Non-reactive interaction of molecules with a surface: periodic or cluster approach?

Marie GUITOU

Laboratoire MSME, Theoretical Chemistry

Université Paris-Est Marne-la-Vallée, France

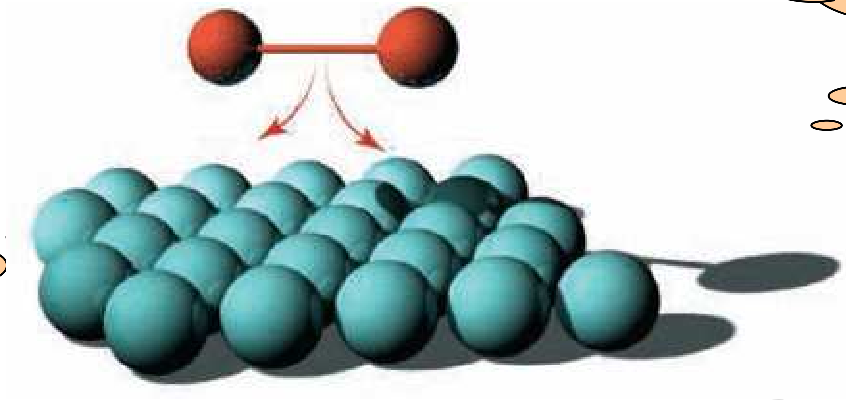
St Petersburg – 16/09/2013

Molecule – surface interactions

Surface
catalysis

Molecule/Surface

reaction

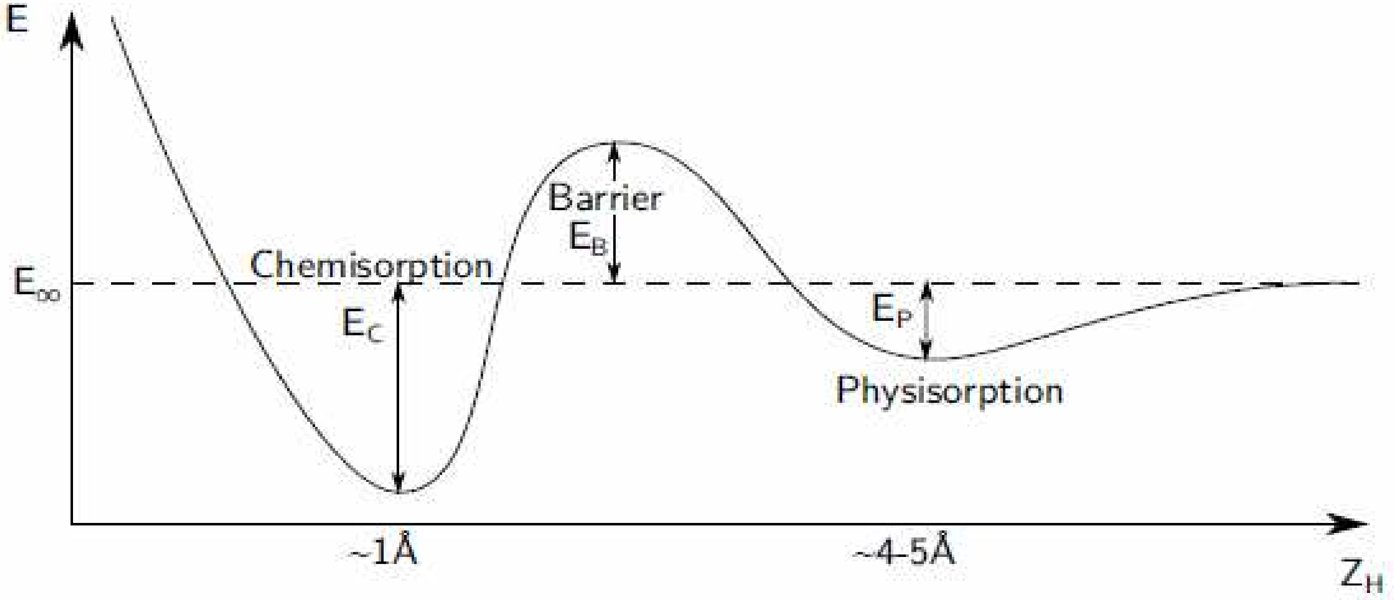


storage
in solid

Astrophysics :
gas/solid interaction

Spectroscopy

Several interaction domains



H$_2$-metal interactions

For Cu: $E_C < E_\infty$

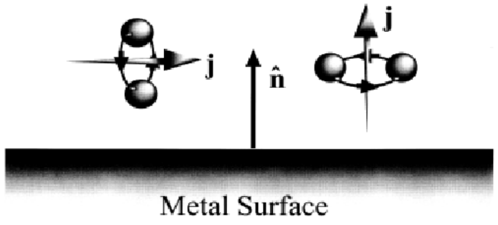
(for Ag: $E_C > E_\infty$)

$E_P \sim$ meV

$E_C, E_B \sim$ eV

Several steps in the interaction process

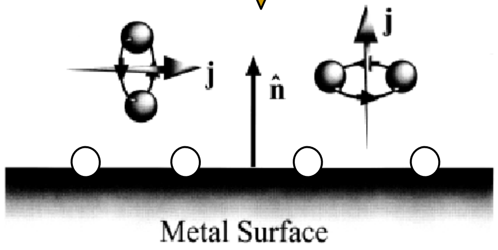
I



Physisorption

Dissociation

II

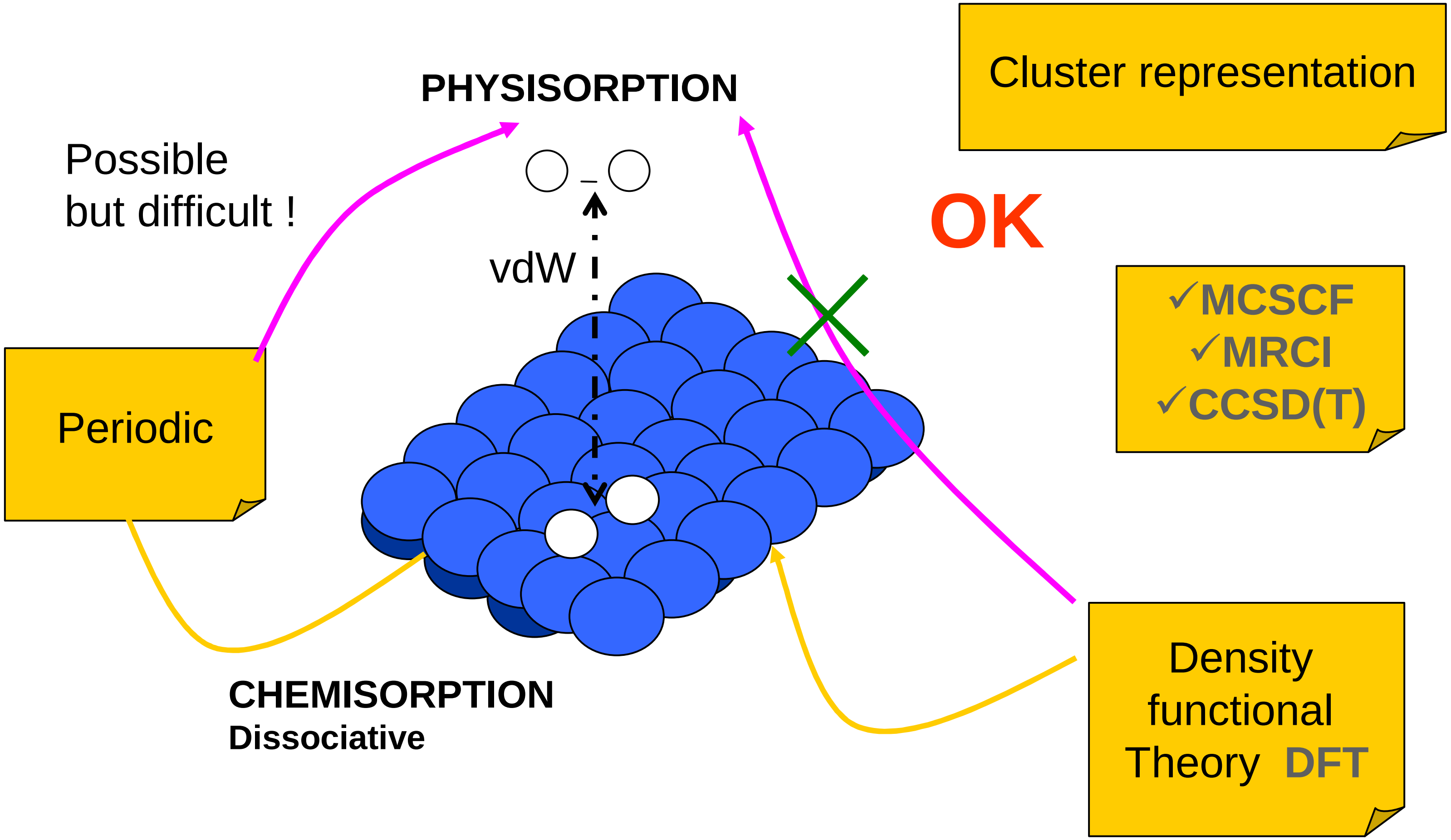


Physisorption of further molecules

III

Interaction energy of further layers

Choice of the computational method



PHYSISORPTION

Cluster representation

Possible
but difficult !

OK

vdW

✓MCSCF
✓MRCI
✓CCSD(T)

Periodic

CHEMISORPTION
Dissociative

Density
functional
Theory **DFT**

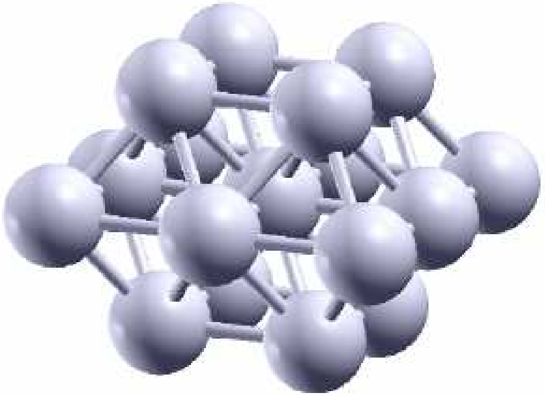
Some aspects of the periodic (Slab) model for the physisorption

The generally used method is DFT with various functionnals among which : PBE, PBEsol (especially adapted to solids),
+ eventually Grimme correction for long range interactions.

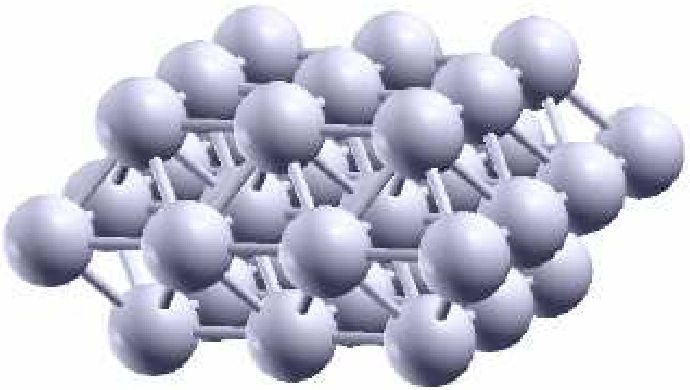
Different choices for the electronic calculation:
- Plane waves for the electron description – code VASP
- Localized atomic orbitals for the electrons – code CRYSTAL, this is preferred for molecular processus.

Appropriate choice of the unit cells for the periodic representation

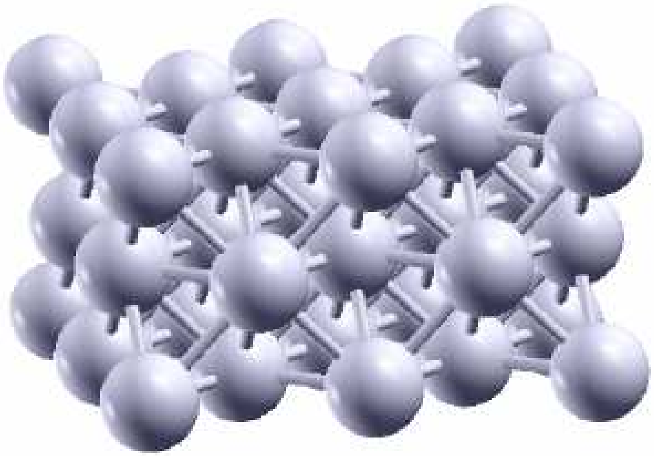
Periodic – Slab model of the surface



Cell 1



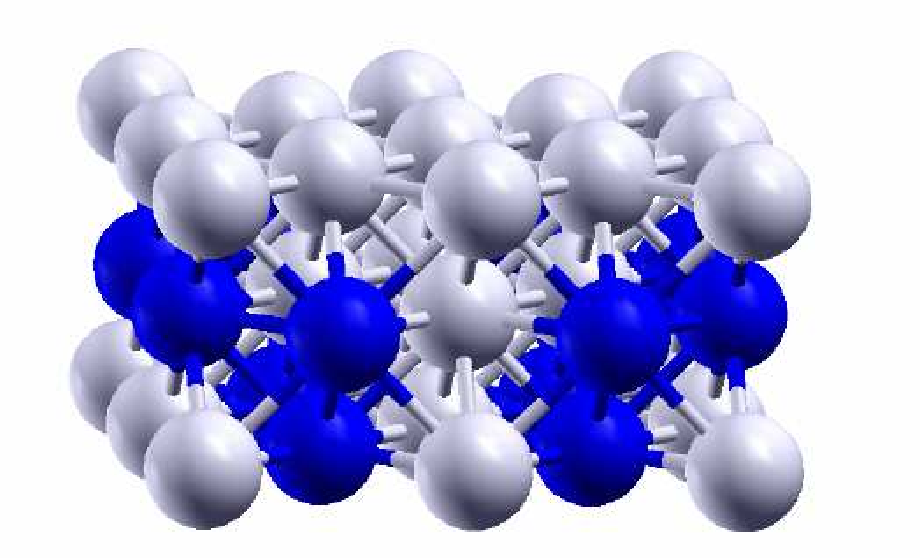
Cell 2

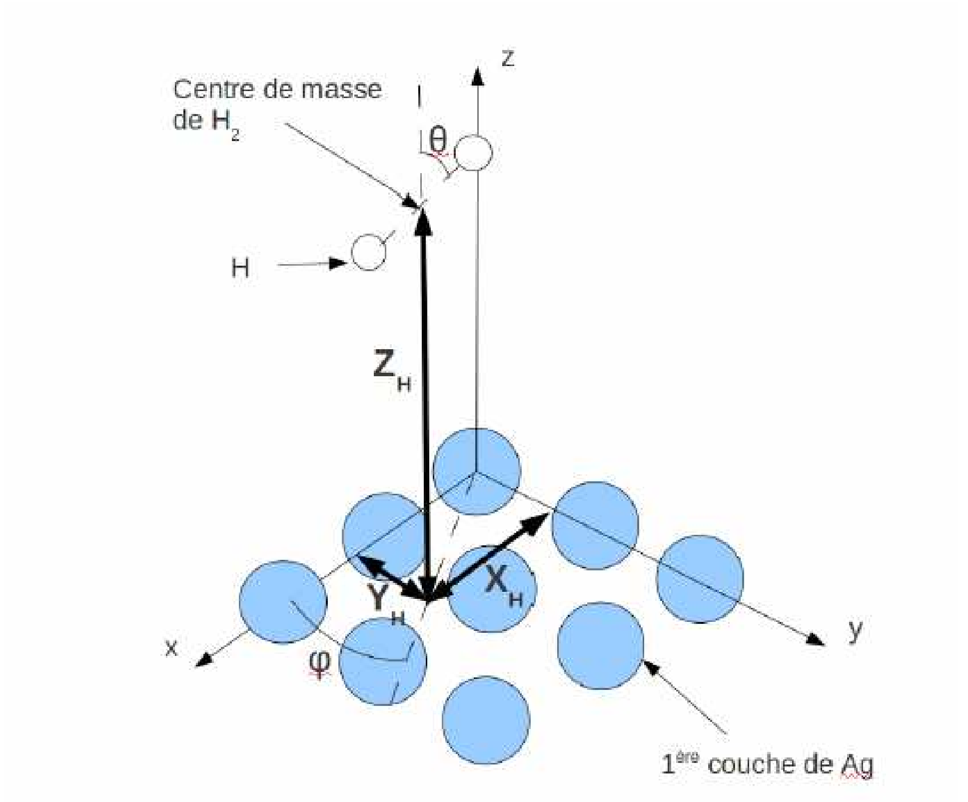


Cell 3

Definition of the unit cells for the periodic representation:
different sizes of cell and 3 layers for the Slab

Details of the periodic calculation (cell 3)





Cu/Ag $(n\text{-}1)s^2(n\text{-}1)p^6(n\text{-}1)d^{10}ns^1$

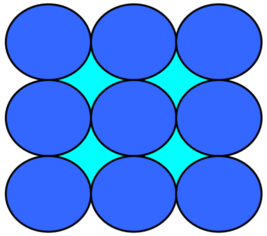
-Grey atoms : all electrons calculation
-Blue atoms : pseudopotentiel with 19 explicit electrons

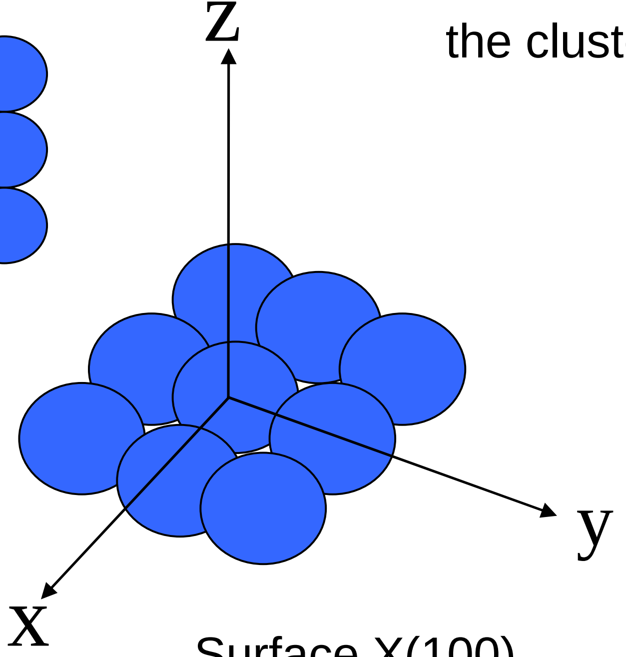
VASP or CRYSTAL

Coordinate system (X,Y,Z,θ,φ),
Including lateral displacements
$d_{H\text{-}H}$ is fixed

A cluster to model the surface (constraints)

Main concerns :
Size - big enough cluster to be representative
Limit the border effects - consider the central part of the cluster


(9,4,9)



Surface X(100)

Representation of the metallic (100) surface by a cluster composed of 22 atoms in 3 layers (9,4,9)

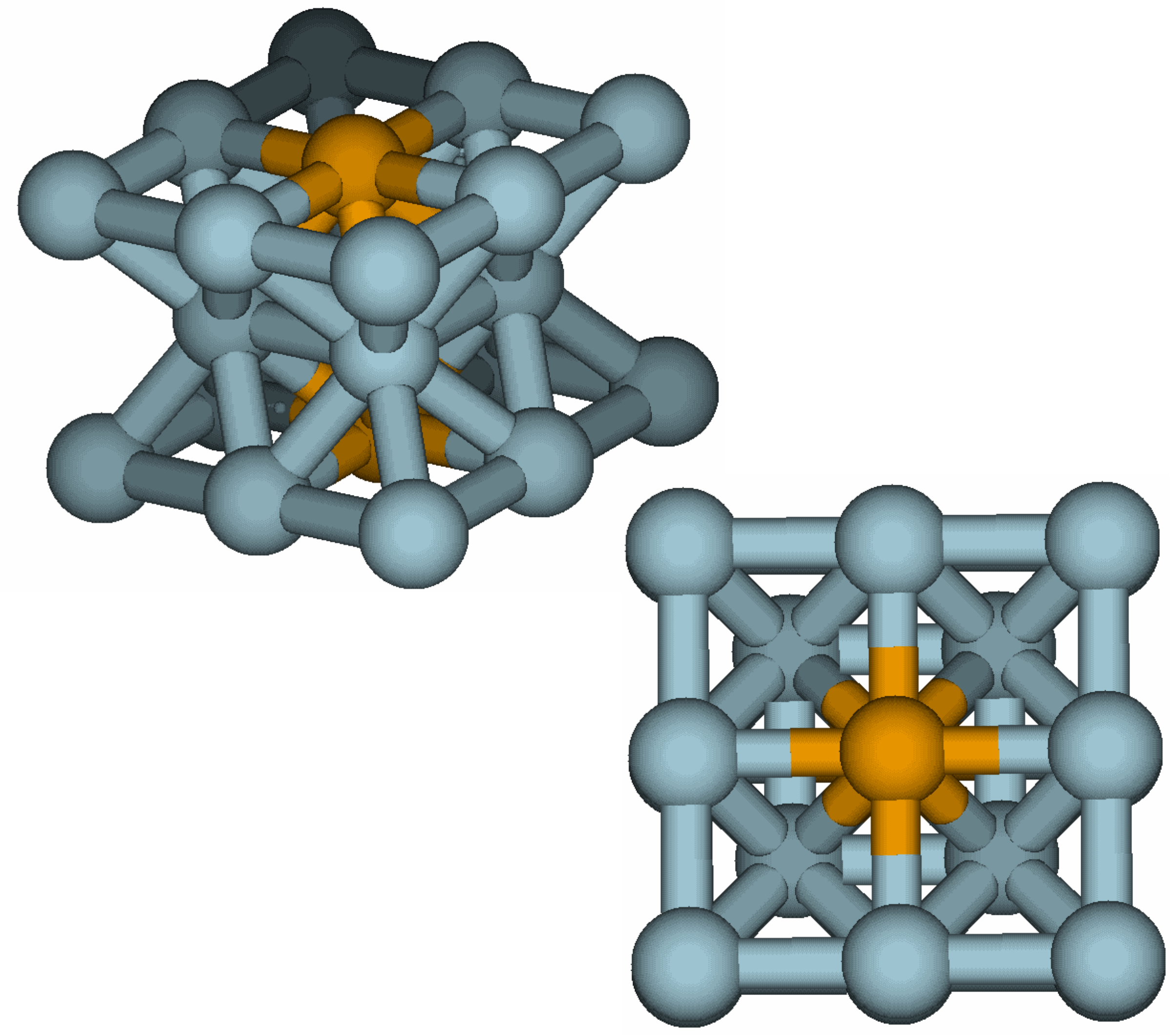
Advantage: Z- symmetry
no artificial polarisation (μ_z=0)

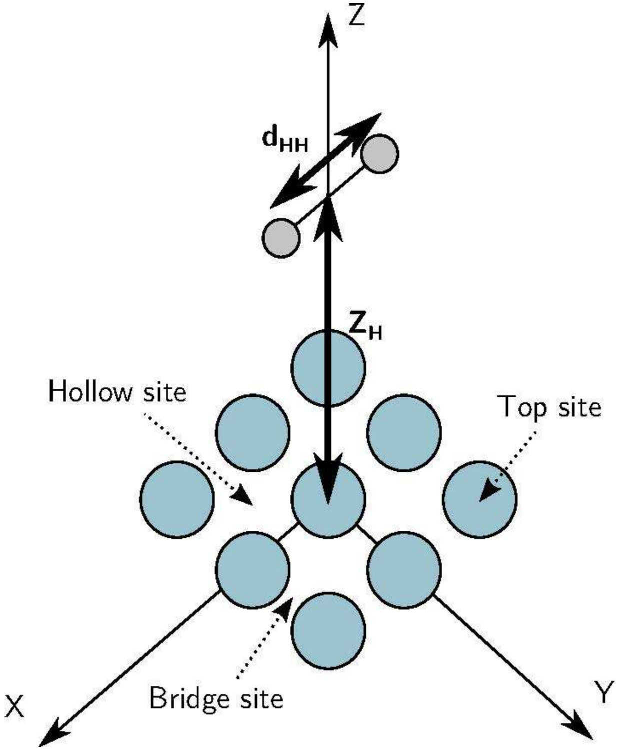
Cu/Ag $(n-1)s^2(n-1)p^6(n-1)d^{10}ns^1$

● Pseudopotentiel with 19 explicit electrons for the central atoms

● Pseudopotentiels with 1 explicit electron for the outer atoms

Cluster Cu_{22}/Ag_{22} and H_2



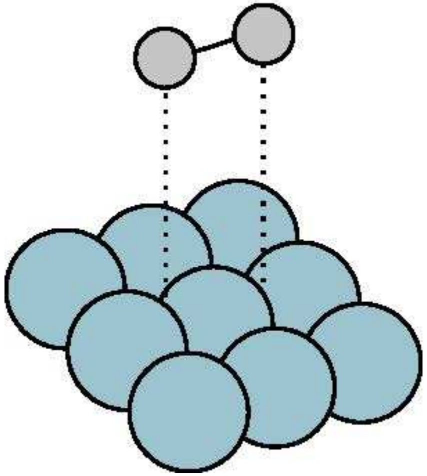


Coordinate system, (Z,θ,φ), no lateral displacement, $d_{H\text{-}H}$ is fixed

Several investigated geometries

Parallel approaches

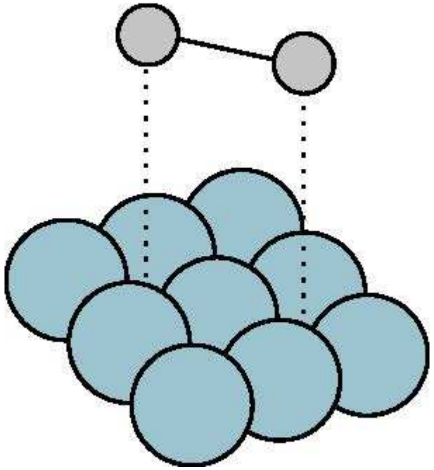
Perpendicular approach



H_2 in **btb**

Bridge-top-bridge

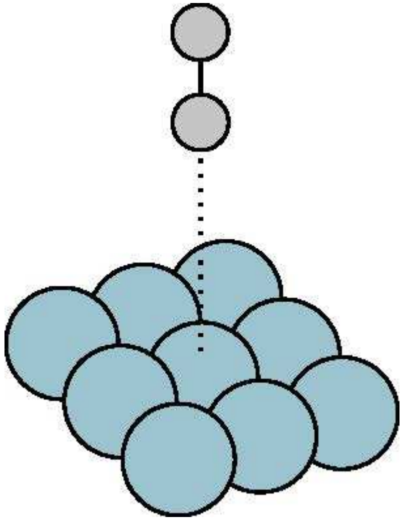
θ =90° Φ =0°



H_2 in **hth**

hollow-top-hollow

θ =90° Φ =45°



H_2 in **top**

θ =0° Φ =0°

Physisorption

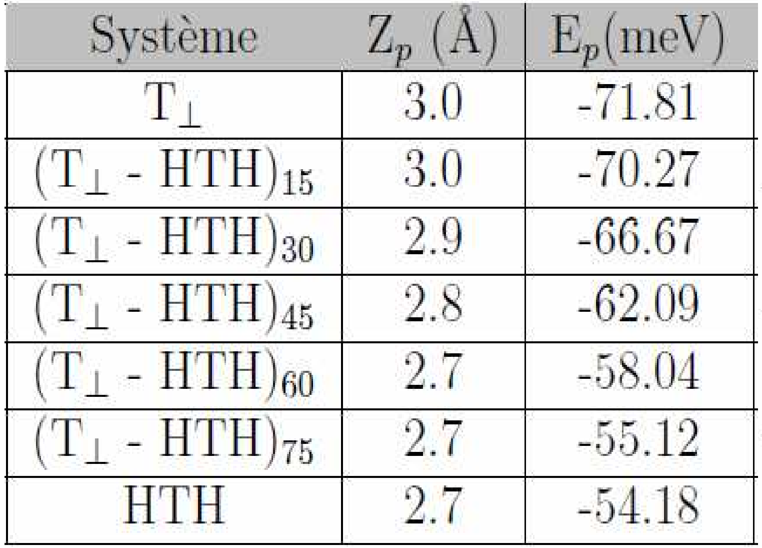
Shape of the Potential Energy Surface

First layer interaction of H_2 with the (100) Ag surface of CFC

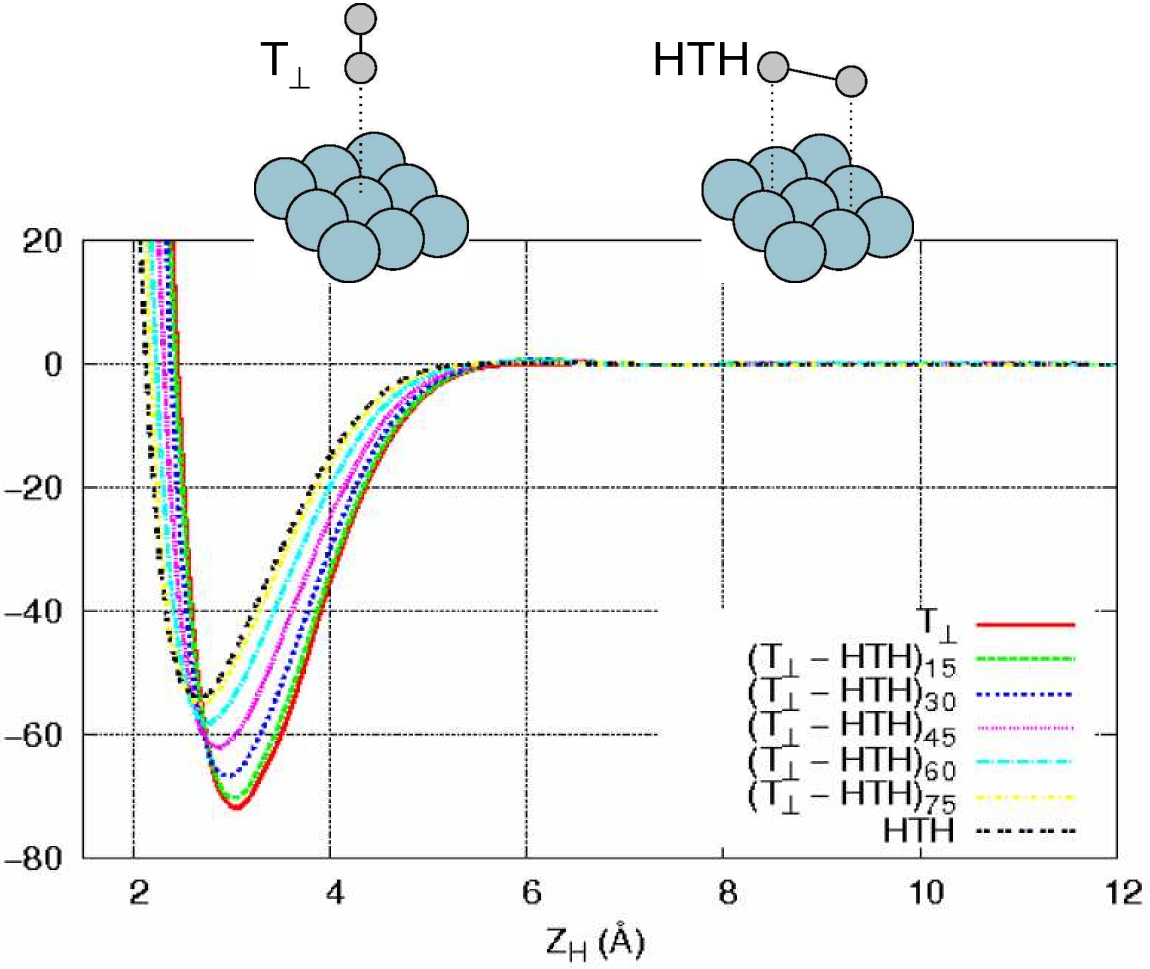
Periodic model

Periodic (DFT) results obtained with CRYSTAL, cell-3, PBEsol, rotations θ

Rotation of H_2 from vertical $T_\perp$ to parallel HTH to the surface, $V(Z,\theta)$, $\varphi=45$

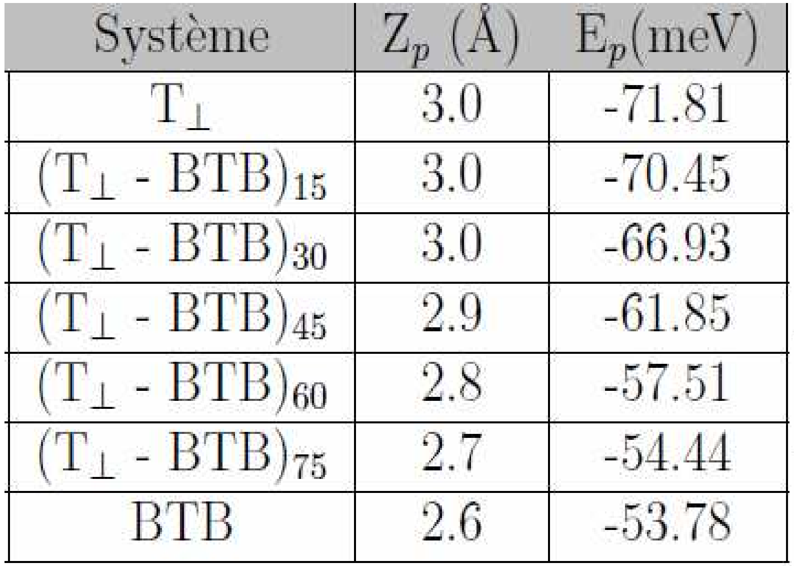


Système	Z_p (Å)	E_p(meV)
$T_\perp$	3.0	-71.81
$(T_\perp$ - HTH$)_{15}$	3.0	-70.27
$(T_\perp$ - HTH$)_{30}$	2.9	-66.67
$(T_\perp$ - HTH$)_{45}$	2.8	-62.09
$(T_\perp$ - HTH$)_{60}$	2.7	-58.04
$(T_\perp$ - HTH$)_{75}$	2.7	-55.12
HTH	2.7	-54.18

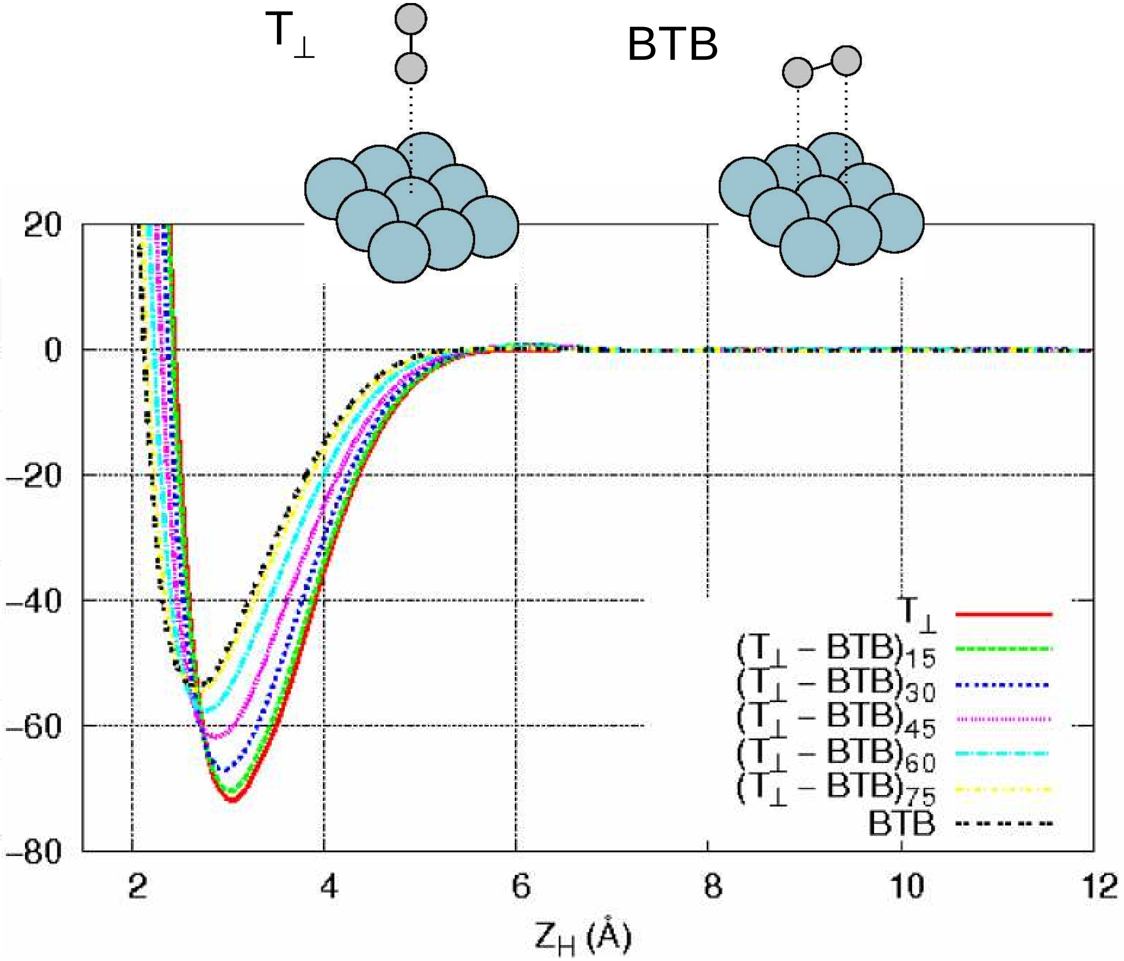


Periodic (DFT) results obtained with CRYSTAL, cell-3, PBEsol, rotations θ

Rotating the H_2 from vertical $T_\perp$ to parallel BTB to the surface, V (Z,θ), φ=0



Système	Z_p (Å)	E_p(meV)
$T_\perp$	3.0	-71.81
$(T_\perp$ - BTB$)_{15}$	3.0	-70.45
$(T_\perp$ - BTB$)_{30}$	3.0	-66.93
$(T_\perp$ - BTB$)_{45}$	2.9	-61.85
$(T_\perp$ - BTB$)_{60}$	2.8	-57.51
$(T_\perp$ - BTB$)_{75}$	2.7	-54.44
BTB	2.6	-53.78



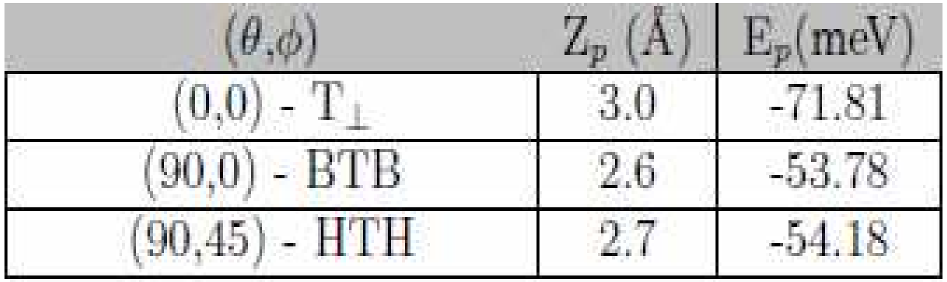
Periodic (DFT) results obtained with CRYSTAL, for H_2 on top of a metallic atom

Main results for the centre of mass of H_2 positionned on top of a metallic atom:

1) The more stable position corresponds to the perpendicular $T_\perp$ approach, in good agreement with the values of the polarisabilities of H_2

$\alpha_\perp = 4{,}84$ $\alpha\| = 6{,}30$

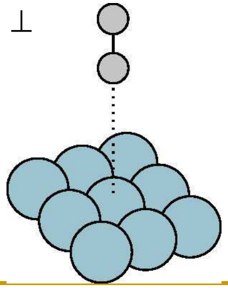
$\alpha\| / \alpha\perp = 1{,}30$ $E_T/E_{BTB} = 1{,}33$



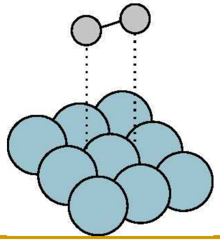
(θ,ϕ)	Z_p (Å)	E_p(meV)
(0,0) - $T_\perp$	3.0	-71.81
(90,0) - BTB	2.6	-53.78
(90,45) - HTH	2.7	-54.18

2) The rotation with φ is almost isotropic for the parallel positions (BTB and HTH)

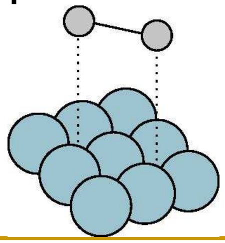
$T_\perp$



BTB



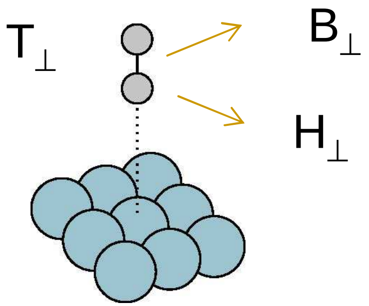
HTH



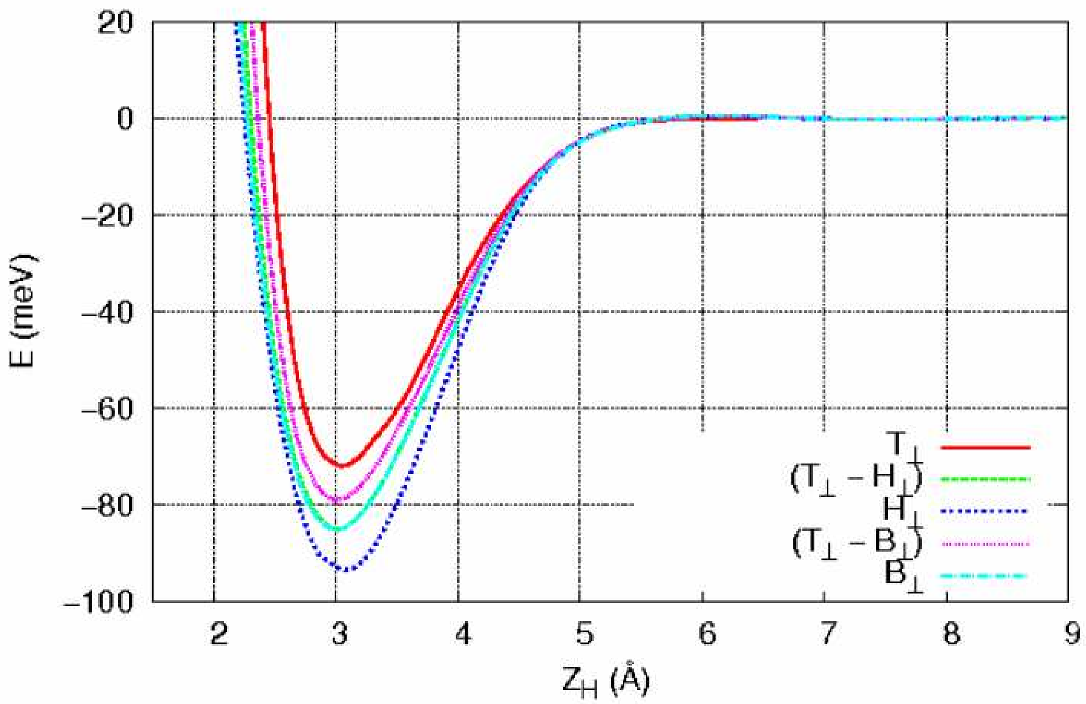
Periodic (DFT) results obtained with CRYSTAL, cell-3, PBEsol, translations of perpendicular H_2

For H_2 perpendicular to the surface on top of various sites:
Top T, Hollow H, Bridge B and intermediate ones.

The more metallic atoms are involved, the stronger is the interaction.



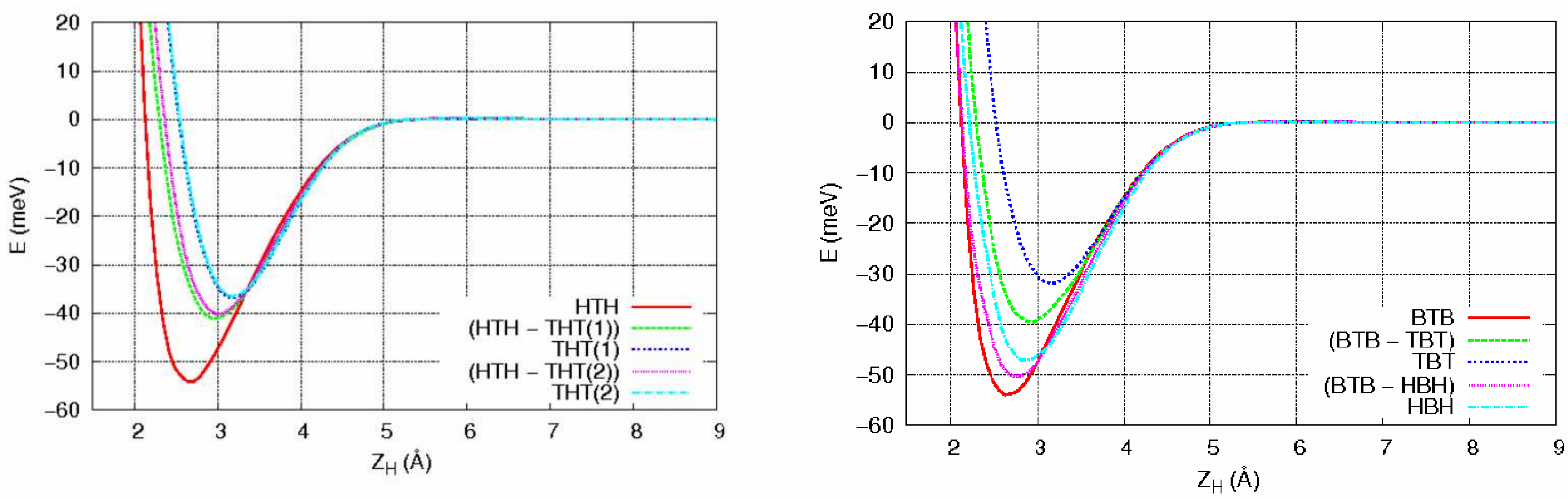
Système	Z_p (Å)	E_p(meV)
$T_\perp$	3.0	-71.81
($T_\perp$ - $H_\perp$)	3.0	-84.77
$H_\perp$	3.0	-93.39
($T_\perp$ - $B_\perp$)	2.95	-78.76
$B_\perp$	2.95	-84.85



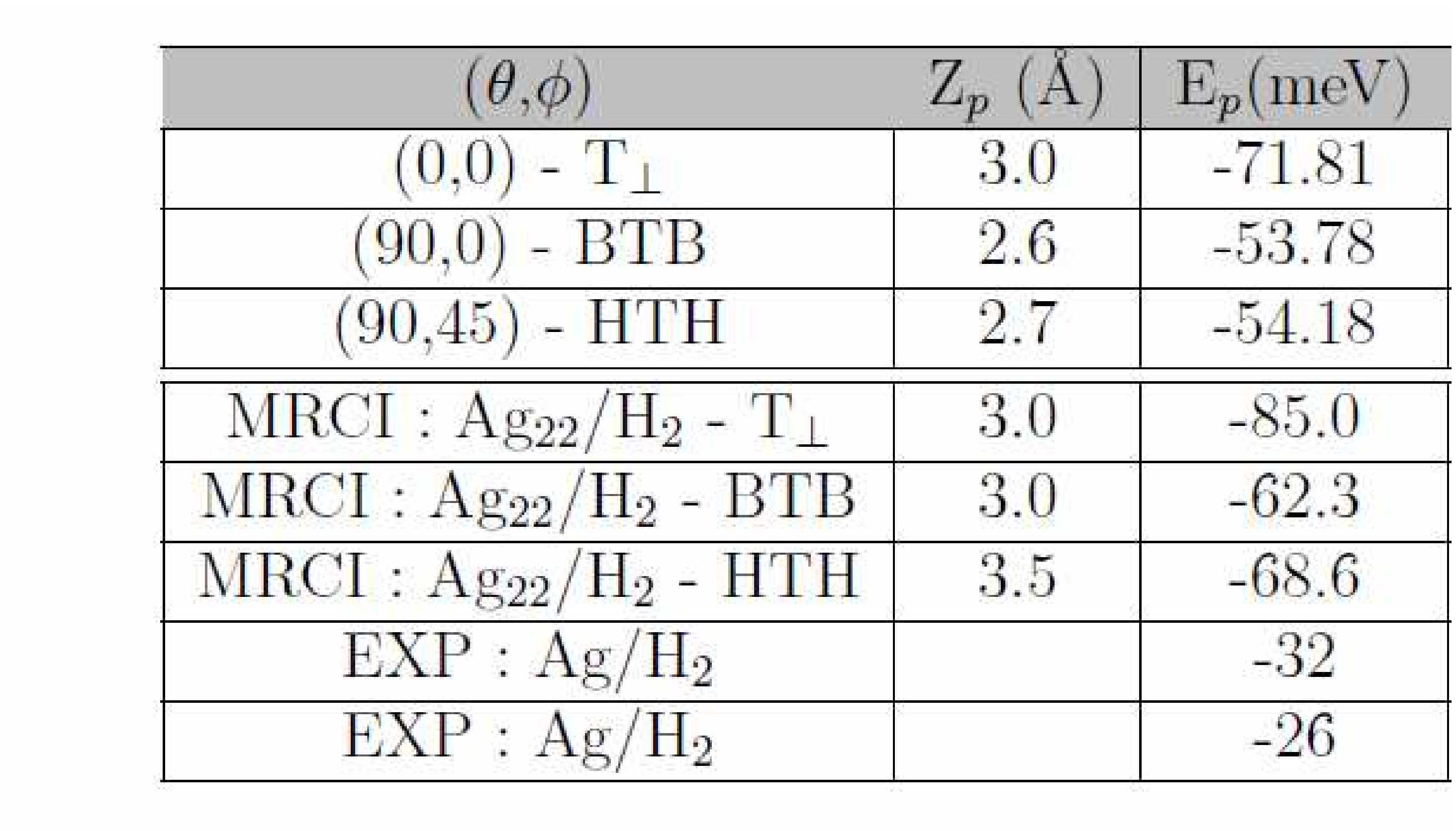
Periodic (DFT) results obtained with CRYSTAL, cell-3, PBEsol, translations of parallel positions

For H_2 parallel to the surface on top of various sites:
Top T, Hollow H, Bridge B and intermediate ones.

The more stable situations correspond to positions of the center of mass of H_2 on top of a metallic atom.



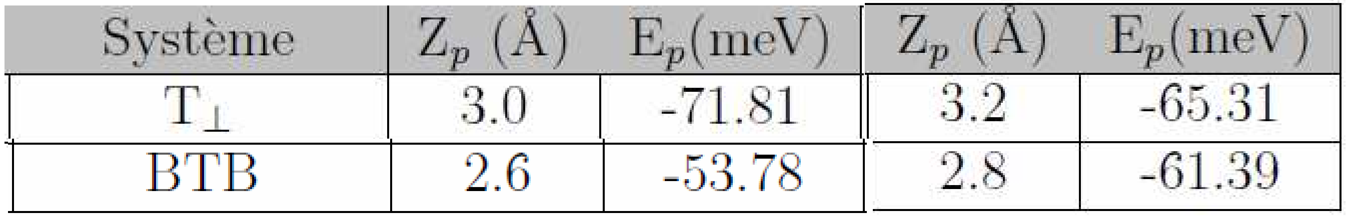
Comparison of periodic (DFT) results obtained with CRYSTAL and cluster model (MRCI) H_2@Ag(100)



(θ,ϕ)	Z_p (Å)	E_p(meV)
(0,0) - $T_\perp$	3.0	-71.81
(90,0) - BTB	2.6	-53.78
(90,45) - HTH	2.7	-54.18
MRCI : Ag_{22}/H_2 - $T_\perp$	3.0	-85.0
MRCI : Ag_{22}/H_2 - BTB	3.0	-62.3
MRCI : Ag_{22}/H_2 - HTH	3.5	-68.6
EXP : Ag/H_2		-32
EXP : Ag/H_2		-26

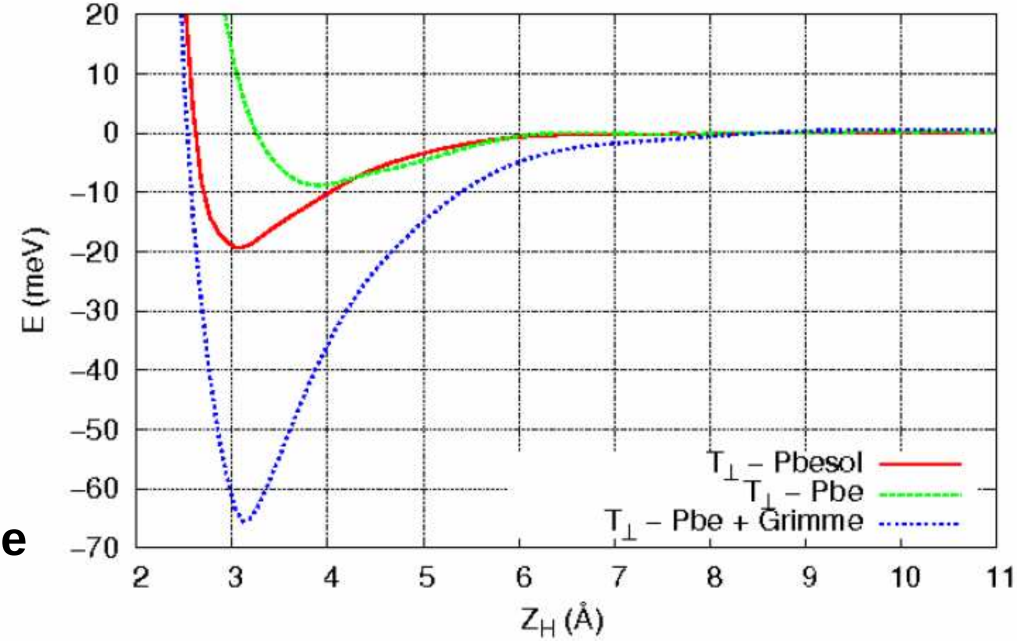
Exp: diffusion of H_2 molecules on Ag surface(111)

Comparison of the results with CRYSTAL and VASP



	CRYSTAL		**VASP**	
Système	Z_p (Å)	E_p(meV)	Z_p (Å)	E_p(meV)
$T_\perp$	3.0	-71.81	3.2	-65.31
BTB	2.6	-53.78	2.8	-61.39

VASP, with plane waves, can provide comparable results with CRYSTAL when using PBE + Grimme correction.



CRYSTAL seems more appropriate

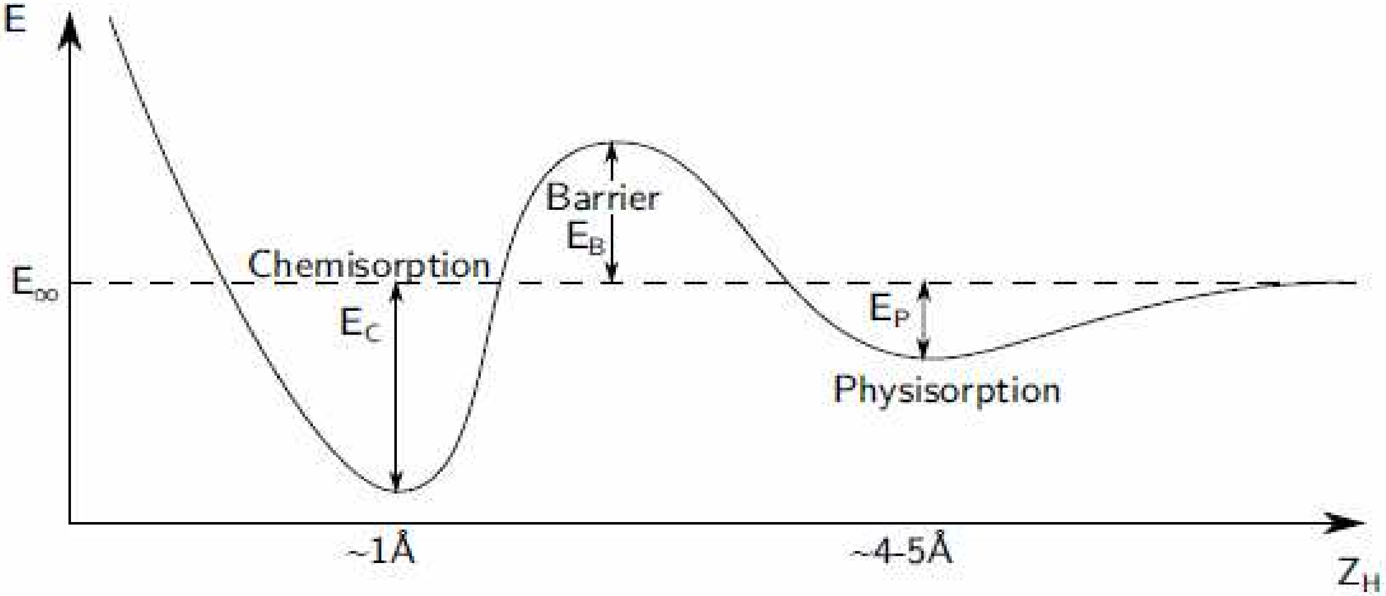
Physisorption, chemisorption

First layer interaction of H_2 with the (100) Cu surface

Cluster model

Physisorption well requires longer range with Cu than with Ag

H$_2$-metal interactions



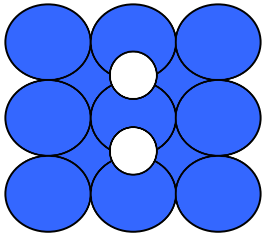
For Cu: $E_C < E_\infty$

$E_P \sim$ meV

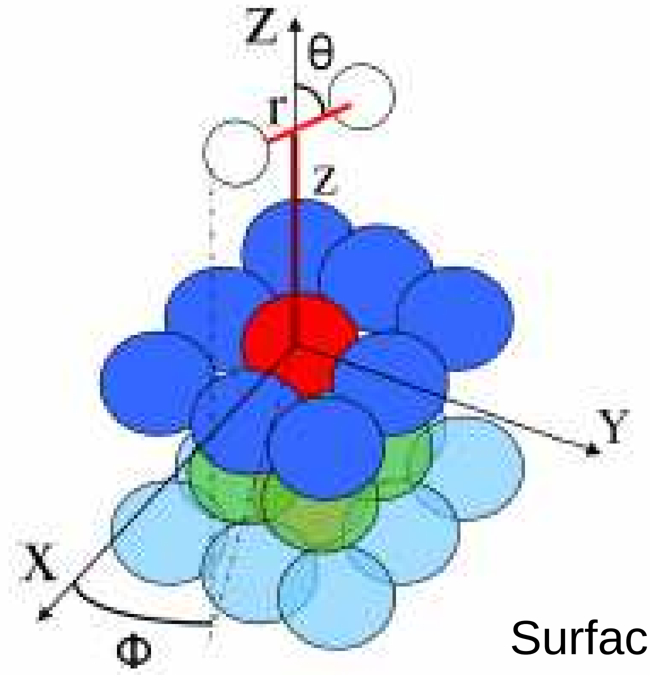
$E_C, E_B \sim$ eV

(for Ag: $E_C > E_\infty$)

Parameters of H_2/surface system



(9,4,9)



Surface
(100)

○ H atom

● Cu atom

(x, y, Z) : Centre of mass H_2
$r = r_{HH}$: distance H-H
θ : angle (H-H / axe Z)
Φ : angle (H-H / axe X)

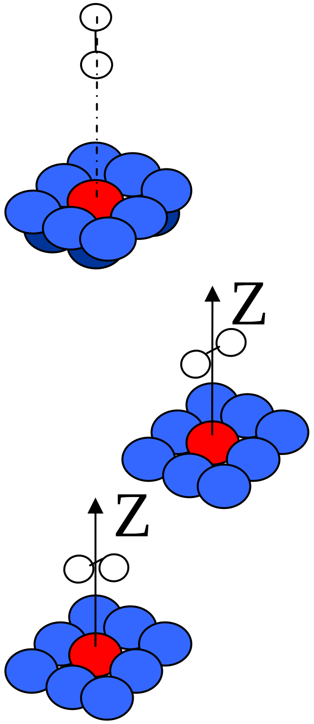
MRCI+Q, CCSD(T), DFT

$$\boxed{V_{6D}(Z, x, y, r_{HH}, \theta, \phi)}$$

Molpro version 2010 : H.-J. Werner et P. Knowles www.tc.bham.ac.uk/molpro

Physisorption energy of H_2@Cu

$$E_p = E_{min} - E_{ref}$$



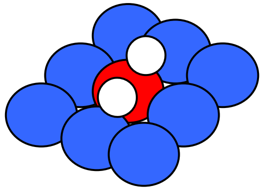
CCSD(T)	E_p (meV)	Z_p (Å)
top	**- 45.0**	**4.0**
btb	**-8.0**	**4.5**
hth	**-7.9**	**4.6**

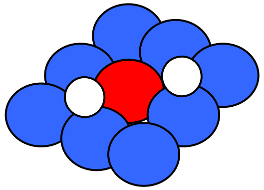
H-H distance remains at 0.74Å
E_{exp} ~ -31 meV, Andersson et al, RPB 1988

$\alpha_{para}(H_2) > \alpha_{perp}(H_2)$

Barrier and Chemisorption energies H_2@Cu

Approach	BTB			HTH
Method	MRCI +Q	CCSD(T)	DFT*	CCSD(T)
Barrier	**Z = 1.3 Å** **$r_{(H-H)}$= 0.80 Å** **E = 0.6 eV**	**Z = 1.4 Å** **$r_{(H-H)}$= 0.80 Å** **E = 0.4 eV**		**Z = 1.8 Å** **$r_{(H-H)}$= 0.80 Å** **E = 0.3 eV**
Chemisorption	**Z = 1.0 Å** **$r_{(H-H)}$= 2.5 Å** **E = -0.4 eV**	**Z = 1.0 Å** **$r_{(H-H)}$= 2.5 Å** **E = -0.5 eV**	**Z = 1.0 Å** **$r_{(H-H)}$= 2.5 Å** **E = -0.9eV (B3LYP)** **E = -1.0eV (PBE0)** **E = -0.47eV (WB97XD)**	**Z = 0.3 Å** **$r_{(H-H)}$= 3.1 Å** **E = -0.7 eV**



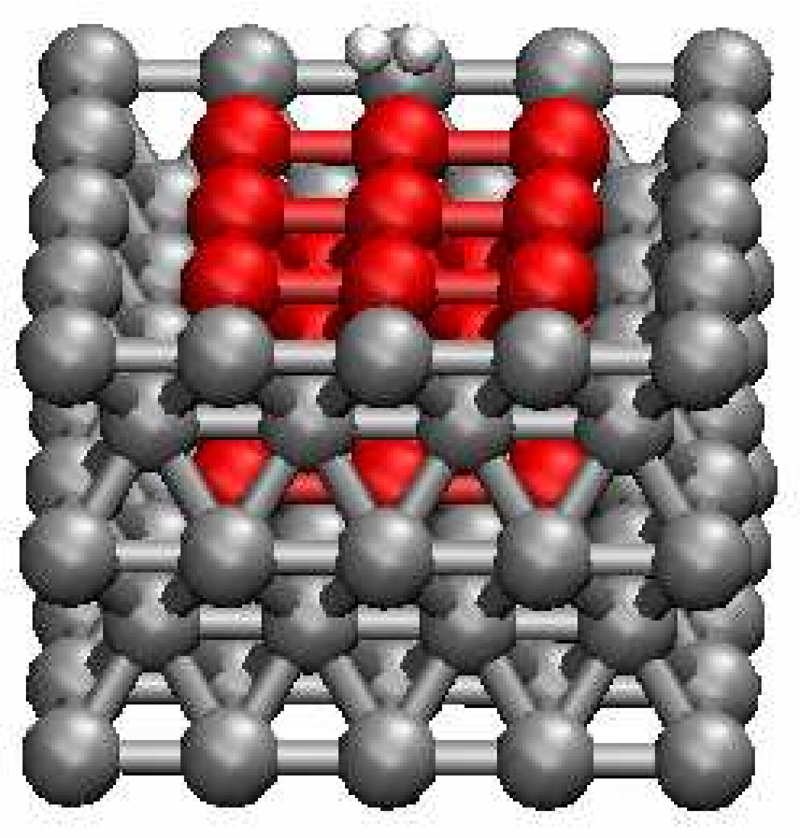


***19/1 pseudo**
19/19 E = - 0.27 eV

Delocalisation correction by embedding the cluster

Physisorption, barrier, chemisorption

Embedded cluster into a periodic system

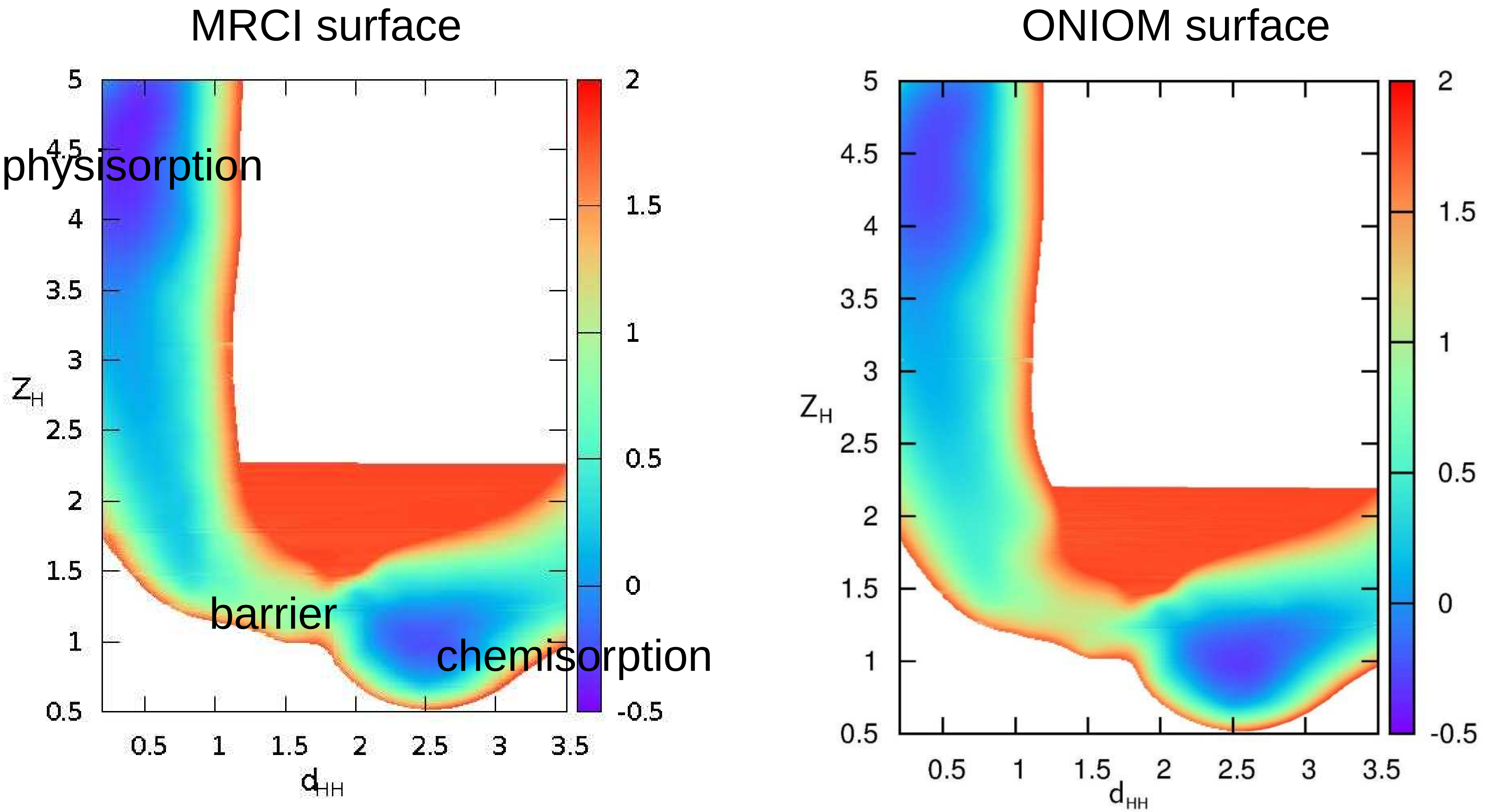


To correct for the delocalization effect in the metal the cluster is embedded in a periodic system. **ONIOM Method**

$$E_{HL/LH} = E_{HL}(\text{cluster}) - E_{LL}(\text{cluster}) + E_{LL}(\text{Slab})$$

Periodic code VASP:
-Low level calculation (LL) DFT (PBE).
-High level calculation CCSD(T) or MRCI+Q
- In the slab calculation the unit cell is defined by the 22 atoms cluster surrounded by 5 layers of copper atoms..

2D Potential energies V(Z,r_{HH}), parallel approach



- Chemisorption well deeper with ONIOM (-0.05 eV)

-Higher barrier with ONIOM (+0.21 eV)

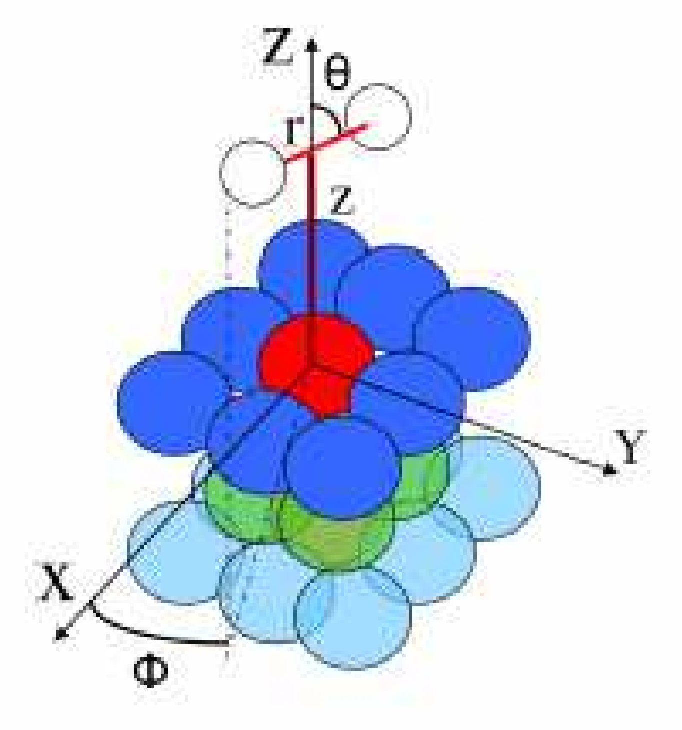
-No reliable access to the physisorption region

Checking the accuracy of the physisorption well

Rotational spectroscopy of physisorbed H_2@Cu

Framework of the spectroscopic treatment

The H_2 molecule centre-of-mass is **constrained on the Z axis**, on top of the central Cu atom. An accurate description of the 4D interaction potential $V(Z,r,\theta,\varphi)$ is obtained with CCSD(T) calculation.



The $r_{H\text{-}H}$ **parameter can be fixed** at the equilibrium geometry of H_2 molecule for large Z values. H_2 is considered as a rigid rotor.

The variations of V with the angle ϕ are very small ($<1 cm^{-1}$) and are neglected.

The potential is strongly anharmonic and anisotropic with respect to Z and θ variables.

Equation of the motion of the H_2 molecule

The motion of H_2 on the surface can thus be solved with a 2D Hamiltonian, where the motion associated with the angle ϕ - helicopter rotation above the surface – is represented by the quantum number *m*, a ‘good’ quantum number.

$$\hat{H}_{2D} = -\frac{1}{4m_H}\frac{\partial^2}{\partial Z^2} + \frac{1}{m_H r_0^2}\left[-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{m^2}{\sin^2\theta}\right] + V_{2D}(Z,\theta)$$

Spectroscopic wavefunctions are represented, for the rotational motion, with associated Legendre functions, labelled with *m*.

$$\phi_{klm}(Z,\theta) = \chi_k(Z)\Theta_{lm}(\theta)$$

Expansion of the $V_{2D}(Z,\theta)$ potential in the physisorption region

$$\begin{aligned} V_{2D}(Z,\theta) &= V_0(Z) + \sin^2\theta\left[V_{\pi/2}(Z) - V_0(Z) + \right. \\ &\left. 2\cos^2\theta\left(V_{\pi/4}(Z) - V_{\pi/2}(Z) - V_0(Z)\right)\right] \end{aligned}$$

with

$$V_{2D}(Z,\theta) = V_{2D}(Z,\pi-\theta)$$

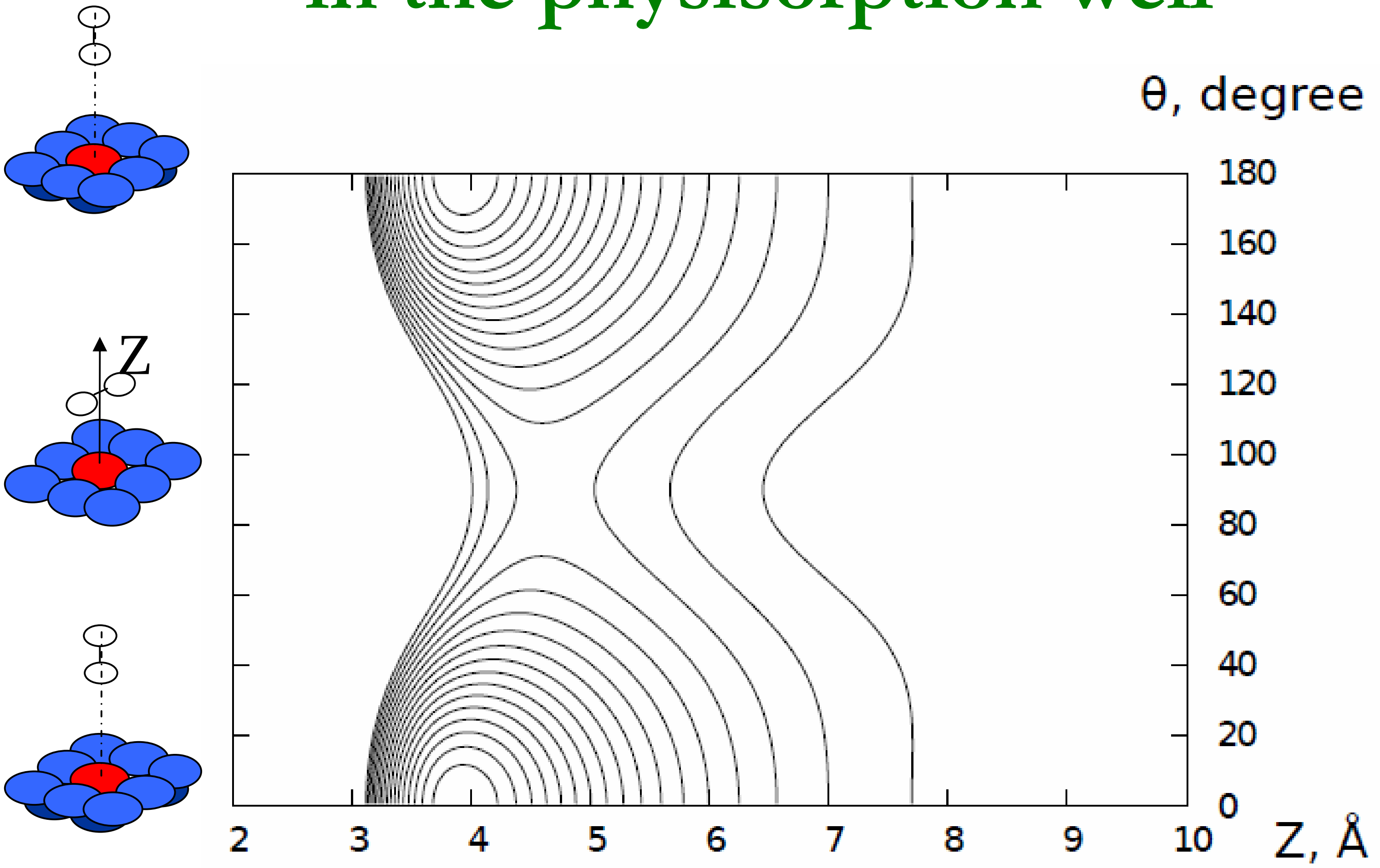
Analytic expansion of the van der Waals Z dependent term, developed in Morse type coordinate series

$$V(Z) = C_0(1-y^2) + D_e y^2 + C_3(y^3 - y^2)$$

$$y = 1 - \exp(-a(Z - Z_0))$$

	$\theta = 0$	$\theta = \frac{\pi}{2}$	$\theta = \frac{\pi}{4}$
Z_0 (Å)	3.9126	4.6515	4.2301
a (Å^{-1})	0.92520	0.96568	0.79377
C_0 (cm^{-1})	0	293.873	197.189
D_e (cm^{-1})	362.756	362.756	362.756
C_3 (cm^{-1})	39.424	4.266	-14.471

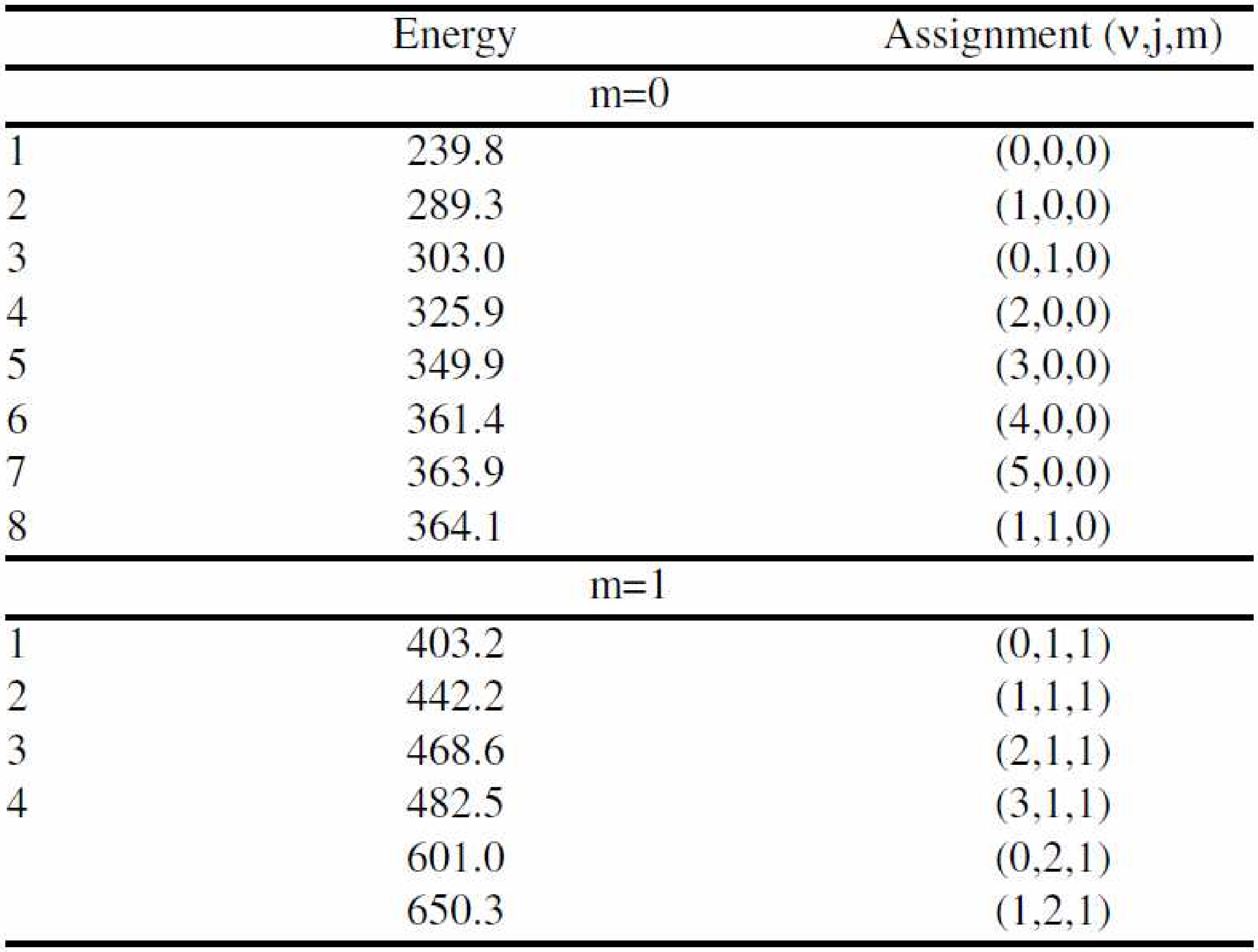
Contour plot of the $V_{2D}(Z,\theta)$ potential in the physisorption well



Distance between lines equals 2.5 meV = 20cm^{-1}

Energies (in cm^{-1}) of the first ro-vibrational levels

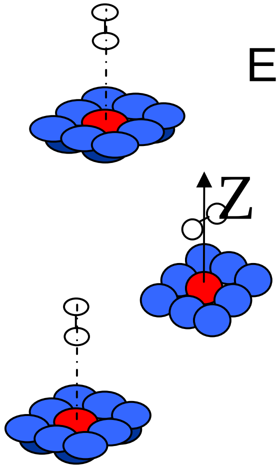
(v for stretching, j for rotation θ, and m for ϕ)

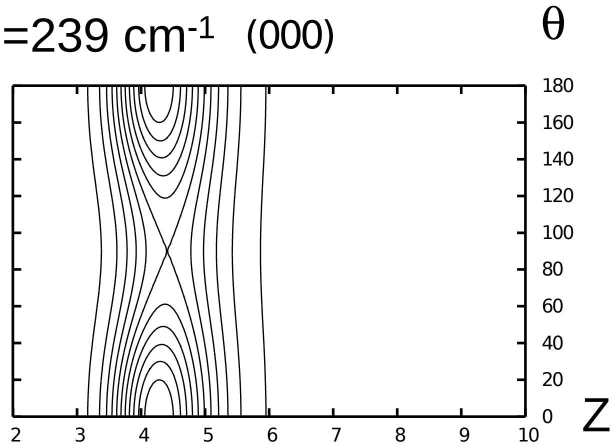


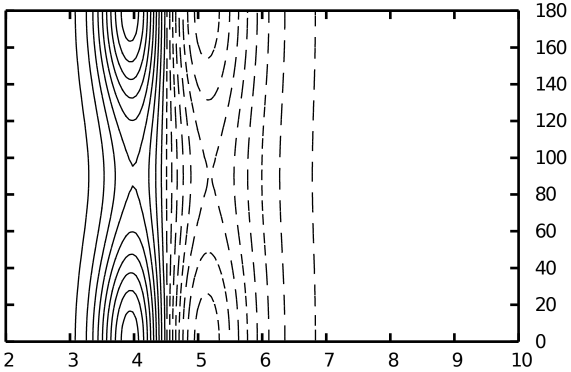
	Energy	Assignment (ν,j,m)
	m=0	
1	239.8	(0,0,0)
2	289.3	(1,0,0)
3	303.0	(0,1,0)
4	325.9	(2,0,0)
5	349.9	(3,0,0)
6	361.4	(4,0,0)
7	363.9	(5,0,0)
8	364.1	(1,1,0)
	m=1	
1	403.2	(0,1,1)
2	442.2	(1,1,1)
3	468.6	(2,1,1)
4	482.5	(3,1,1)
	601.0	(0,2,1)
	650.3	(1,2,1)

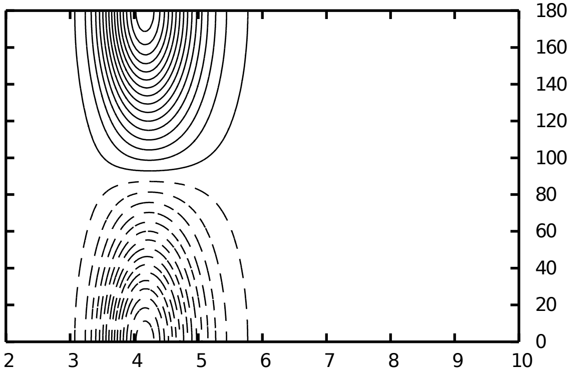
Contour plots of ro-vibrational wavefunctions

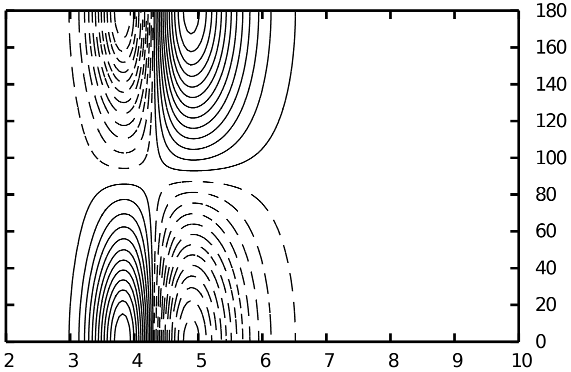
m=0, no-helicopter rotation of H_2



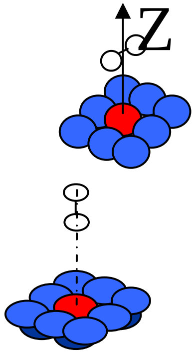

E=239 cm^{-1} (000)


E=289 cm^{-1} (100)

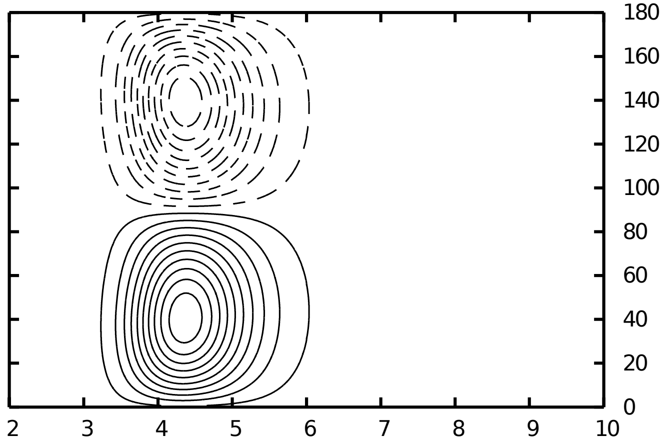

E=303 cm^{-1} (010)


E=364 cm^{-1} (110)

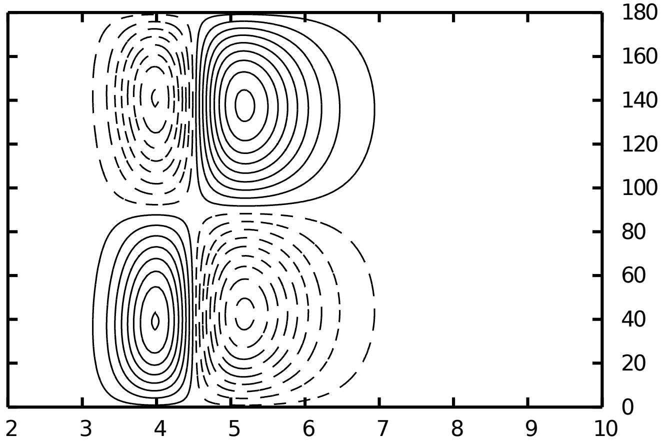
Contour plots of ro-vibrational wavefunctions m=1, including helicopter rotation of H_2



E=601cm^{-1} (021)



E=650 cm^{-1} (121)

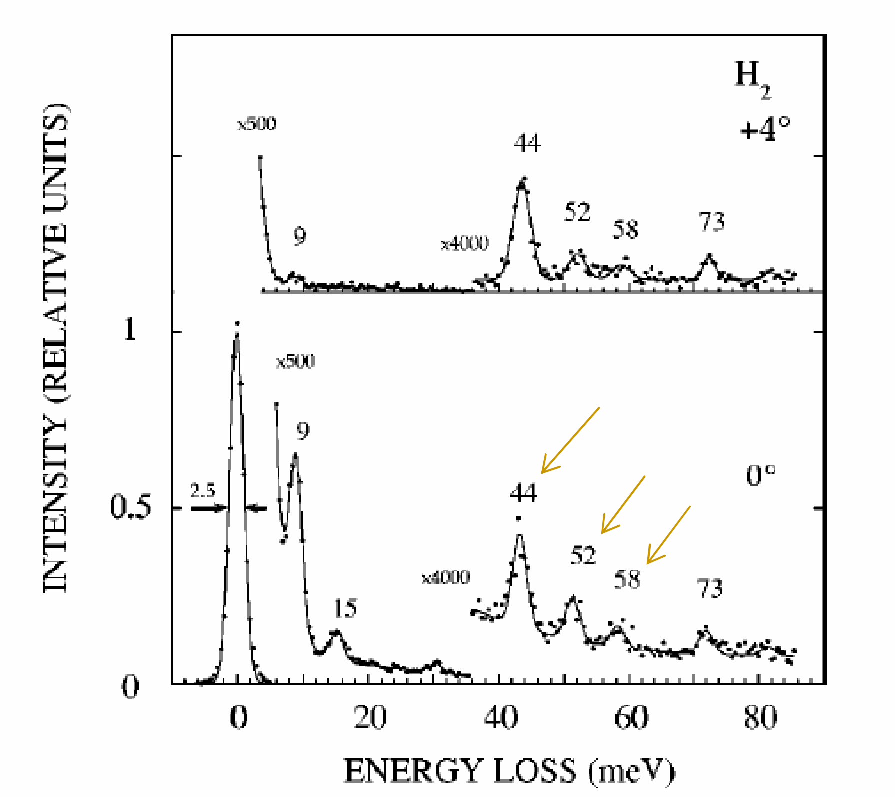


Comparison calculation/experiment

Measurements of Electron-Energy-Loss Spectroscopy EELS, on Cu(100) surface, showing j=0→2 rotational transitions in H_2

Conditions : 10^{-11} Torr and T~10K.
3eV electron beam

Transition	E_{cal} (meV)	E_{exp} (meV)
(000)→(021)	44	44
(000)→(121)	51	52
(000)→(221)	56	58



K. Svensson, J. Bellman, A. Hellman, and S. Andersson PHYSICAL REVIEW B **71**, 245402 (2005)

Conclusions

✓It is still a challenge to have a full description of the interaction of a molecule with a surface for all distances within one given method. So far, with DFT methods, no functional is able to cover the whole range of distances and the long distances are difficult to obtain when metals are involved

✓Short and intermediate range, interesting for reactivity on surface and catalysis, can be described with periodic approaches or cluster representation with embedding correction for more accurate description of the processes.

✓Long range interaction, needed for non reactive dynamics on surfaces, multilayers problems, nano-fluidic etc.., can be approached by cluster representation using highly correlated wavefunctions. Spectroscopy can be a good tool to check the performance of the techniques.

Acknowledgments

- MLV:
    - Eddy Bernard
    - Céline Houriez
    - Sacha Mitrushchenkov
    - Gilberte Chambaud

- ENS Lyon
    - Florian Göltl
    - Philippe Sautet

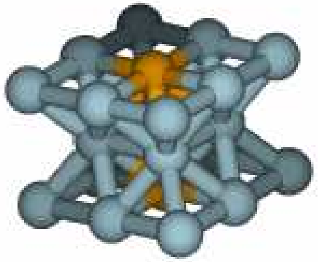
- Herzen University
- Univ. Marne La Vallée
- CNRS
- ANR DYQUMA

Thank you for your attention

Basis sets

Stuttgart group's ECP:

2 levels of description:



- Central atoms of the 2 external layers of the cluster : **19 explicit electrons**
  Cu1 : [Ne]$3s^2 3p^6 3d^{10} 4s^1$ (ECP10MDF)
- Other atoms of the cluster: **1 explicit electron**
  Cu2 : [Ar]$4s^1$ (ECP28SDF)

Basis sets:

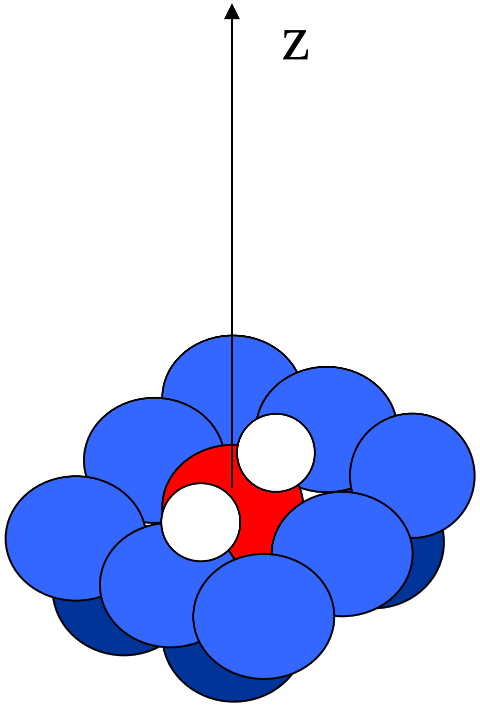
- Cu1: basis corresponding to the 19 electrons ECP (s, p, d functions)
- Cu2: same basis but with only s and p functions
- H atoms: aug-cc-pVTZ (s, p, d)

(We use the same basis sets for all levels of theory)

Second layer interaction of H_2 with the Cu (100) surface

Physisorption

Polarisation of the surface by chemisorbed H_2

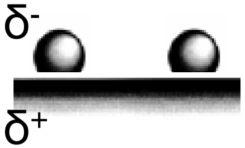


Dipole moment along the Z axis

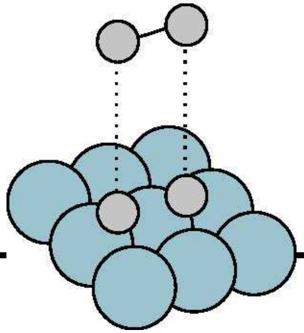
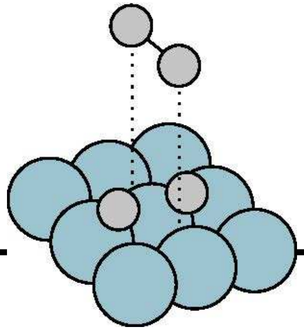
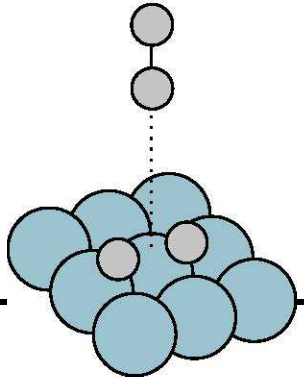
(MRCI)

μ_Z= 3.1 Debye

Polarisation of surface atoms



Physisorption H_2/H-H-Cu(100)

CCSD(T)			
E (meV)	-24.4 (-8)*	-20.7 (-8)*	-68.6 (-45)*
Z (Å)	3.9 (4.5)*	4.0 (4.5)*	3.7 (4.0)*

*Physisorption of the first layer
First H_2 molecule fixed at the btb minimum
Larger interaction in the second layer, closer approach

[1] C. Houriez, E. Bernard, F. Göltl, Ph. Sautet, M. Guitou et G. Chambaud (RCTF – Marseille, 07 – 2012)