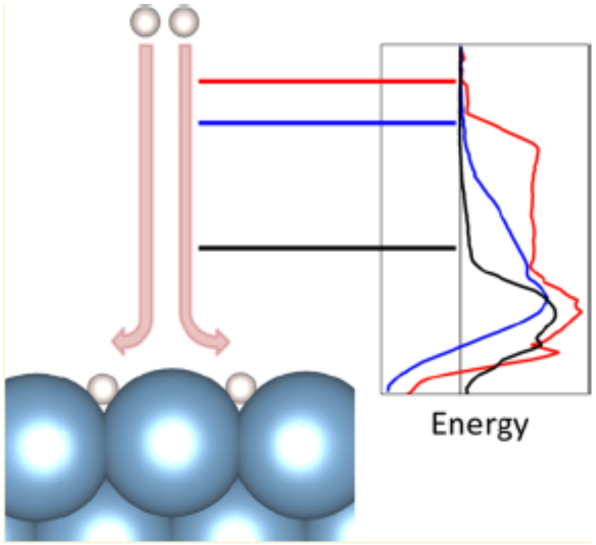
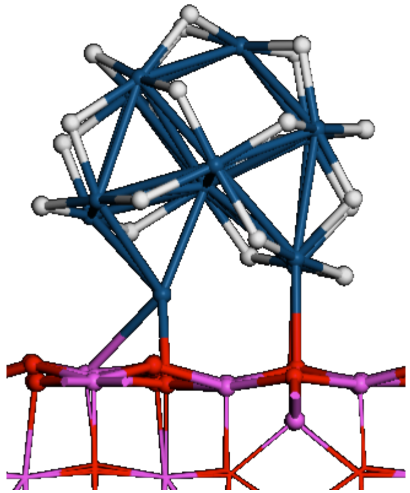
Modelling heterogeneous catalysis: what challenge for first principle calculations?



Philippe Sautet

Institute of Chemistry
University of Lyon



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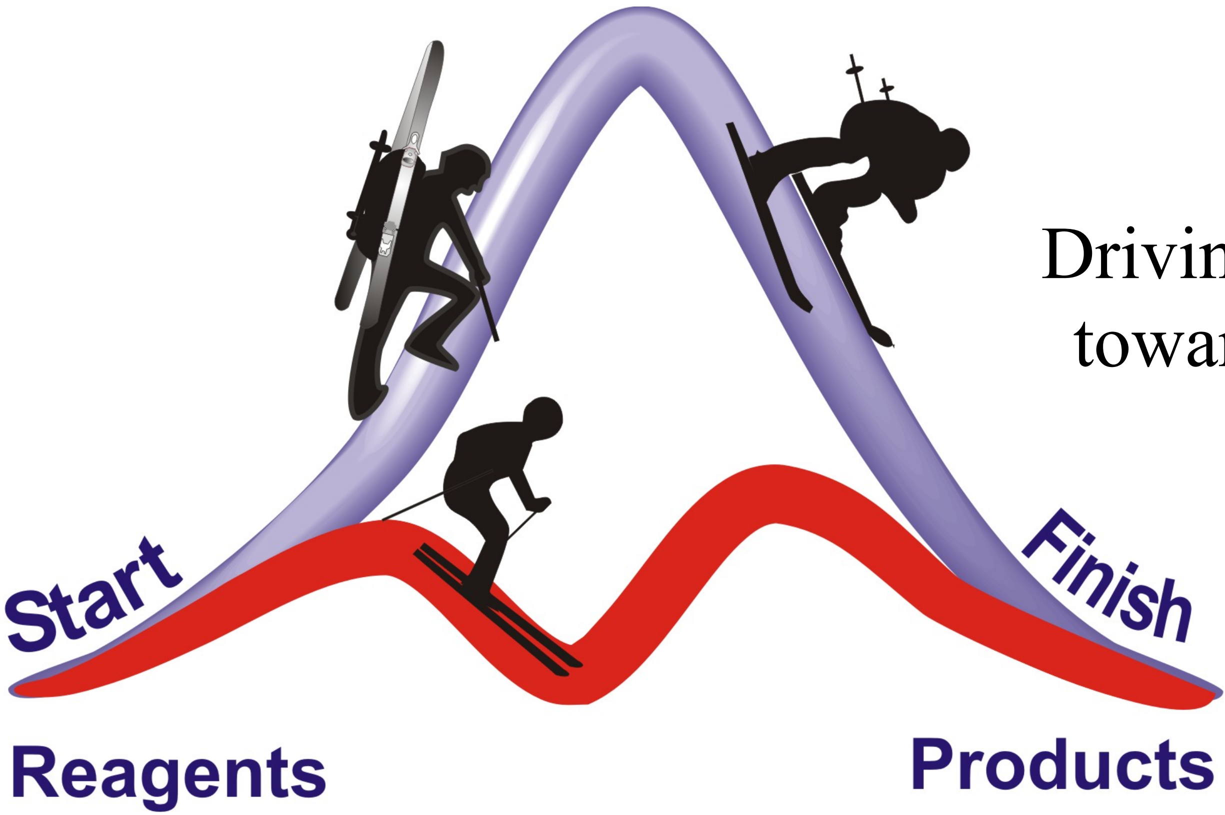
Making chemical reactions easier with catalysis

Lowering the energy barrier, finding an easy path



Driving chemical reaction towards wanted product

without catalyst

with catalyst

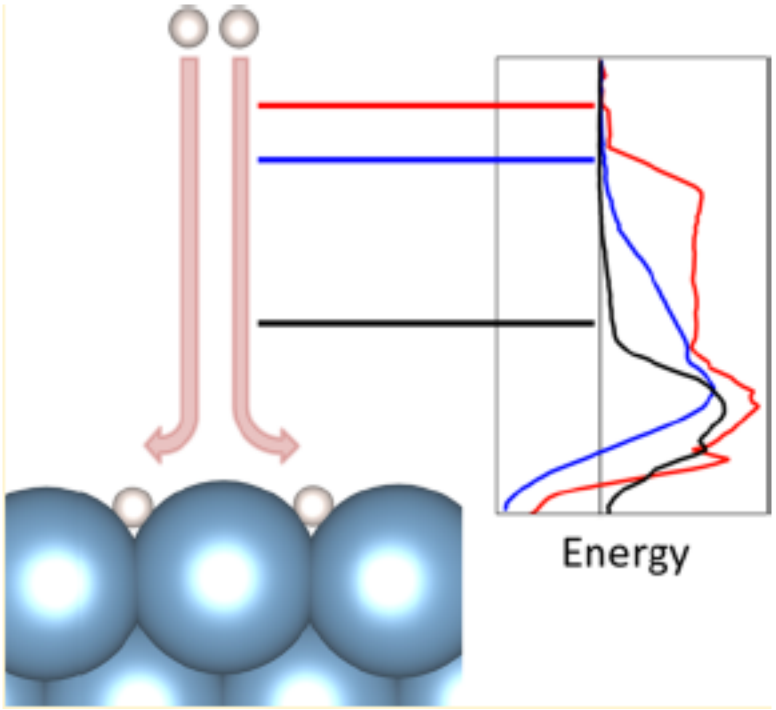
Ecoefficient chemistry with catalysis ... and simulations

Chemical plant of the 21st century

•Softs conditions
• total selectivity
•No waste

Design of efficient catalysts
Understanding mechanisms at the molecular scale
Molecular simulation is a key approach

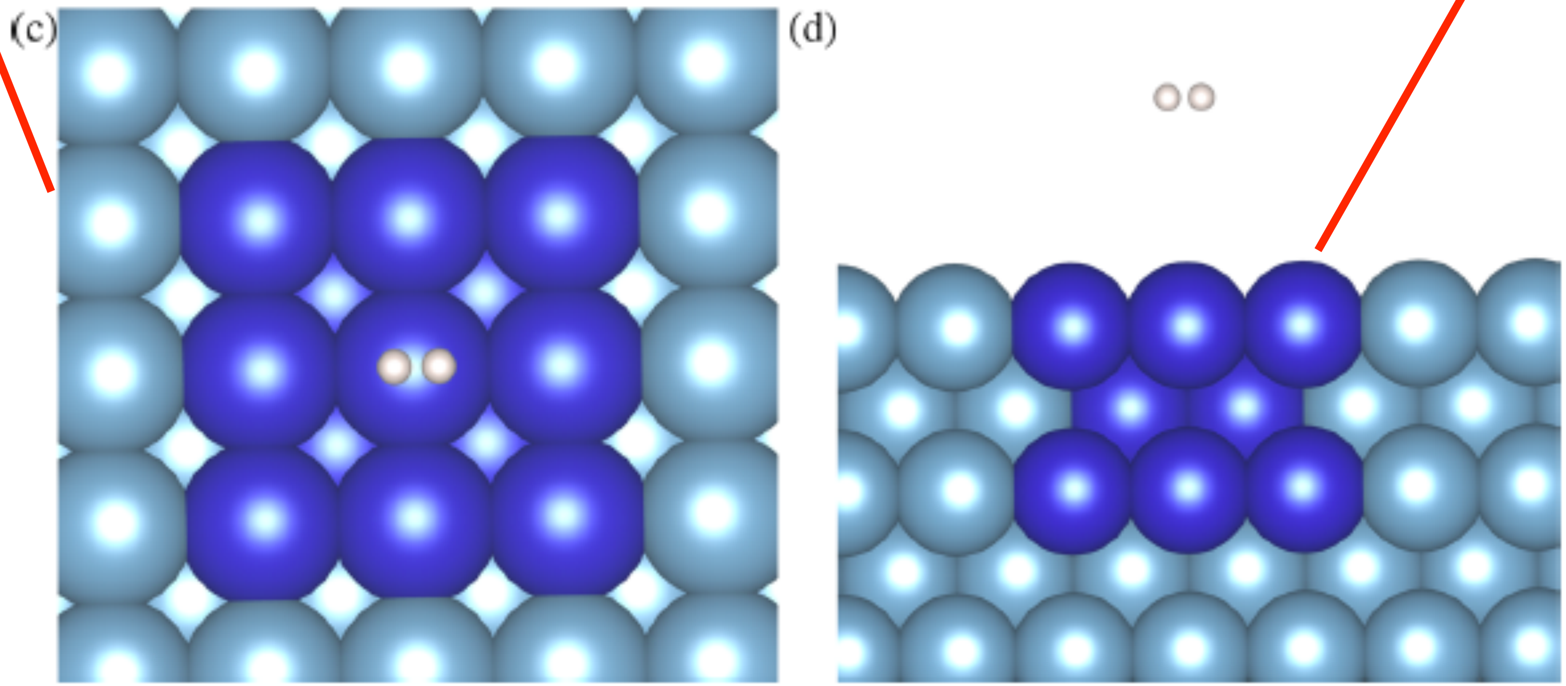
Reaction pathways at surfaces



H_2 on Cu(100): hybrid approach

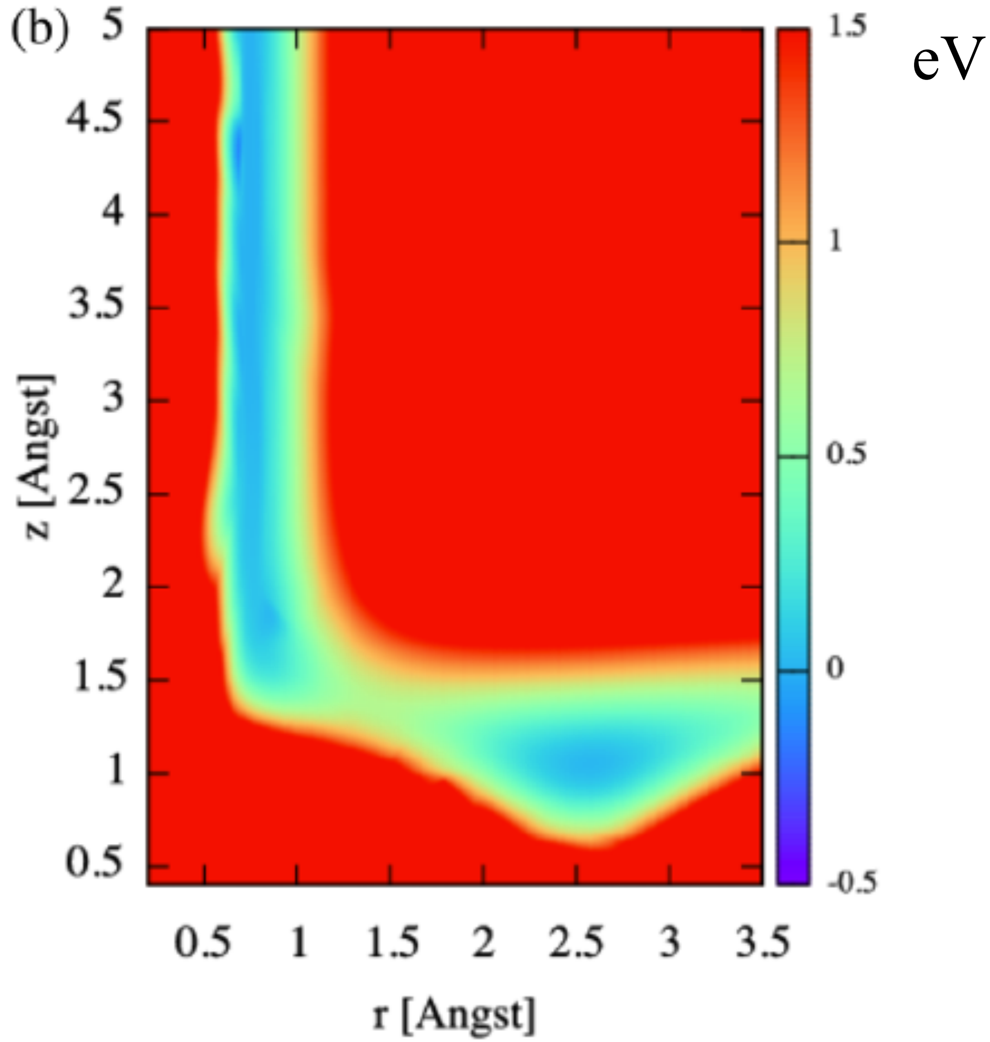
Cu_{22} cluster : MRCI+Q
or CCSD(T) or PBE

5 layers 3x3 Cu (100) surface: PBE



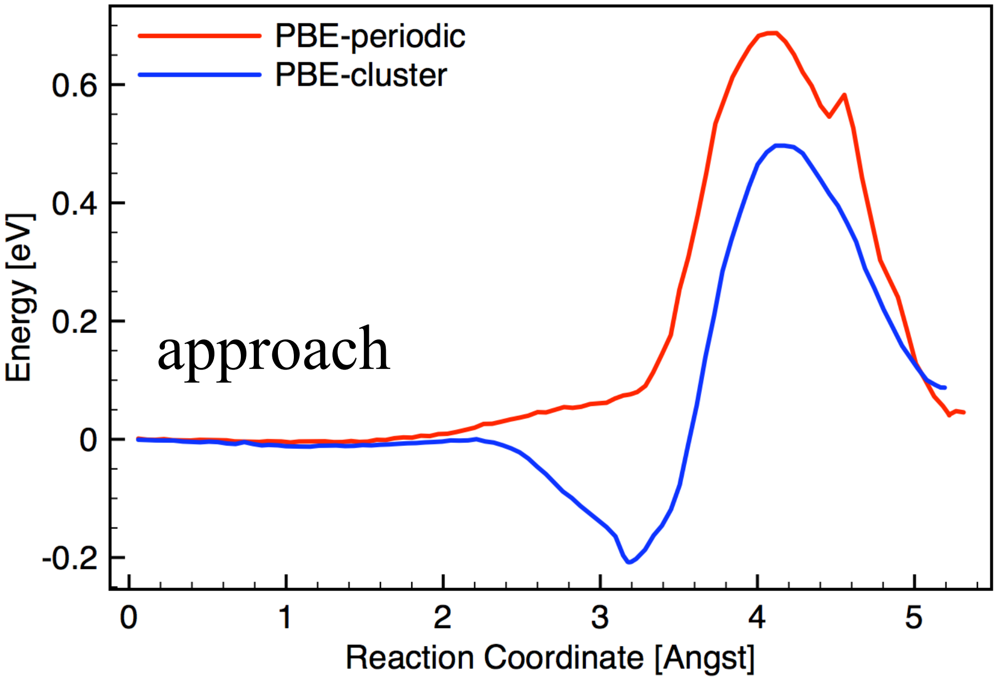
ONIOM type embedding

Potential energy surface



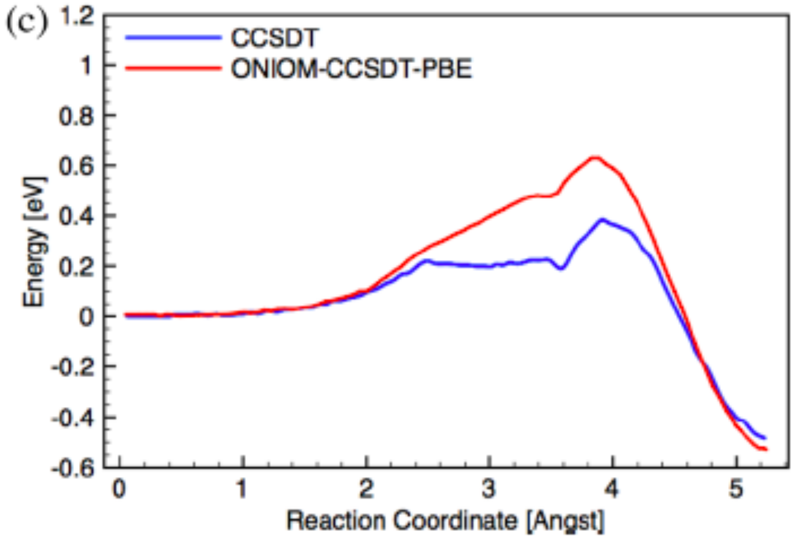
PBE/PBE

TS r=1.48 Å
Z=1.33 Å
E^{TS}=0.69 eV

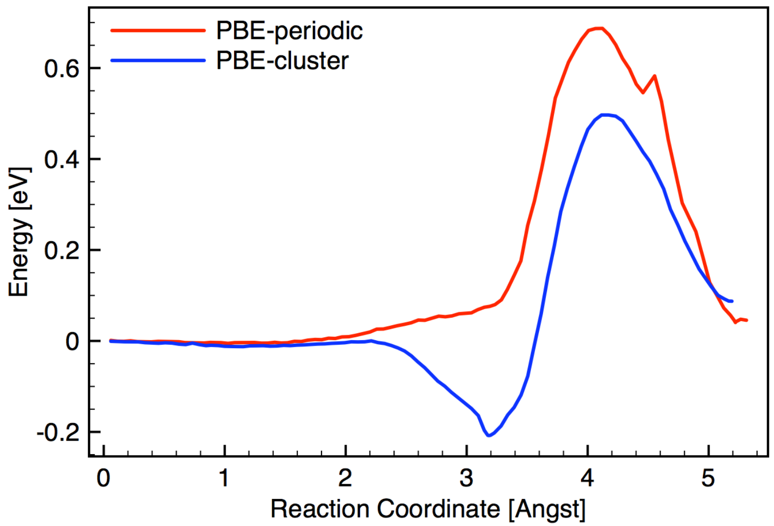


min r=2.49 Å
Z=1.01 Å

CCSD(T)/PBE

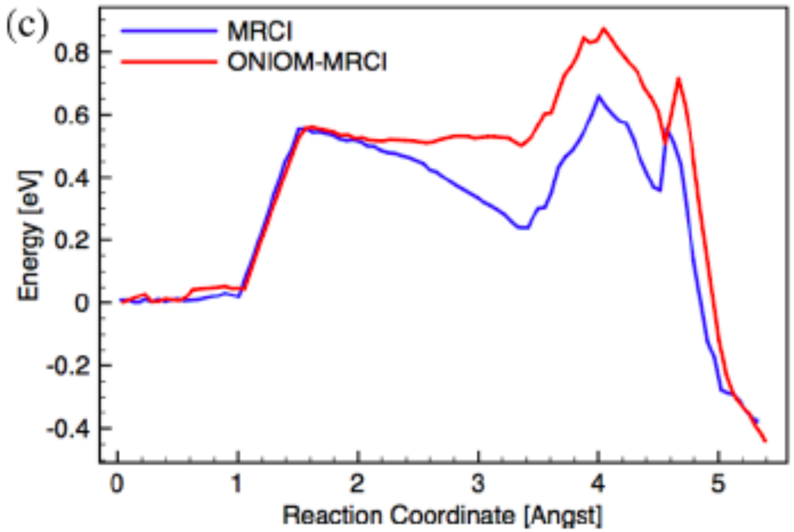


TS r=1.41 Å
Z=1.19 Å
E^{TS}=0.63 eV

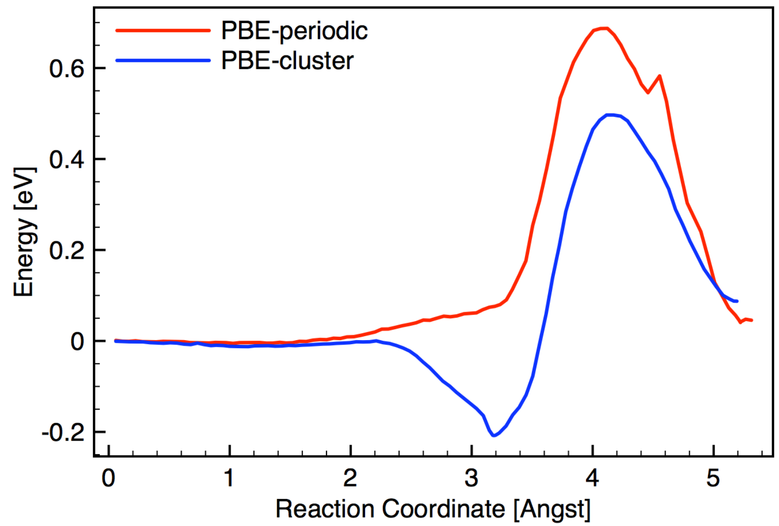


TS r=1.48 Å
Z=1.33 Å
E^{TS}=0.69 eV

MRCI+Q/PBE



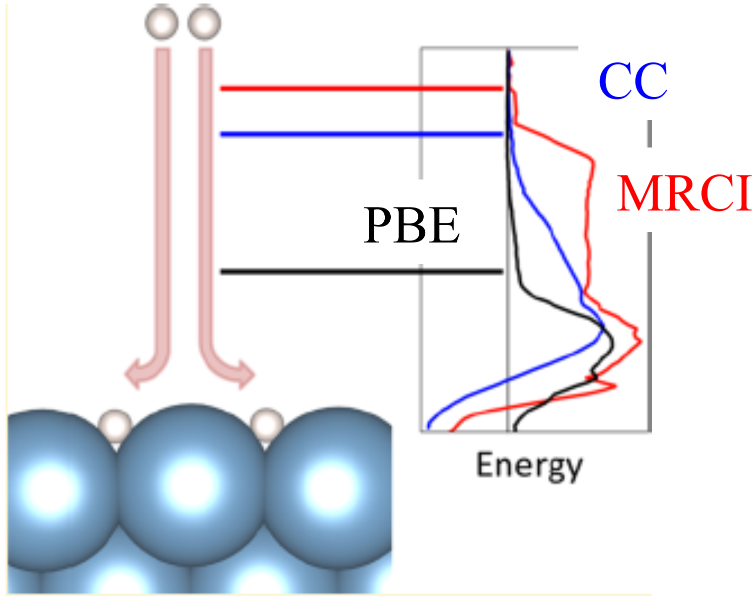
TS r=1.39 Å
Z=1.29 Å
E^{TS}=0.87 eV



TS r=1.48 Å
Z=1.33 Å
E^{TS}=0.69 eV

Diaz et al. SRP-DFT
E^{TS}=0.87 eV

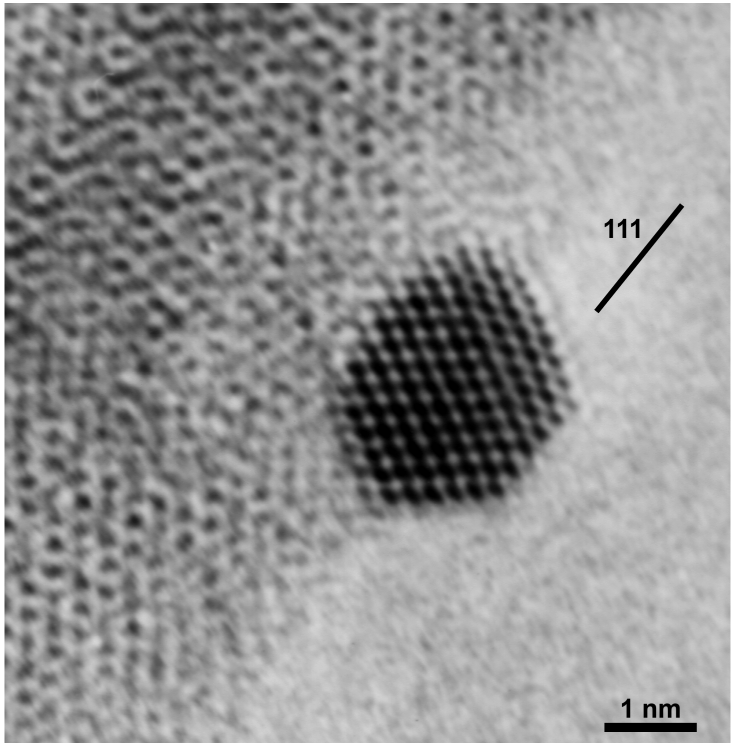
H_2 on Cu(100)



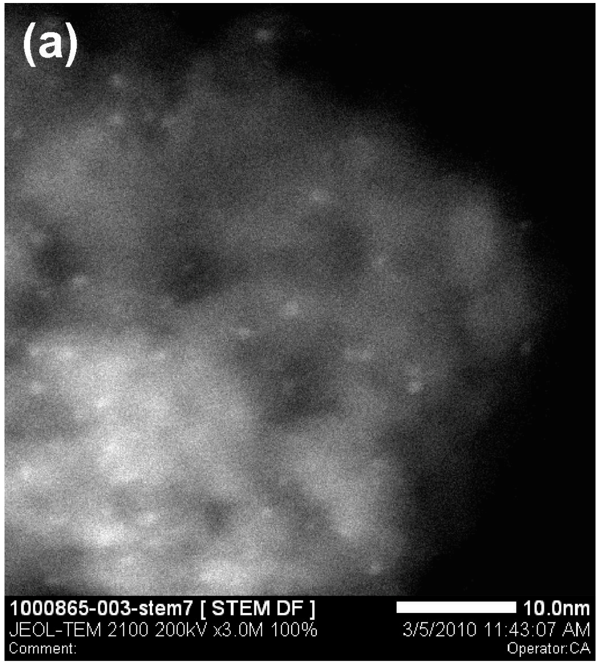
- Hybrid QM/QM' scheme
- Cluster energies need to be corrected
- Much broader barrier with explicitly correlated calculations
- Activation energy with MRCI+Q / PBE in excellent agreement with best estimate of experimental value
- DFT/PBE is (only) 0.18 eV away

F. Göltl, C. Houriez, M. Guitou, G. Chambaud and P. Sautet J. Phys. Chem. C. 118, 5374-5382 (2014)

Pt particles on γ-alumina



Particle size 0.6 – 1.1 nm

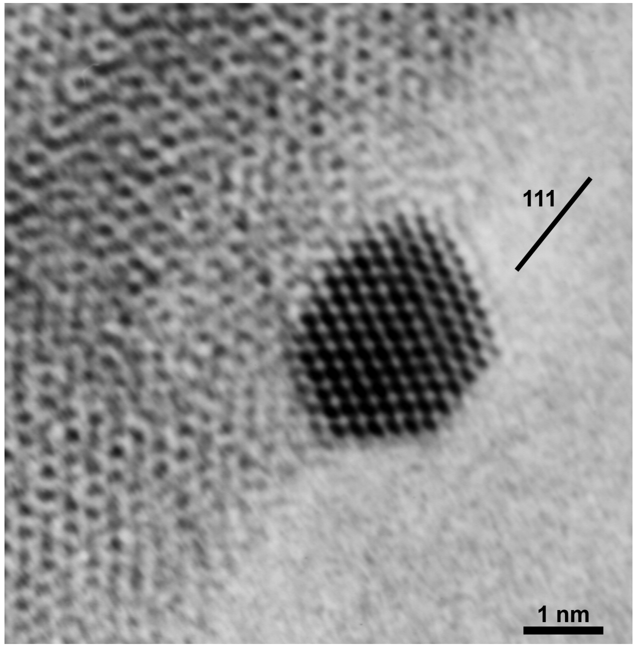


A. Jael et al, J. Catal. 272 (2010) 275

$Pt_{10} – Pt_{20}$

Supported particles: open questions

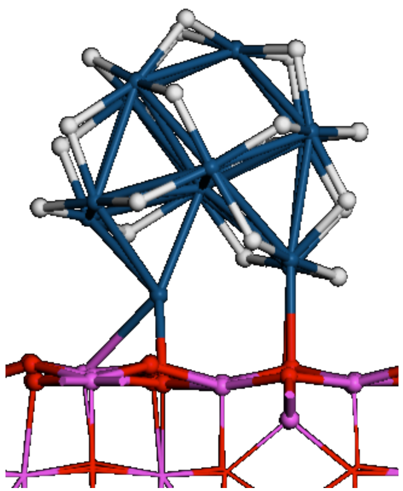
- Influence of size
- Shape, various sites
- Influence of support
  Electronic transfer
- Specific chemisorption properties
- Catalytic reactivity



Nano-particle of Pt on Alumina

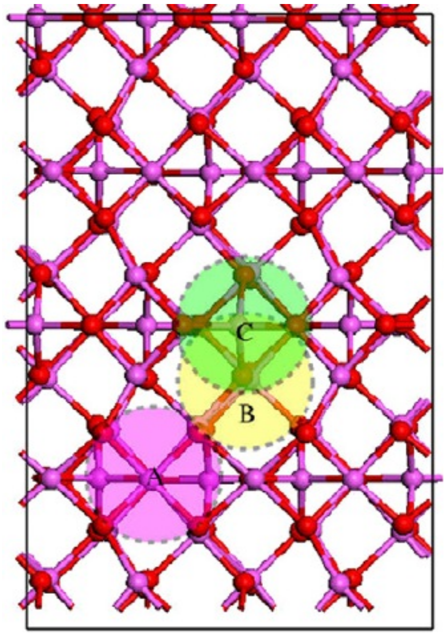
Theoretical Methods

- Catalyst: nanoparticle deposited on extended support
- Density functional theory
  GGA: Perdew-Wang 91 or PBE
- Structural exploration with MD
- Combination with thermodynamics



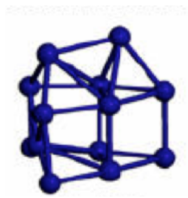
Pt_{13} particles on the γ-Al_2O_3 support

(100)



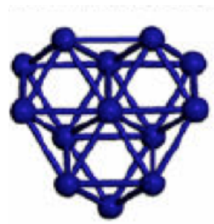
(100) is fully dehydrated

relevant Pt_{13} shapes

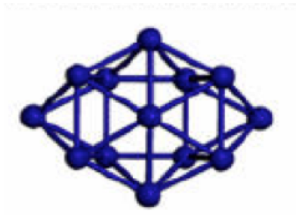


3D
0 $kJ.mol^{-1}$

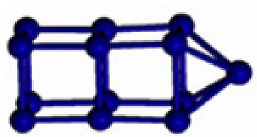
3D'
+12



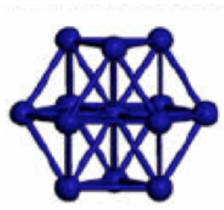
BP 7+6
+128



+150



+163



3
7
3

CUB
+322

In vacuum

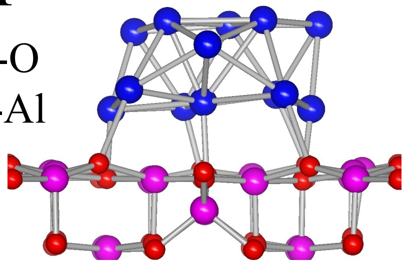
C-.H. Hu, C. Chizallet, ..., P. Sautet, H. Toulhoat, P. Raybaud, J. Catal. 274 (2010) 99

Pt_{13} particles on γ-Al_2O_3 (100)

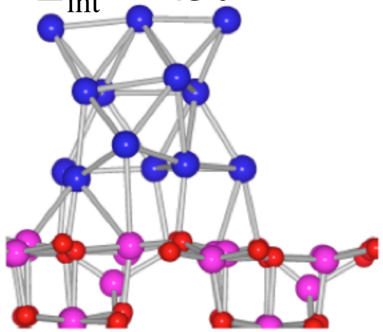
E = 0 kJ.mol^{-1}
(E_{gas} = +136)
E_{int} = -783

BP

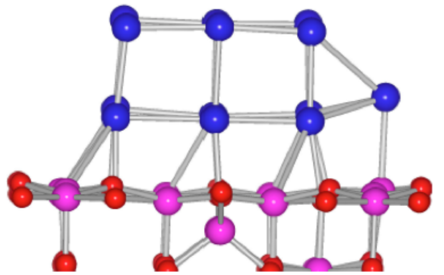
8 Pt-O
6 Pt-Al

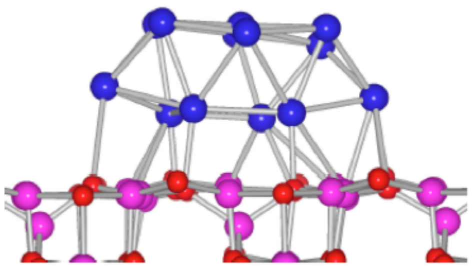


E = +25
(E_{gas} = +12)
E_{int} = -430

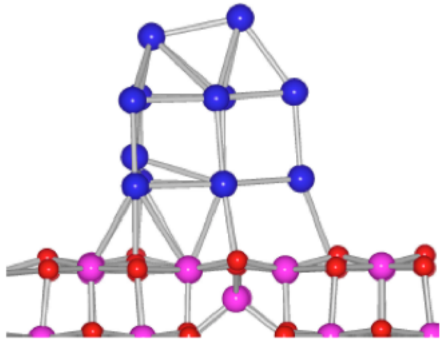


E = +26
(E_{gas} = +163)
E_{int} = -704

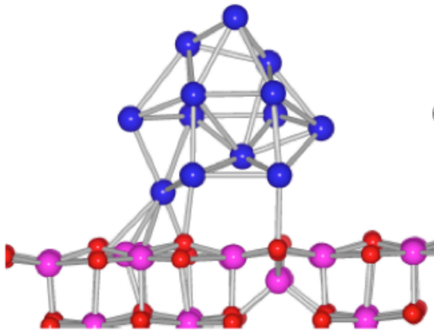




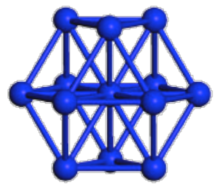
E = +62
(E_{gas} = +150)
E_{int} = -646



E = + 62
(E_{gas} = 0)
E_{int} = -300



E = +150
(E_{gas} = +322)
E_{int} = -331



CUB

Al O Pt

C-H. Hu, C. Chizallet, C. Mager-Maury, M. Corral-Valero, P. Sautet, H. Toulhoat and P. Raybaud, **Journal of Catalysis** 274, 99-110 (2010)

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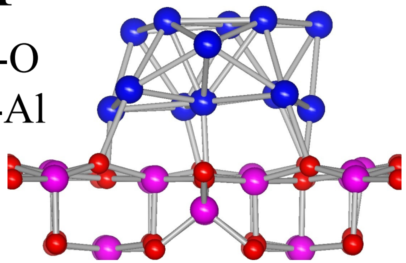

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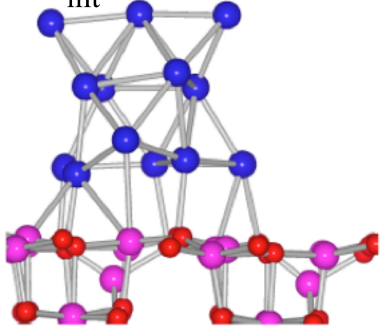

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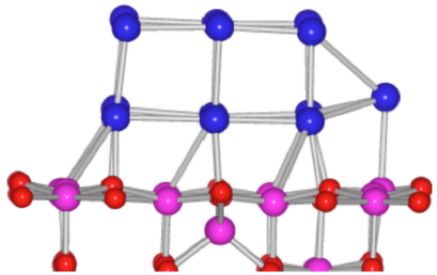

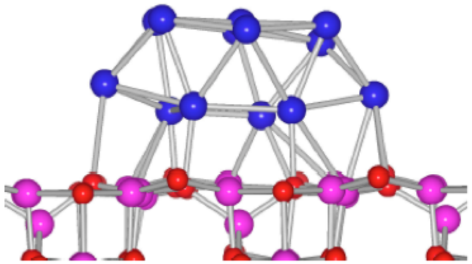

$E = +62$
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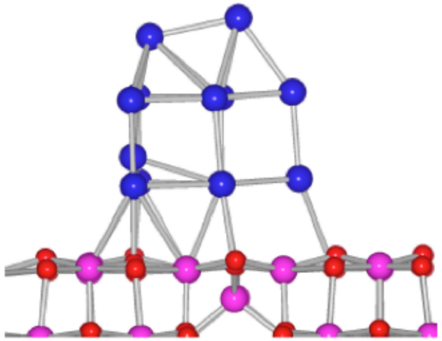
$E_{int} = -646$



$E = +62$
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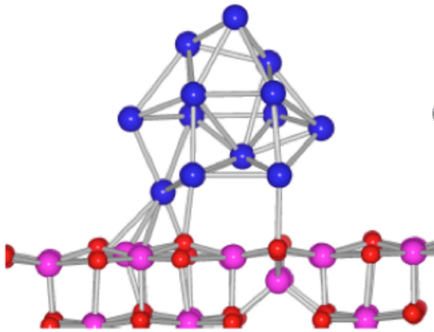
$E_{int} = -300$



$E = +150$
($E_{gas} = +322$)
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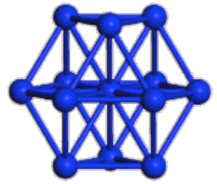

CUB

Al O Pt

C-H. Hu, C. Chizallet, C. Mager-Maury, M. Corral-Valero, P. Sautet, H. Toulhoat and P. Raybaud, **Journal of Catalysis** 274, 99-110 (2010)

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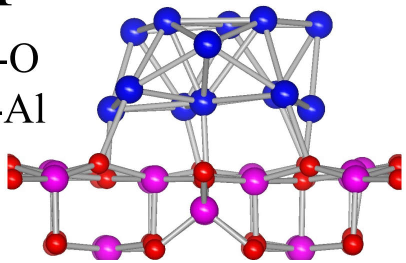

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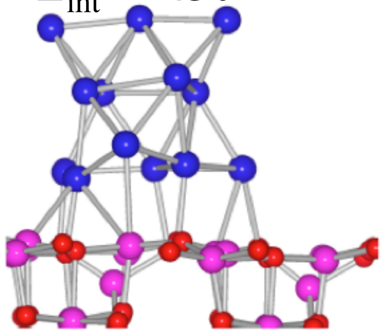

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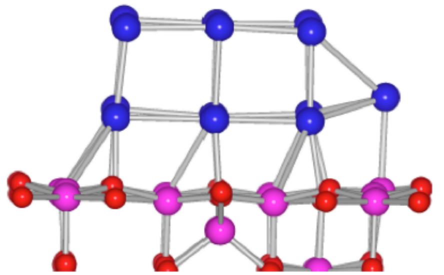

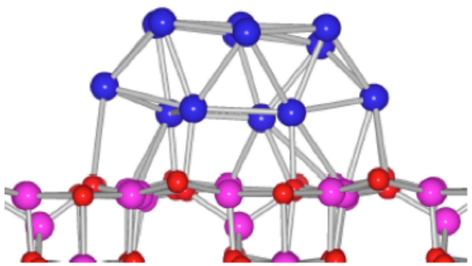

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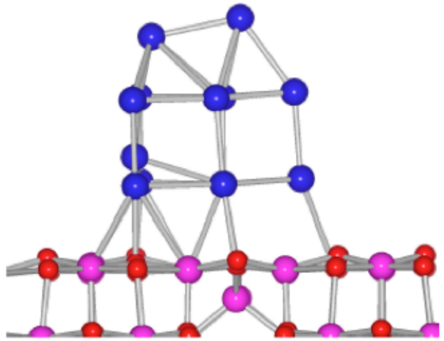

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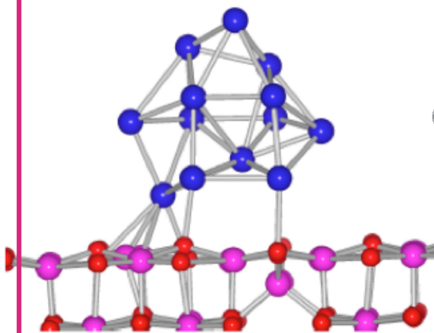

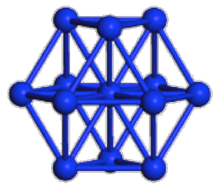

CUB

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Al O Pt

C-H. Hu, C. Chizallet, C. Mager-Maury, M. Corral-Valero, P. Sautet, H. Toulhoat and P. Raybaud, **Journal of Catalysis** 274, 99-110 (2010)

Modeling catalysis under operando conditions

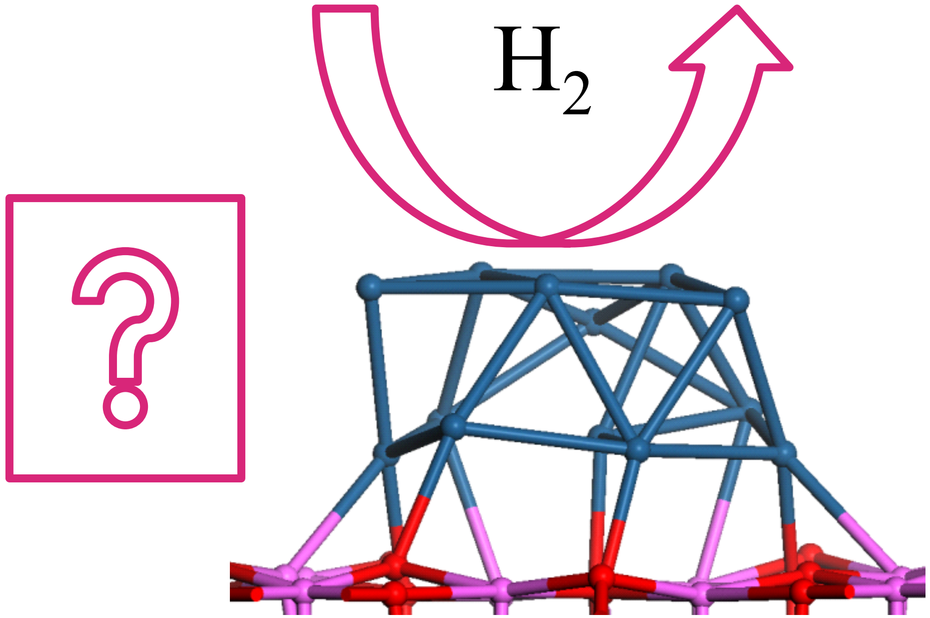
Realistic
Relevant
Insight

Conditions: T, P, rate, flow, liquid

Model: catalyst nature and geometry: slab, supported cluster
Kinetic model, KMC lattice
Reactor model

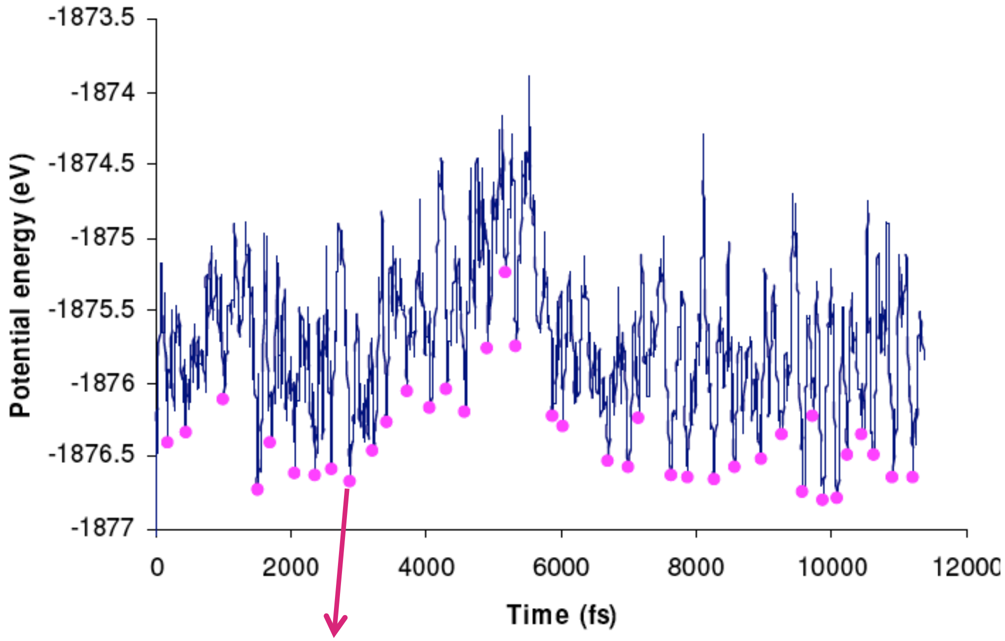
T, P : structure of catalyst in situ (Ab initio atomistic thermodynamics)
Relation with experimental characterisation

Pt_{13} on γ-Al_2O_3 under a pressure of H_2

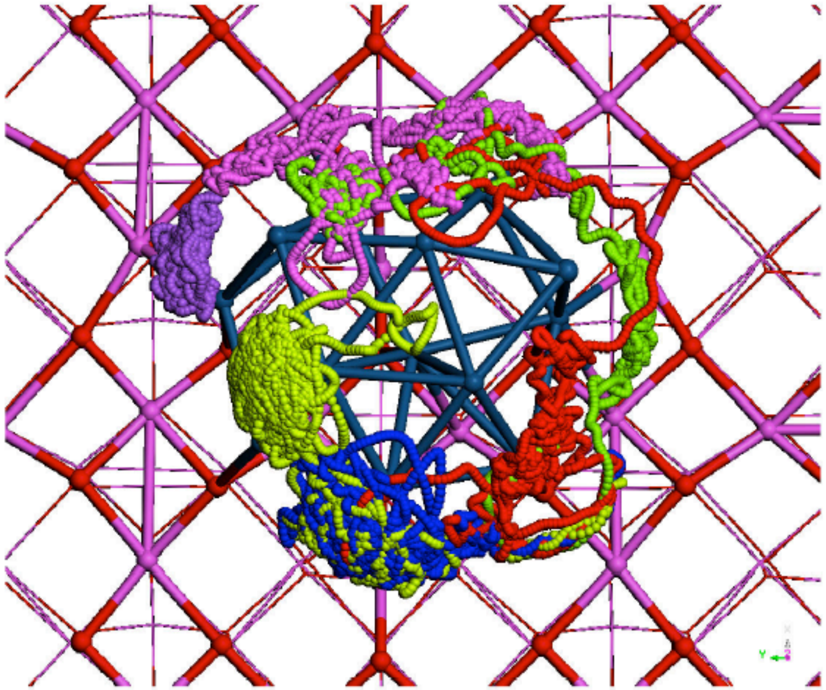


Number of H atoms as a function of (P, T) ?

Pt_{13} + 6 H on γ-Al_2O_3 (100)



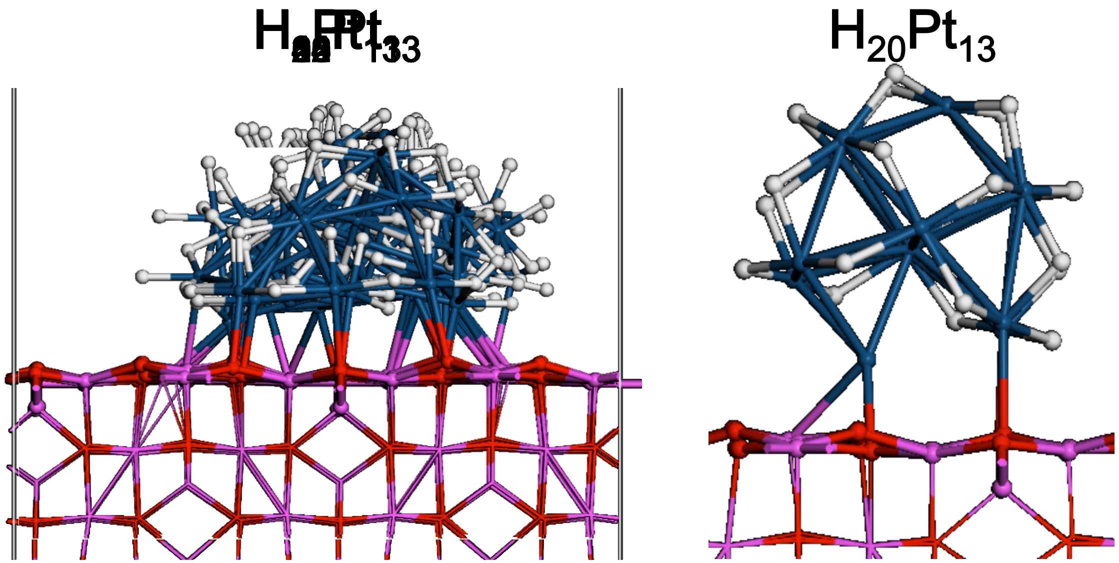
Subsequent complete optimisation



Velocity scaled MD, 1200 K, 12 ps, m_H=10
Pt_{13} and alumina frozen

C. Mager-Maury, C. Chizallet, P. Sautet, P. Raybaud ChemCatChem 3 (2011) 200

Hydrogen adsorption: Pt_{13}/(100) $\gamma-Al_2O_3$



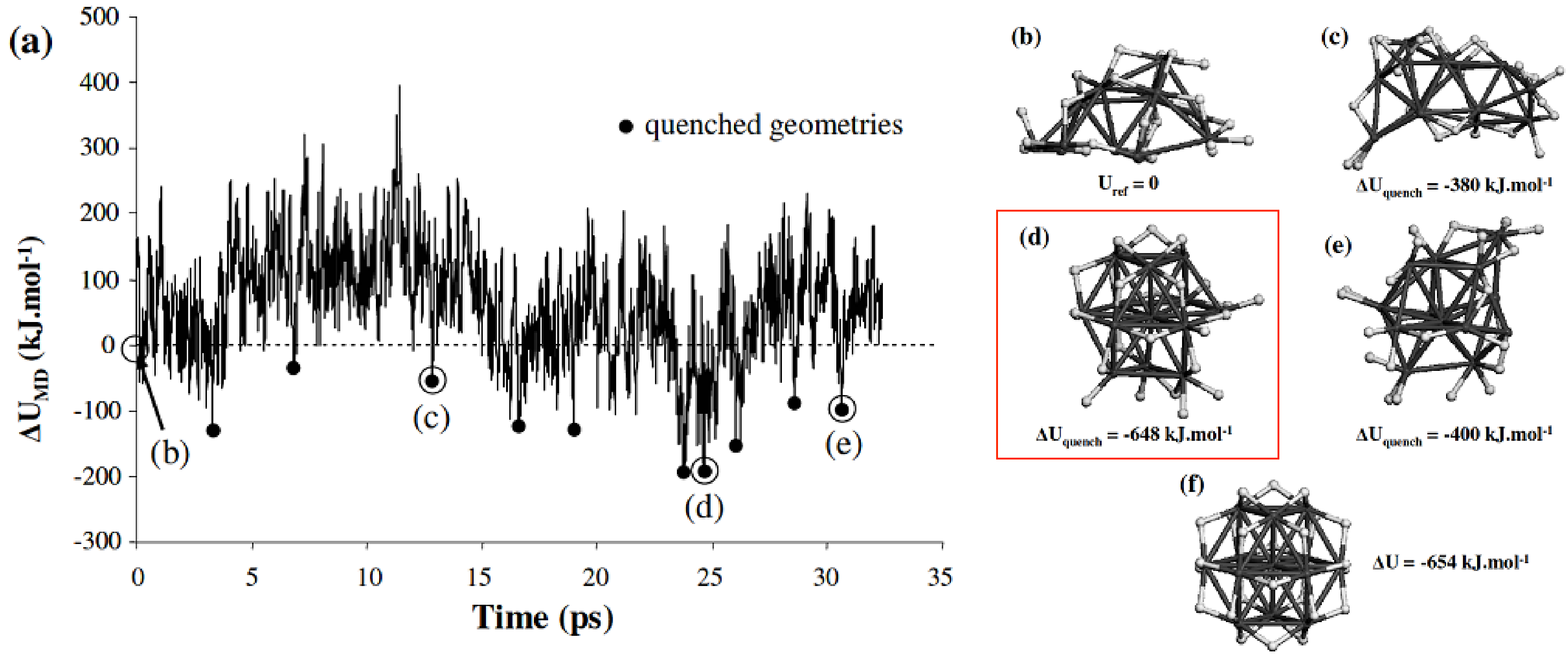
Strong structural deformation of the Pt_{13} cluster
Weakening of the metal support interaction

⇒ Change of the morphology under reductive environment
⇒ Cuboctahedron is stabilized at high p(H_2)

C. Mager-Maury, C. Chizallet, P. Sautet, P. Raybaud ChemCatChem 3 (2011) 200

Hydrogen adsorption: structural reconstruction

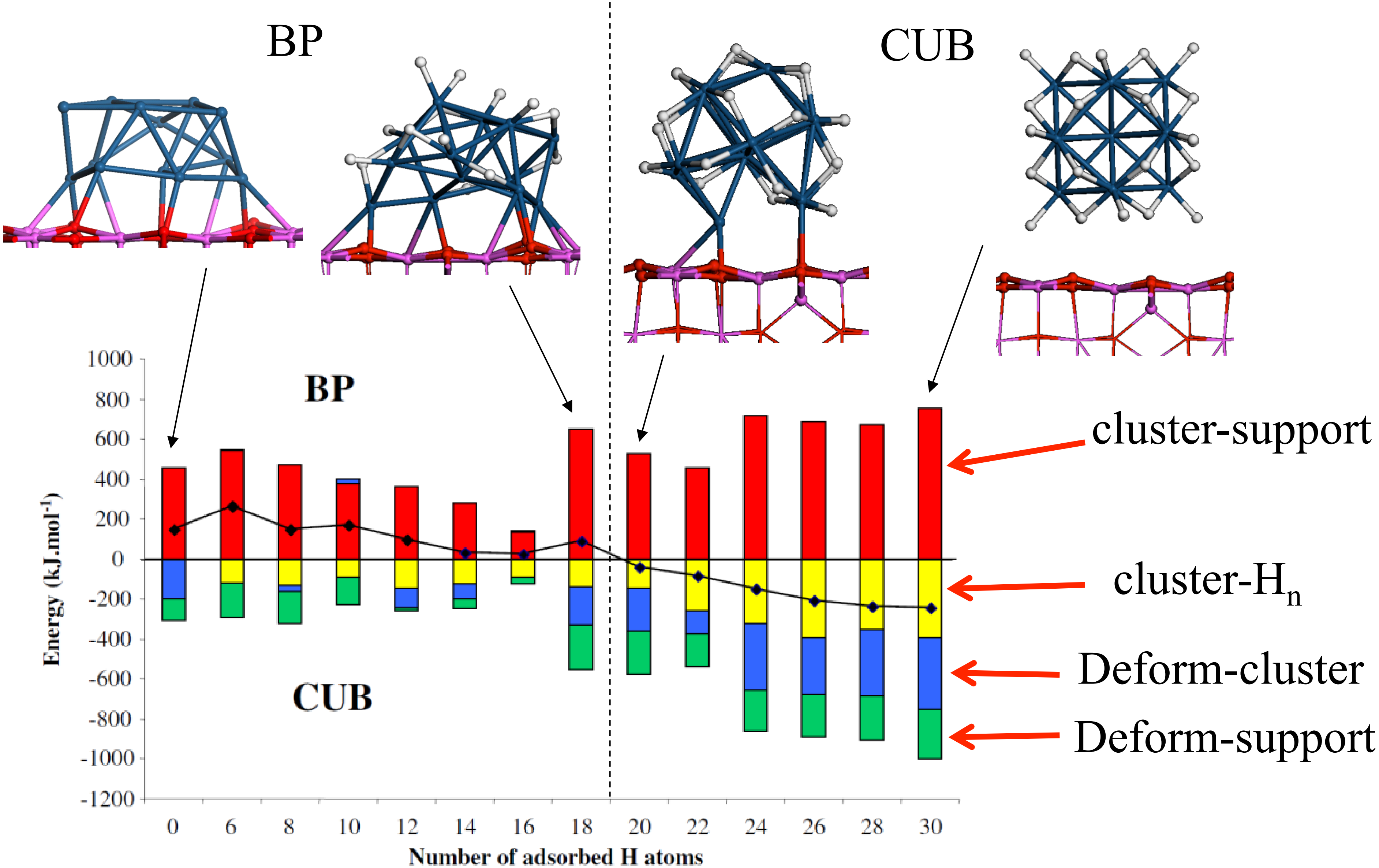
Gas phase molecular dynamic at n(H)=24



From BP to CUB transformation

C. Mager-Maury, C. Chizallet, P. Sautet, P. Raybaud ChemCatChem 3 (2011) 200

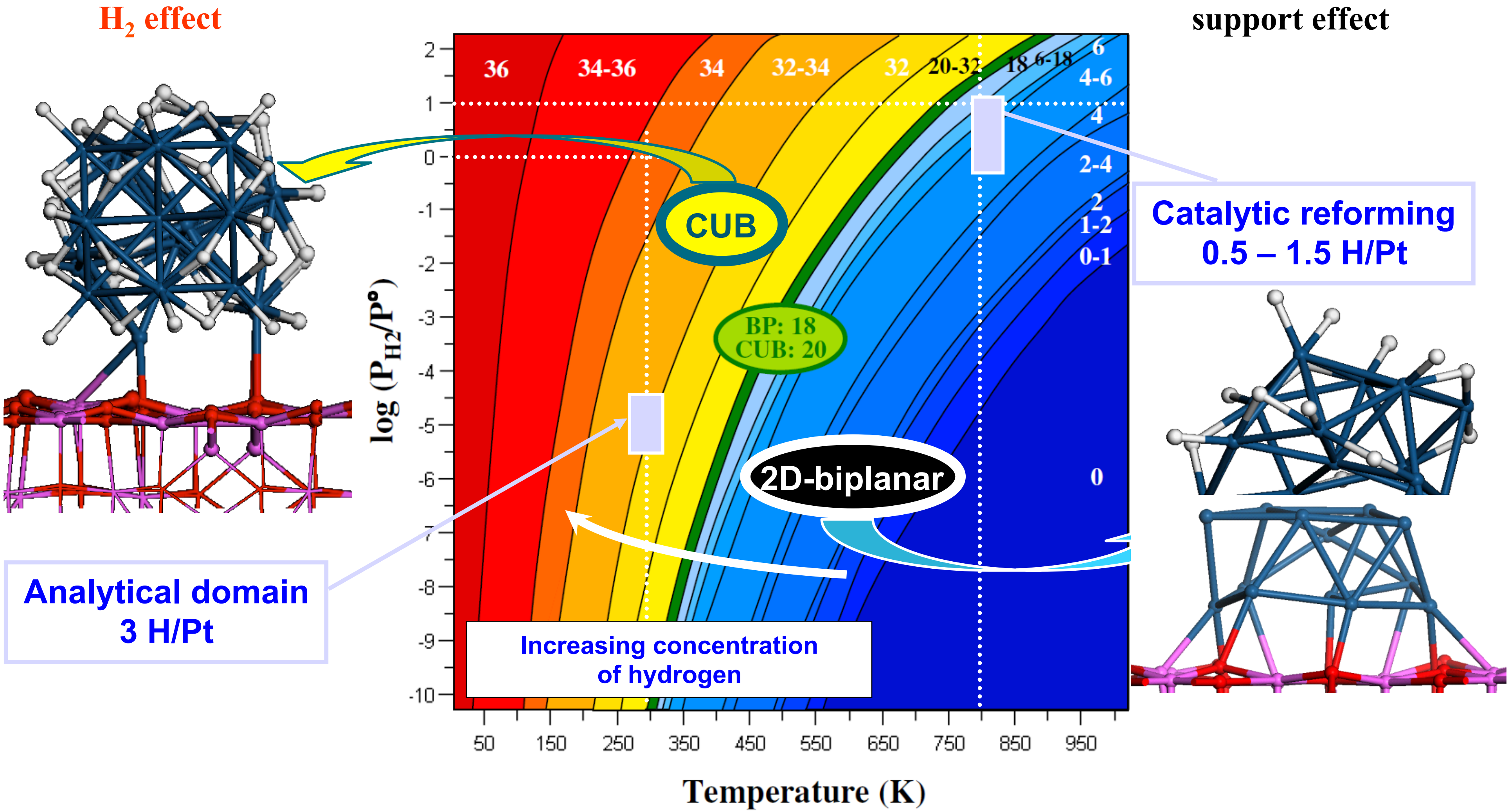
Effect of Hydrogen: structural reconstruction



C. Mager-Maury, C. Chizallet, P. Sautet, P. Raybaud ChemCatChem 3 (2011) 200

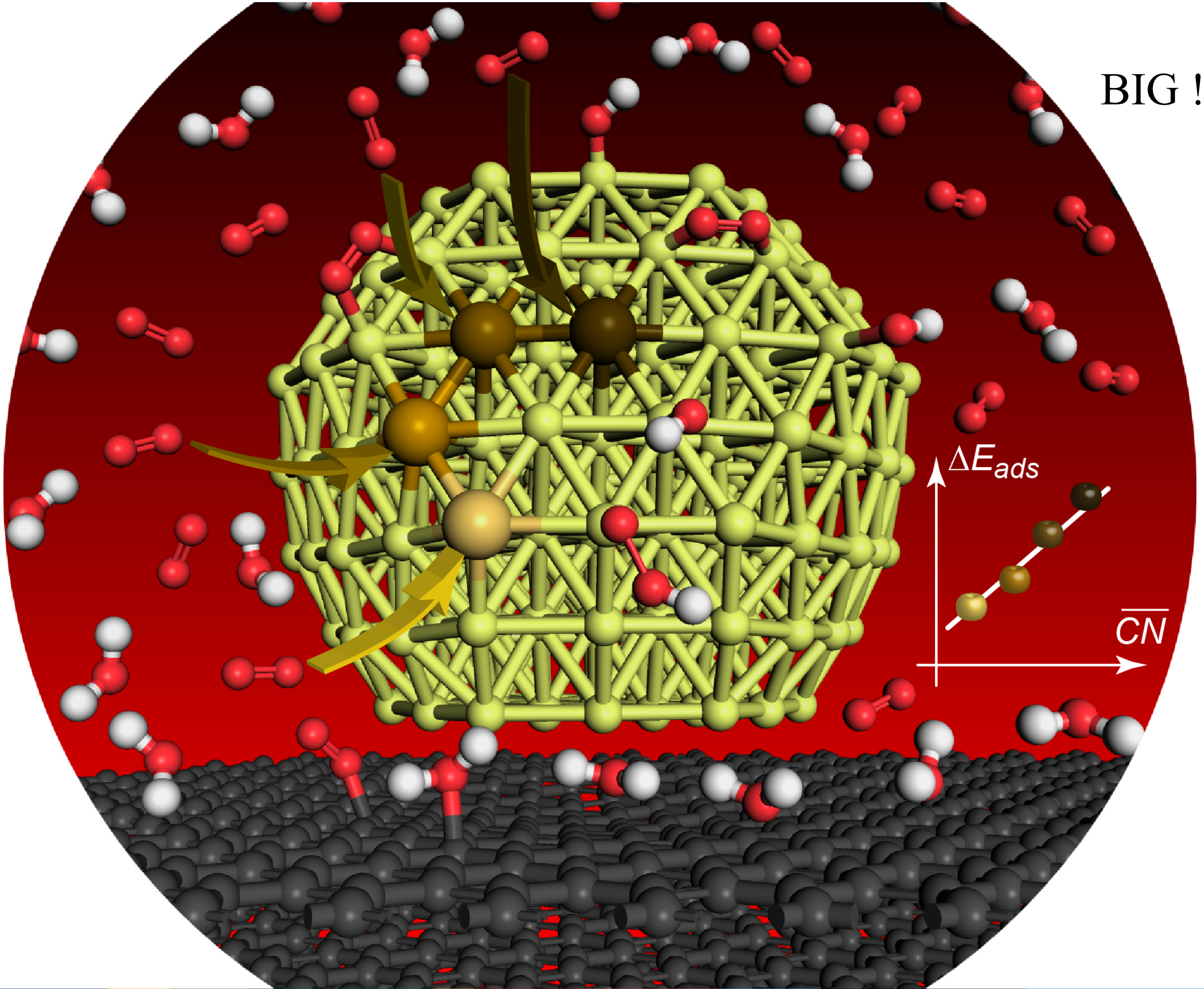
Influence of H_2 on the structural properties of $Pt_{13}/\gamma\text{-}Al_2O_3\text{-}(100)$

Phase diagram of $Pt_{13}\text{-}H_n/(100)\ Al_2O_3$ as a function of T and P



C. Mager-Maury, C. Chizallet, P. Sautet, P.Raybaud ChemCatChem 3 (2011) 200

BIG !



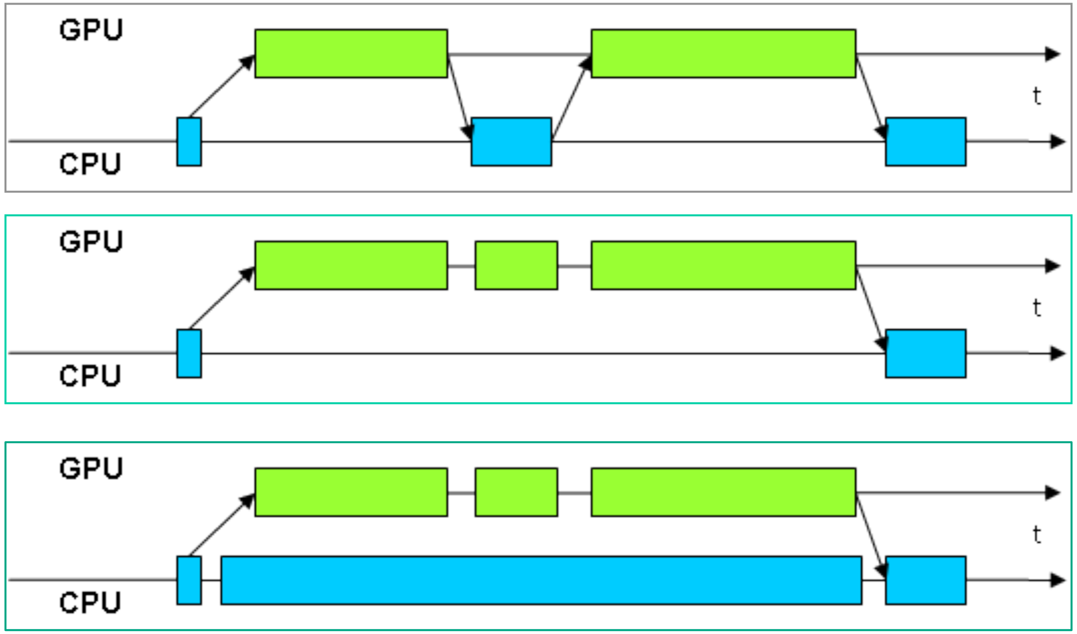
Porting VASP to GPU

- First step
  - FFTW -> CUFFT
  - BLAS -> CUBLAS
- Second step: minimizing data transfer time
  - By computing in parallel with CPU
  - By porting functions called between GPU calls

BAD !

Good

Better



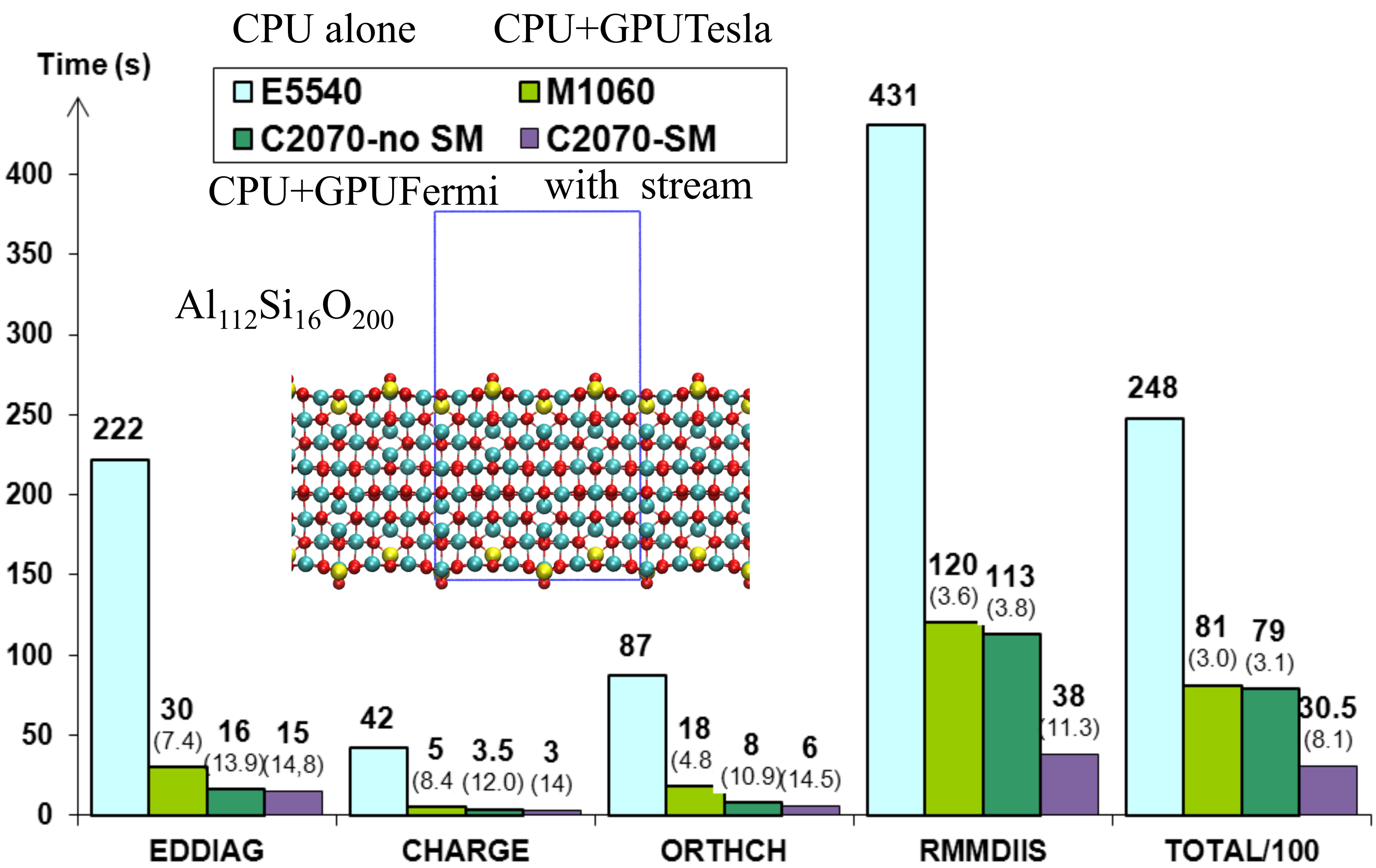
Porting VASP to GPU

- First step
  - FFTW -> CUFFT
  - BLAS -> CUBLAS
- Second step: minimizing data transfer time
  - By computing in parallel with CPU
  - By porting functions called between GPU calls
- Third step: specific optimizations
  - EDDAV
  - EDDIAG and RMMDIIS
  - POTLOK, ORTHCH and CHARGE

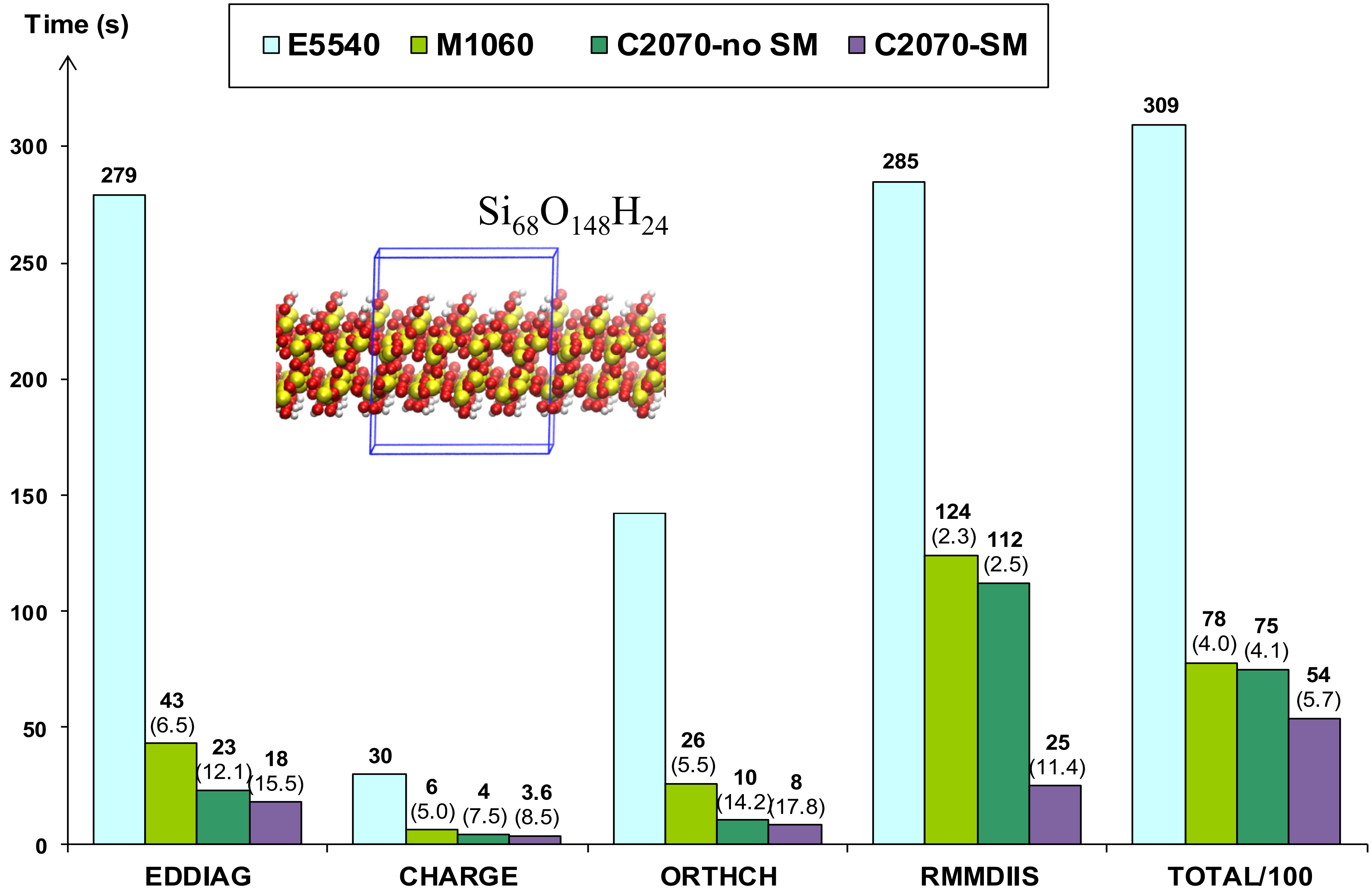
  $\Rightarrow$ Take home: Fill the GPU as much as possible using “streams”

Hacene, M.; Anciaux-Sedrakian, A.; Rozanska, X.; Klahr, D.; Guignon T.; Fleurat-Lessard, P. J. Comput. Chem. (2012)

Some results



Some results



Conclusion/Perspectives

- On penultimate generation of GPUs (Fermi):
  - No loss in scalability
  - Acceleration between 5.7 and 8.0
- Project with G. Kresse and Nvidia (Leader P. Fleurat-Lessard)
  - Merging our code with GPU exact exchange (M. Hutchinson, M. Widom)
  - Going to VASP 5.3, CUDA 5. to use fully the latest GPUs (K20)
  - Porting post-HF: MP2 and RPA

Hacene, M.; Anciaux-Sedrakian, A.; Rozanska, X.; Klahr, D.; Guignon T.; Fleurat-Lessard, P. J. Comput. Chem. (2012)

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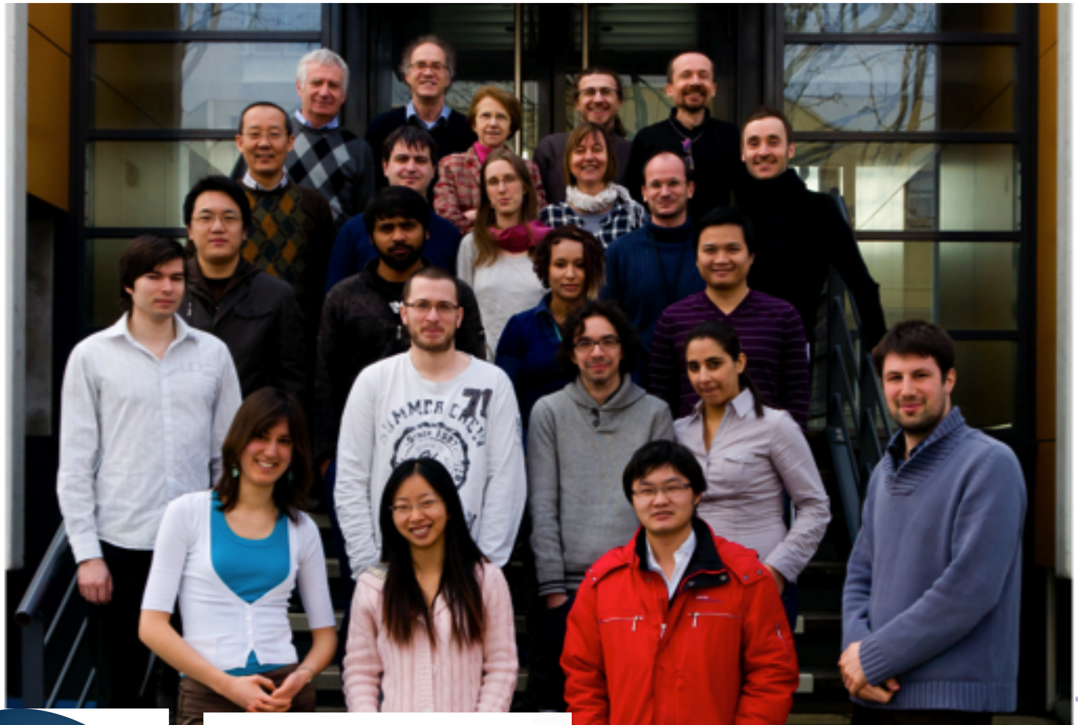
IFPEN: P. Raybaud, C. Chizallet, M. Digne

Marne-La-Vallée: G. Chambaud, M. Guitou



Région Rhône-Alpes

FLMSN