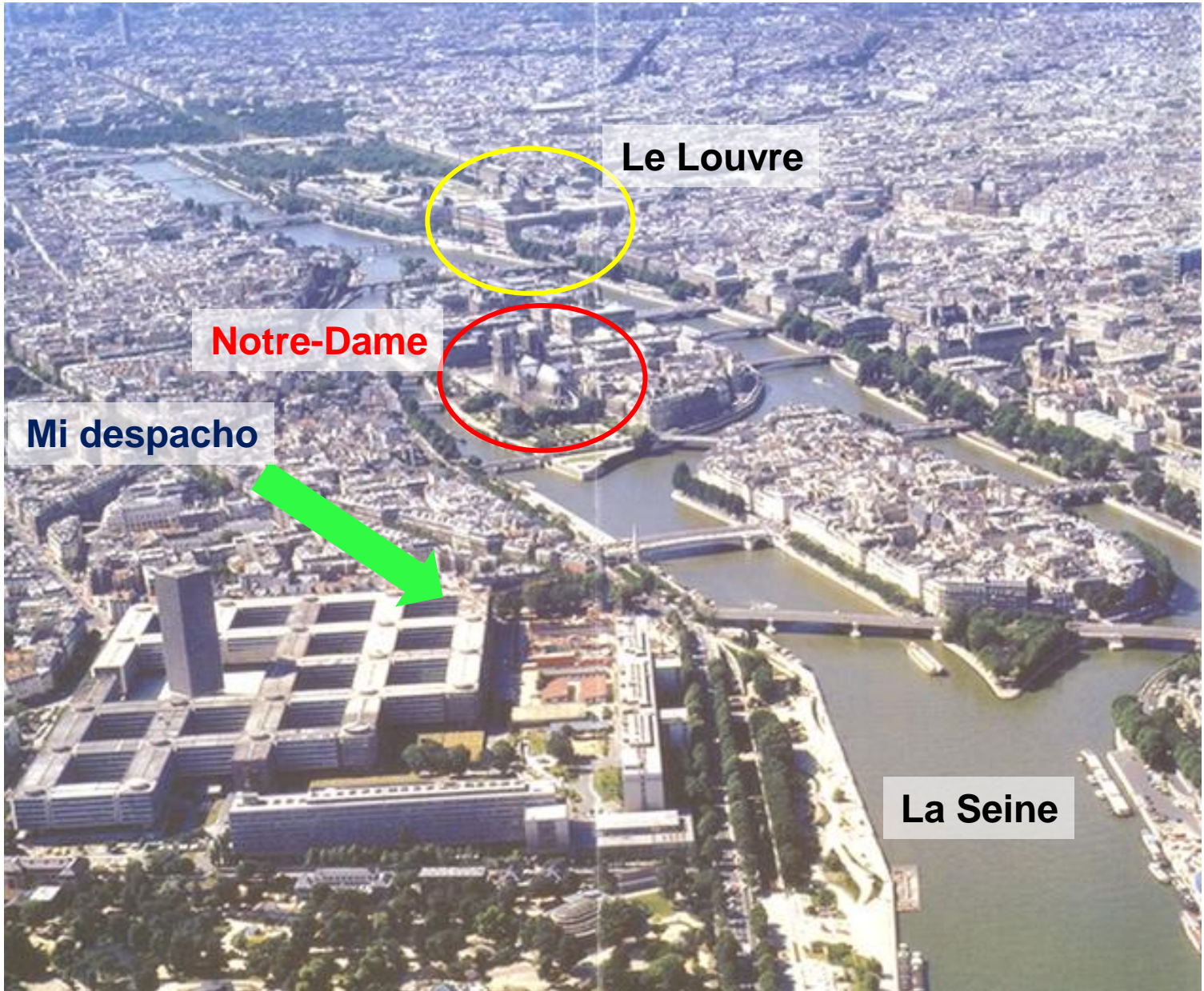


# Modelling surfaces: models and applications

*CTTC School  
Current Topics in  
Theoretical Chemistry*

***M. Calatayud***  
**[calatayu@lct.jussieu.fr](mailto:calatayu@lct.jussieu.fr)**  
Laboratoire de Chimie Théorique  
Sorbonne Université Paris

Quito 30<sup>th</sup> June 2019



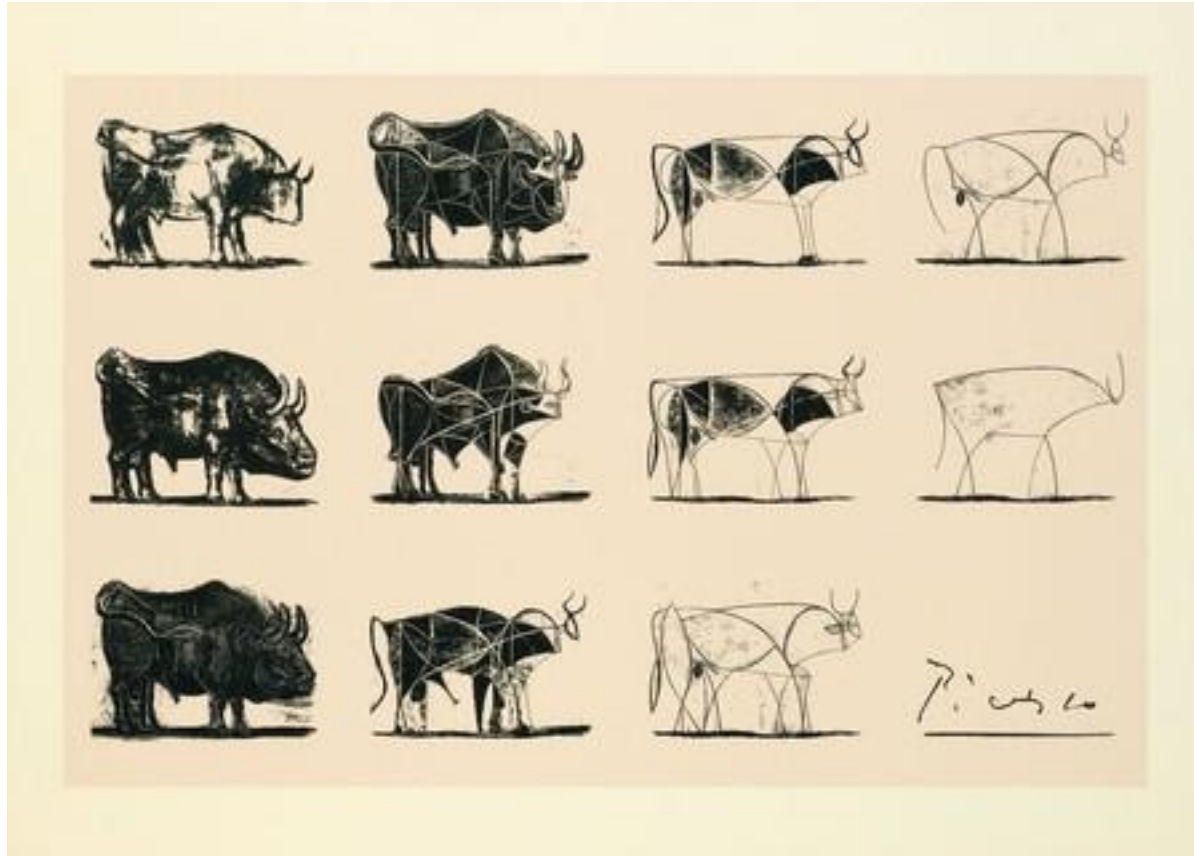
Le Louvre

Notre-Dame

Mi despacho

La Seine

# What is modelling?

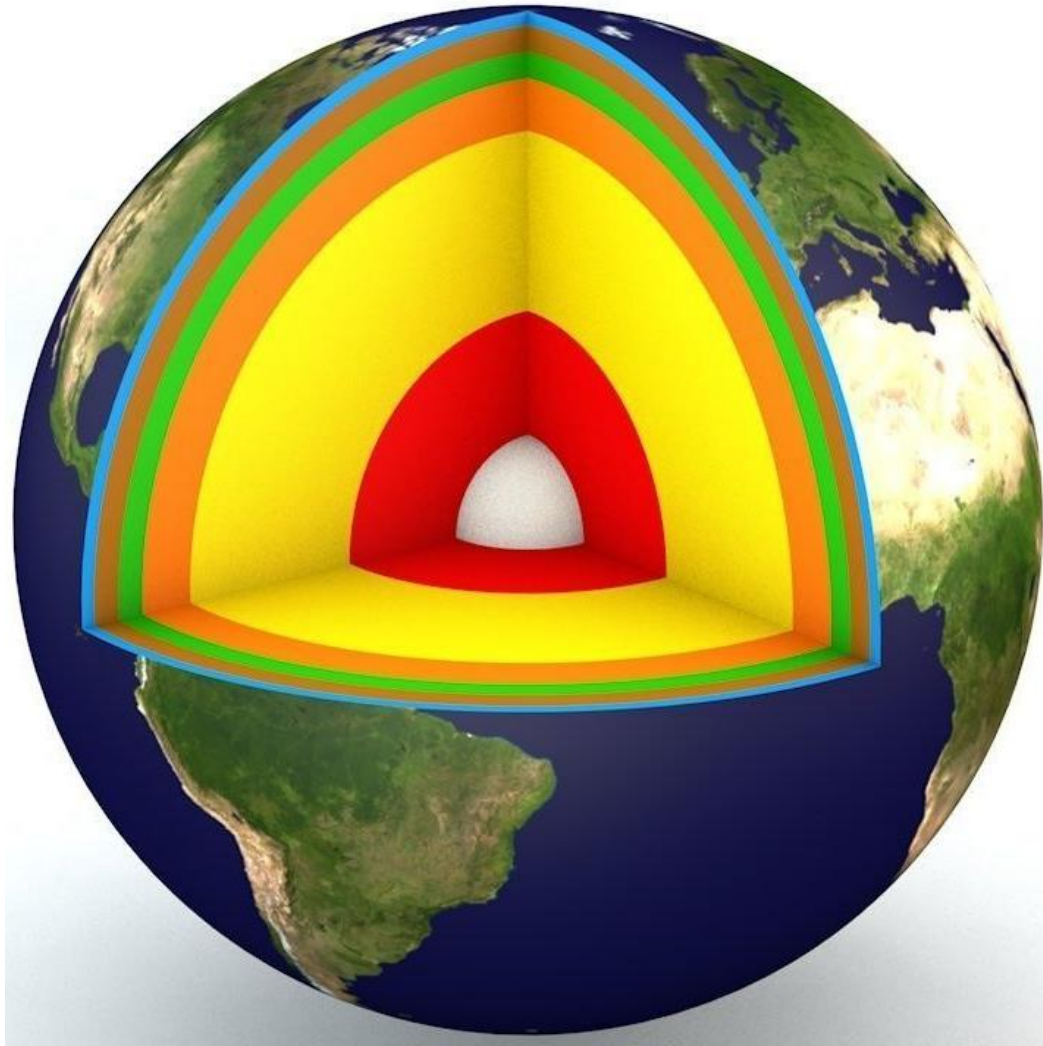


Model: ideal or simplified system

Helps understanding, predicting rather than describing in detail



# What are surfaces?



Regions where the solid ends -> interface with vacuum/gaz/liquid/solid  
Anisotropy, low coordination -> increased reactivity  
It concerns a small number of atoms compared to bulk

## Modelling solid state

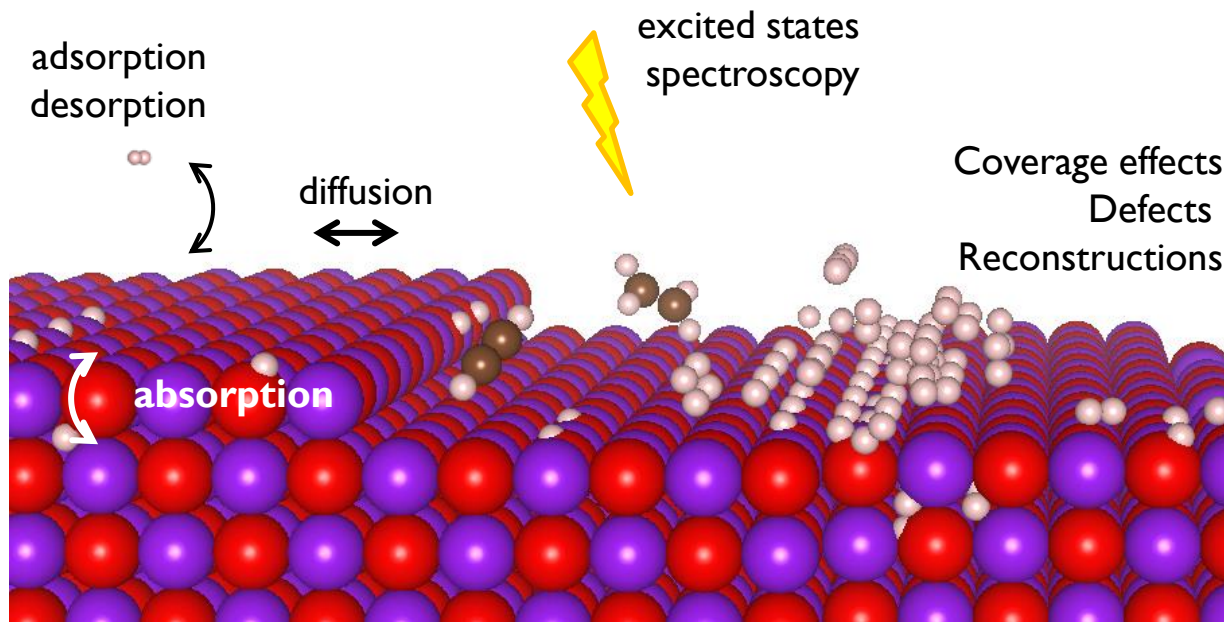
- Methods for solids [Juan Peralta](#)
- Surfaces: models and applications [M. Calatayud](#)
  - Introduction
  - Models
  - Properties
  - Applications
  - Software

### Goal

Get familiar with surface modelling  
[structure - properties](#)

# **I: Introduction**

# Modelling solid surfaces



What do we want to study?

How accurate?



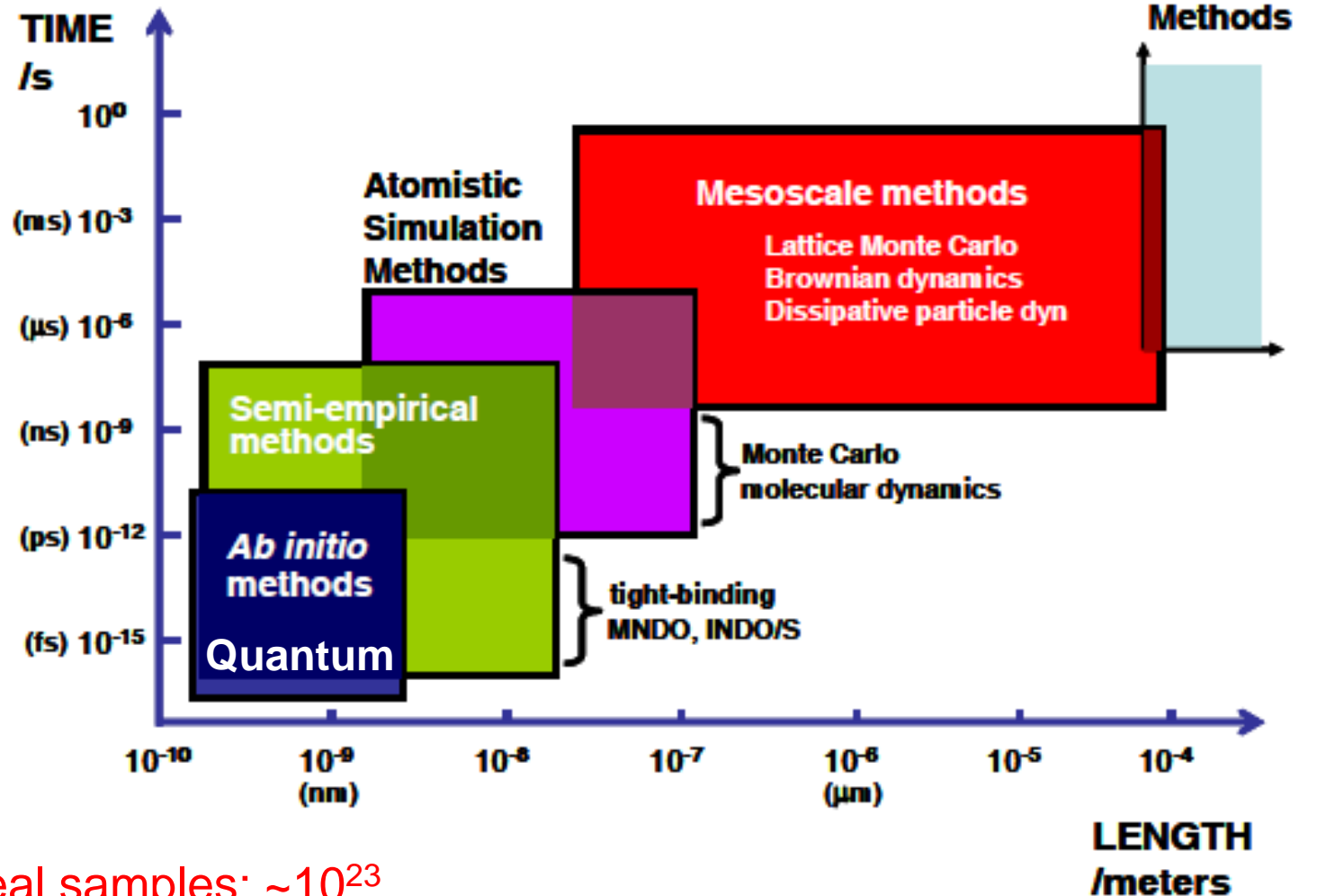
Choice of model  
& method

# Methods, scales and phenomena

Electrons: spectroscopy,  
chemical bond, reactivity  
1-500 atoms

Atoms: growth, segregation  
Growth, segregation  
1000-10000 atoms/particles

Protein adsorption,  
nanoparticles agregation,  
phase transition >20 000  
particles



Real samples:  $\sim 10^{23}$



# Each system its approach

The exact “solution” does not exist! We need:  
**approximations that are reasonable**  
**know the conditions of applicability**

## Physico-chemical laws - Methodology

Simplified forms = easier or faster to solve

ex. Acidic pH neglects  $[\text{OH}^-]$   $\text{pH}_{\text{HCl}} = -\log ([\text{HCl}]/c^\circ)$   
Perfect gaz law  $pV=nRT$  for non-interacting particles  
Born-Oppenheimer approximation nuclei vs e-

## Structural model

Reduce complexity to focus on a particular aspect

ex. size: Use an aminoacid to model a protein  
composition: neglect impurities to model water  
geometry: consider a solid periodic

# Each system its approach



# First step: defining the questions

## What is the phenomena I want to study?

Define the system, property...

verify experimental distances, predict reactivity...

## What level of accuracy I need?

Very accurate for comparison with exp

Accurate to study trends

Low accuracy to have a guess starting structure

## What are my ressources and my constraints?

Literature: structure, composition, previous data

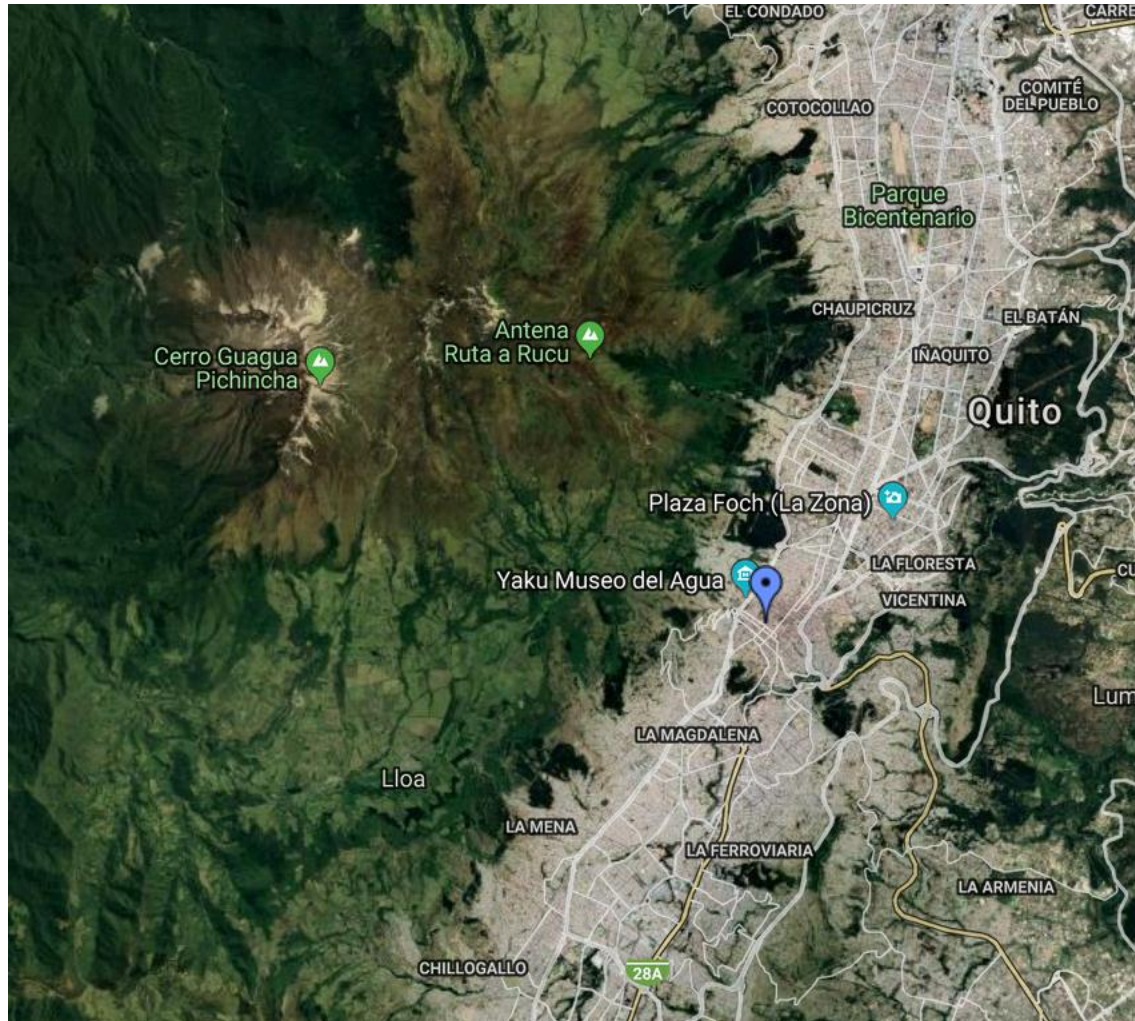
Technical: computers, software, skills

Others: deadlines, money...

**Do it BEFORE you start!!**

# **Structural models for surfaces**

# A real surface



Is not homogeneous

Is not perfect

in composition or structure

Determine the property and the accuracy

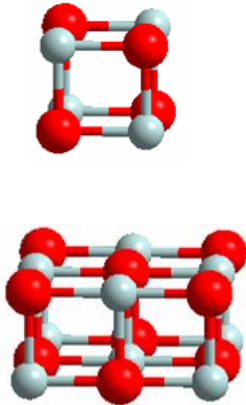


Build the model

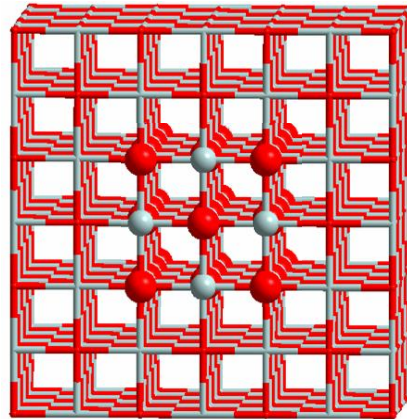


# Models

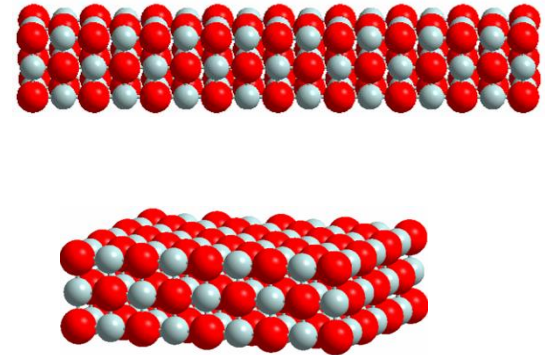
cluster



embedded cluster



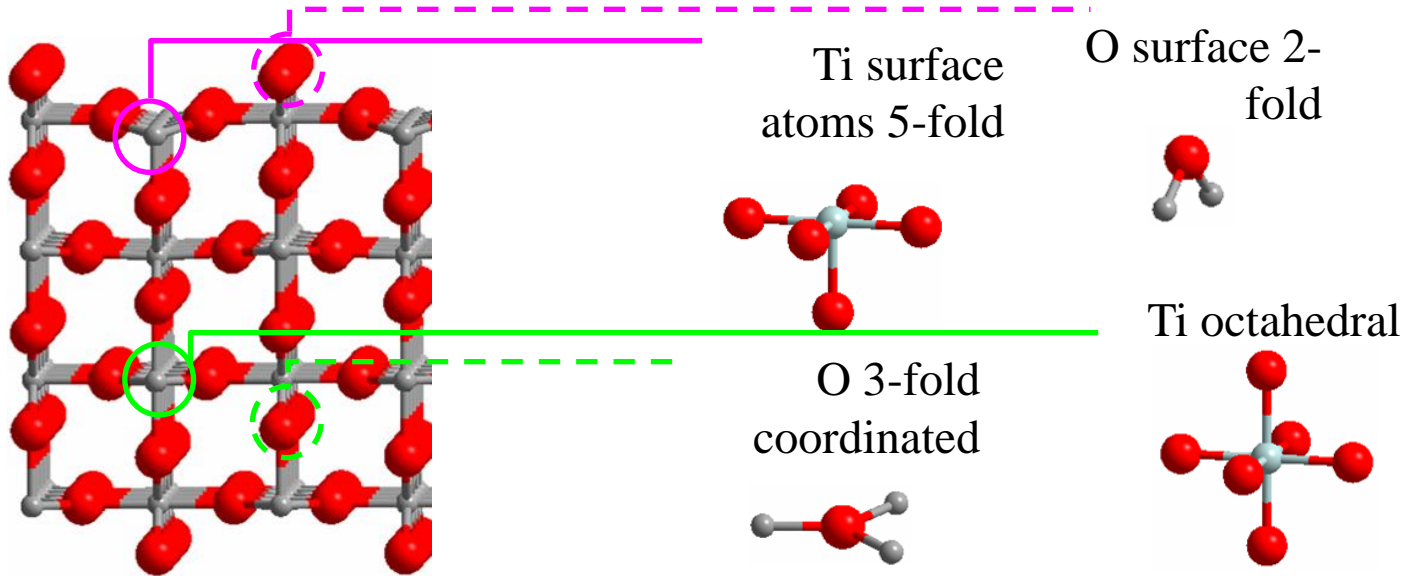
periodic



<b>size</b>	small	medium	infinite/large
<b>methods</b>	sophisticated CI, CCSD(T) MC atomic orbitals	mixed QM/MM ONIOM AO+point charges	less accurate DFT, MM, semiemp. Monte Carlo plane waves/AO
<b>Problems</b>	edge effect	boundary region	concentration ↑
<b>Applications</b>	local phenomena fine structure	semi-local adsorption, enzymes, etc.	periodic crystals, surfaces,...

The model must be carefully chosen depending on the properties to be studied!

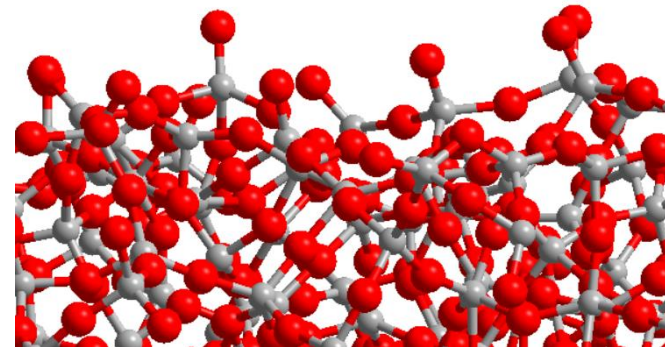
# Characterizing a surface - structure



Orientation along direction  $[hkl]$   
plane  $(hkl)$  for crystals

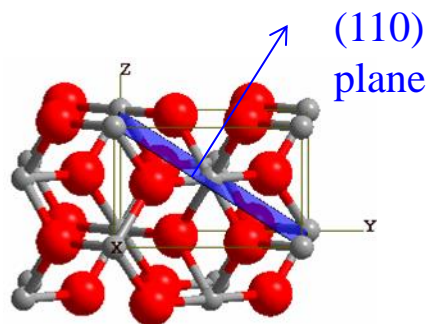
Termination - where to cut  
Coordination of surface atoms, polarity...  
Thickness  
Composition  
stoichiometry, defects, capping...

Also applies for amorphous systems

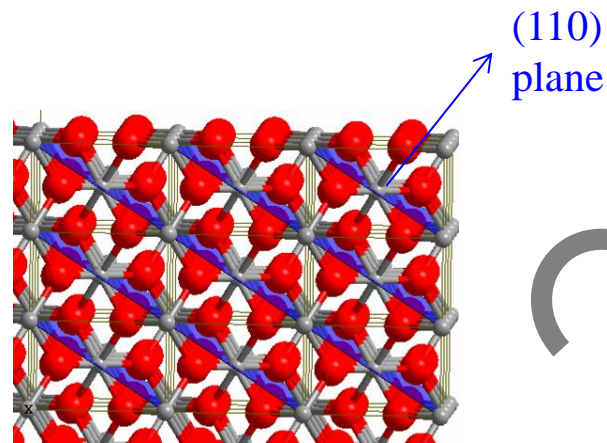


# Creating a surface *in silico*

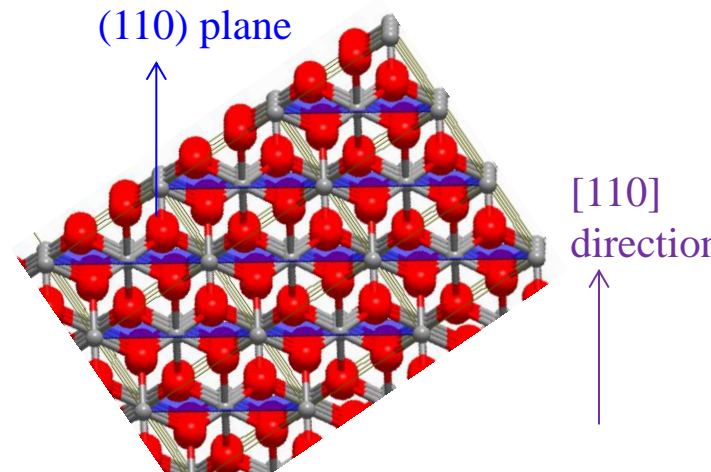
Ex. Rutile  $\text{MO}_2$



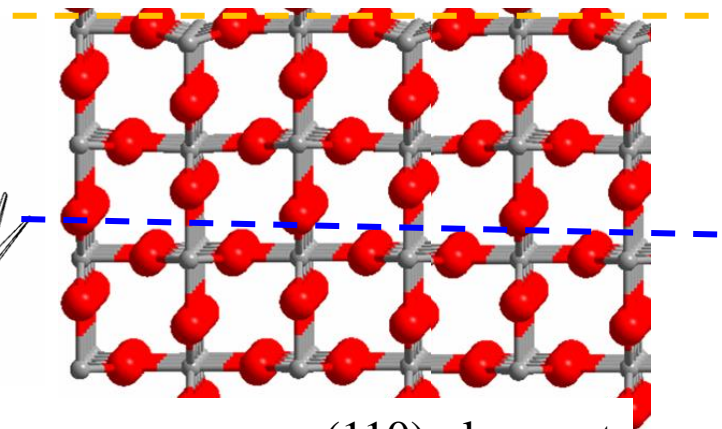
Bulk unit cell



(110) planes



{110} plane family oriented



Termination 1

Termination 2

(110) plane cut

cut the Ti-O bonds

The smaller the number of bonds cut, the more stable the surface  
The atoms at the surface are less coordinated (less stable) than in the bulk

# Properties

# Properties

- Energy

- Optimization
- Surface energy



relaxation-reconstruction  
shape prediction, adsorption mode ...

- Vibrational frequencies

- Electronic structure

- Band structure
- DOS, COOP
- STM



Conductivity, band gap  
Molecular orbital analysis  
bond characterization...

- Catalysis and chemical reactivity

- Adsorption
- Energetic barriers



Adsorption mechanism  
Surface reactivity, diffusion  
Heterogeneous catalysis, tribology



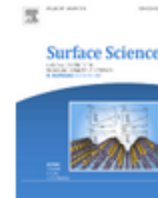
# Exemple 1: studying adsorption

- Building a model for the surface  
cluster vs periodic
- Determining the adsorption mode  
based on energy, method dependent, comparison with experiment
- Explaining the interaction  
analysis of the electronic structure







Surface Science

Volume 530, Issues 1–2, 20 April 2003, Pages 71–87



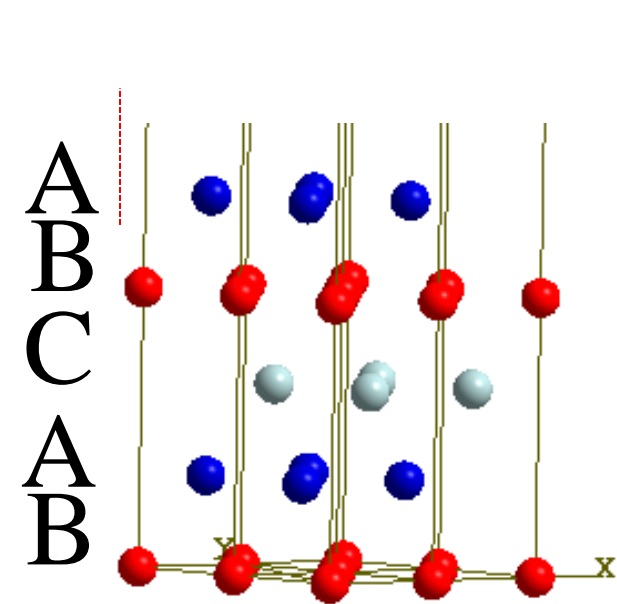
---

## Site preference of CO chemisorbed on Pt(1 1 1) from density functional calculations

Alfred Gil <sup>a</sup>, Anna Clotet <sup>a</sup>, Josep M. Ricart <sup>a</sup>  , Georg Kresse <sup>b</sup>, Maite Garcí&#x0301;a-Hernández <sup>c</sup>, Notker Rösch <sup>c</sup>, Philippe Sautet <sup>d, e</sup>  

[https://doi.org/10.1016/S0039-6028\(03\)00307-8](https://doi.org/10.1016/S0039-6028(03)00307-8)

# The adsorption sites in fcc metals

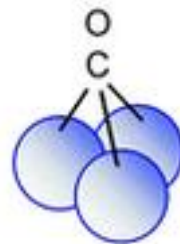
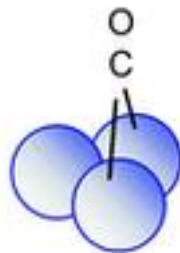
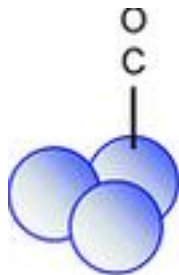
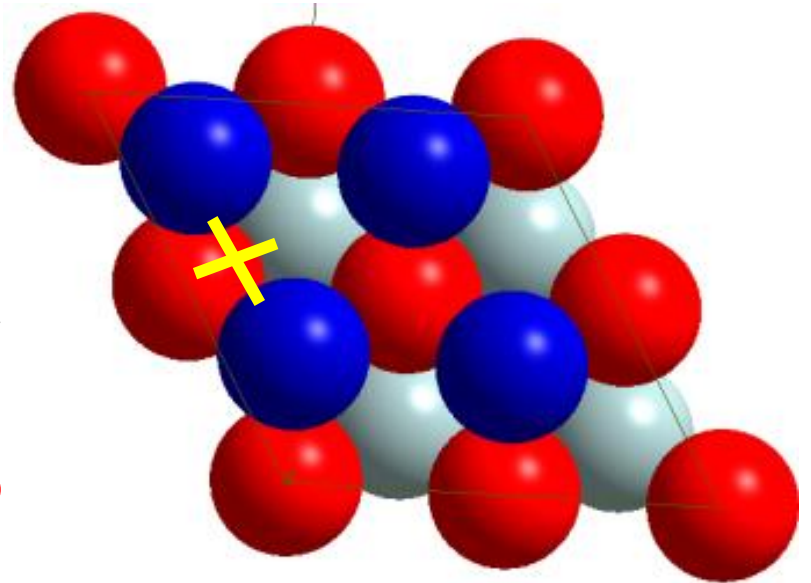


Top

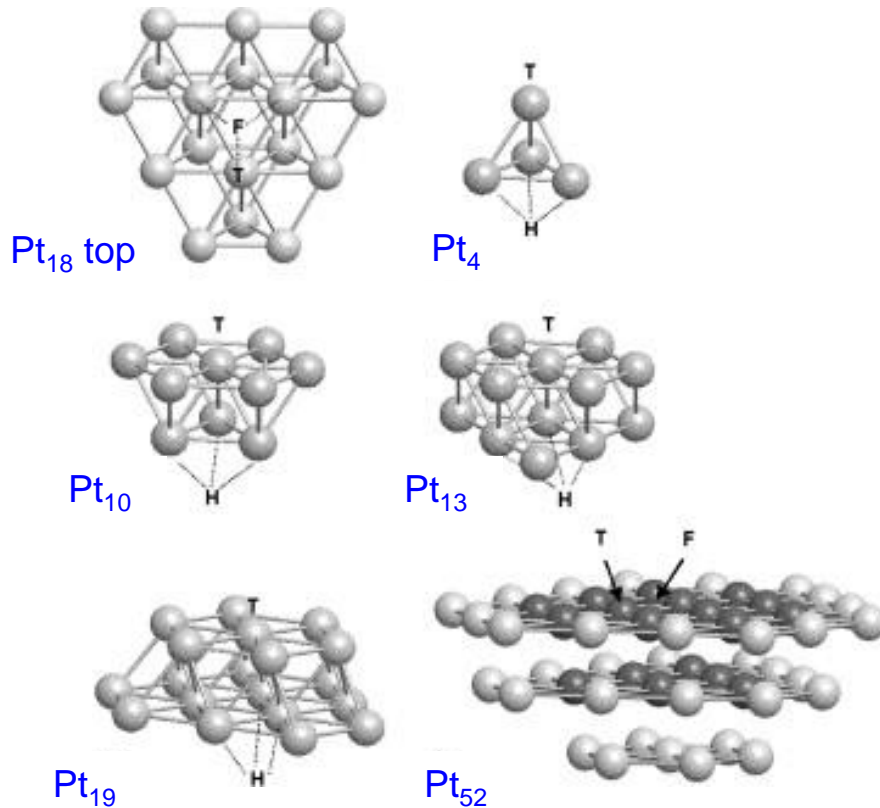
Bridge

Hollow fcc

Hollow hcp

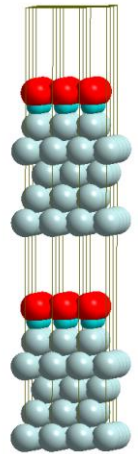
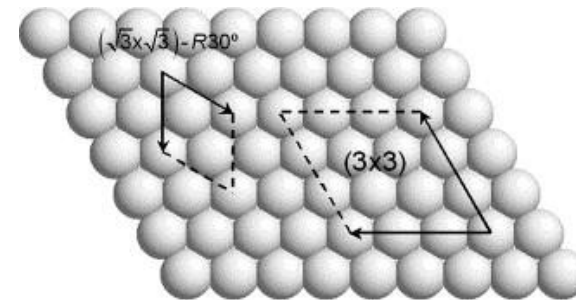


## Cluster models



- small clusters do not correctly describe the substrate environment → **not adequate for adsorption energies**
- larger clusters results  $\approx$  periodic

## Periodic models



both types of model favour CO adsorption at the hollow site instead of on-top → **disagreement with experiment**

**Methods make the difference**  
hybrid functionals including a part of the exact exchange decrease the energy difference between the two positions, suggesting a stabilization of the on top site relative to the threefold hollow site in the limit of extended models

**Modelling allows electronic structure description**

# Bond analysis

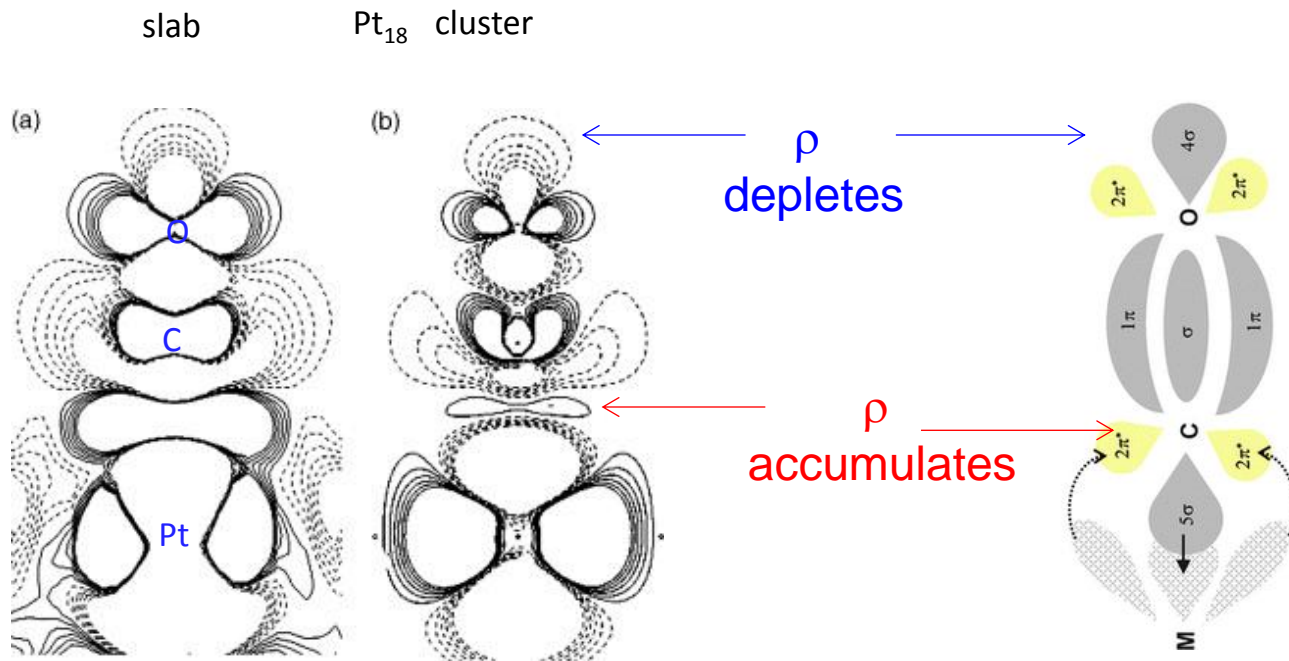


Fig. 3. Electron density difference maps between CO chemisorbed on top at Pt(1 1 1) and the separated fragments computed with the PW91 functional, for (a) plane wave basis set (four layers slab) and (b) localized basis set (Pt<sub>18</sub> cluster model). Solid contours represent zones with accumulated electron density, and dashed contours are associated with zones of depleted electron density.



## Example 2: surface energy

- Determining surface energy  
based on energy
- Relaxation, reconstruction  
based on energy
- Crystal shape  
based on surface energy

# Calculation of surface energy

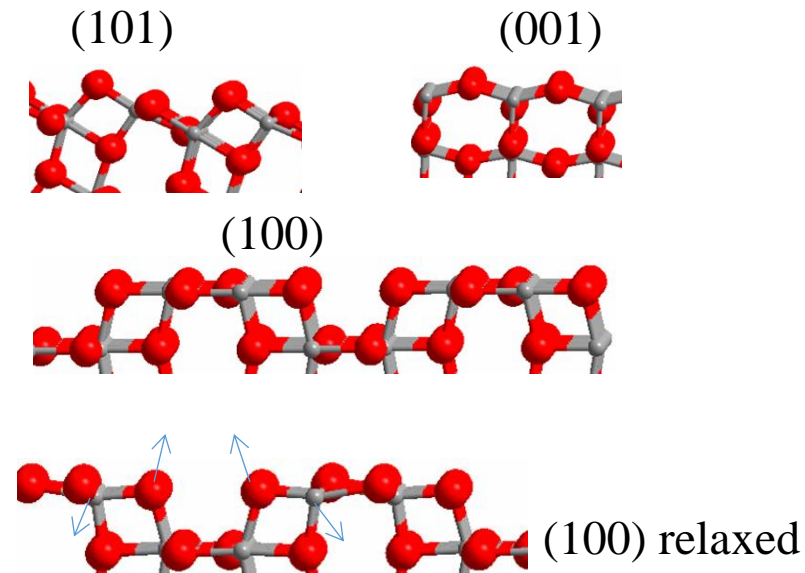
The surface energy can be calculated from ab initio results

$$E_{\text{surf}} = \frac{E_{\text{slab}} - E_{\text{bulk}}}{2A} \quad \text{units: J m}^{-2}$$

The most exposed planes will be the most stable ones  
→ those of lower surface energy

## 1) Comparison of different surfaces

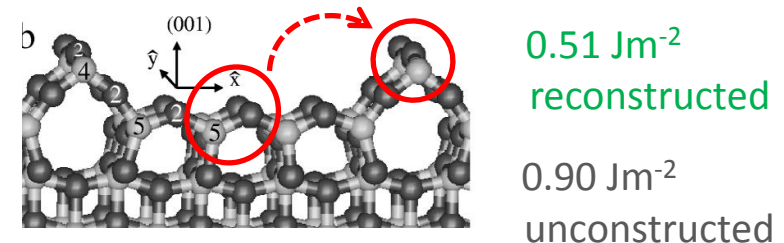
TiO <sub>2</sub> phase	hkl	E <sub>surf</sub> unrelaxed Jm <sup>-2</sup>	E <sub>surf</sub> <b>relaxed</b> Jm <sup>-2</sup>
Anatase	(101)	1.127	0.414
Anatase	(001)	1.011	0.863
Anatase	(100)	1.330	0.463



## 2) Relaxation small rearrangement to decrease energy

## 3) Reconstruction

important rearrangement to decrease energy  
bond break-formation



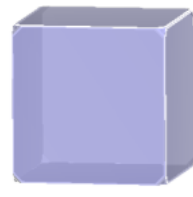
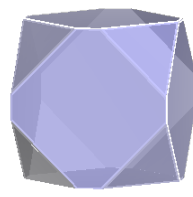
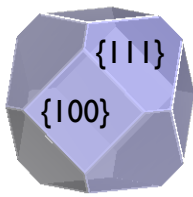
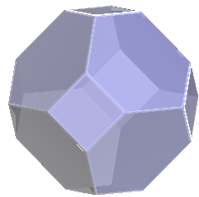
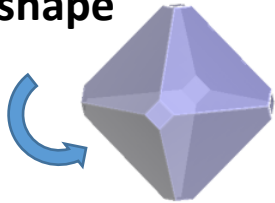
# Crystal shape: a surface property

**Wulff construction:** the surface area is inversely proportional to the surface energy  
The lower energy, the higher area exposed

Predominance  
(111)

fcc metals

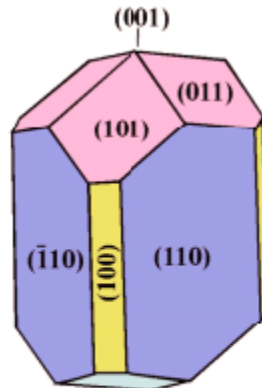
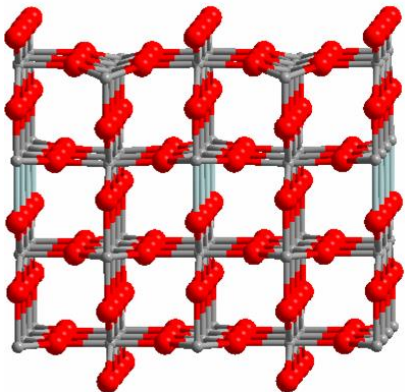
Octahedral shape



Predominance (100)

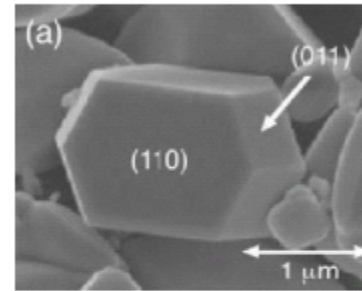
Cubic shape

Rutile  $\text{MO}_2$



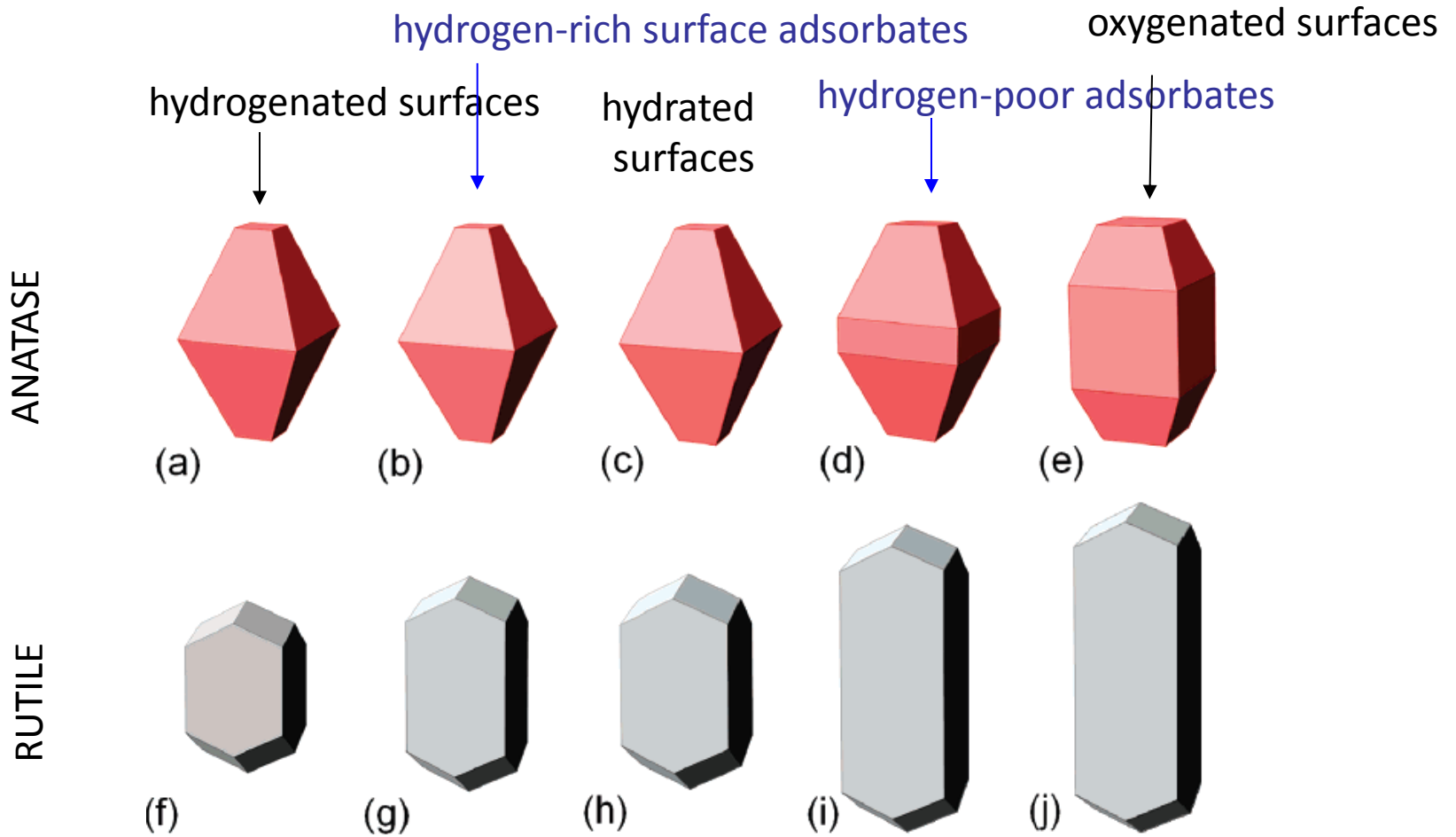
Ramamoorthy and Vanderbilt  
Phys. Rev. B 49, 16721 (1994)

$\text{TiO}_2$  rutile particle



Rutile particle exposing {110}  
and {011} facets.

# Crystal shape: role of termination

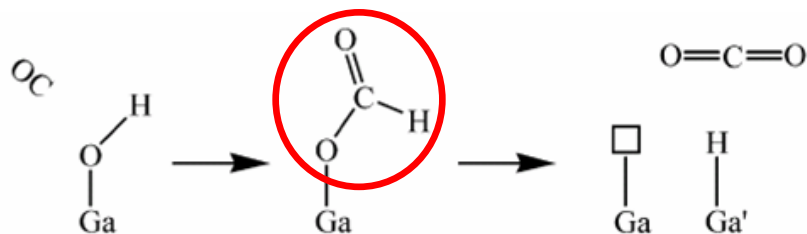
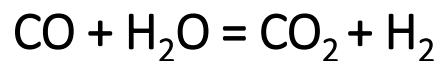


**Prediction of TiO<sub>2</sub> Nanoparticle Phase and Shape Transitions Controlled by Surface Chemistry**

## Example 3: surface reactivity

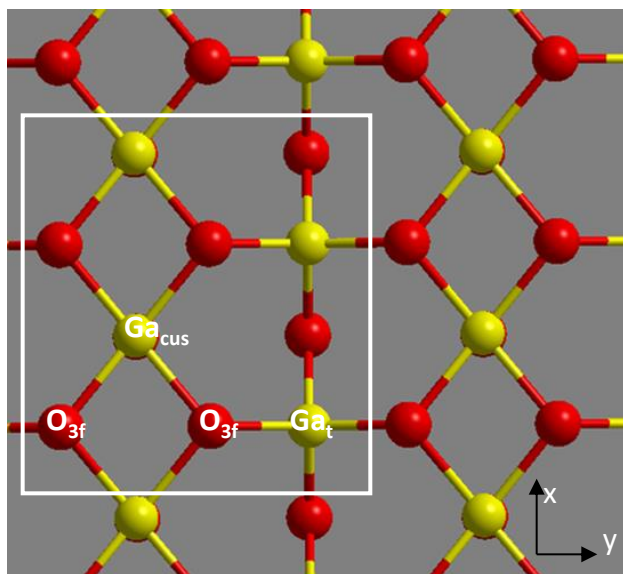
- Building realistic model
  - presence of water
- Adsorption, surface species
  - based on energy, spectroscopic features, comparison exp.
- Chemical reactivity
  - reactants to products mechanism

# Role of formates in the reaction reverse WGS



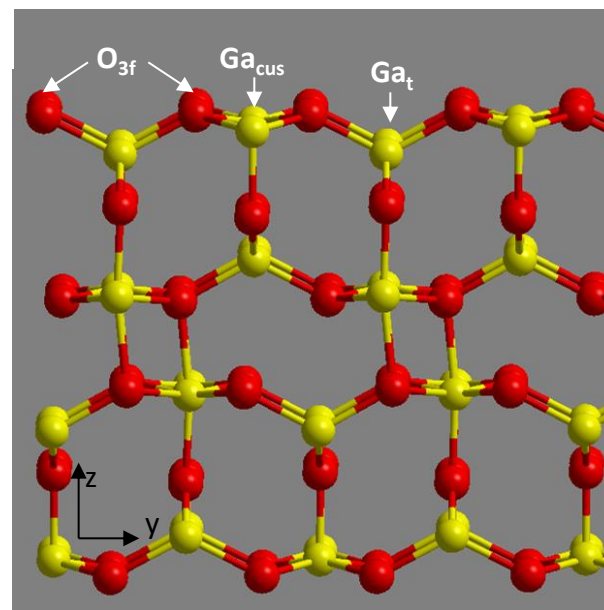
Stability  
Spectroscopy  
→ experiment  
Reaction mechanism

Top view



Hydroxyl groups present

Side view



- $\text{H}_2 = \text{H}^+ + \text{H}^-$
- $\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$

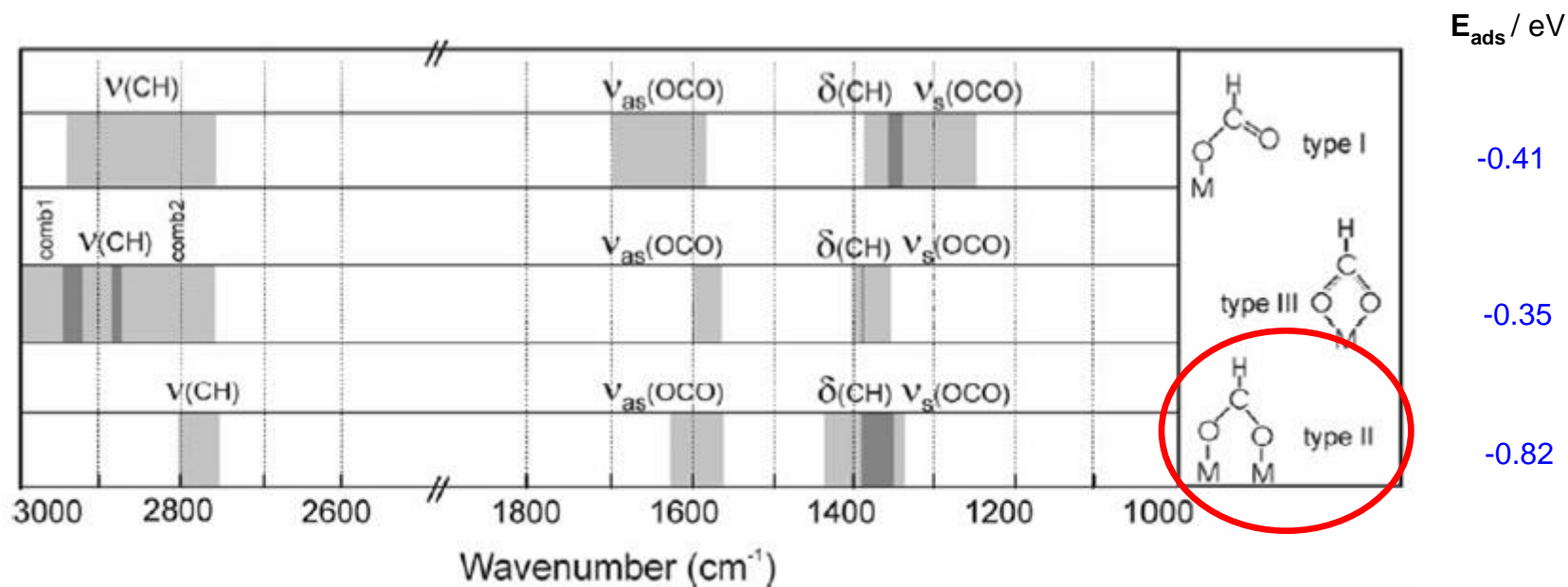


# Formates infra-red assignement

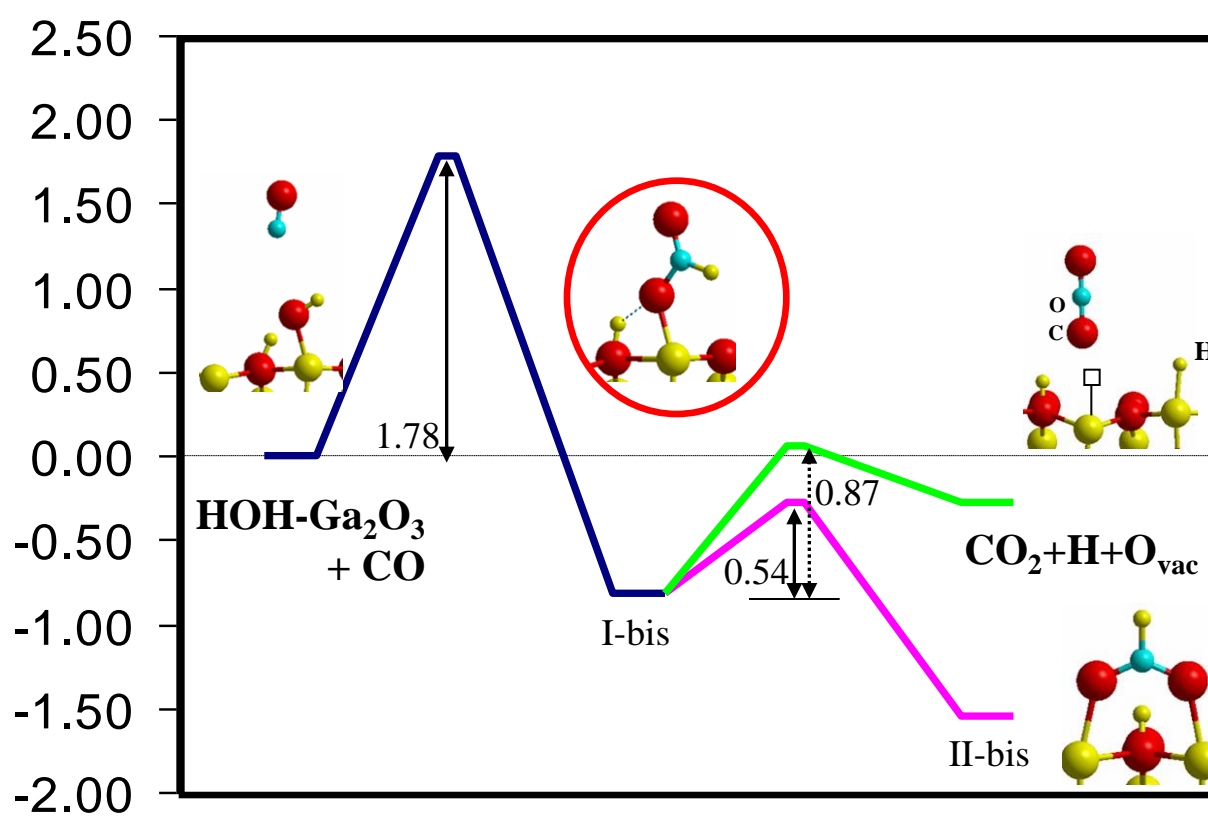
Based on stability (energy) and spectroscopic signature

**Table 1** Calculated and experimental harmonic frequencies for the formate ( $\text{HCOO}^-$ ) species

Vibrational mode	Infrared frequencies of formate species/ $\text{cm}^{-1}$							
	I		II		III		IV	
	Calcd	Exptl <sup>a</sup>	Calcd	Exptl <sup>a</sup>	Calcd	Exptl <sup>a</sup>	Calcd	Exptl <sup>a</sup>
C–H stretching	2923	2910	2973	2915	3011	2895	3062	n.d.
COO asym stretching ( $\nu_{\text{as}}$ )	1634	1665	1538	1580	1581	1600	1624	n.d.
C–H bending	1341	1350	1354	1385	1250	1355	1294	n.d.
COO sym stretching ( $\nu_{\text{s}}$ )	1252	1305	1310	1369	1324	1332	1187	n.d.
$\Delta\nu = \nu_{\text{as}} - \nu_{\text{s}}$	<b>382</b>	<b>360</b>	<b>228</b>	<b>211</b>	<b>257</b>	<b>268</b>	437	—



# Reaction mechanism



Key intermediates: monocoordinated formates

# Conclusion



Modelling is about capturing essential features!

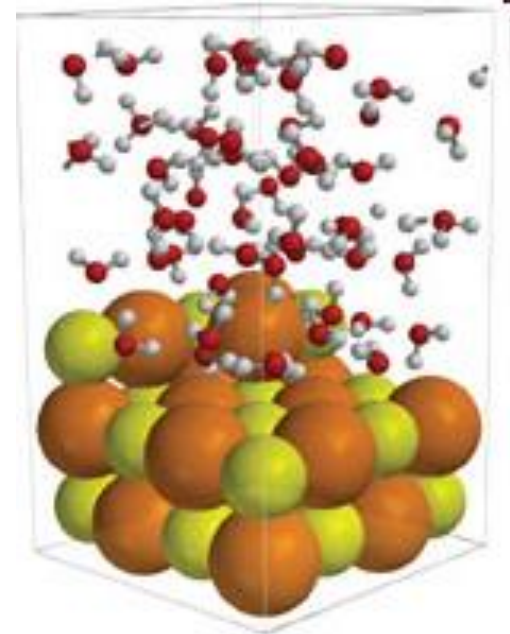
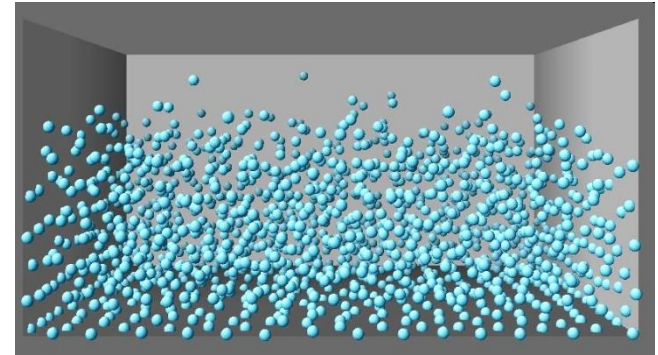
# **Software & tools**

- Molecular Mechanics
- Quantum Chemistry
- Molecular visualization and editing
- Databases etc
  - Nomad repository: structures and files of calculations

Companies – Academics  
Freeware – Web Applications

# Molecular Mechanics

- AMBER
- CHARMM
  
- VMD - Visual Molecular Dynamics
- MOLDY - Free MD program
- GROMACS Molecular Dynamics on Parallel Computers
- GROMOS Dynamic Modelling of Molecular Systems
- MacroModel - Molecular Modelling
- MSI/Biosym Molecular Modelling Software
- NAMD - Scalable Molecular Dynamics
- TINKER package for molecular mechanics and dynamics
- SYBYL - software from Tripos
- TURBOLMOL - Ab initio electronic structure calculations
- X-PLOR- MM program free for Academics
- DNAtools-Web tools to analyze DNA





# Quantum Chemistry

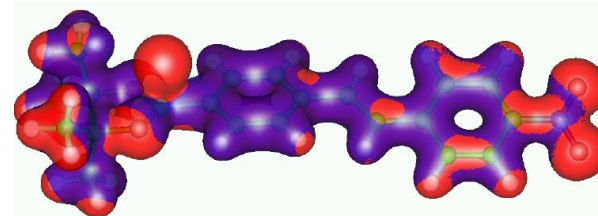
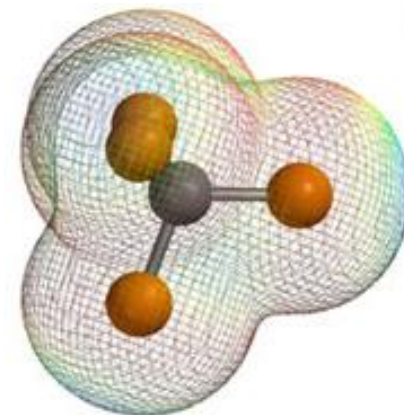
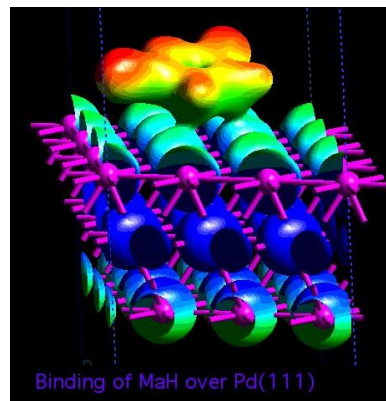
## 1. Finite Size

- GAMESS
- Gaussian
- ADF

## 2. Periodic

- VASP, CP2K
- WIEN2K, SIESTA, DACAPO
- CRYSTAL

- MOLCAS Quantum chemistry software at Lund University
- MOLPRO an ab initio package
- GAMESS-UK
- HyperCube Inc.
- ATMOL an ab initio program
- CADPAC -- The Cambridge Analytic Derivatives Package
- COLUMBUS general ab initio electronic structure calculations
- DeFT A gaussian density functional program
- Python source code for computational chemistry



# Molecular visualization and editing

## Molecules

- Molden
- Jmol
- GaussView
- ECCE
- Avogadro
- Arguslab
- VMD
- VegaZZ
- DeepView
- Discovery Studio
- MolView and Molview Lite - Macintosh

## Periodic Systems

Materials Studio  
Crystal Maker  
VMD  
ModelView  
MOLDRAW (Molecules and crystals)  
Molekel (Molecules and crystals)  
VESTA

# Selection!

# Molecular visualization and editing

## MOLDEN

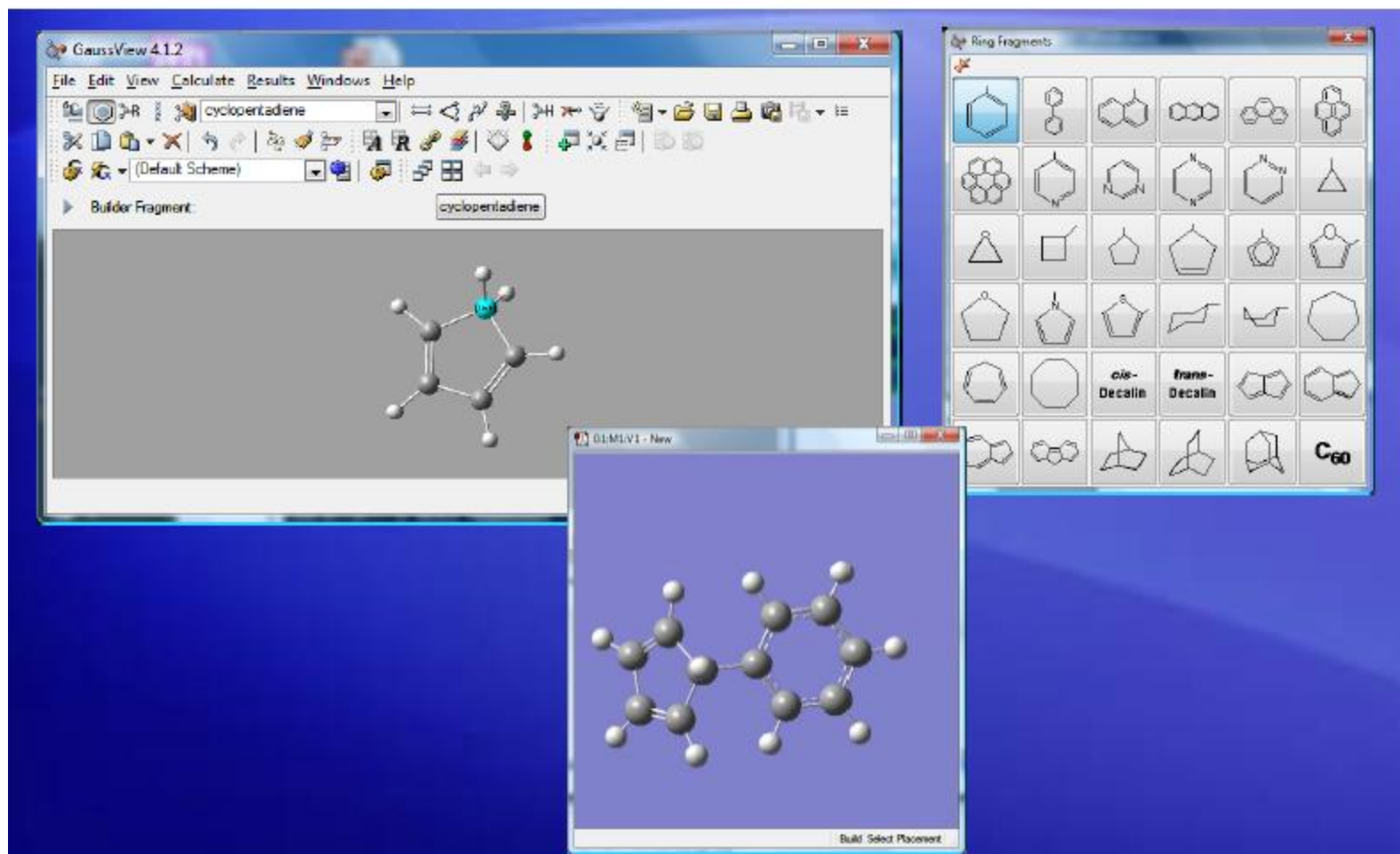
The screenshot displays the MOLDEN software interface, which is used for molecular visualization and editing. It consists of several windows:

- Molden Control:** A panel on the left containing various controls:
  - Select Point:** Buttons for 'First', 'Next', 'Prev', and 'None'.
  - Miscellaneous:** Buttons for 'Dens. Mode', 'Read', 'Write', 'ZMT Editor', and 'PostScript'.
  - Draw Mode:** Checkboxes for 'Solid', 'StickColor', 'Shade', 'Perspect.', 'Label', and 'BackBone'.
  - Render Forces:** A checkbox for 'Forces' and buttons for 'Dist. Scale', 'Angle Scale', and 'Update'.
  - Calculate:** Buttons for 'Distance', 'Angle', and 'Dihedral'.
  - Convergence:** Buttons for 'S.F. Conv.', 'Geom. Conv.', and 'Zoom' (with 'In', 'Out', and 'Fit' sub-buttons).
  - Status line:** A text box at the bottom showing 'No coordinates found!'.
- Z-Matrix Editor:** A central window for editing molecular parameters. It has columns for 'BondLength', 'BondAngle', and 'Dihedral'. The table below shows the current data:

	BondLength	BondAngle	Dihedral
C			
H 1	1.089000		
H 1	1.089000	109.471001	
O 1	1.220000	120.0	120.0 0
- MOLDEN:** A window on the right showing a 3D ball-and-stick model of a molecule (likely formaldehyde, CH<sub>2</sub>O) with a red oxygen atom, a brown carbon atom, and two white hydrogen atoms.

# Molecular visualization and editing

## Gaussview



# Molecular visualization and editing

Vesta

Avogadro

VMD

CONTICAR - VESTA

File Edit View Objects Utilities Help

a b c a\* b\* c\* Step (\*): 45.0 Step (px): 10 Step (%): 10

Tools Style Objects V205\_1L\_new.vasp CONTICAR

Structural models

- Show models
- Show dot surface

Style

- Ball-and-stick
- Space-filling
- Polyhedral
- Wireframe
- Stick

Volumetric data

- Show sections
- Show isosurfaces
- Surface coloring

Style

- Smooth shading
- Wireframe
- Dot surface

Crystal shapes

- Show shapes

Style

- Unicolor
- Custom color
- Wireframe

Properties...

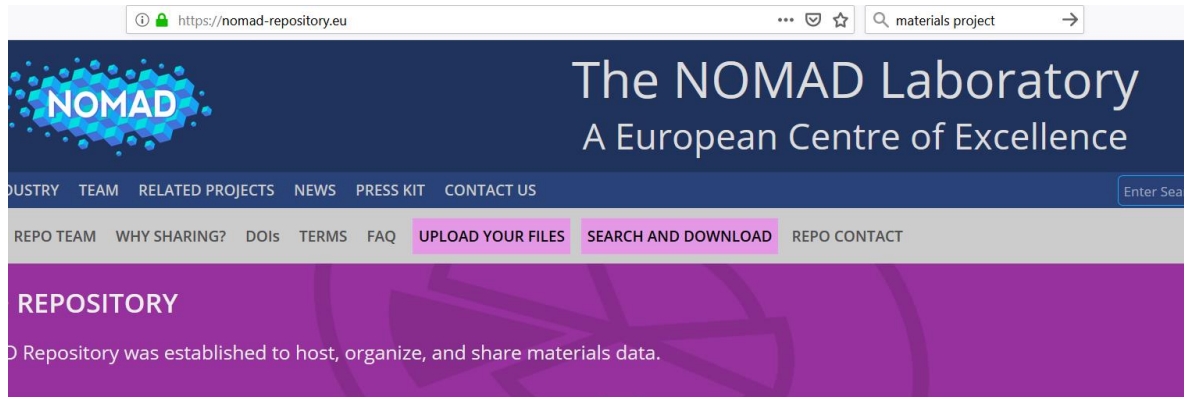
Boundary... Orientation...

Number of polygons and unique vertices on isosurface = 0 (0)  
166 atoms, 280 bonds, 36 polyhedra; CPU time = 8 ms

117	C	C1	0.43375	0.27977	0.60660	1.000	1.000	1a	1
118	C	C2	0.56252	0.29778	0.62752	1.000	1.000	1a	1

Output Summary Comment

# Databases, repositories

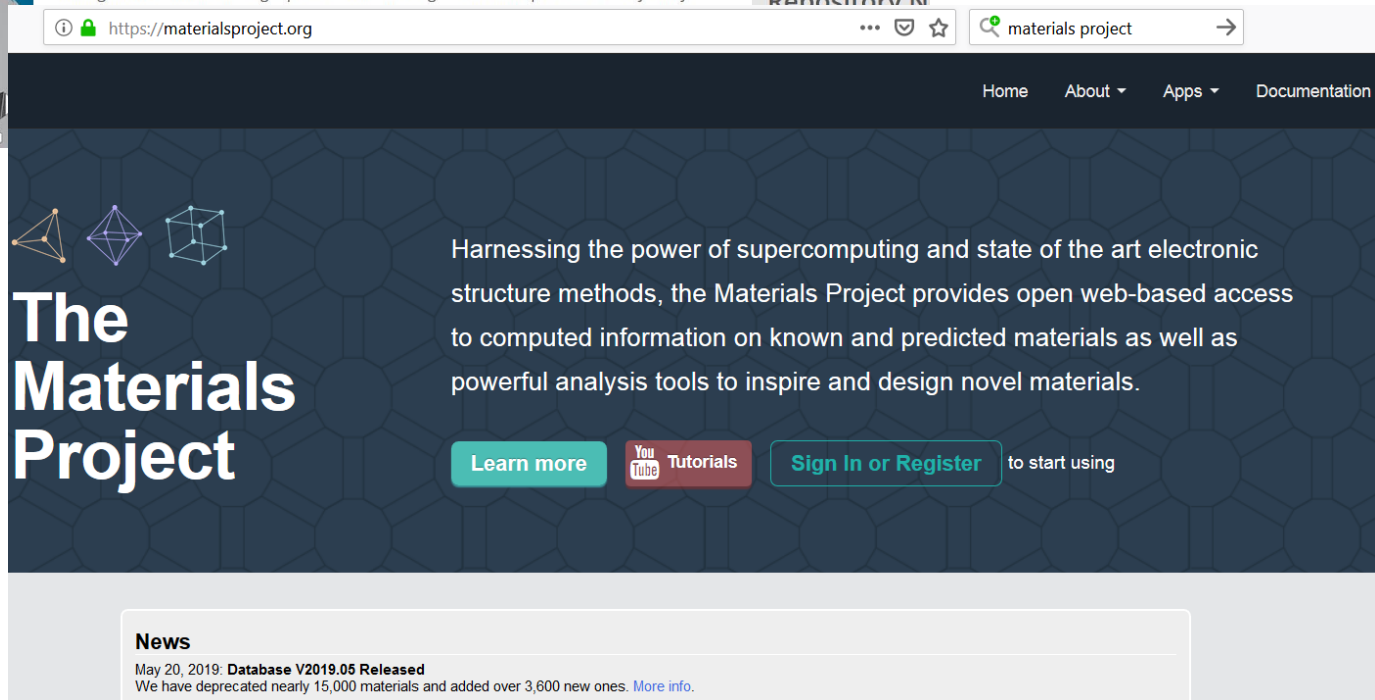


The screenshot shows the homepage of the NOMAD Laboratory. The browser address bar displays "https://nomad-repository.eu" and the search bar contains "materials project". The main header features the NOMAD logo and the text "The NOMAD Laboratory A European Centre of Excellence". A navigation menu includes "INDUSTRY", "TEAM", "RELATED PROJECTS", "NEWS", "PRESS KIT", and "CONTACT US". A secondary menu below it lists "REPO TEAM", "WHY SHARING?", "DOIs", "TERMS", "FAQ", "UPLOAD YOUR FILES", "SEARCH AND DOWNLOAD", and "REPO CONTACT". A purple banner below the menu reads "REPOSITORY" and "The NOMAD Repository was established to host, organize, and share materials data."



NOMAD copes with the increasing demand and requirement of storing scientific data and making them available for longer periods. This rule of good scientific practice is set by many

Repository N



The screenshot shows the homepage of the Materials Project. The browser address bar displays "https://materialsproject.org" and the search bar contains "materials project". The navigation menu includes "Home", "About", "Apps", and "Documentation". The main content area features a dark blue background with a hexagonal pattern and the text "The Materials Project". Below this, a paragraph reads: "Harnessing the power of supercomputing and state of the art electronic structure methods, the Materials Project provides open web-based access to computed information on known and predicted materials as well as powerful analysis tools to inspire and design novel materials." Three buttons are visible: "Learn more", "YouTube Tutorials", and "Sign In or Register to start using". A "News" section at the bottom left contains the text: "May 20, 2019: Database V2019.05 Released We have deprecated nearly 15,000 materials and added over 3,600 new ones. More info."