Modelling surfaces: models and applications

CTTC School
Current Topics in
Theoretical Chemistry

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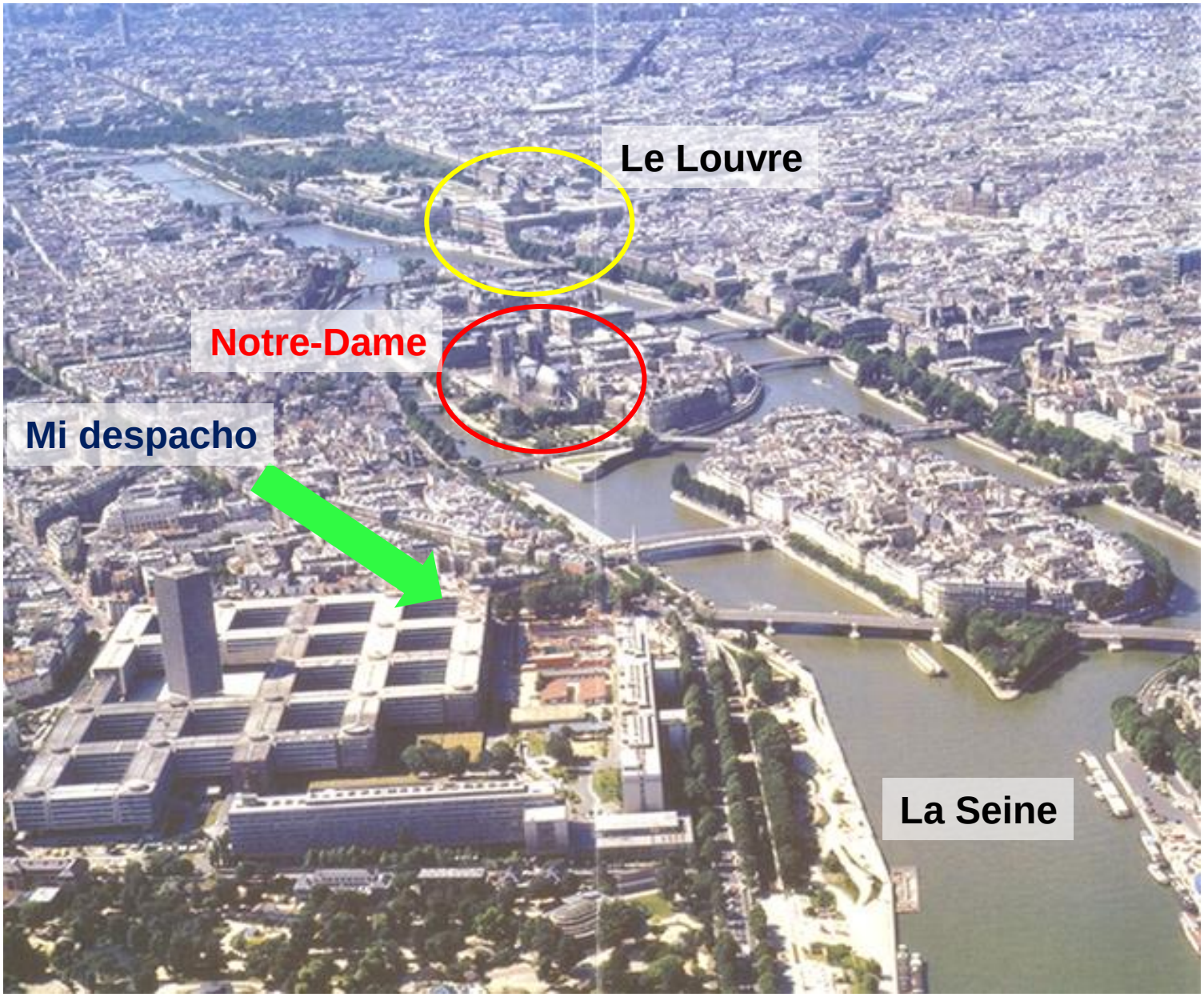
Quito 30th June 2019

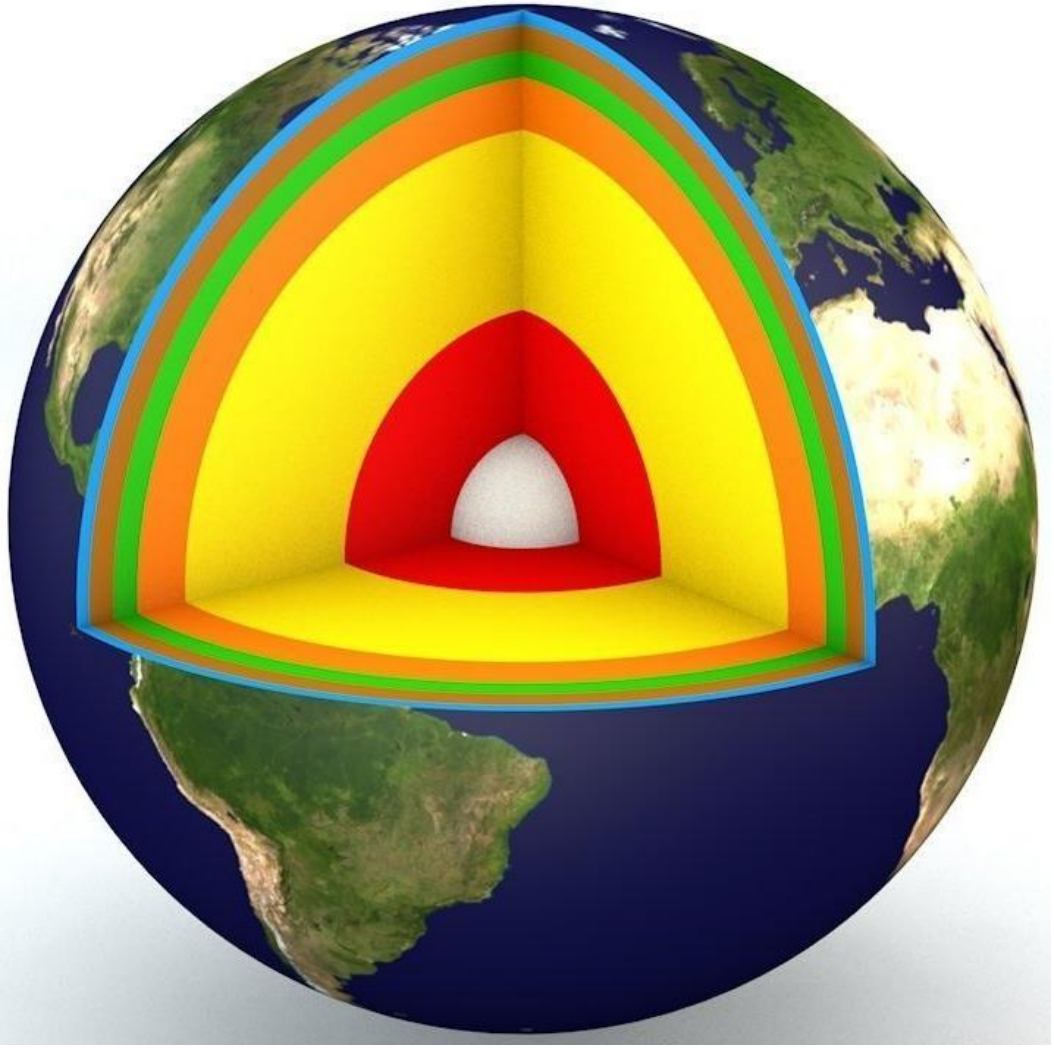

Le Louvre
Notre-Dame
Mi despacho
La Seine

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

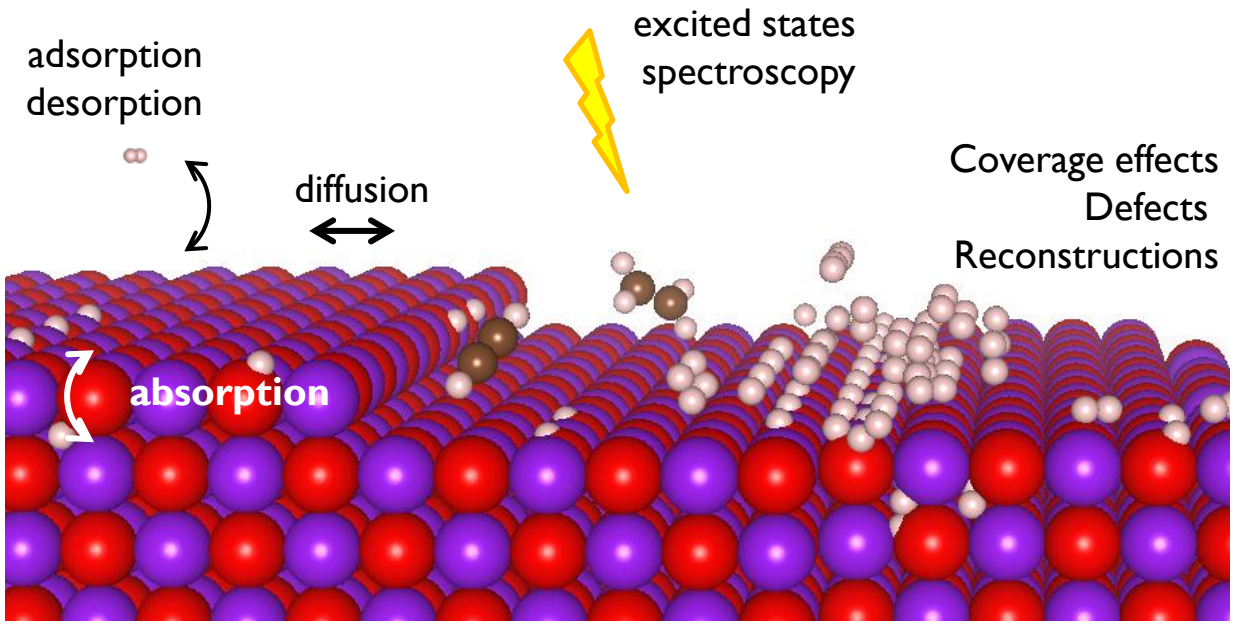
- Methods for solids Juan Peralta
- Surfaces: models and applications M. Calatayud
  - Introduction
  - Models
  - Properties
  - Applications
  - Software

Goal

Get familiar with surface modelling
structure - properties

I: Introduction

Modelling solid surfaces



What do we want to study?

How accurate?

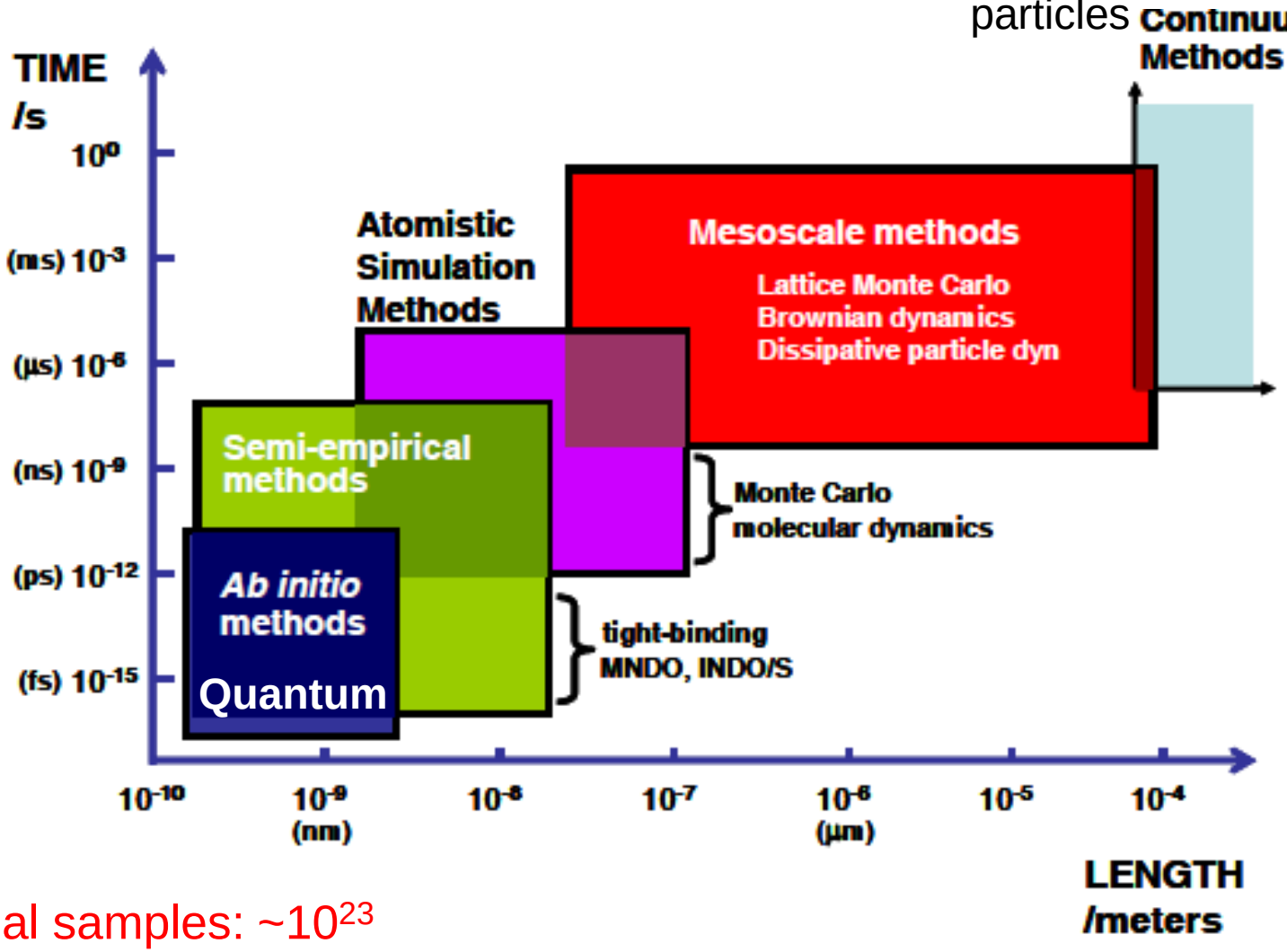
→ **Choice of model & method**

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: ~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 $[OH^-]$ $pH_{HCl} = -\log([HCl]/c°)$
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

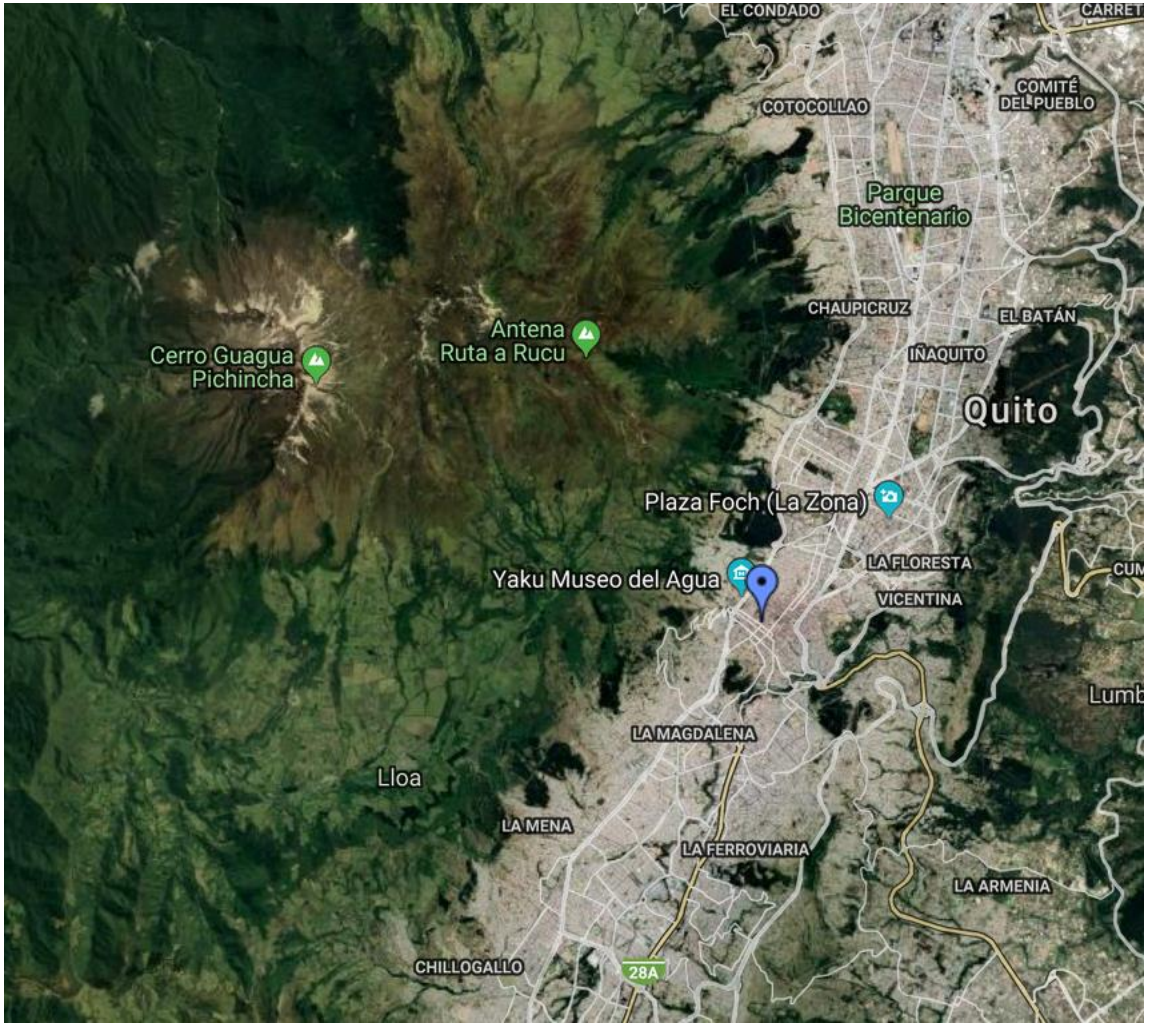
What are my ressources and my constraints?

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

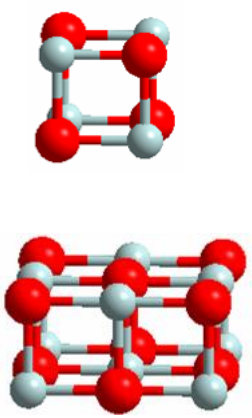
in composition or structure

Determine the property and the accuracy

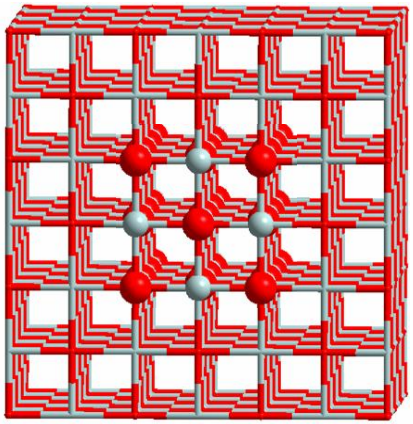
Build the model

Models

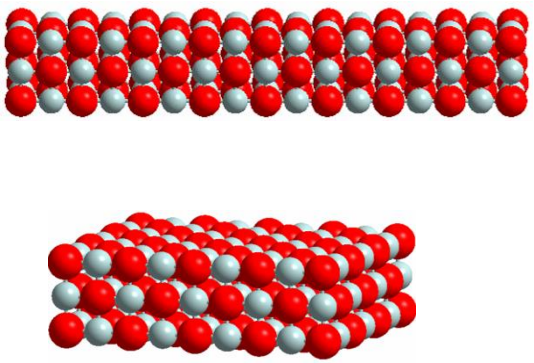
cluster



embedded cluster



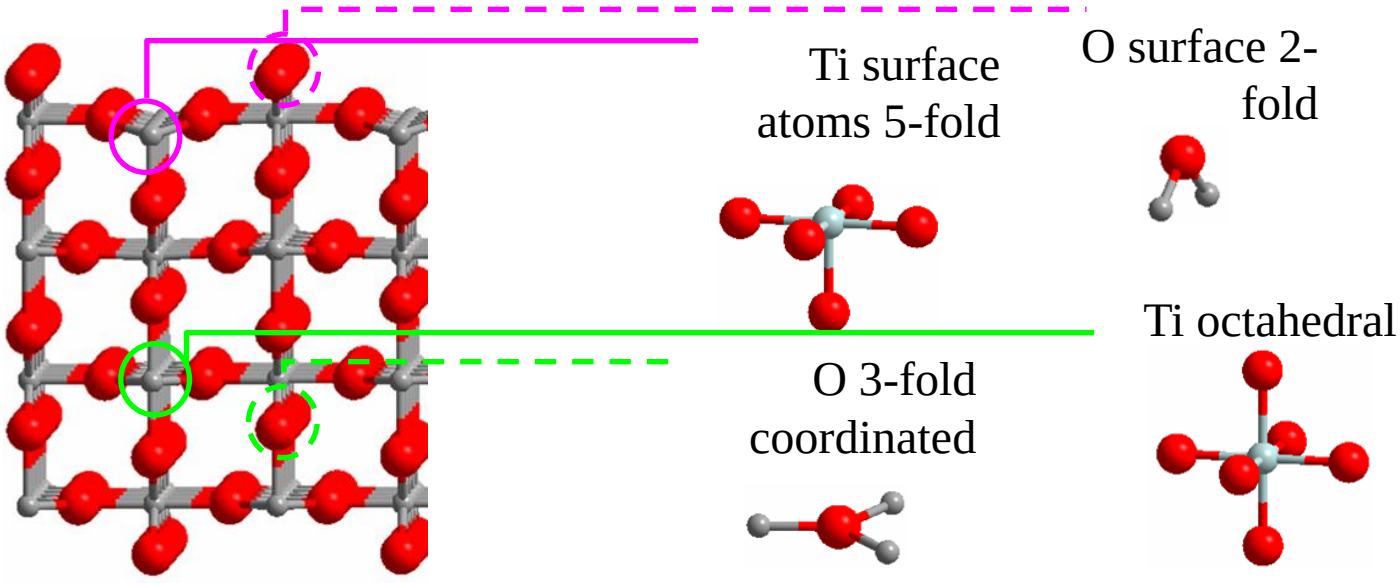
periodic



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

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

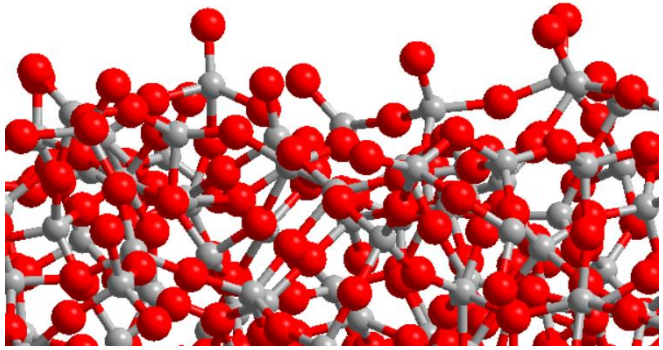
Characterizing a surface - structure



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

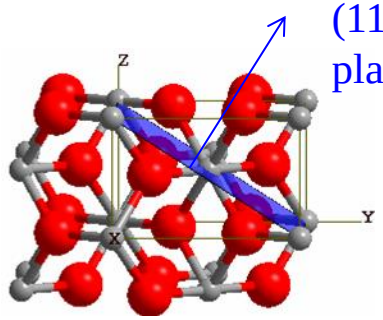
Termination - where to cut
Coordination of surface atoms, polarity…
Thickness
Composition
stoichiometry, defects, capping…

Also applies for amorphous systems

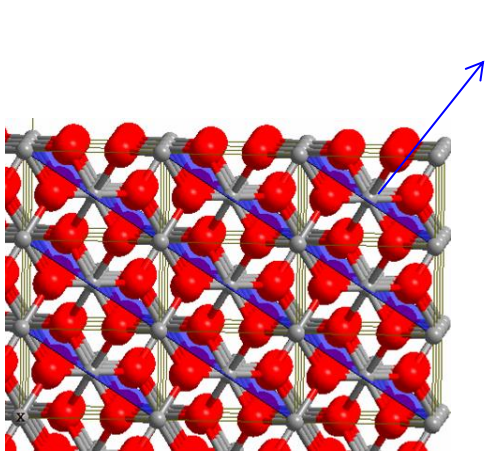


Creating a surface *in silico*

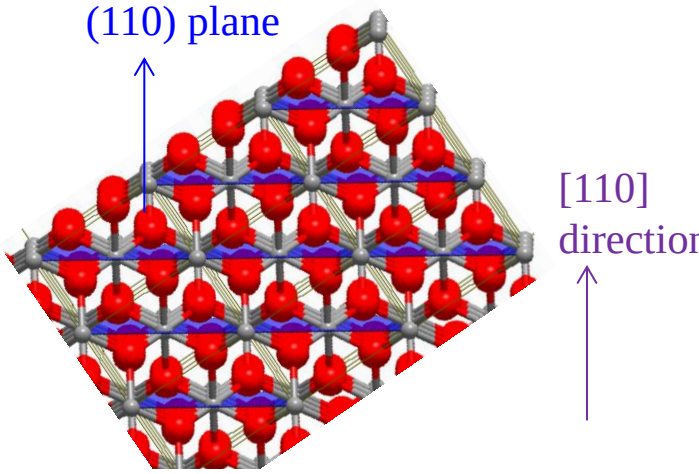
Ex. Rutile MO_2



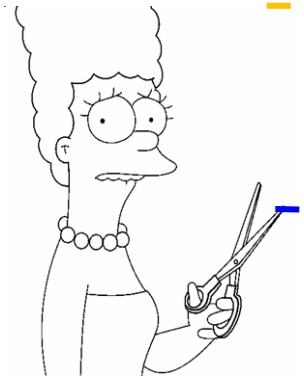
Bulk unit cell



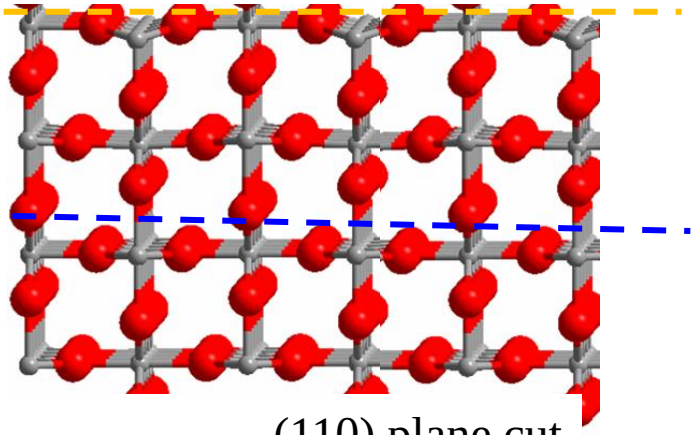
(110) planes



{110} plane family oriented



cut the Ti-O bonds



(110) plane cut

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
- Vibrational frequencies

relaxation-reconstruction
shape prediction, adsorption mode …

- 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

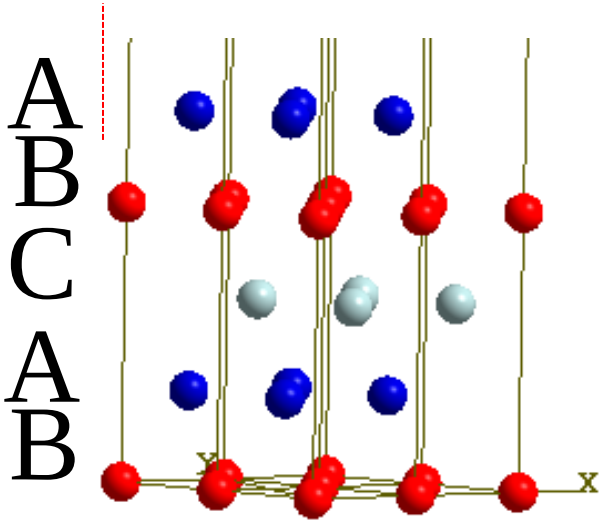
Volume 530, Issues 1–2, 20 April 2003, Pages 71-87

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

Alfred Gil [a], Anna Clotet [a], Josep M. Ricart [a] ✉, Georg Kresse [b], Maite Garcı́a-Hernández [c], Notker Rösch [c], Philippe Sautet [d, e] ✉

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

The adsorption sites in fcc metals

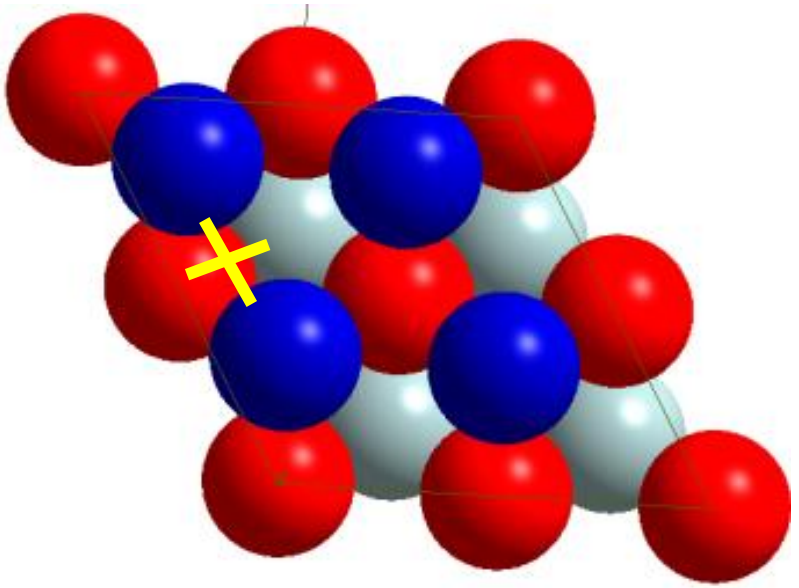


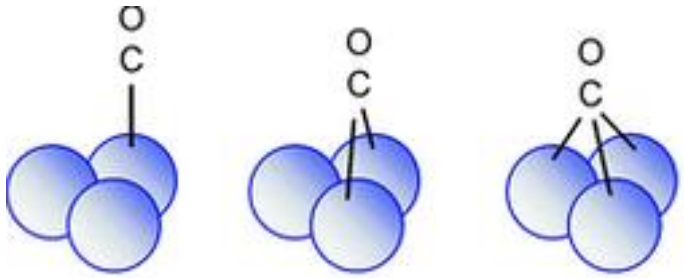
Top

Bridge

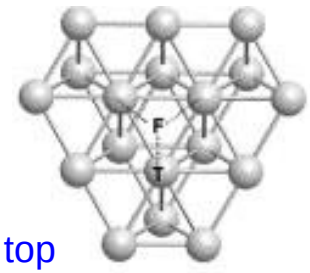
Hollow fcc

Hollow hcp



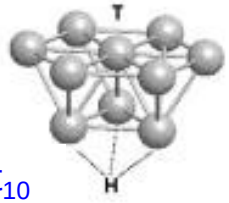


Cluster models

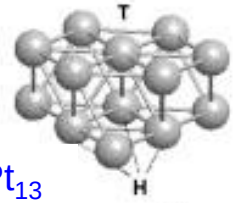


Pt_{18} top

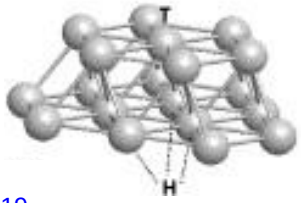
Pt_4



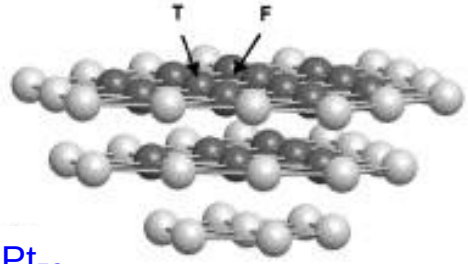
Pt_{10}



Pt_{13}



Pt_{19}

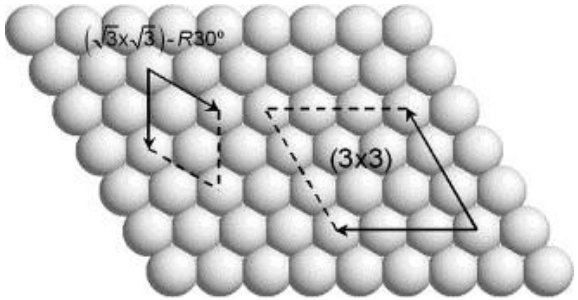


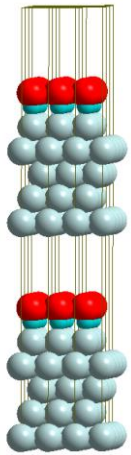
Pt_{52}

- small clusters do not correctly describe the substrate environment → not adequate for adsorption energies

- larger clusters results ≈ 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

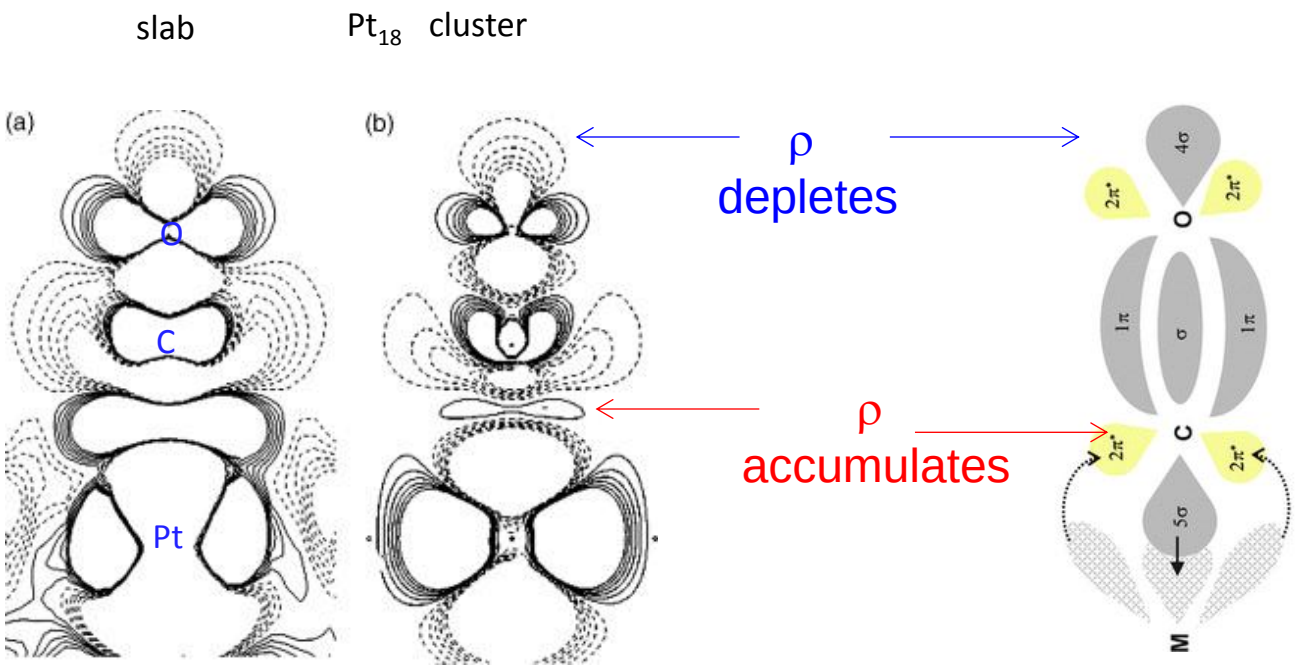


Fig. 3. Electron density difference maps between CO chemisorbed on top at Pt(1 1 1) and the separated fragments computed with the PW91 functional, for (a) plane wave basis set (four layers slab) and (b) localized basis set (Pt_{18} cluster model). Solid contours represent zones with accumulated electron 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

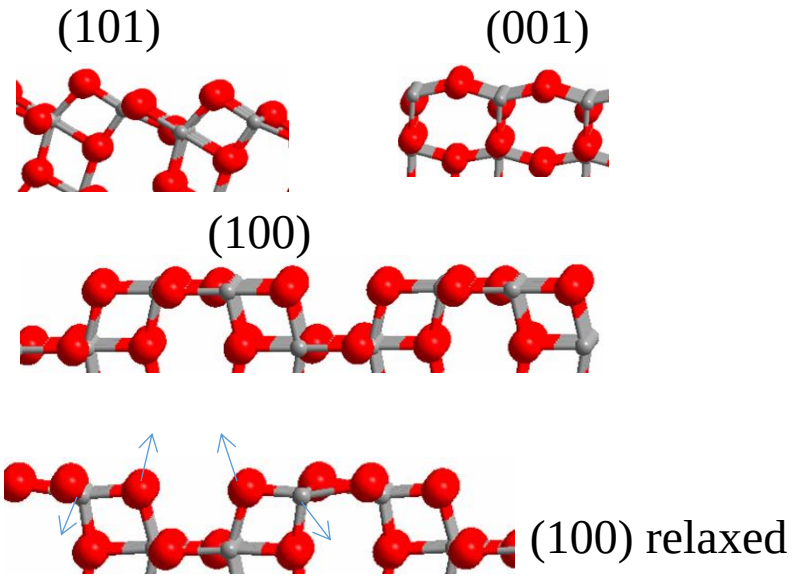
$$E_{surf} = \frac{E_{slab} - E_{bulk}}{2\,A}$$ units: J m^{-2}

The most exposed planes will be the most stable ones

→ those of lower surface energy

1) Comparison of different surfaces

TiO_2 phase	hkl	E_{surf} unrelaxed Jm^{-2}	E_{surf} **relaxed** Jm^{-2}
Anatase	(101)	1.127	0.414
Anatase	(001)	1.011	0.863
Anatase	(100)	1.330	0.463

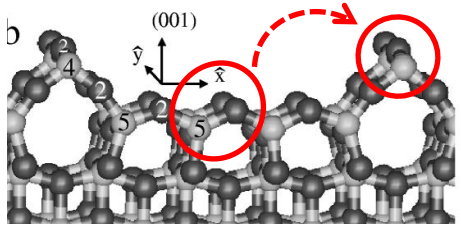


2) Relaxation small rearrangement to decrease energy

3) Reconstruction

important rearrangement to decrease energy

bond break-formation



Phys. Rev. Lett. 87 (2001) 266105

0.51 Jm^{-2} reconstructed

0.90 Jm^{-2} unconstructed

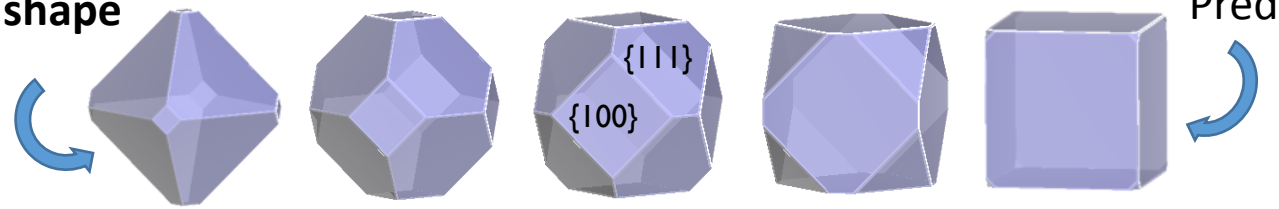
Crystal shape: a surface property

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

Predominance
(111)

fcc metals

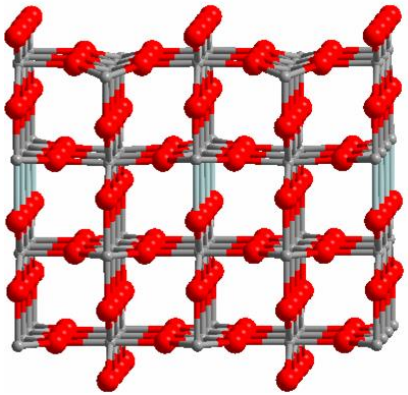
Octahedral shape

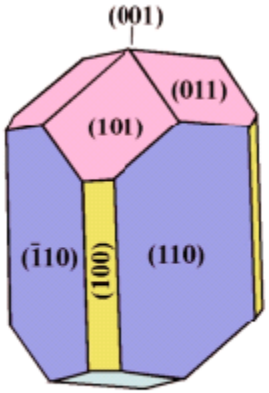


Predominance **(100)**

Cubic shape

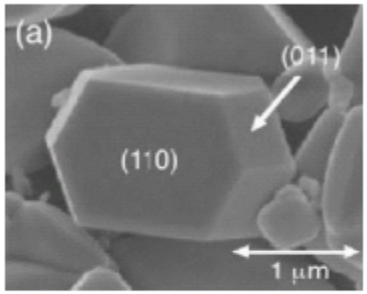
Rutile MO_2





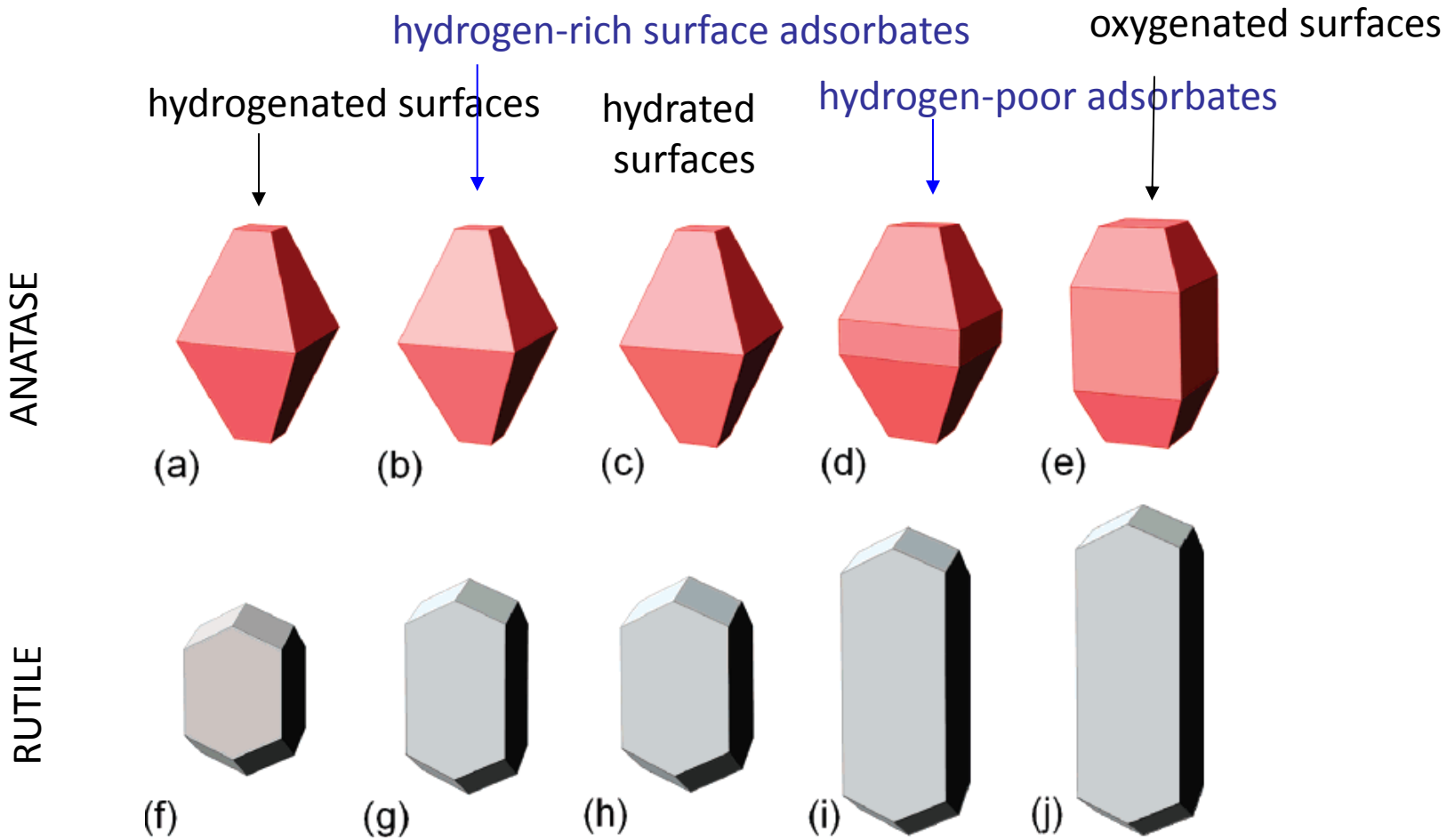
Ramamoorthy and Vanderbilt
Phys. Rev. B 49, 16721 (1994)

TiO_2 rutile particle



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

Crystal shape: role of termination



Prediction of TiO_2 Nanoparticle Phase and Shape Transitions Controlled by Surface Chemistry

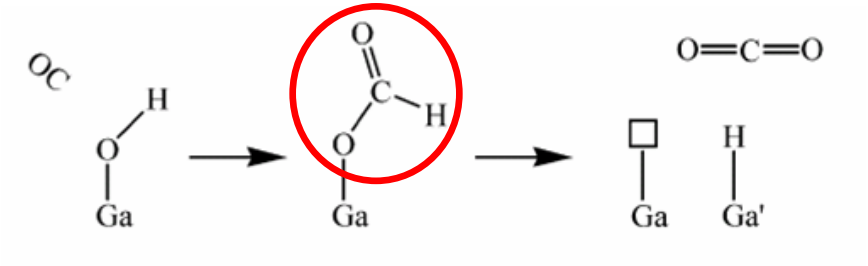
Barnard and Curtiss Nano Lett., Vol. 5, No. 7, **2005**

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

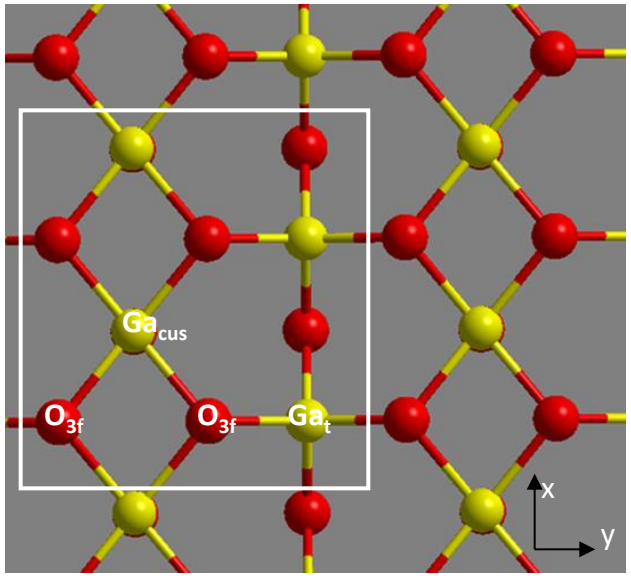
Role of formates in the reaction reverse WGS

$$CO + H_2O = CO_2 + H_2$$

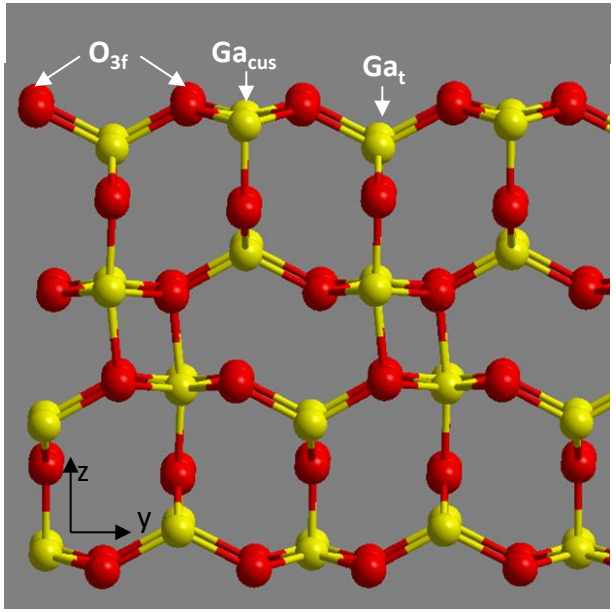


Stability
Spectroscopy
→ experiment
Reaction mechanism

Top view



Side view



Hydroxyl groups present

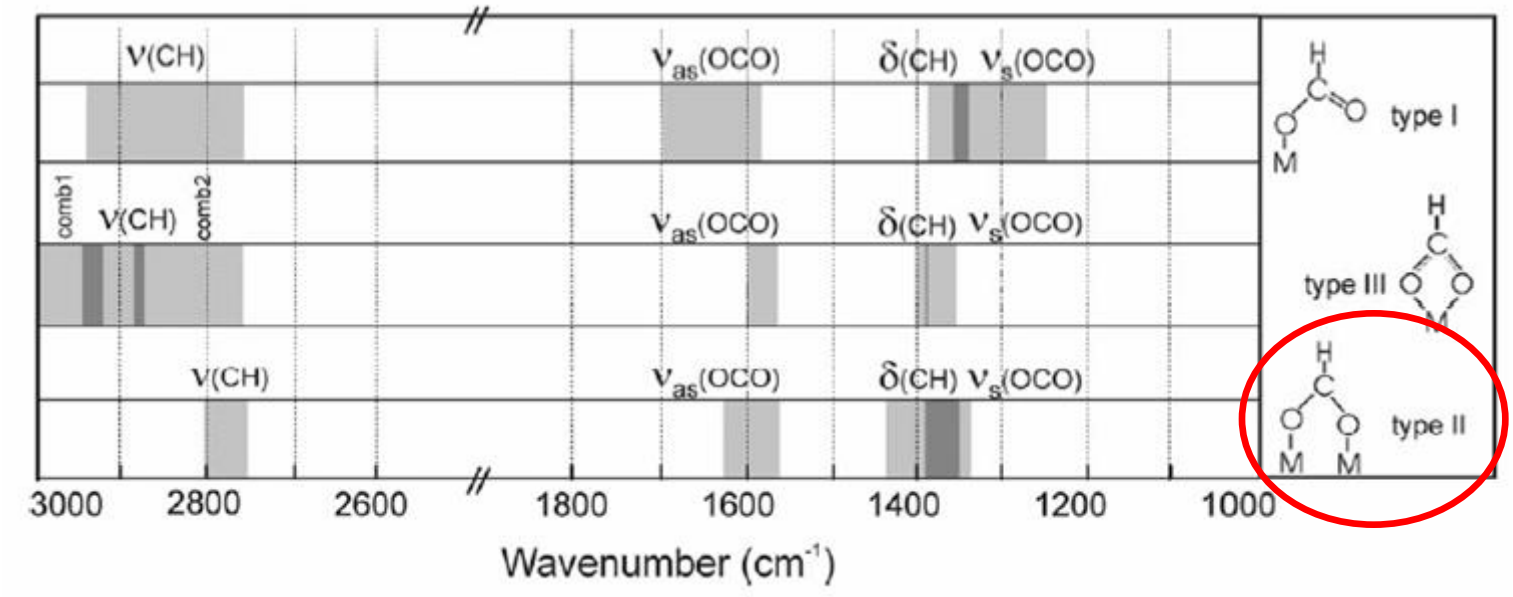
- $H_2 = H^+ + H^-$
- $H_2O = H^+ + OH^-$

Formates infra-red assignement

Based on stability (energy) and spectroscopic signature

Table 1 Calculated and experimental harmonic frequencies for the formate ($HCOO^-$) species

	Infrared frequencies of formate species/cm^{-1}							
	I		II		III		IV	
Vibrational mode	Calcd	Exptl[a]	Calcd	Exptl[a]	Calcd	Exptl[a]	Calcd	Exptl[c]
C–H stretching	2923	2910	2973	2915	3011	2895	3062	n.d.
COO asym stretching (ν_{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 (ν_s)	1252	1305	1310	1369	1324	1332	1187	n.d.
$\Delta\nu = \nu_{as} - \nu_s$	382	360	228	211	257	268	437	—



E_{ads} / eV

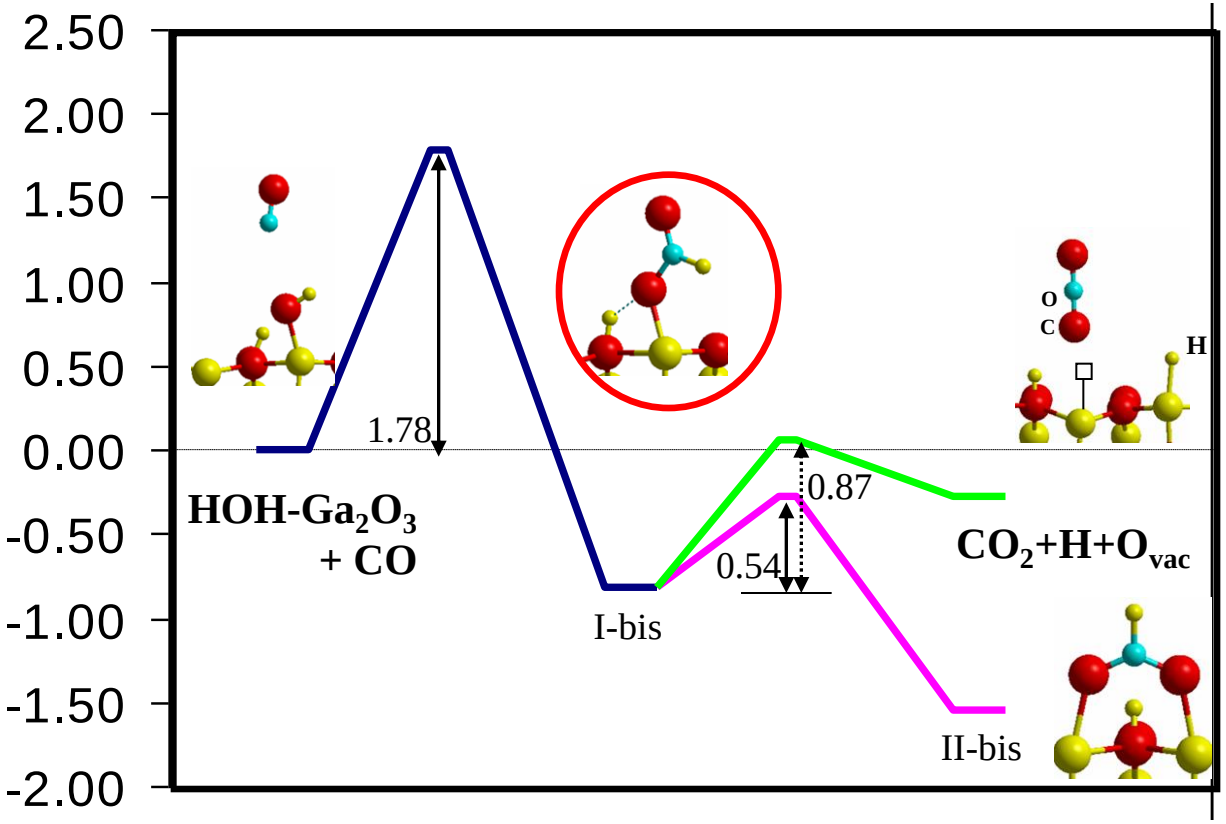
-0.41

-0.35

-0.82

M. Calatayud et al. Phys. Chem. Chem. Phys. 11 (2009) 1397

Reaction mechanism



Key intermediates: monocoordinated formates

M. Calatayud et al. Phys. Chem. Chem. Phys. 11 (2009) 1397

Conclusion

Modelling is about capturing essential features!

Software & tools

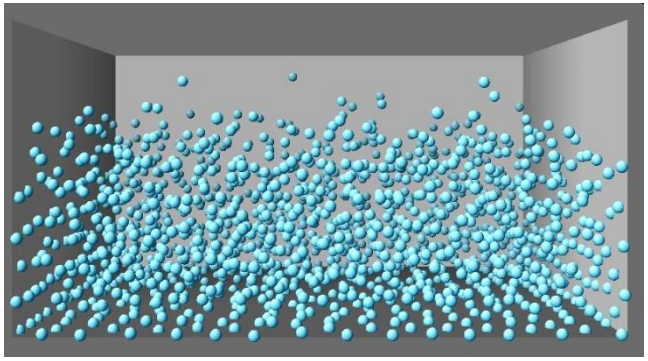
- Molecular Mechanics
- Quantum Chemistry
- Molecular visualization and editing
- Databases etc
  - Nomad repository: structures and files of calculations

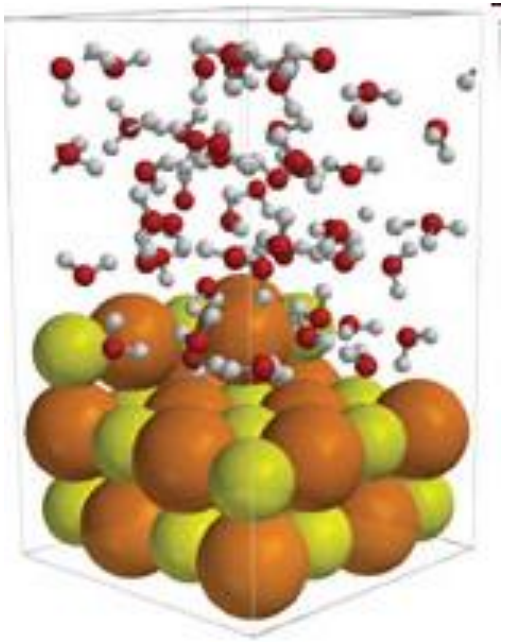
Companies – Academics
Freeware – Web Applications

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

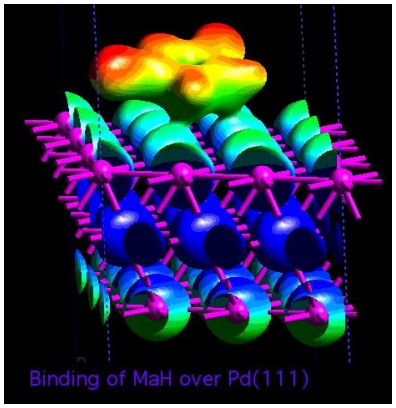


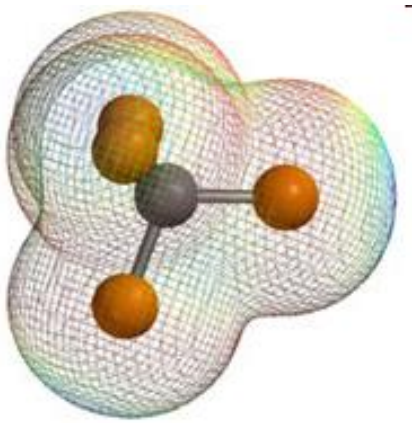


Quantum Chemistry

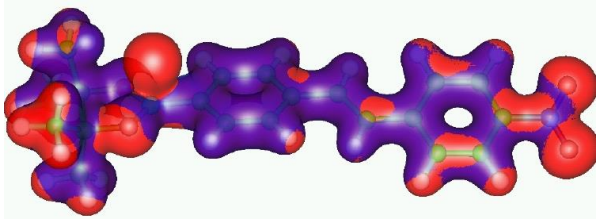
1. Finite Size
- GAMESS
- Gaussian
- ADF

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

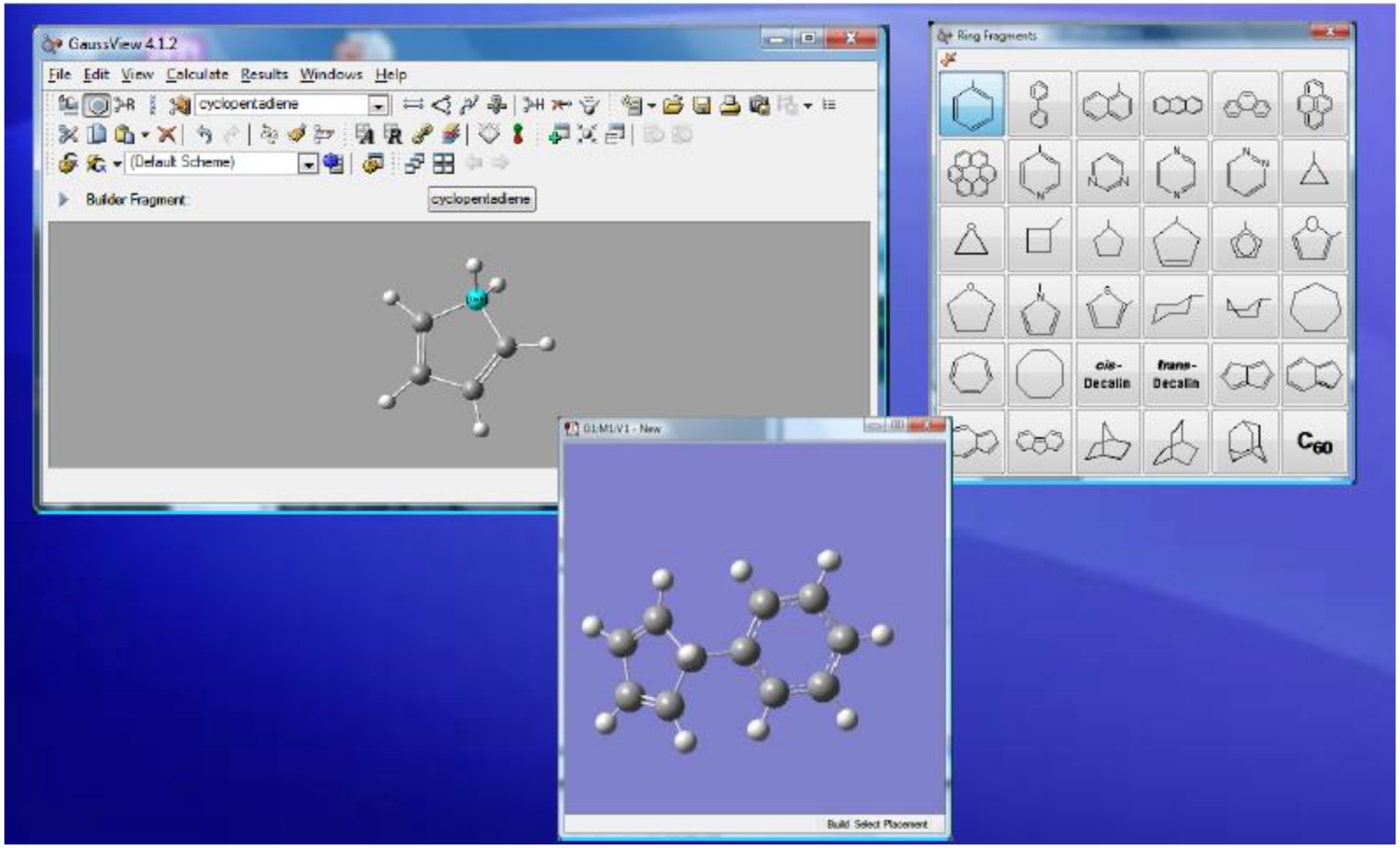
Selection!

Molecular visualization and editing

MOLDEN

Molecular visualization and editing

Gaussview

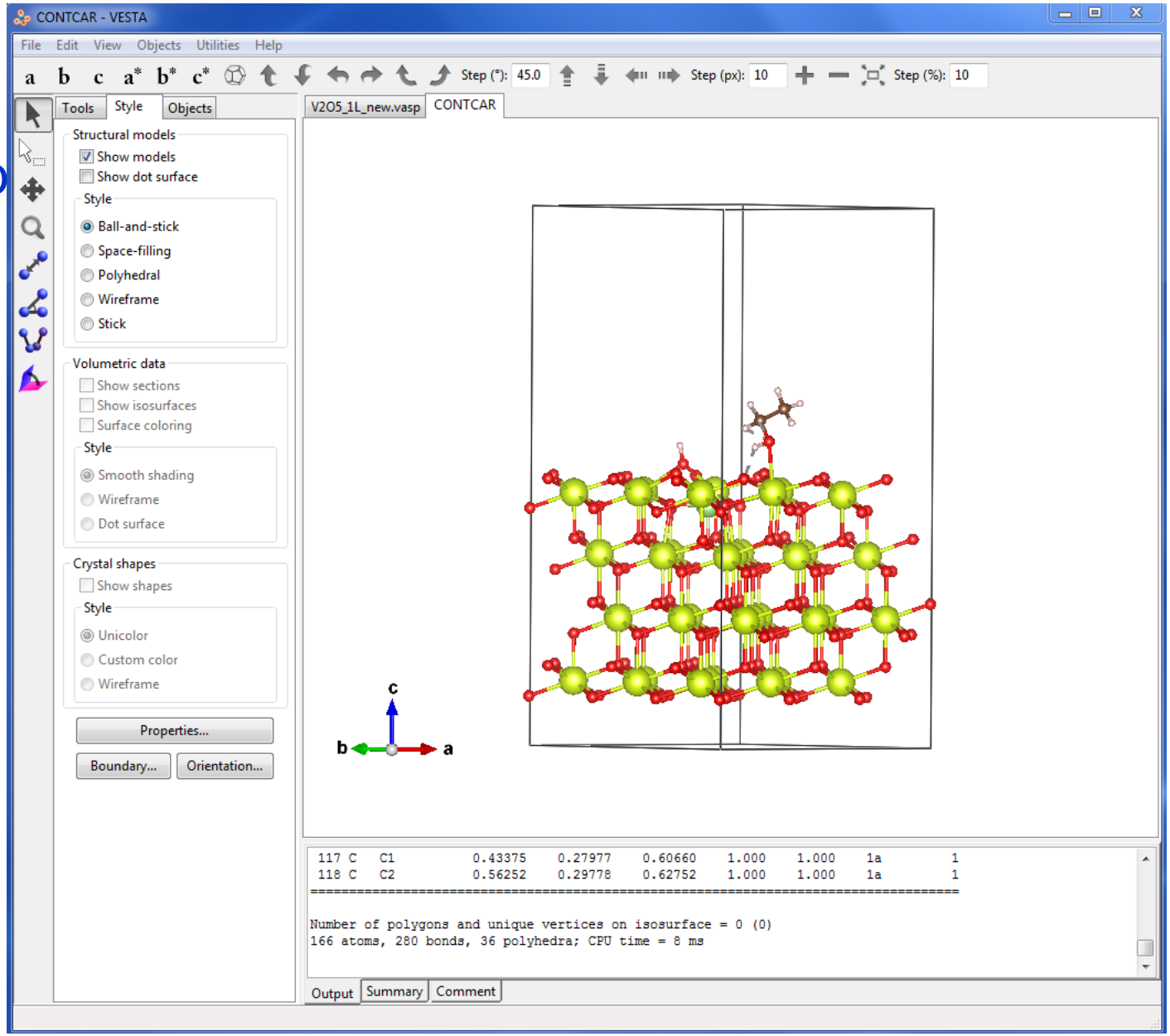


Molecular visualization and editing

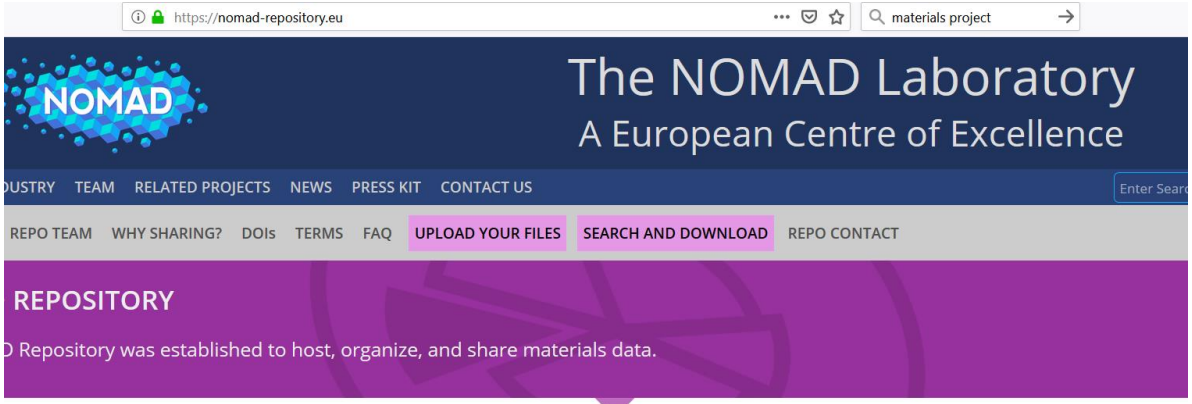
Vesta

Avogadro

VMD



Databases, repositories



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