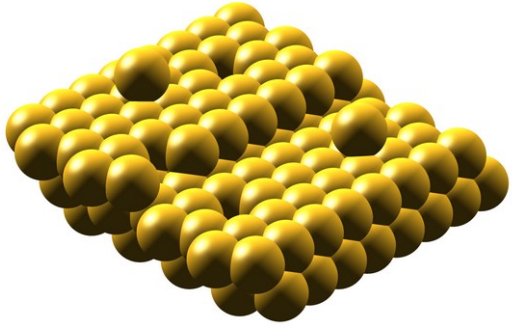


THROUGH ME THE WAY TO THE ETERNAL PAIN, [...] THROUGH ME THE WAY THAT RUNS AMONG THE LOST.

BEFORE ME NOTHING BUT ETERNAL THINGS[...] ABANDON EVERY HOPE, WHO ENTER HERE.

Divina Commedia, Inferno, Canto III

I Circle: The Surface



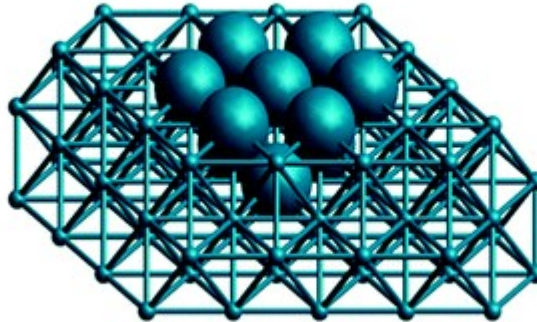
Surface Modeling

Different surface models for a fcc(111) surface

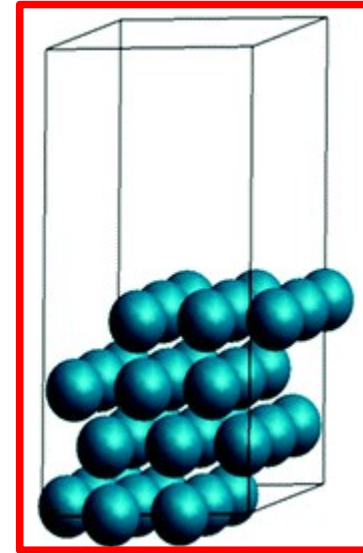
cluster model



embedded cluster approach

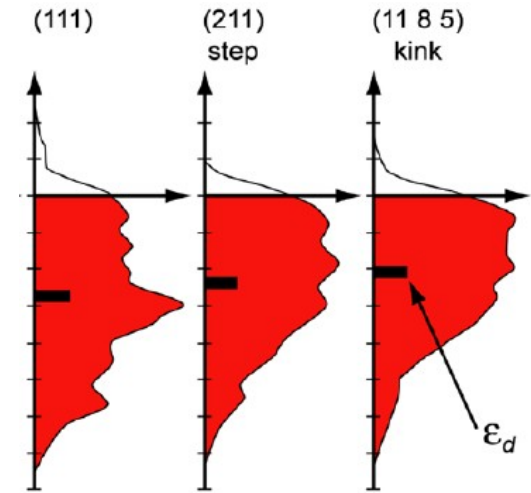
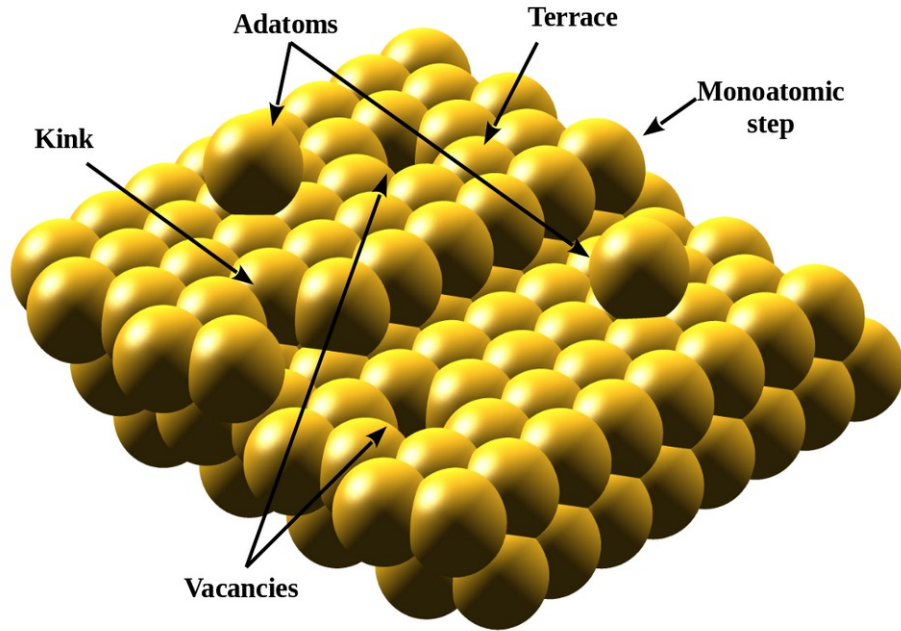


periodic slab model with unit cell indicated



Periodic models must be preferred if possible to avoid finit size effects

Surface Defects

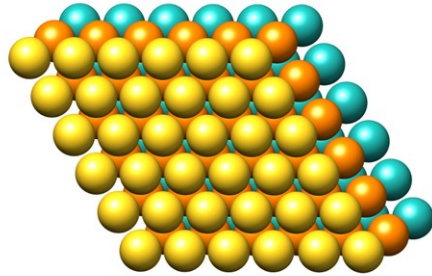


DOS of a Pt(111) surface

Presence of defects → Different Electronic Structure → Different reactivity

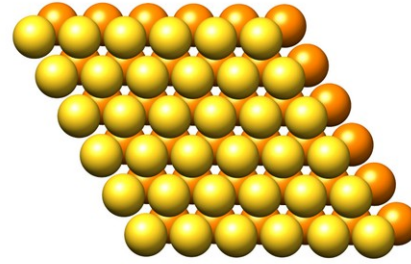
Number of Layers

FCC (111)

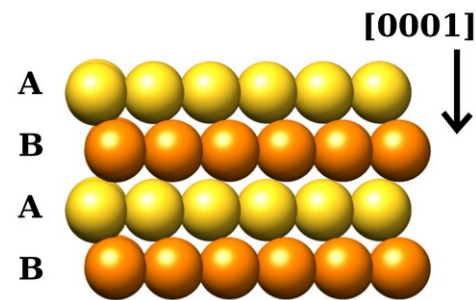
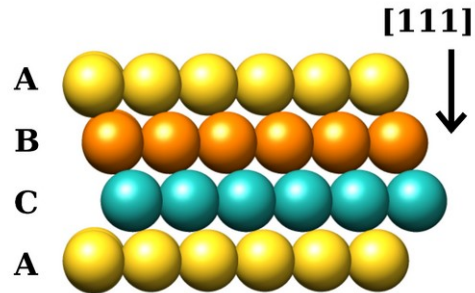


At least three layers
required for an FCC
surface

HCP (0001)

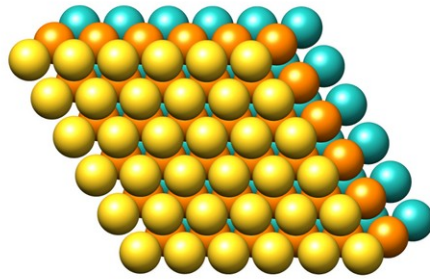


HCP requires four
layers to conserve
symmetry

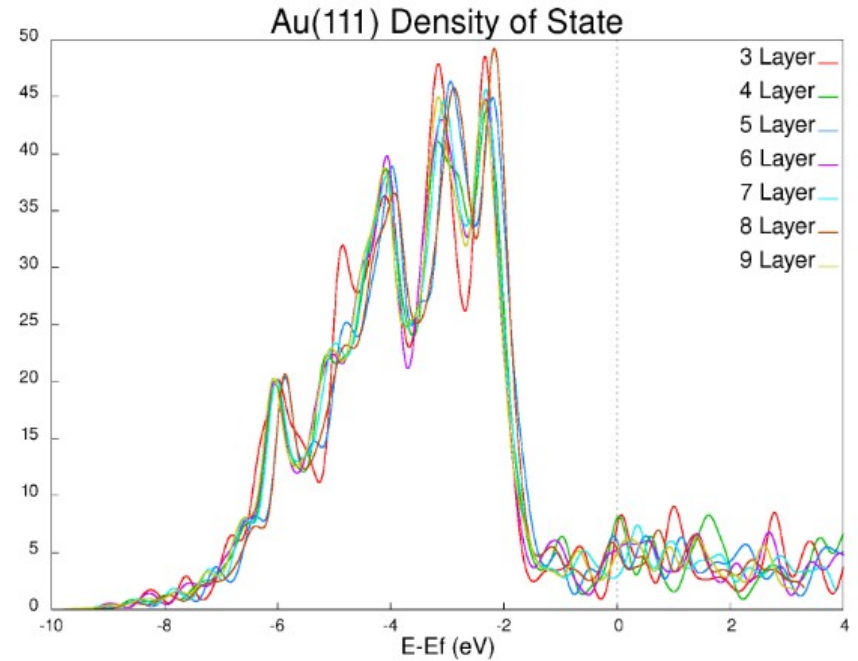
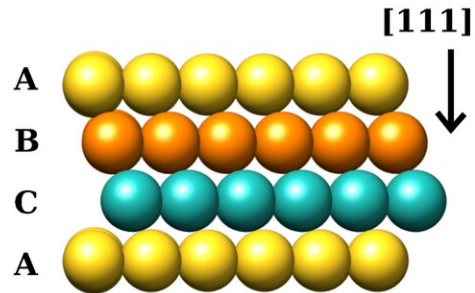


Number of Layers

FCC (111)



At least three layers
required for an FCC
surface



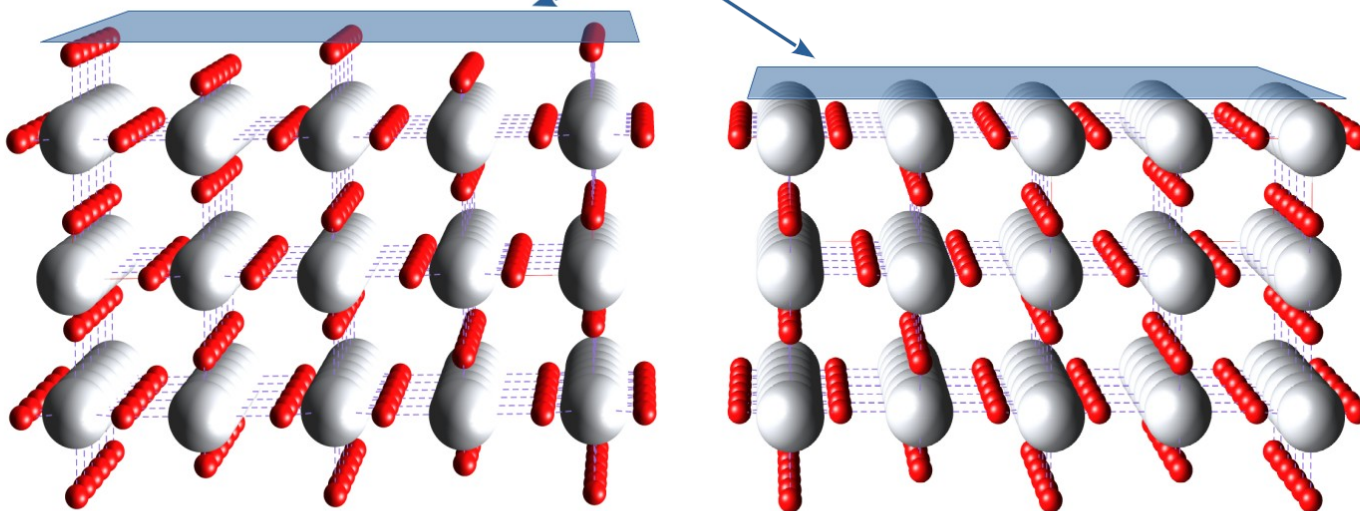
Lunghi and Totti *J. Mater. Chem. C*, 2015, 3, 7294-7304

Termination Layer

Saturated: more stable!

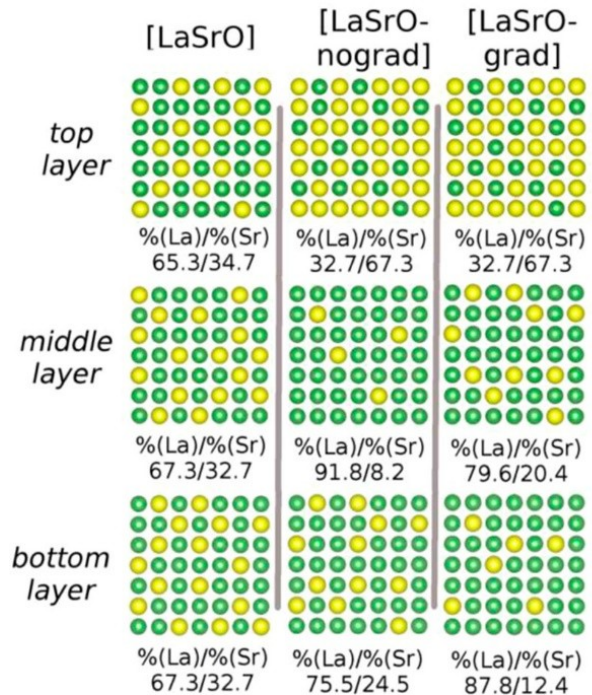
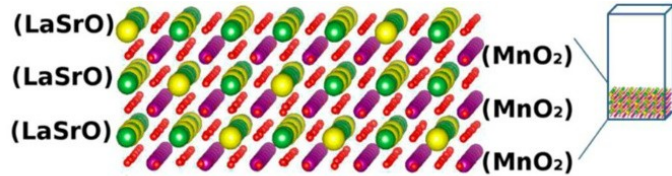
Cutting Planes

Unsaturated: more reactive!



Two possible termination layers in rutile TiO₂ (110)

A Complicated Case: LSMO



LSMO surface: Sr-rich with respect to the bulk

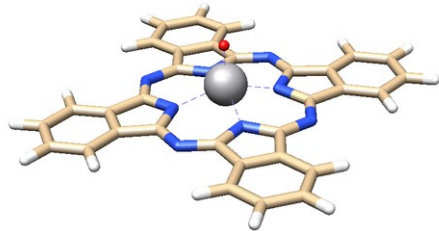
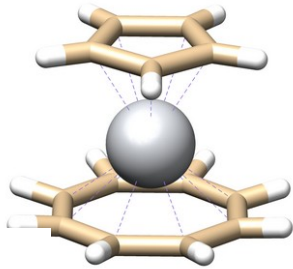
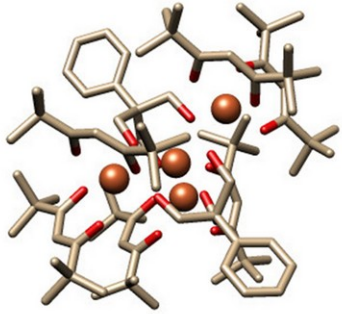
Necessity to model complex phenomena such as concentration gradients from the bulk to the surface layers

LaSrO slab: rich in Sr ions, more stable than the layers with a stoichiometric concentration, in agreement with the experimental data

Poggini *et al.*, *J. Phys. Chem. C*, 2014, 118, 1363.

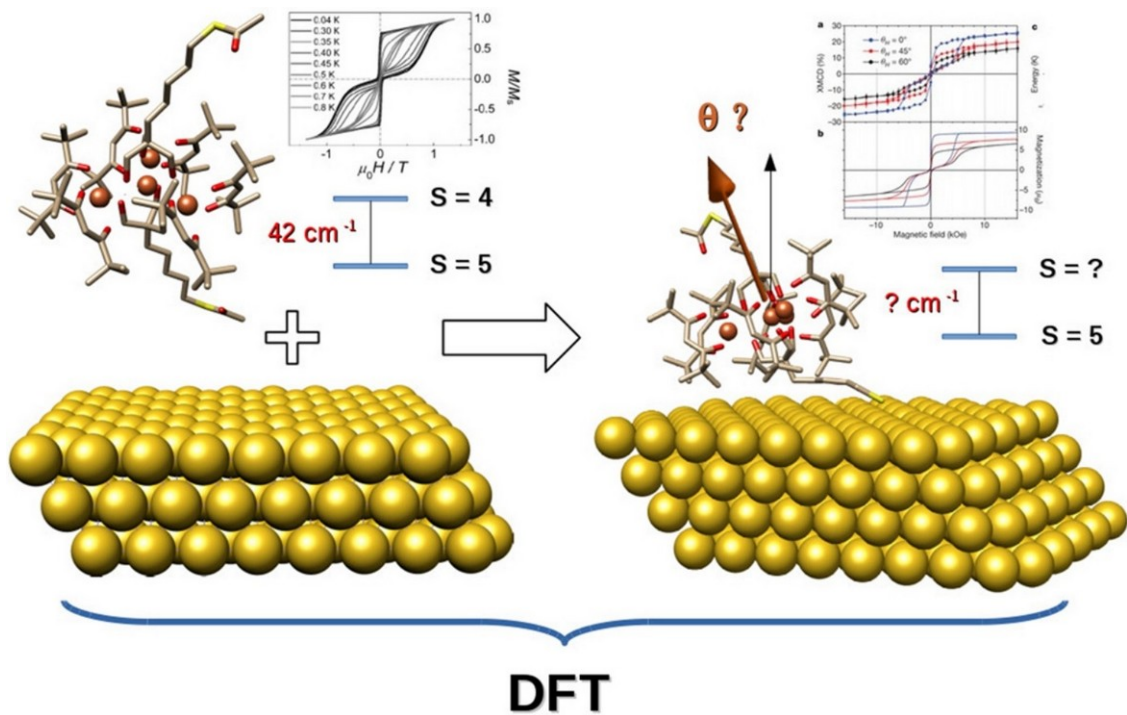
II Circle: The Molecule

Molecules are objects quite volatile...



Which approach for molecular Magnets?

- A computational protocol which is able to accurately account for the evolution of the molecular properties from bulk to adsorbed scenario for both surface and molecule → **Homogeneity!**



In a reasonable amount of time!

Totti et al. *Coord. Chem. Rev.* 2015, 289–290, 357-378

Correct DFT Orbital Energies: Self Interaction

DFT: overdelocalization of the electronic charge density



Occupied eigenstates of molecules are pushed to higher energies



DFT + U approach → provides both a self-interaction correction for the total energy functional and the corresponding KS orbital energies through an effective correction term U

Advantages:

Efficiency → No extra computation time requested other than DFT

Accuracy → High if small geometrical deviations are expected

Disadvantages:

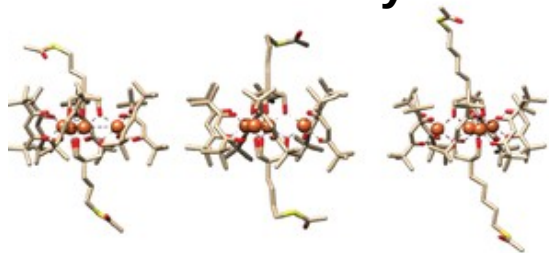
Parametric → Set up derivation U/J or U_{eff} values and limited to few set of orbitals

Accuracy → Medium/Low if large geometrical deviations are expected

How to Tune the U value?

On the basis of experimental data!

Optimized Geometry vs X-Ray



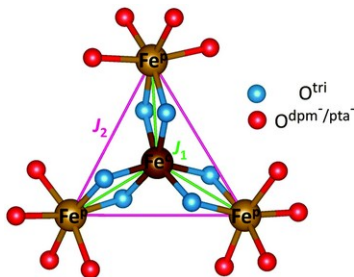
$\text{Fe}_4\text{C}_3\text{SAc}$

$\text{Fe}_4\text{C}_4\text{SAc}$

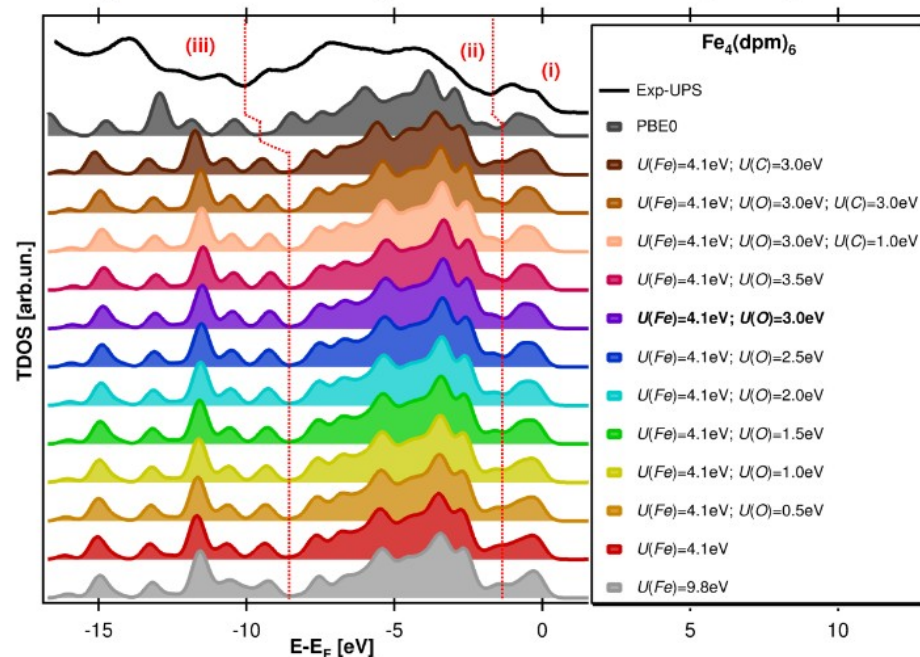
$\text{Fe}_4\text{C}_5\text{SAc}$

Simulated vs Experimental Exchange

	$U(\text{Fe})$, eV	$U(\text{O})$, eV	$U(\text{C})$, eV	J_1 , cm^{-1} (optimized)	J_1 , cm^{-1} (X-ray)
	9.8	-	-	17.66	-
	-	-	-	31.68	32.59
	0.5	-	-	28.86	-
	1.0	-	-	26.18	-
	1.5	-	-	23.62	-
	2.0	-	-	21.20	-
	2.5	-	-	18.89	-
	3.0	-	-	16.70	16.95
	3.5	-	-	14.63	14.79
	3.0	1.0	-	16.59	-
	3.0	3.0	-	16.37	-
	-	3.0	-	31.26	-
	PBE0			13.83	14.43
	Experimental ⁶			16.37(12)	



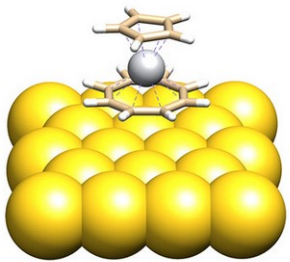
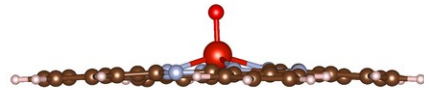
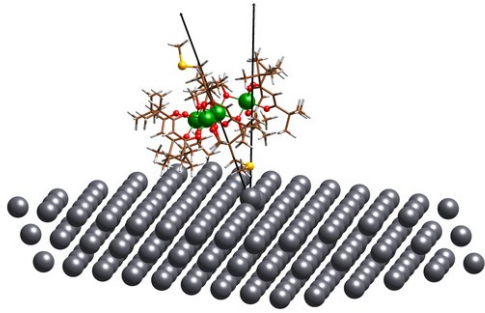
DOS vs UPS



Ninova et al. *J. Mater. Chem. C*, 2014,2, 9599-9608

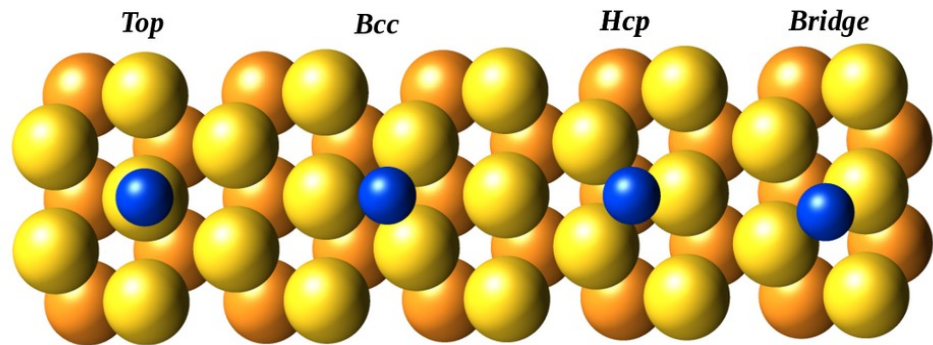
Poggini et al. *Adv. Mater. Interfaces*, 2021, 8, 2101182

III Circle: The Molecule@Surface

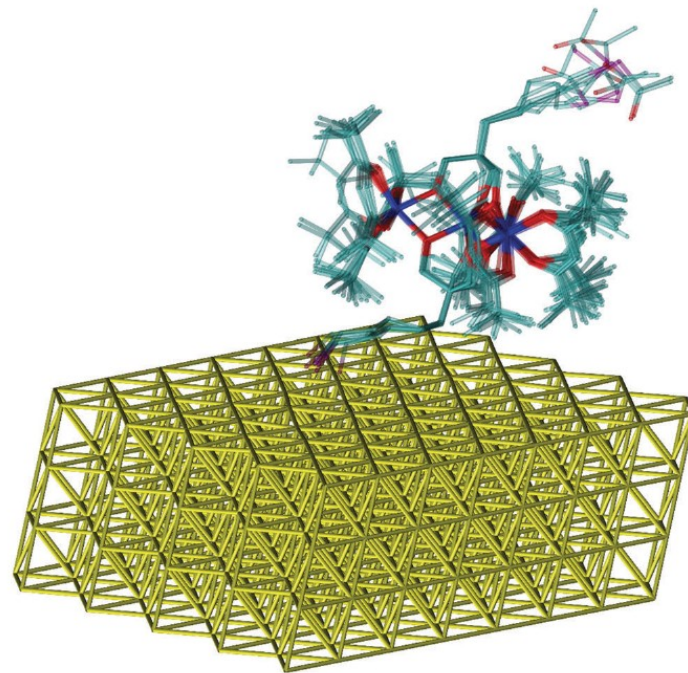


Adsorption process: geometrical issues

Multiple Adsorption sites: major problem for chemisorption and small molecules

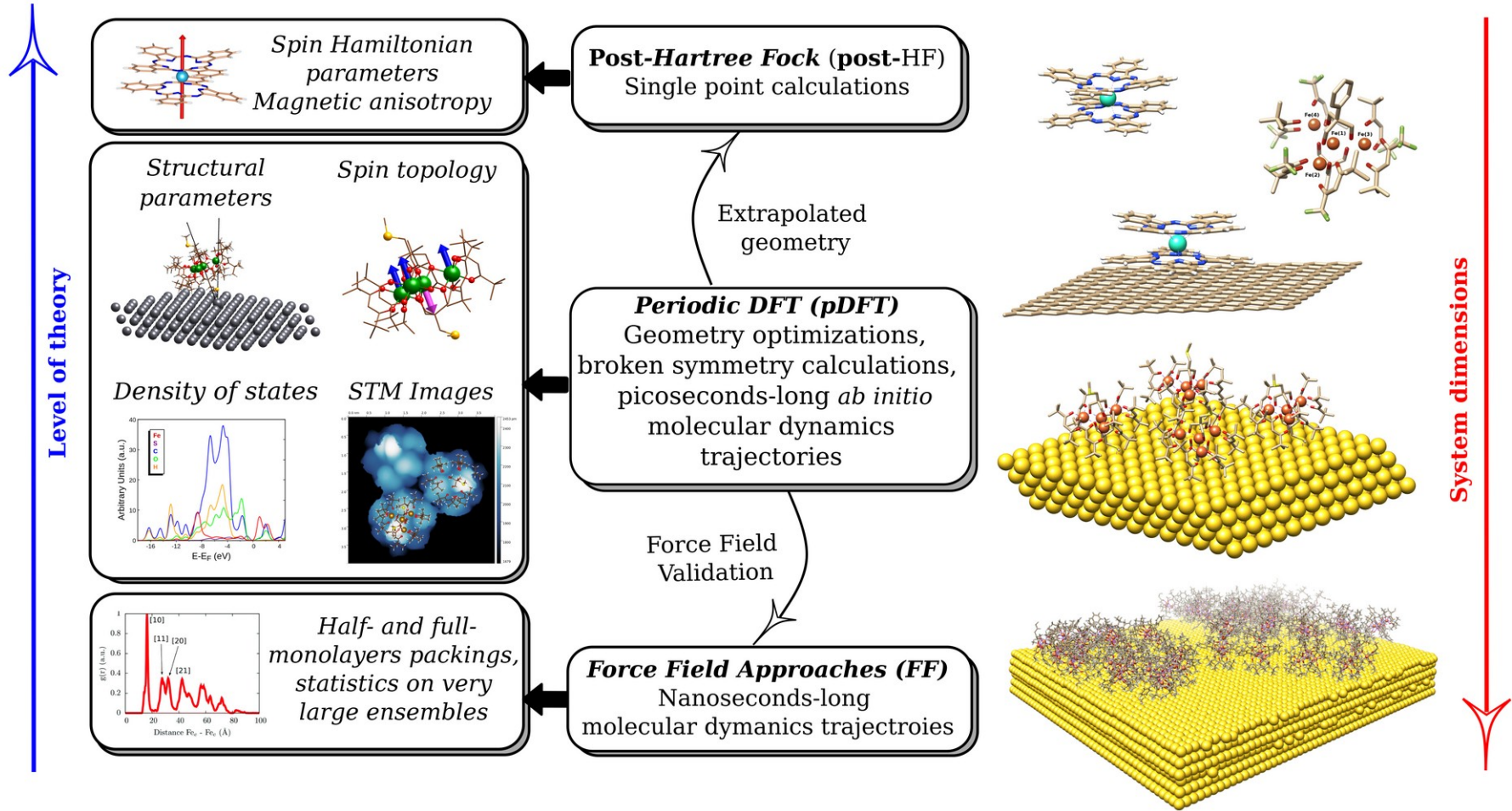


Several Conformational minima
(major problem for large systems)

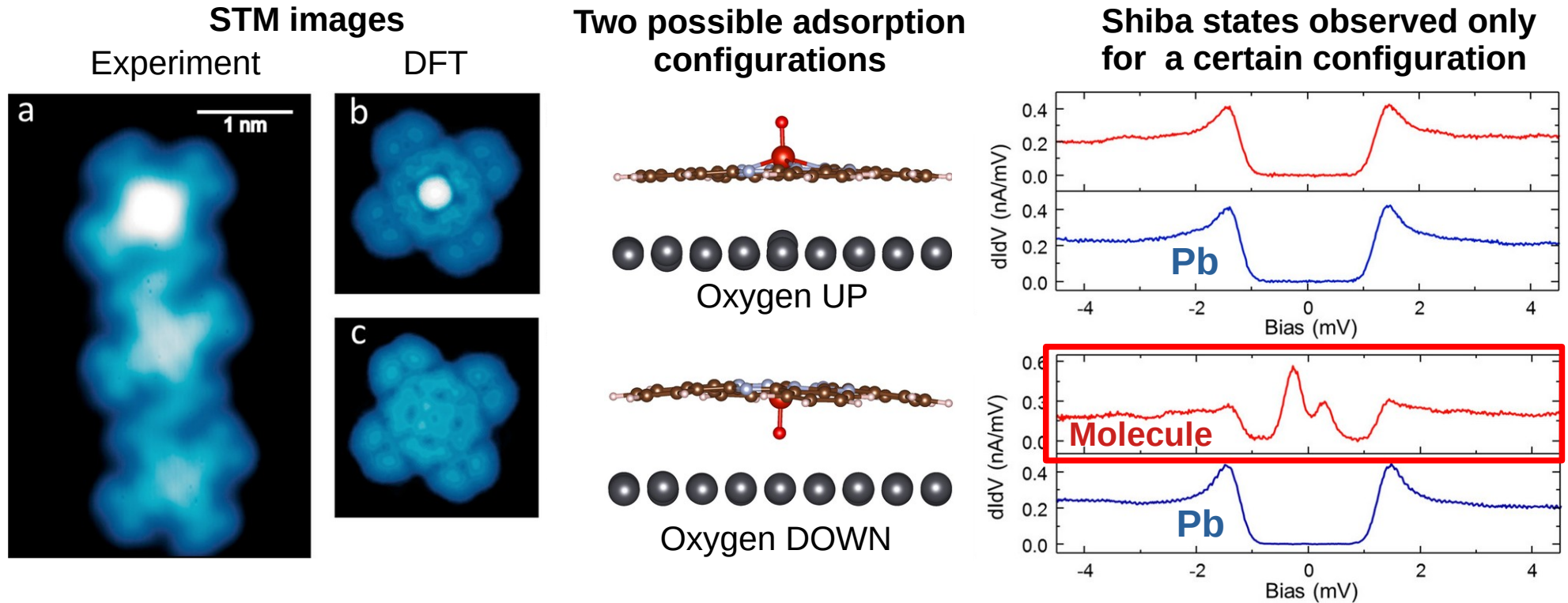


Lunghi et al *J. Mat. Chem. C*, 2015, 3, 7294

Which Approach for Molecular Magnets?



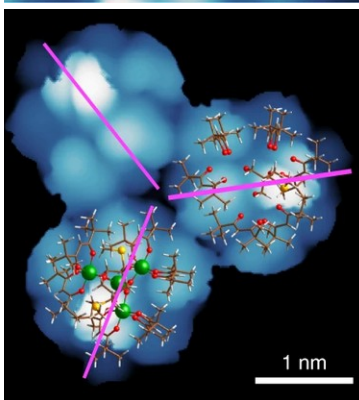
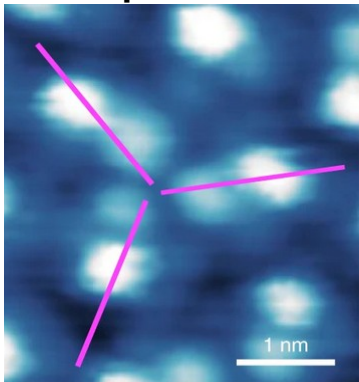
Geometry Optimizations of Single Molecules



Malavolti, Briganti, *et al* *Nano Lett.* 2018, 18, 7955–7961.

Geometry Optimizations of Cluster of Molecules

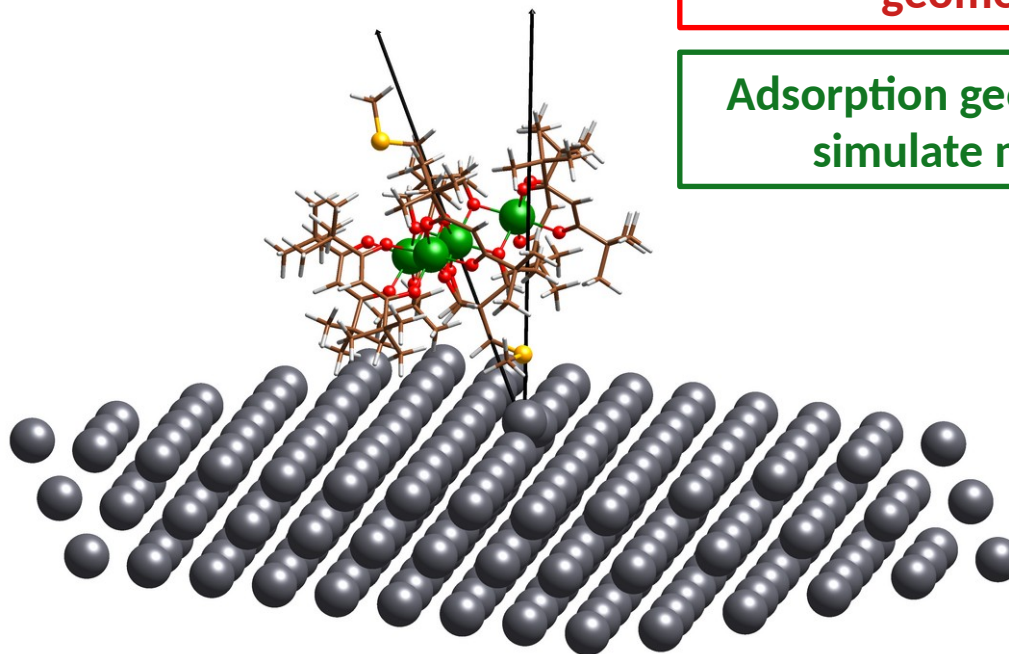
Experiment



Simulated
by Periodic DFT

Simulation of the packing
geometry by DFT

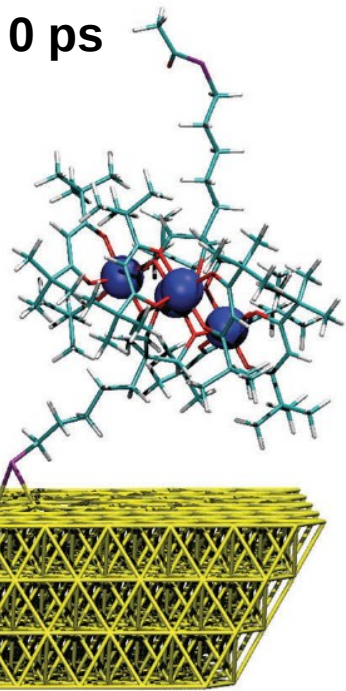
Adsorption geometry allowed to
simulate magnetic data



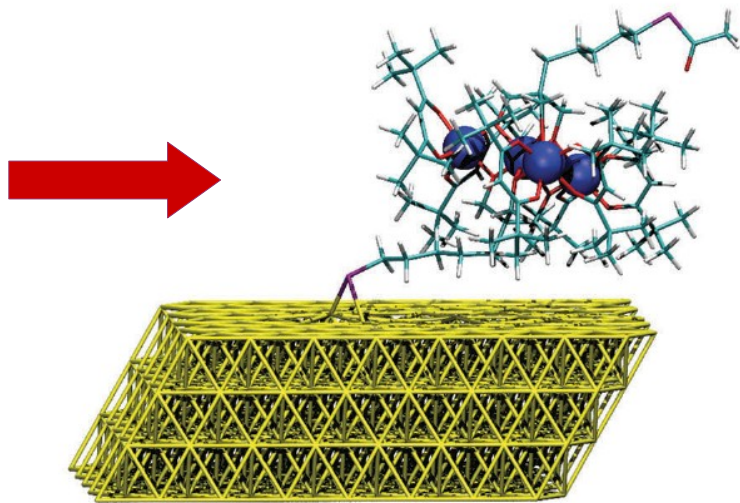
Fe_4SMe Molecule on $\text{Pb}(111)$

Ab Initio Molecular Dynamics

0 ps



0.5 ps



Pro: Larger conformational space

Contra:

- Only one or few molecules
- Few picoseconds
- Computationally expensive

Geometry Optimization

Mannini et al. *Nature*, 2010, 468, 417

Ab Initio Molecular Dynamics

A. Lunghi et al. *J. Mater. Chem. C*, 2015, 3, 7294

L. Poggini et al. *Adv. Mater. Interfaces*, 2021, 8, 2101182

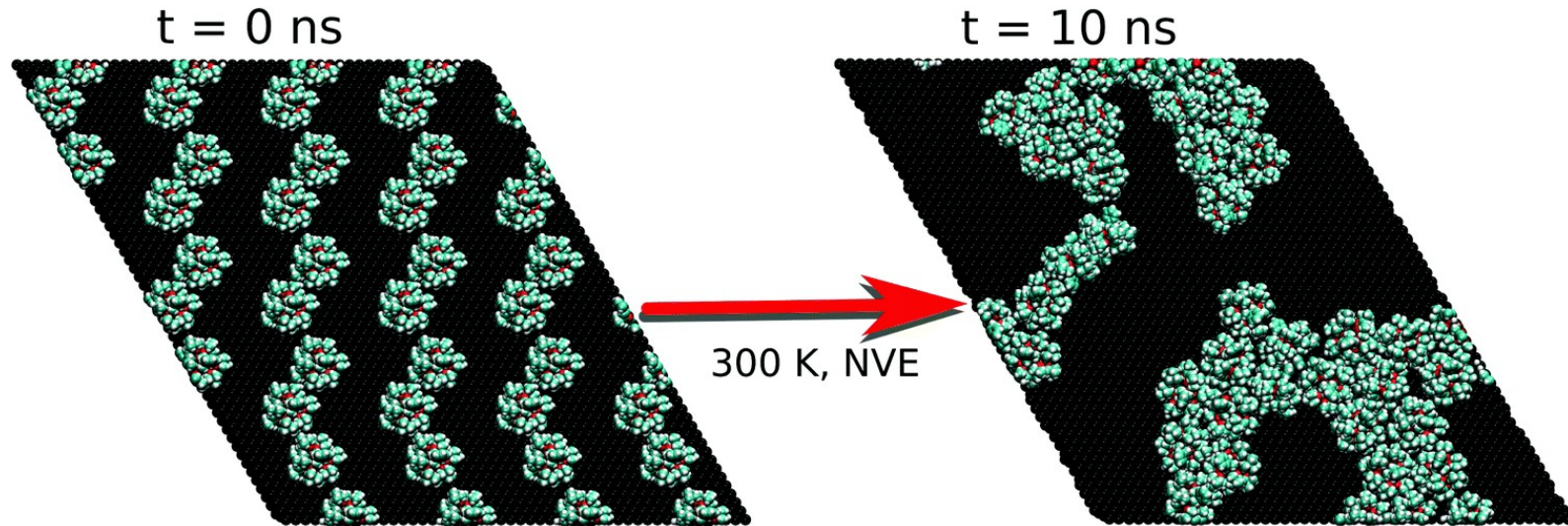
Force Field Molecular Mechanics

PRO

- Walker time around nanoseconds vs picoseconds
- Hundreds of molecules

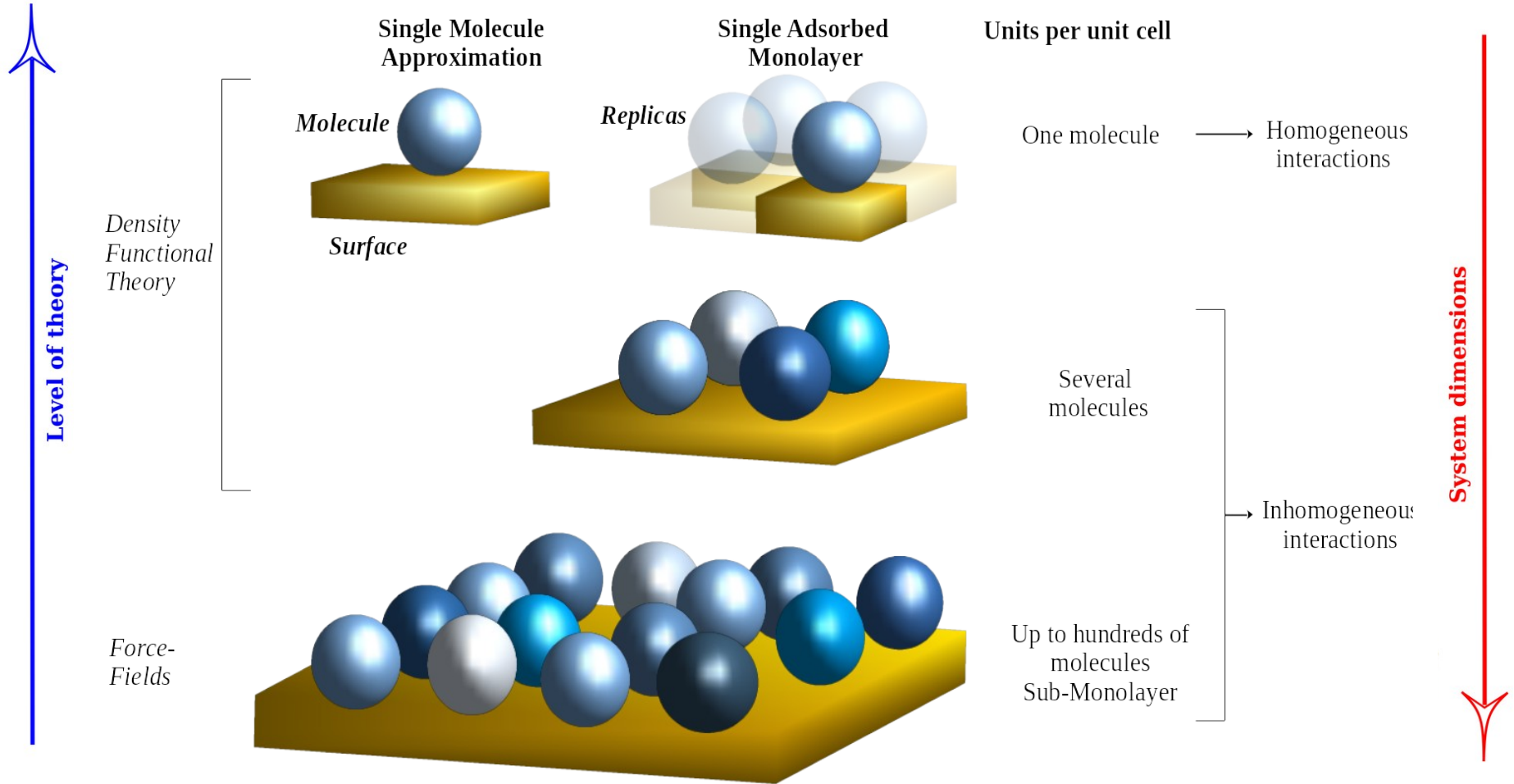
CONTRA

- Accuracy?
- Necessity to fit an *ad hoc* force field: parametrization and validation time demanding

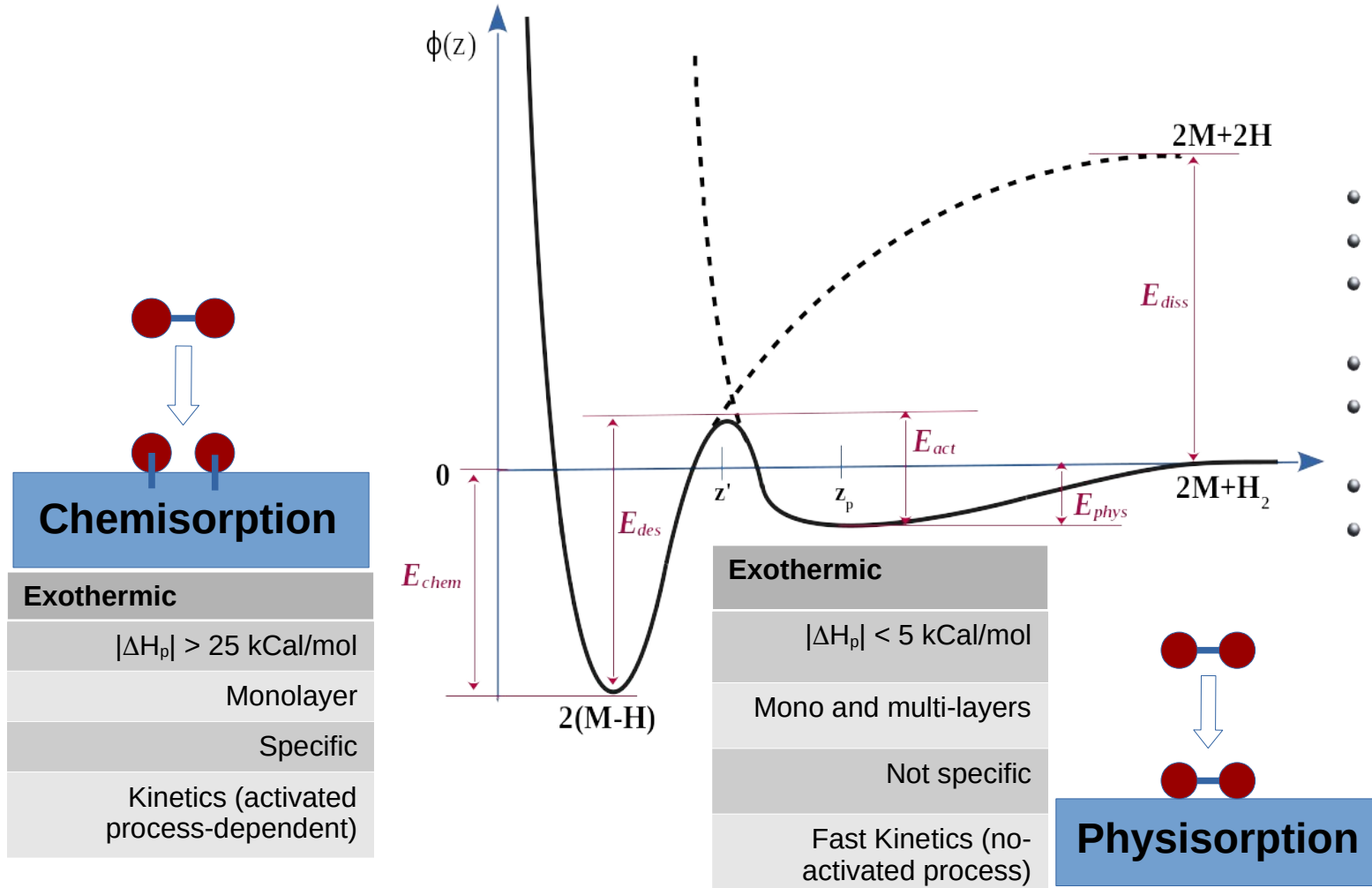


Fernandez-Garcia *et al.*, *Nanoscale*, 2018, 10, 4096

Modelling approximations



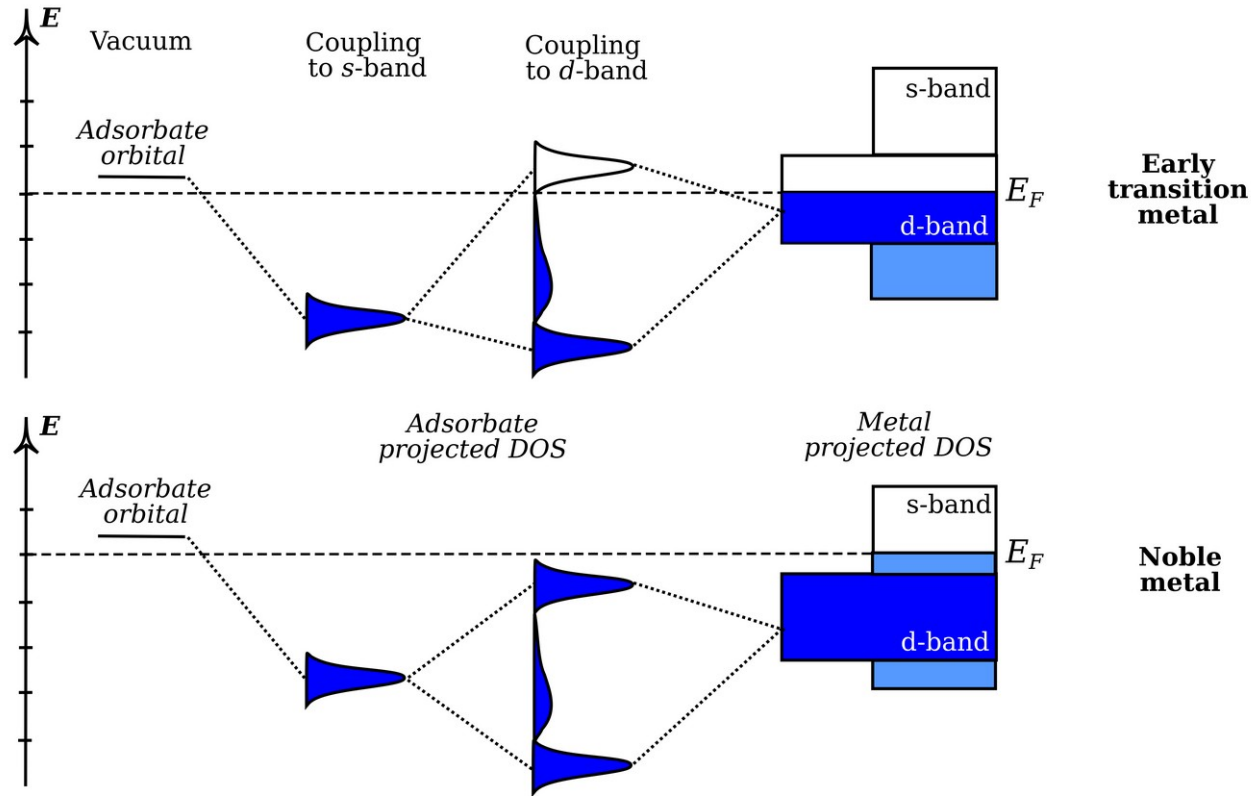
Nature of the Interaction



Interaction $H_2@Metal$

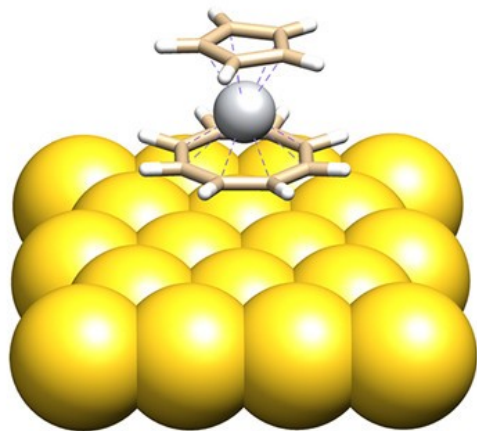
- $z_p \rightarrow$ physisorption distance
 - $z' \rightarrow H_2 \leftrightarrow 2H$
 - $E_{diss} \rightarrow$ dissociation energy in the gas phase
 - $E_{phys} \rightarrow$ physisorption energy
 - $E_{act} \rightarrow$ activation energy for chemisorption
 - $E_{chem} \rightarrow$ chemisorption energy
 - $E_{des} \rightarrow$ desorption energy
- $(E_{des} = E_{chem} + E_{act})$

Orbital interactions among adsorbate and surface bands

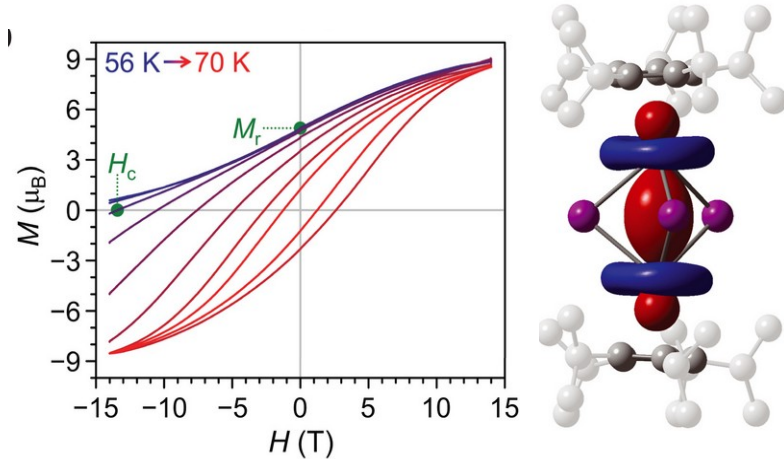


Imbalance of population among bonding and anti-bonding combinations leading to increase of electron density at the interface region.

IV Circle: $[\text{CpTi}(\text{cot})]@Au$, a case study

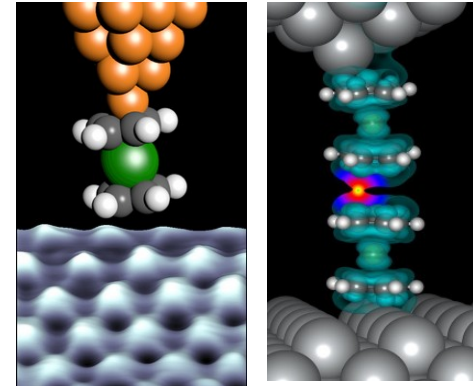


Metallocenes for Molecular Magnetism



Record blocking temperatures and coercive fields

C. Gould *et al.*, **Science**, 2022, 375, 198-202



Atomic spin sensing

B. Verlhac *et al.*, **Science**, 2019, 366, 623-627,
G. Czap *et al.*, **Science**, 2019, 364, 670-673.

Our Damned Molecule: [CpTi(cot)]

(η^8 -cyclooctatetraene)(η^5 -cyclopentadienyl)titanium
Organometallic mixed sandwich complex
 $3d^1$ $S=1/2$

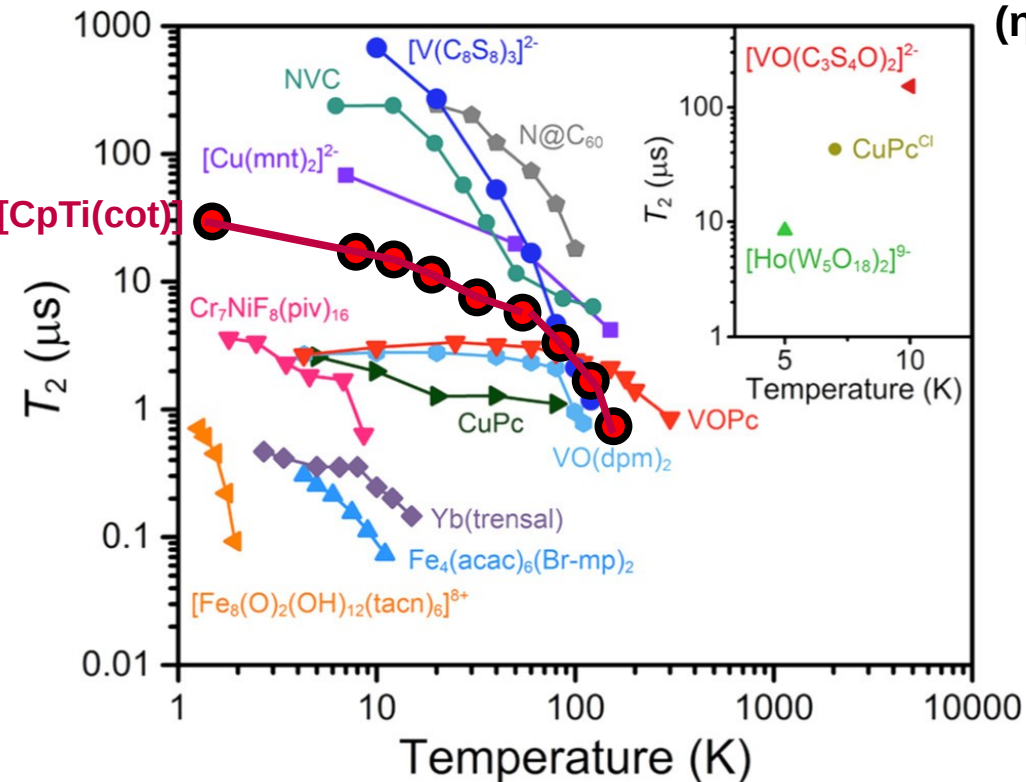
Formally Ti^{III}

Long Coherence times

Sublimable

Fragile molecule from the redox
point of view

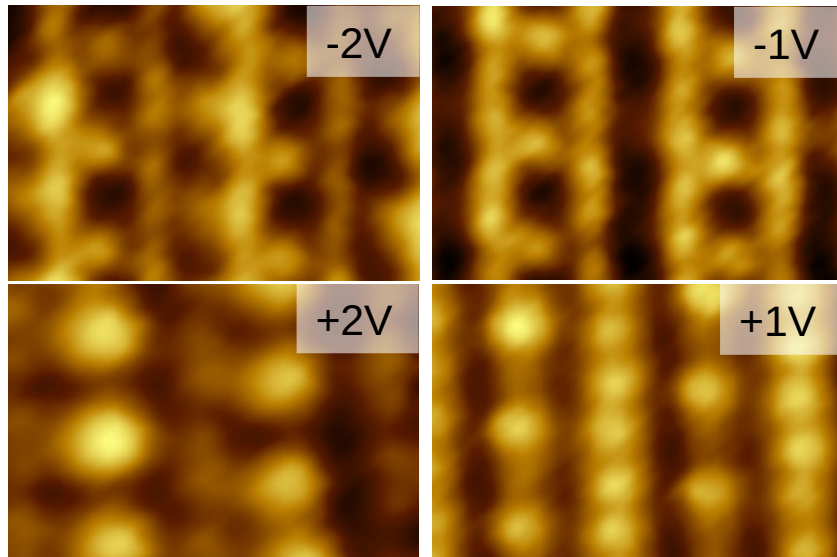
Difficult to manipulate



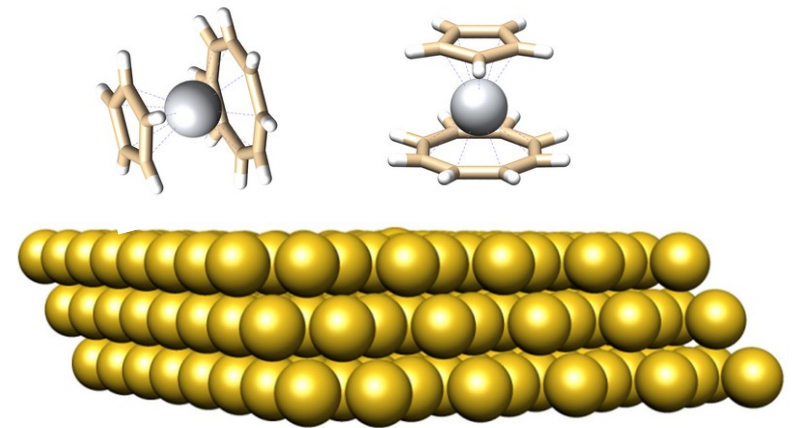
What is happening to [CpTi(cot)] upon grafting?

Scanning Tunneling Microscopy:

- Molecular pattern alternating bright and dark rows
- STM contrast changes with the bias voltage



I) Different adsorption conformations?



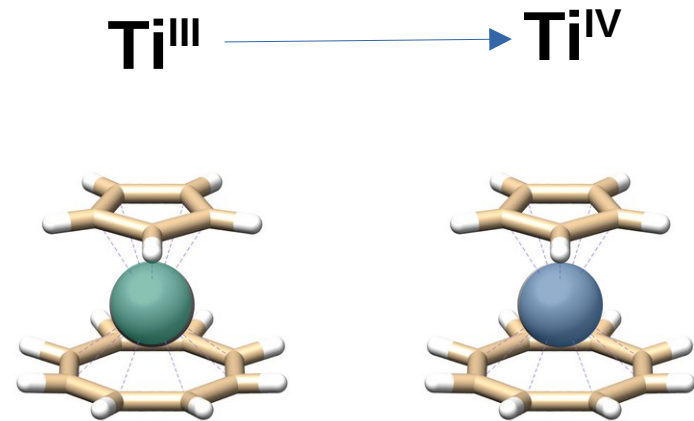
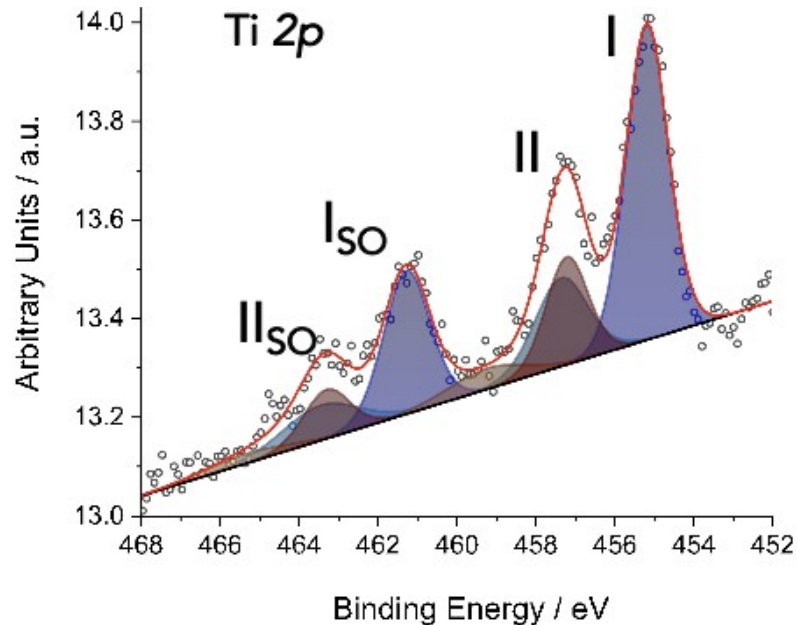
What is happening to [CpTi(cot)] upon grafting?

X-Ray Photoelectron Spectroscopy:

- Two pairs of peaks
- Peculiar intensity ratio



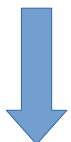
II) Redox Process?



STM Simulation of the isolated molecule

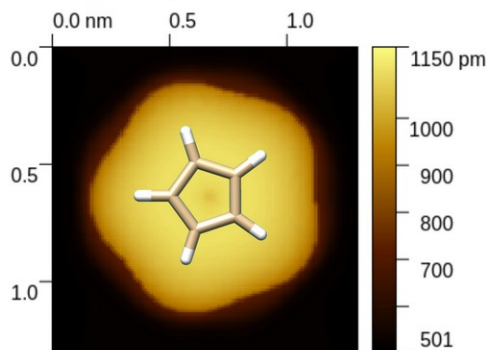
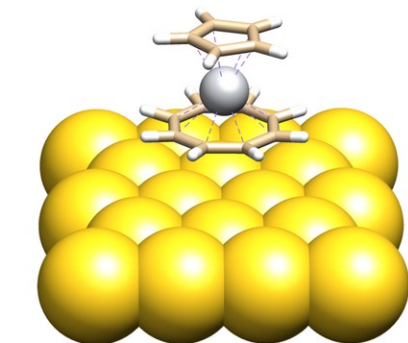
No difference upon varying the bias voltage in contrast with the experimental bias dependence

No significant charge transfer

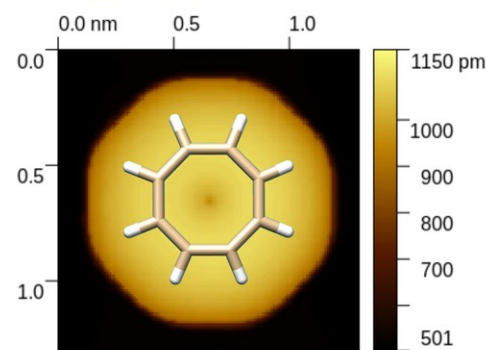
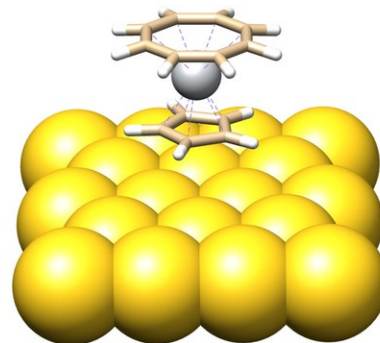


Necessity to
i) go beyond the isolated molecule
ii) simulate the packing on surface

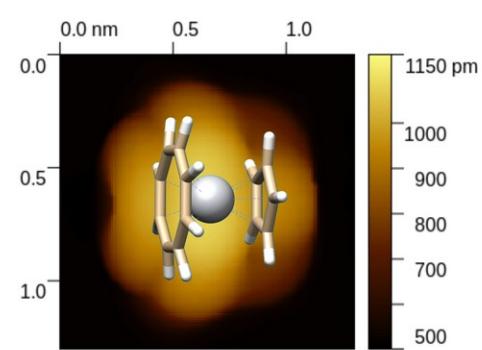
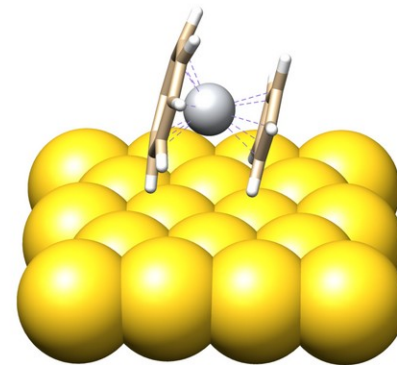
Standing_{cot}
-18.7 kcal/mol



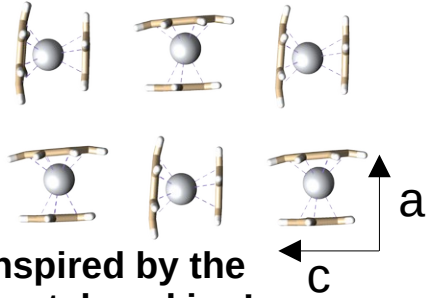
Standing_{Cp}
-12.8 kcal/mol



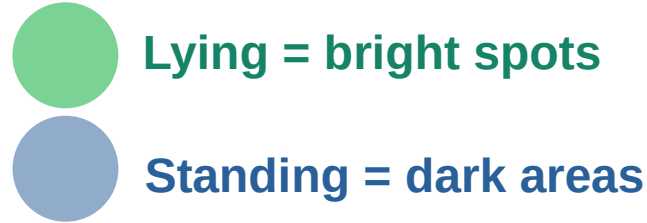
Lying
-13.2 kcal/mol



Beyond the Single Molecule: Simulation of the Adsorbed Monolayer



Inspired by the crystal packing!

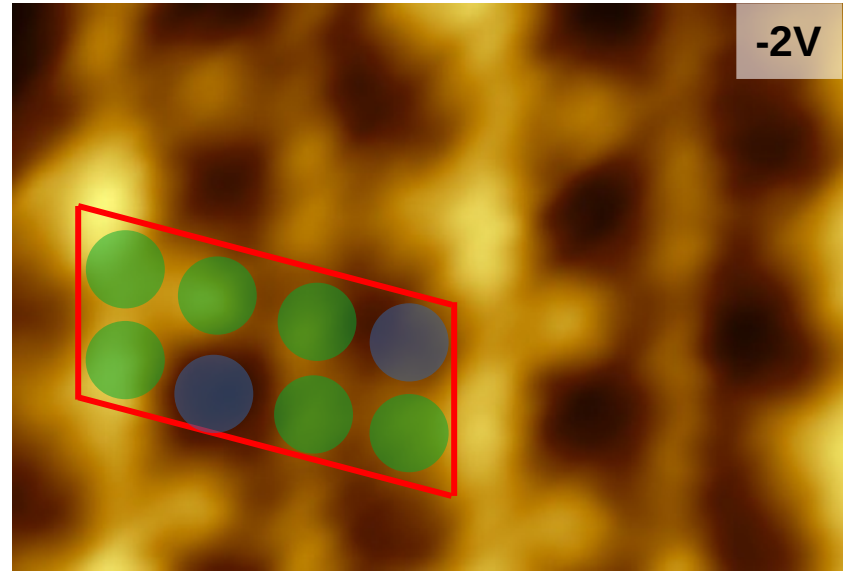
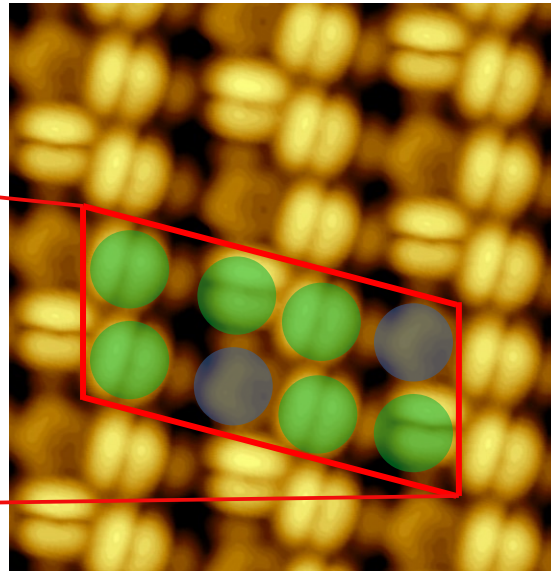
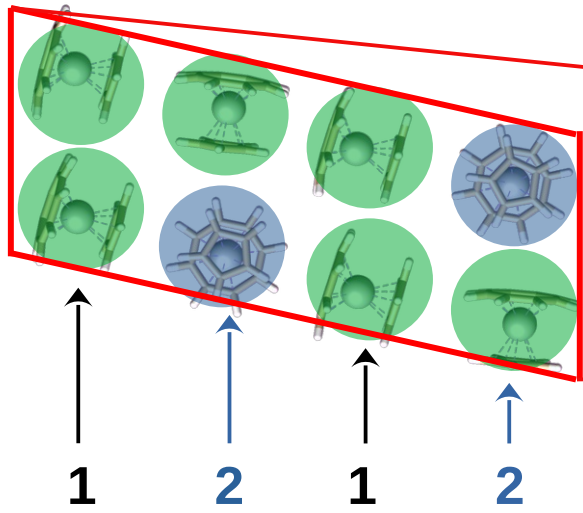


$a = 31.2 \text{ \AA}$

$b = 15.0 \text{ \AA}$

$\gamma = 76.1^\circ$

Negative bias
Filled states




CP2K

Periodic DFT+U / VDZP
 $U_{Ti} = 4 \text{ eV}$

Simulation of the adsorbed monolayer

Lying molecules in row **2B**
lose brightness

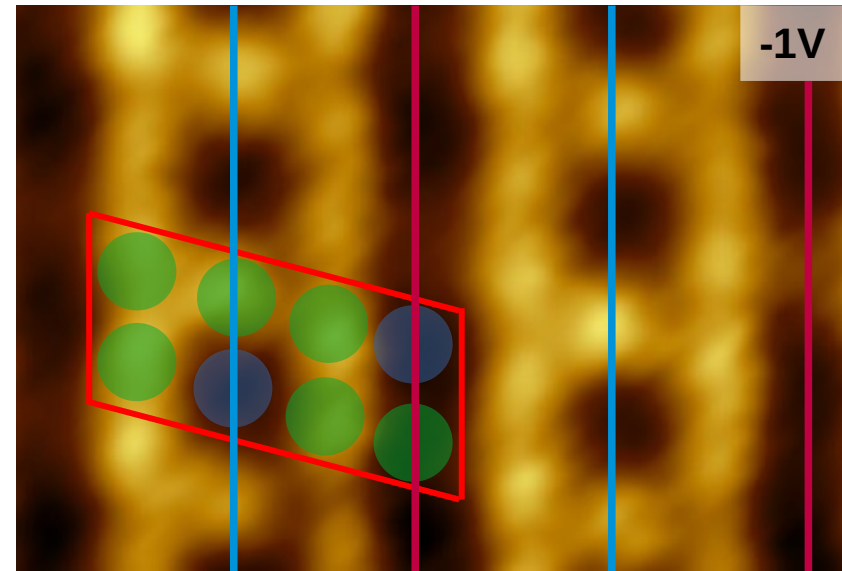
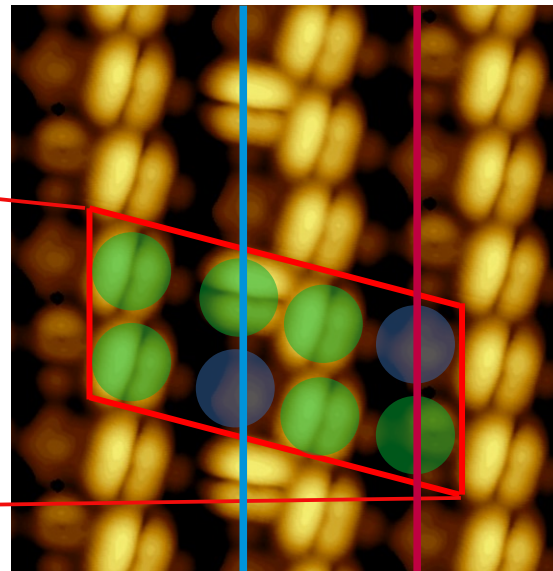
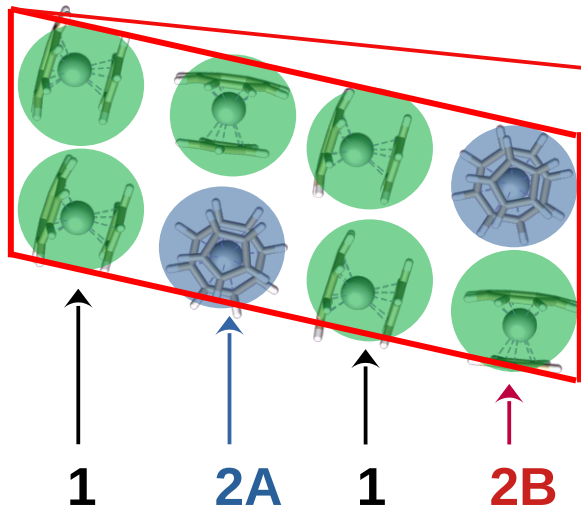
Completely dark **2B** row

 Lying = bright spots

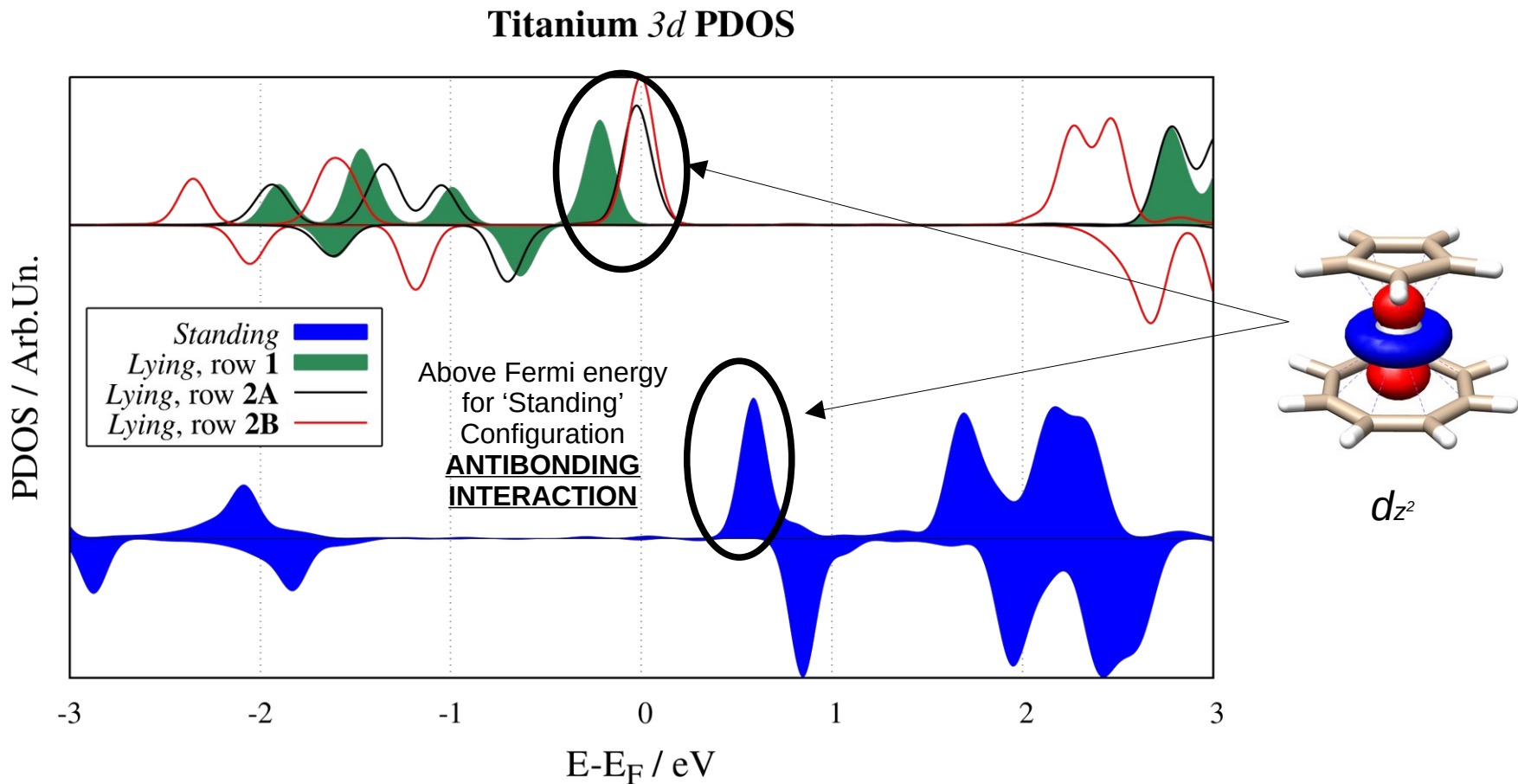
 Standing = dark areas

Negative bias
Filled states

Same composition:
different behaviour!



Orbital Picture: Antibonding Interaction

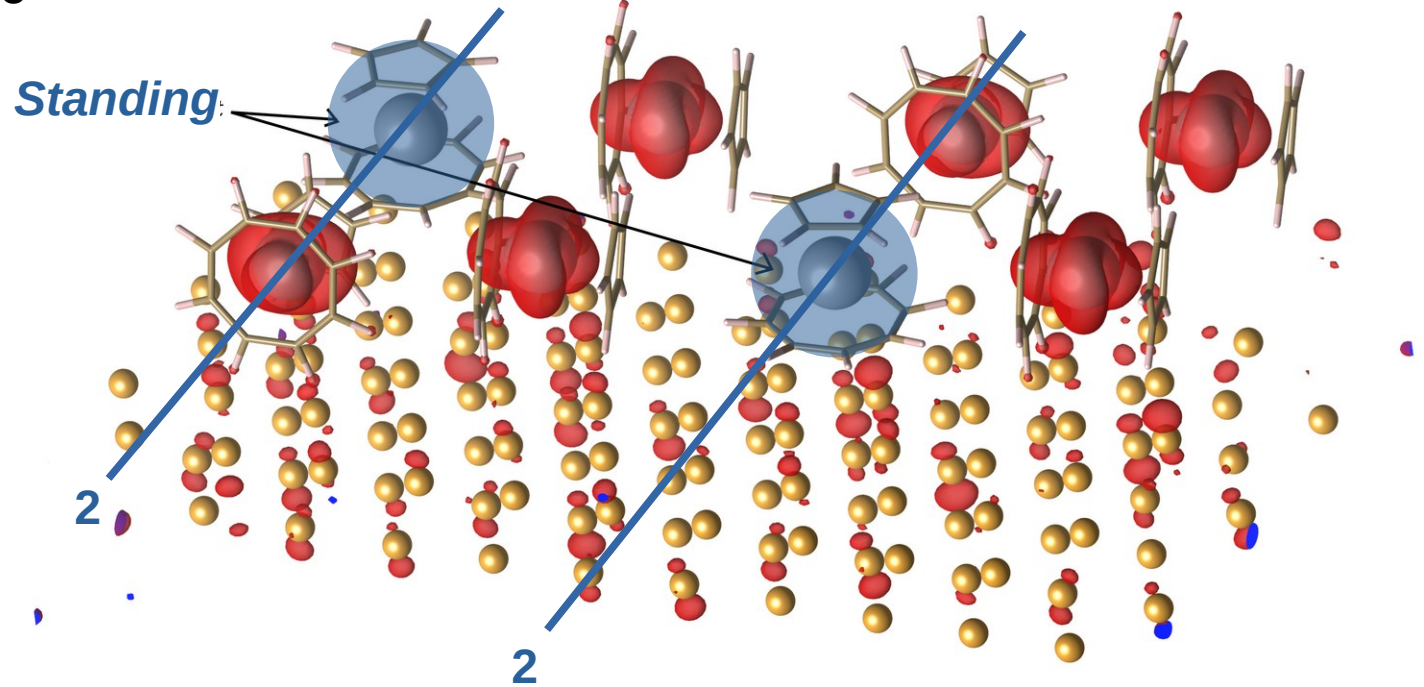


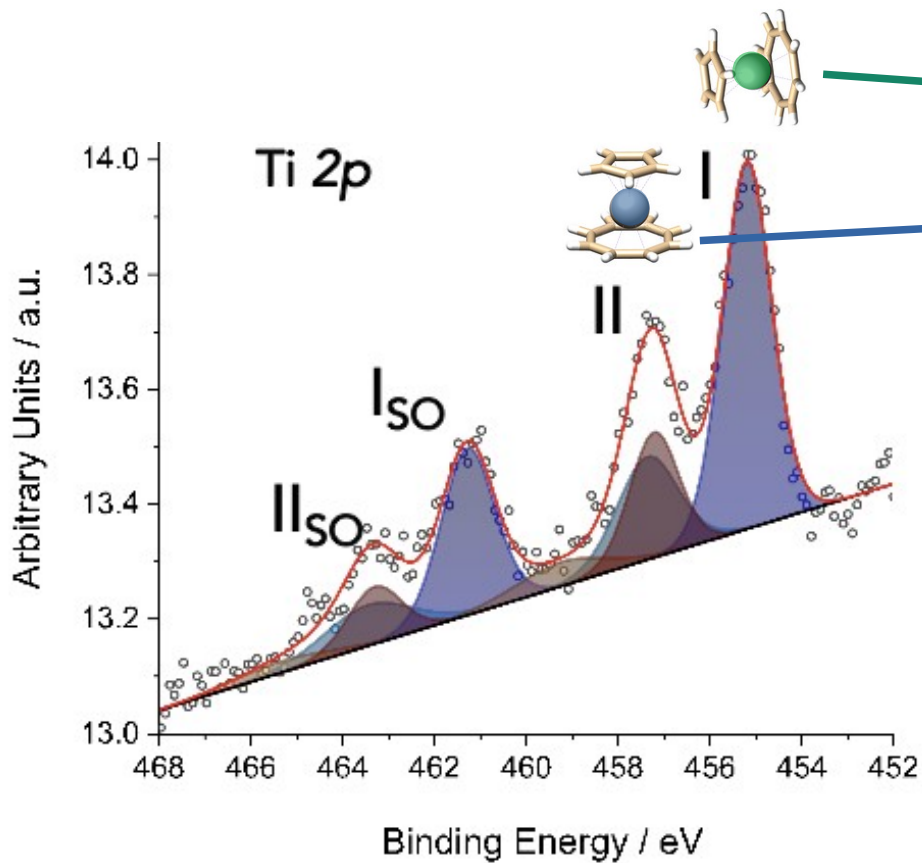
Spin density of the adsorbed monolayer

Standing molecules in row 2: 0.01 unpaired e^- on Ti

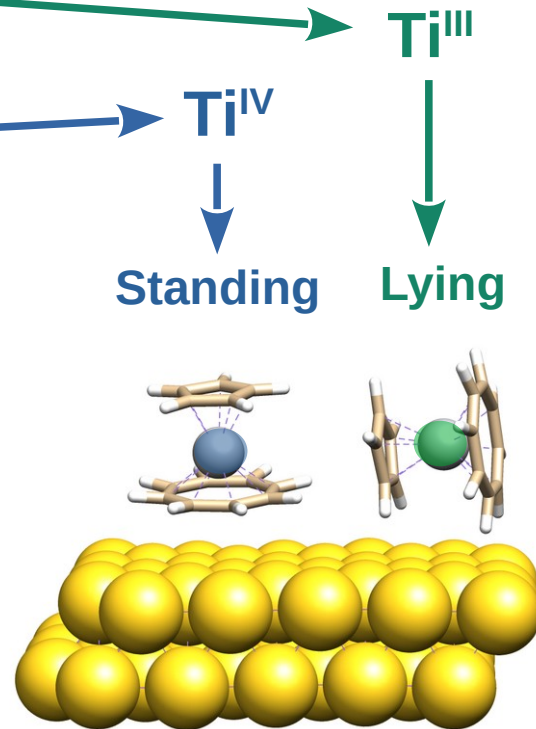
Selective transfer of electronic and spin density from the *standing* molecules to the surface

[CpTi(cot)]@Au(111)



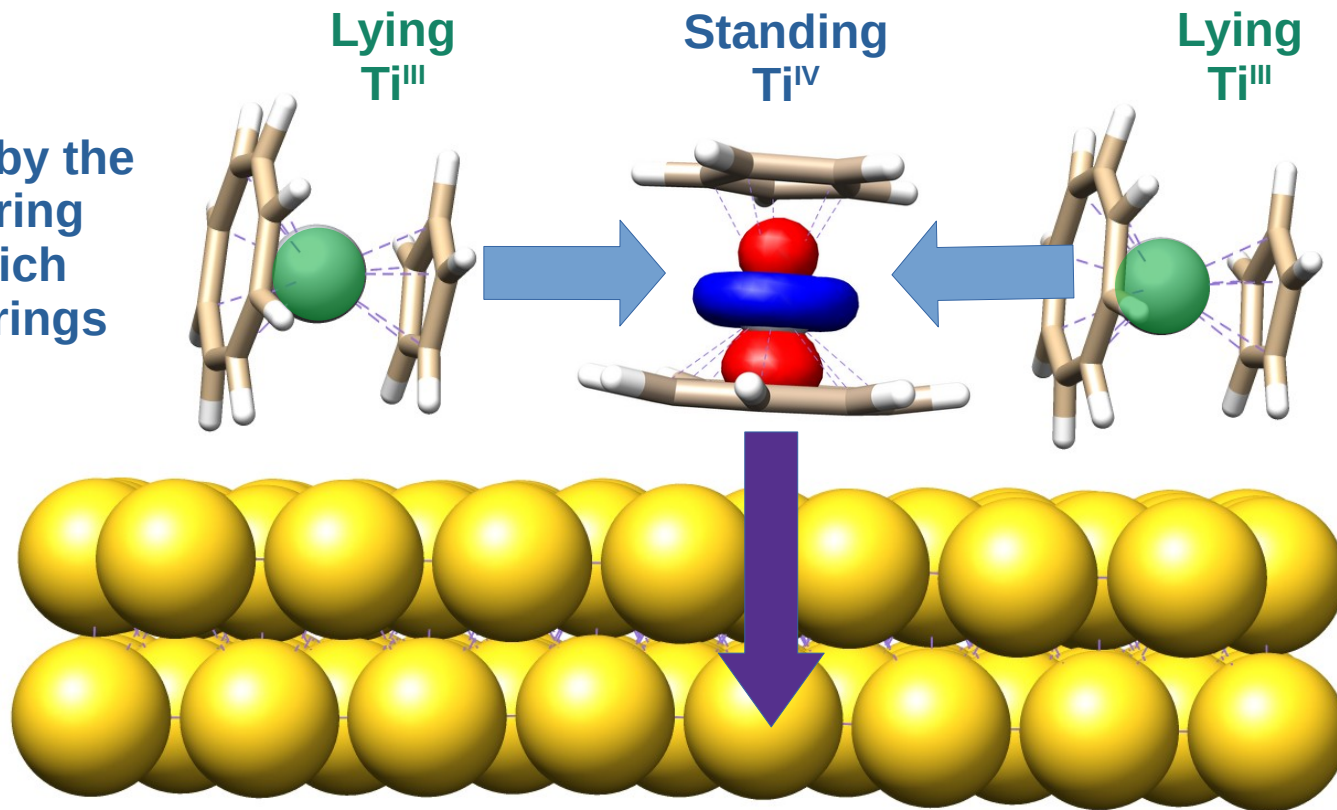


Ab initio calculations:



Why this oxidation?

Electron donation by the neighbouring electron-rich aromatic rings



Electron withdrawal allowed by the surface

Ti^{IV} exists only on surface!

Oxidation state allowed by:

- Surface
- Packing
- Unpaired electron in d_{z^2}

The other Dantes and Virgils



Prof. Roberta Sessoli



Prof. Federico Totti



Dr. Giulia Serrano



Prof. Matteo Mannini



Dr. Andrea Sorrentino



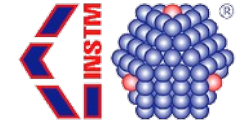
Prof. Jaísa Soares



Luana Camargo



Dr. Lorenzo Poggini



Dr. Alessandro Motta

When You Are Lost in the Experimental Hell...



Search for a Theoretician!

Paradise can be closer than you think!

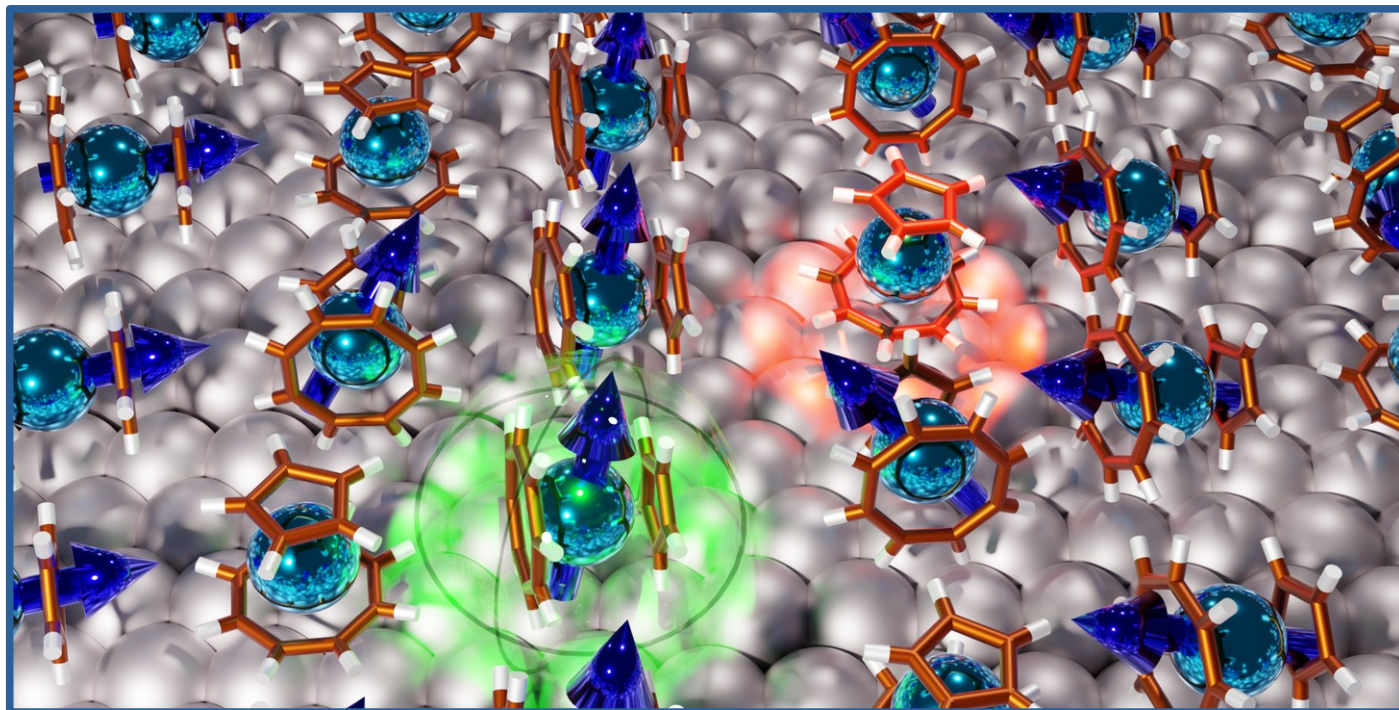


Many thanks for your attention!

*Here force failed my high fantasy; but my
desire and will were moved already—like
a wheel revolving uniformly—by
the Love that moves the sun and the other
stars.*

Divina Commedia, Paradiso, Canto XXXIII

Acknowledgments



Acknowledgments

