GDR ARCHES

Chimisorption d'un second hydrogène en présence d'un premier sur une surface graphitique : conséquences pour la formation de H_2

Damien Bachellerie
Nathalie Rougeau
Victor Sidis
Muriel Sizun
Dominique Teillet-Billy

UNIVERSITE PARIS-SUD XI

CNRS CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

Laboratoire des Collisions Atomiques et Moléculaires

CNRS & Université Paris Sud 11 (UMR 8625) Orsay

Hydrogen atom interaction with carbonaceous surfaces : interest

- hydrogen adsorption on interstellar grains and
  catalytic formation of molecular hydrogen

- hydrogen storage (nanotubes, graphite substrate, …)

- hydrogen interaction with fusion reactor walls

Interstellar medium (ISM)

gas (99%) → H, H_2 } ~ 75% – 90%

He ~ 25% – 10%

dust grains (1%)

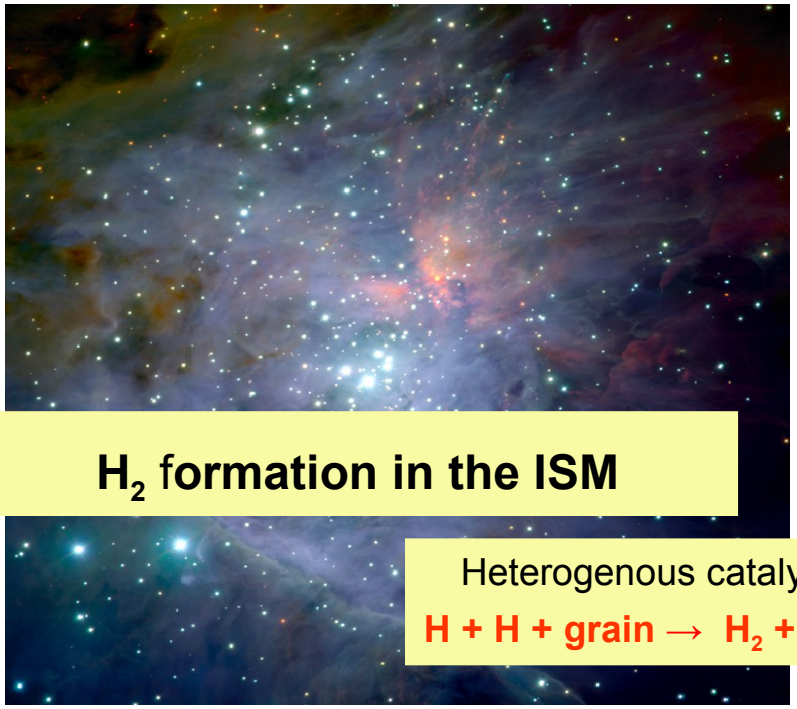
Density < 1000 atoms per cm^3

Temperature : 10K – 100 K

Silicates and carbonaceous material

1nm – 0.1 μm

PAH like



H_2 formation in the ISM

Heterogenous catalysis

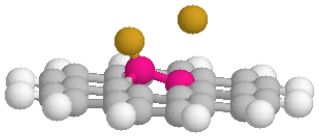
$H + H + grain \rightarrow H_2 + grain$

Present :

Single and Double H atom adsorption
on a cluster model of a graphite surface

Characteristics of H atoms adsorption

- Energy
- Adsorption barrier
- Second adsorption : site and spin effects

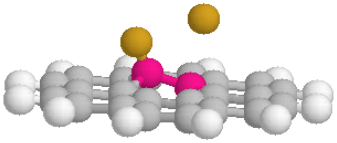


Consequences for the formation of the H_2 molecule
(Eley-Rideal mechanism)

Theoretical approach

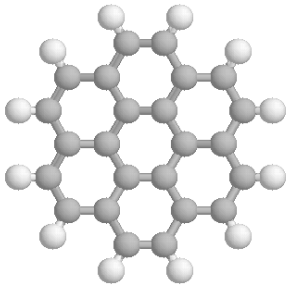
- **DFT** (ADF code/ cluster calculation)
  - DFT : spin unrestricted Kohn-Sham
  - Basis (triple ζ + polarization)TZP Slater-type orbitals
  - Exchange-Correlation interaction functional :

    LSDA + GGA (PW91)



- **Cluster model for graphite surface (PAH)**

  coronene molecule ($\mathbf{C_{24}}H_{12}$)

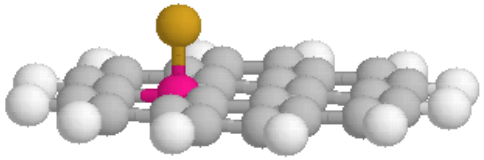


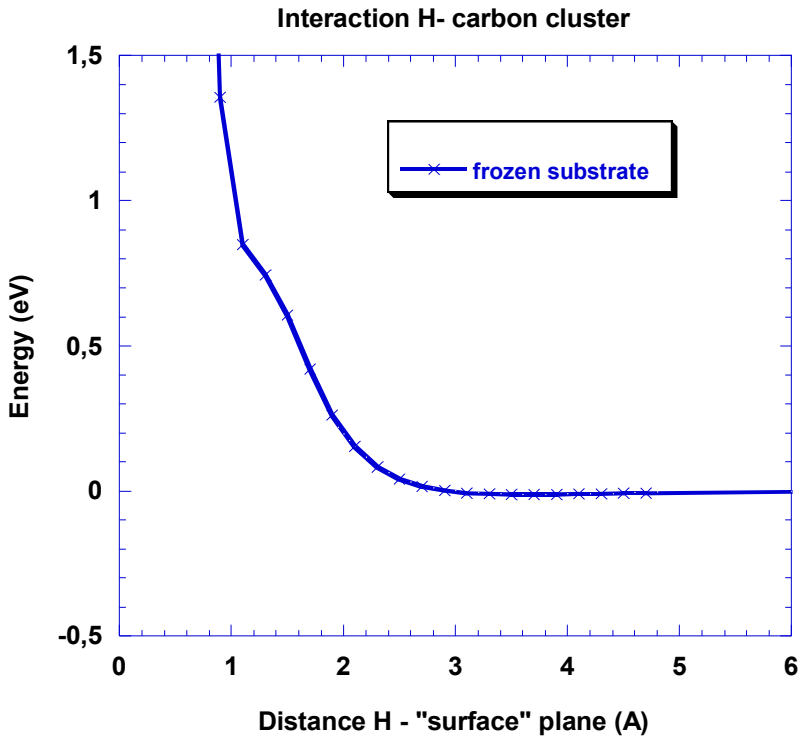
Graphite-like coronene
C-C 1.415 Å

Single H atom adsorption on a cluster model of a graphite surface

(Sidis et al 1999, 2000)

- Without substrate relaxation,
  no chemical adsorption





Single H atom adsorption on a cluster model of a graphite surface

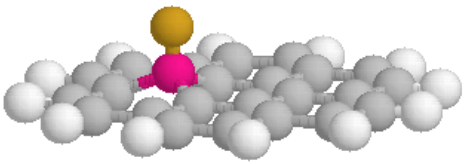
(Sidis et al 1999, 2000)

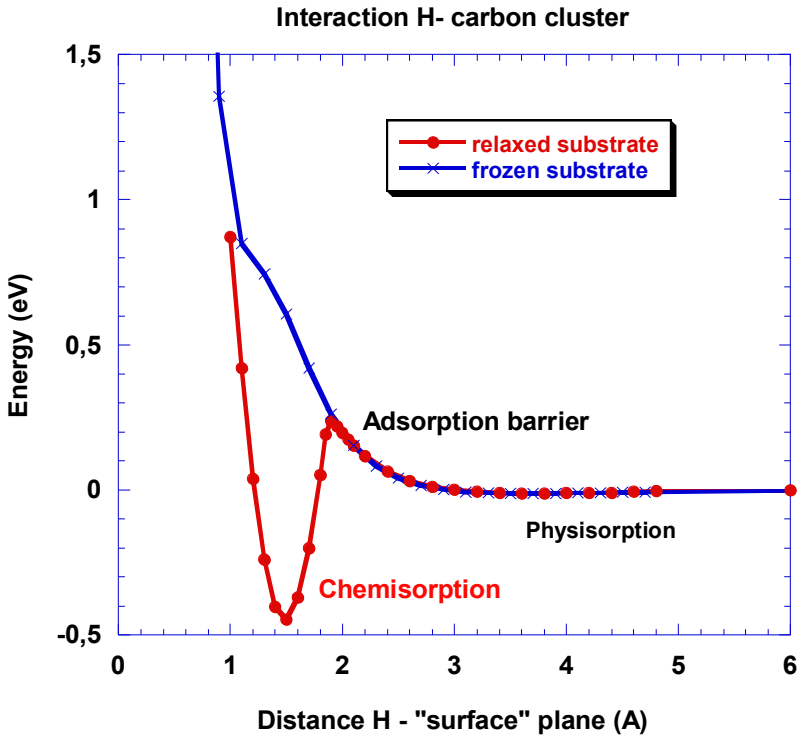
With substrate relaxation

Chemisorption: on top geometry

Characteristics of an H atom adsorption

- Energy	Chemisorption	-0.47 eV
- Geometry	Puckered C	0.36 Å
	C-H distance	1.13 Å
- Adsorption barrier		0.2 eV





-Chemisorption CH bonding ; C $sp^2 \rightarrow sp^3$

-The activation barrier prevents H adsorption in InterStellar Medium

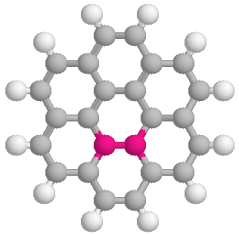
Double H atom adsorption on a cluster model of a graphite surface

Previous work : Miura et al 2003, Ferro et al 2003, Hornekaer et al 2006

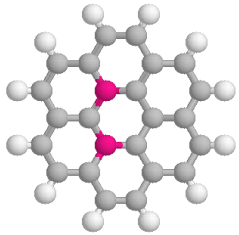
Present : Characteristics of two H atoms adsorption
- Energy
- Adsorption barrier
- Second adsorption : site and spin effects

Sites

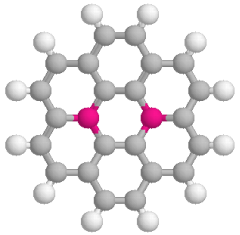
2 atoms on the same carbon ring



ortho
(adjacent)



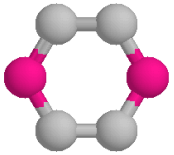
meta



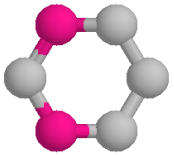
para
(opposite)

Double H atom adsorption on a cluster model of a graphite surface Energy

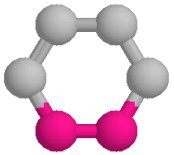
site : **para**
double adsorption energy : **-2.04eV**



site : **meta**
double adsorption energy : **-0.76eV**



site : **ortho**
double adsorption energy : **-2.16eV**



(with respect to 3 isolated fragments)

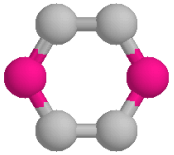
- Stronger chemisorption energy

on ortho and para sites (≈-2eV)

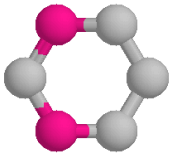
Double H atom adsorption on a cluster model of a graphite surface Energy

Spin ↑↓

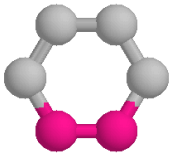
site : **para**
double adsorption energy : **-2.04eV**



site : **meta**
double adsorption energy : **-0.76eV**



site : **ortho**
double adsorption energy : **-2.16eV**

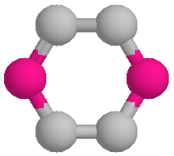
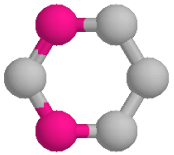
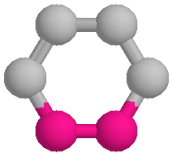


Spin ↑↓
- Stronger chemisorption energy

on ortho and para sites (≈-2eV)

PAH molecule + H + H → spin **paired** state ↑↓
→ spin **unpaired** state ↑↑

Double H atom adsorption on a cluster model of a graphite surface

	Spin ↑↓		Spin ↑↑
site : **para** double adsorption energy : **-2.04eV**			**-1.03 eV**
site : **meta** double adsorption energy : **-0.76eV**			**-0.91 eV**
site : **ortho** double adsorption energy : **-2.16eV**			**-1.13 eV**

Spin ↑↓
- Stronger chemisorption energy on ortho and para sites (≈-2eV)

Spin ↑↑
- Twice single chemisorption irrespective of site (≈-1eV)

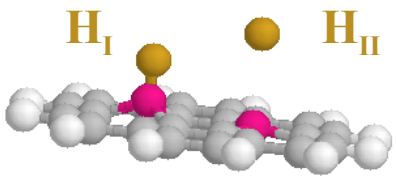
Confirmed on larger clusters (C_{42})

ARCHES : Report on the collaboration with Yves Ferro et al on Wednesday …

Interaction of an H atom with H@coronene

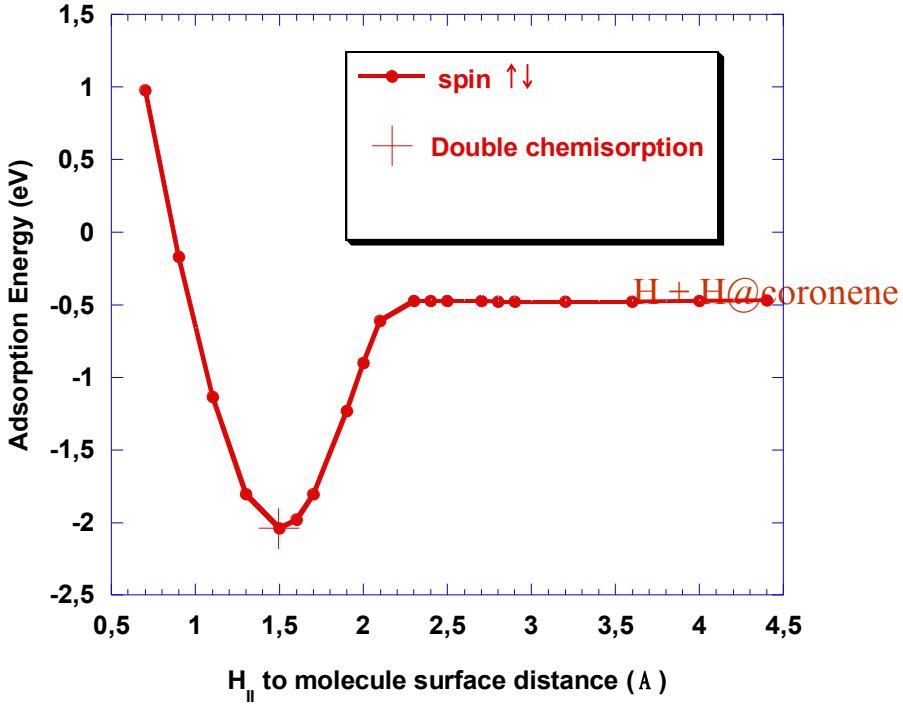
Potential energy curves

site : **para**



H_I : chemisorbed
H_{II} : incoming

H_I C_I C_{II} relaxation allowed



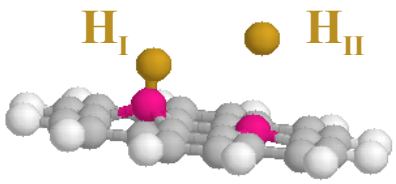
Para site, spin ↑↓ :
No activation barrier for adsorption of the second H atom

Rougeau et al 2006 ; Hornekaer et al 2006

Interaction of an H atom with H@coronene

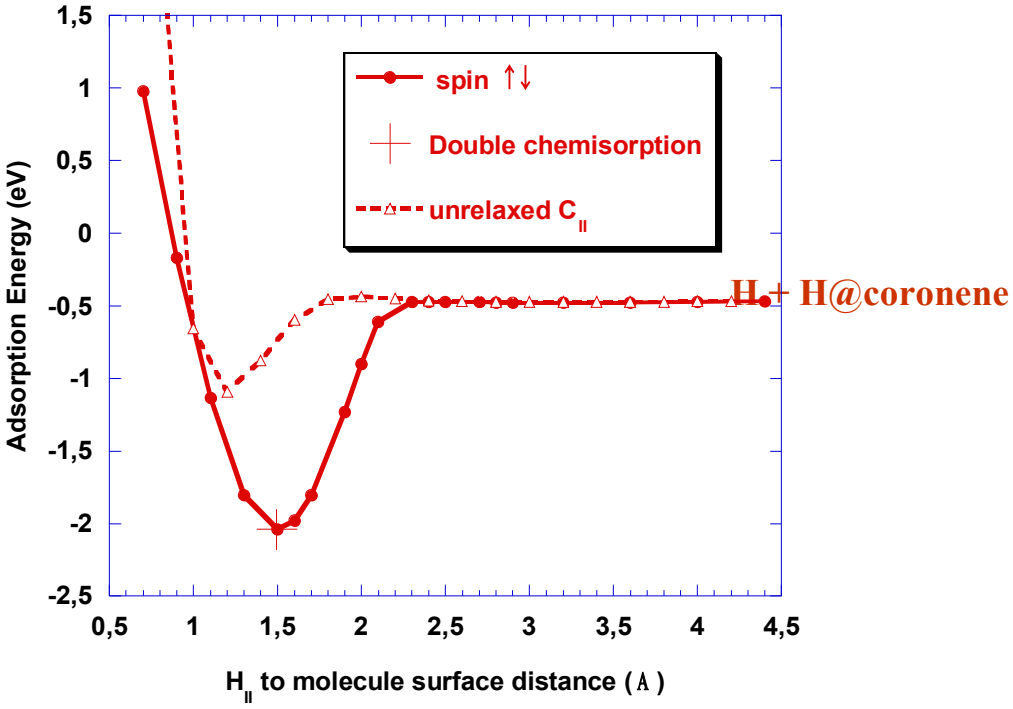
Potential energy curves

site : **para**



H_I : chemisorbed
H_{II} : incoming

H_I C_I C_{II} relaxations allowed



Para site, spin ↑↓ :
Chemisorption strictly on top
No activation barrier for adsorption of the second H atom
Barrier-less chemisorption possible without C_{II} relaxation

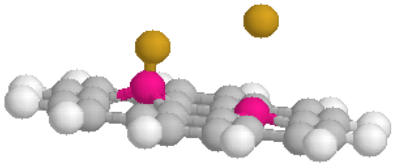
There is an **activation barrier** for the adsorption of a second H for all other cases :

- at **ortho** and **meta** sites for paired ↑ ↓ and unpaired ↑ ↑ spins
- at para site for unpaired ↑ ↑ spins

Interaction of an H atom with H@coronene

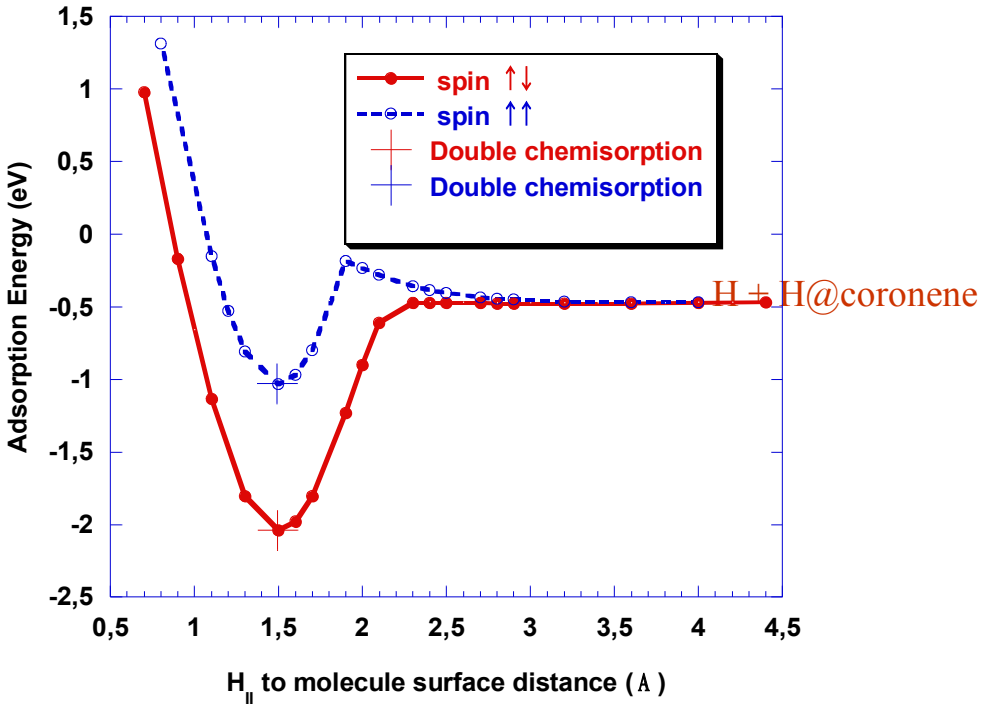
Potential energy curve

site : **para**



↑↑

↑↓



Para site, spin ↑↑ :
Activation barrier similar to the barrier for single atom adsorption

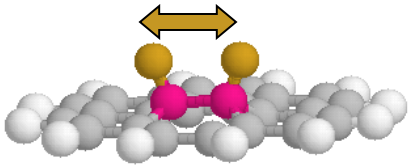
Double H atom adsorption on a cluster model of a graphite surface

Characteristics of two H atoms adsorption
Energy

site : **ortho**

spin : ↑↓

double adsorption energy : **-2.16eV**



spin : ↑↑

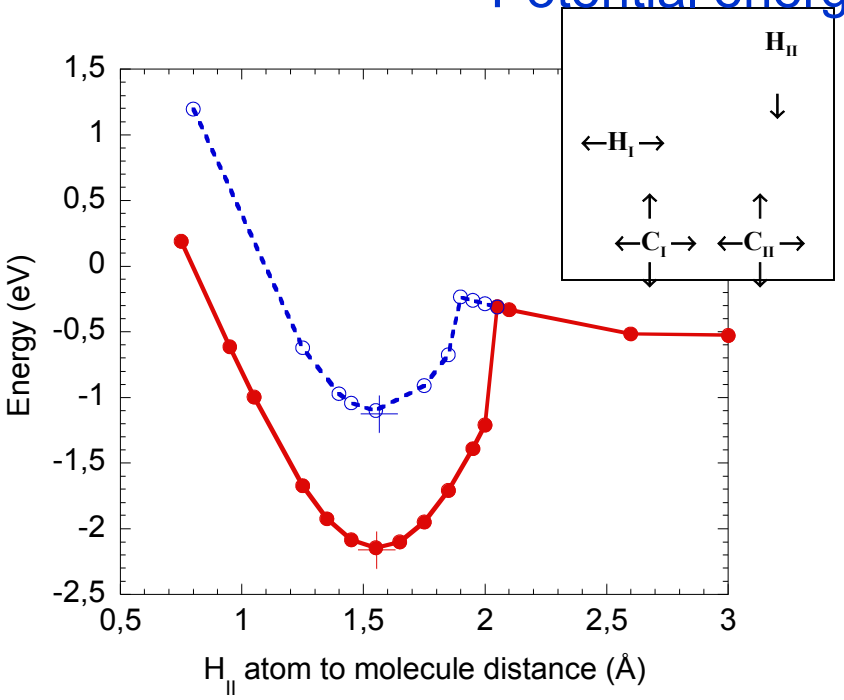
-1.13 eV

Geometry for the double adsorption on ortho : not on top, similar to cis substituted « ethane »
Contribution of CH bonds repulsion to chemisorption energy for ↑↓ : ≈-1eV !

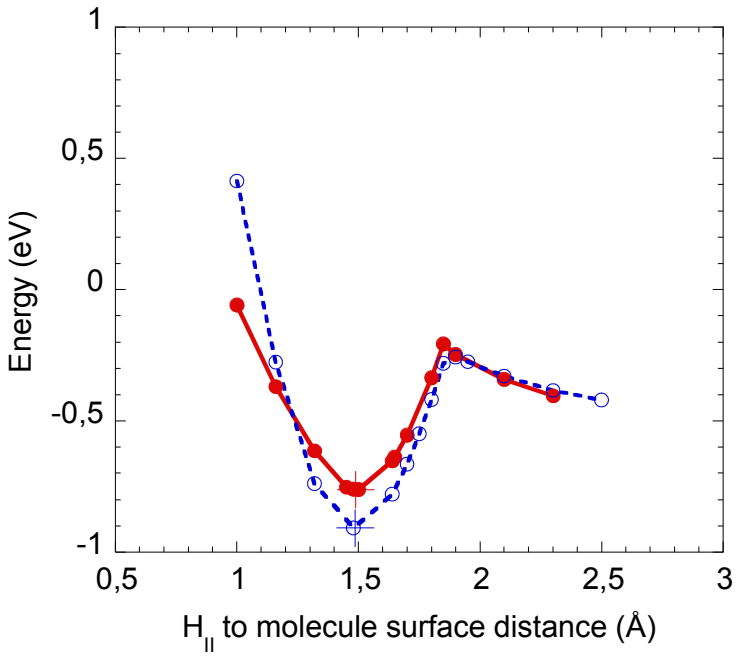
Interaction of an H atom with H@coronene

Potential energy curves

↑↑ ↑↓



Ortho

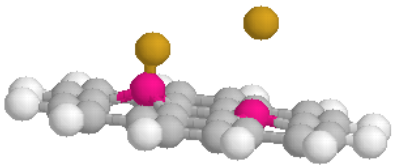


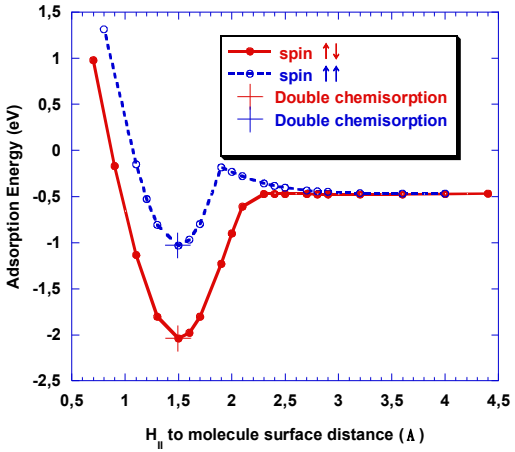
Meta

Ortho and meta sites

There is a **barrier to adsorption** of the second H for **paired ↑↓ and unpaired ↑↑** spin states (height 0.16 to 0.29eV)

Interaction of an H atom with H@coronene



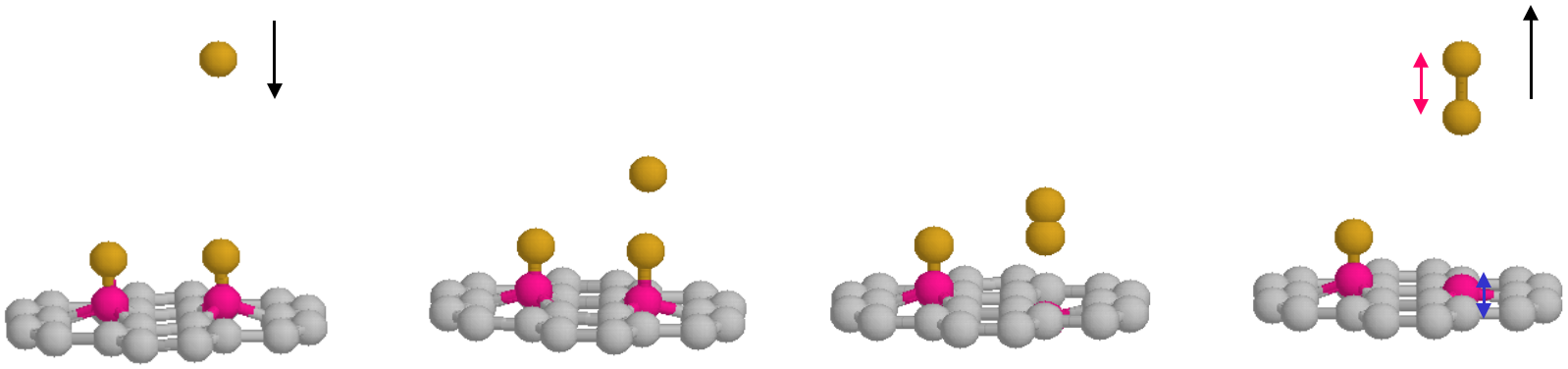


H atoms Adsorption :

-The « impurity/defect » allows an H adsorption without barrier
-With Spin selectivity (paired ↑↓) and site selectivity (para)

This should have consequences on H_2 formation on ISM

Eley-Rideal formation of H_2 involving one of two para-chemisorbed H atoms on a graphite surface.



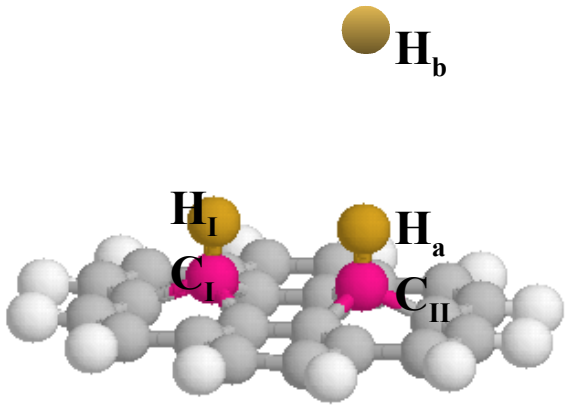
$H_{coll} + H_{\text{chimisorbé /H@graphite}} \longrightarrow H_2$

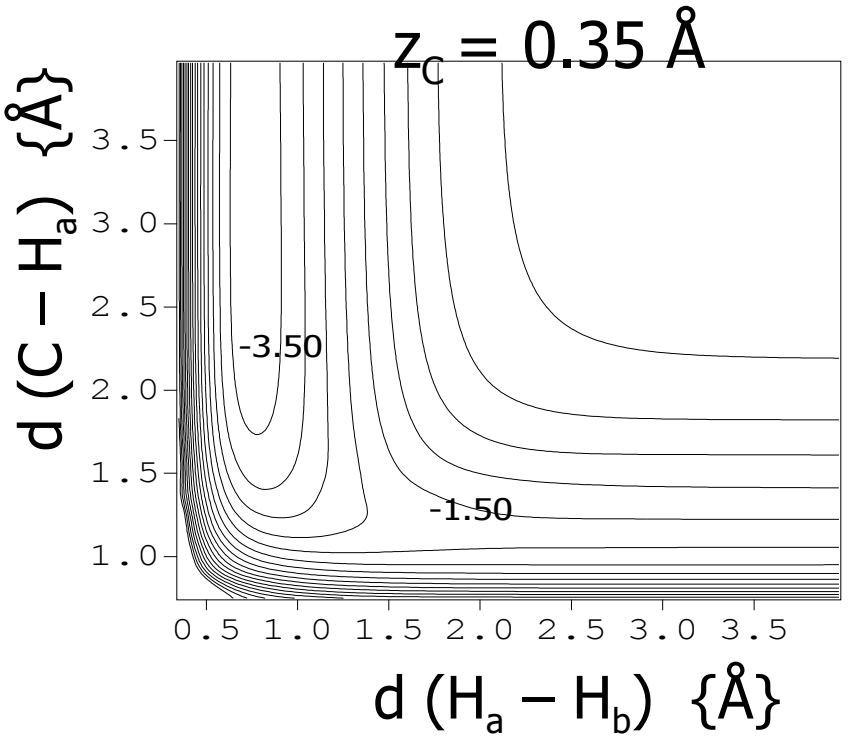
An important question : energy sharing
Internal energy of the nascent molecule, kinetic energy of the molecule, C-surface vibration

Available energy : **3.00eV**+Ecoll+ZPE

Eley-Rideal formation of H_2 involving one of two para-chemisorbed H atoms on a graphite surface

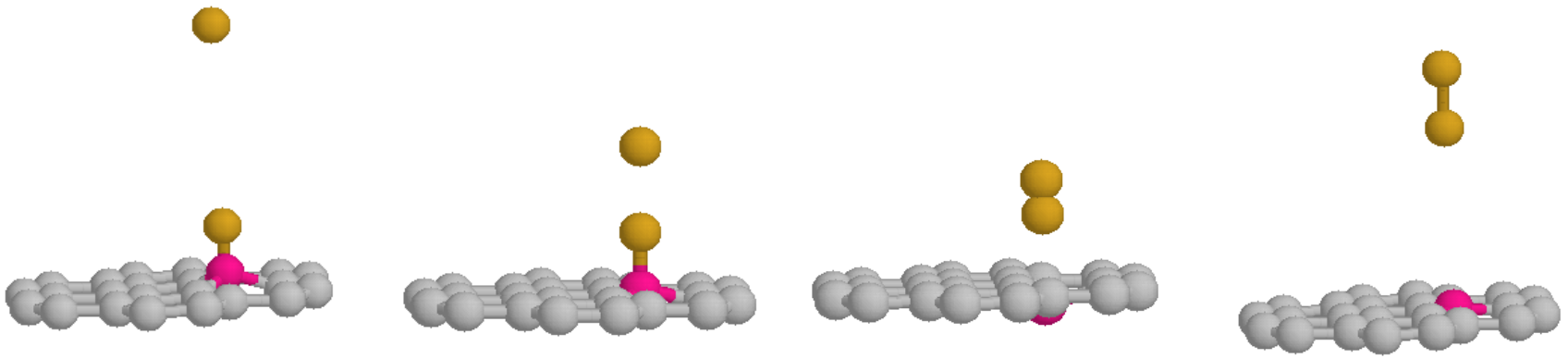
Newly computed 3D (C_{II},H_a,H_b) potential energy surface





Quasi-Classical molecular dynamics

Comparison with the formation of H_2 involving a single H atom chemisorbed on a graphite surface

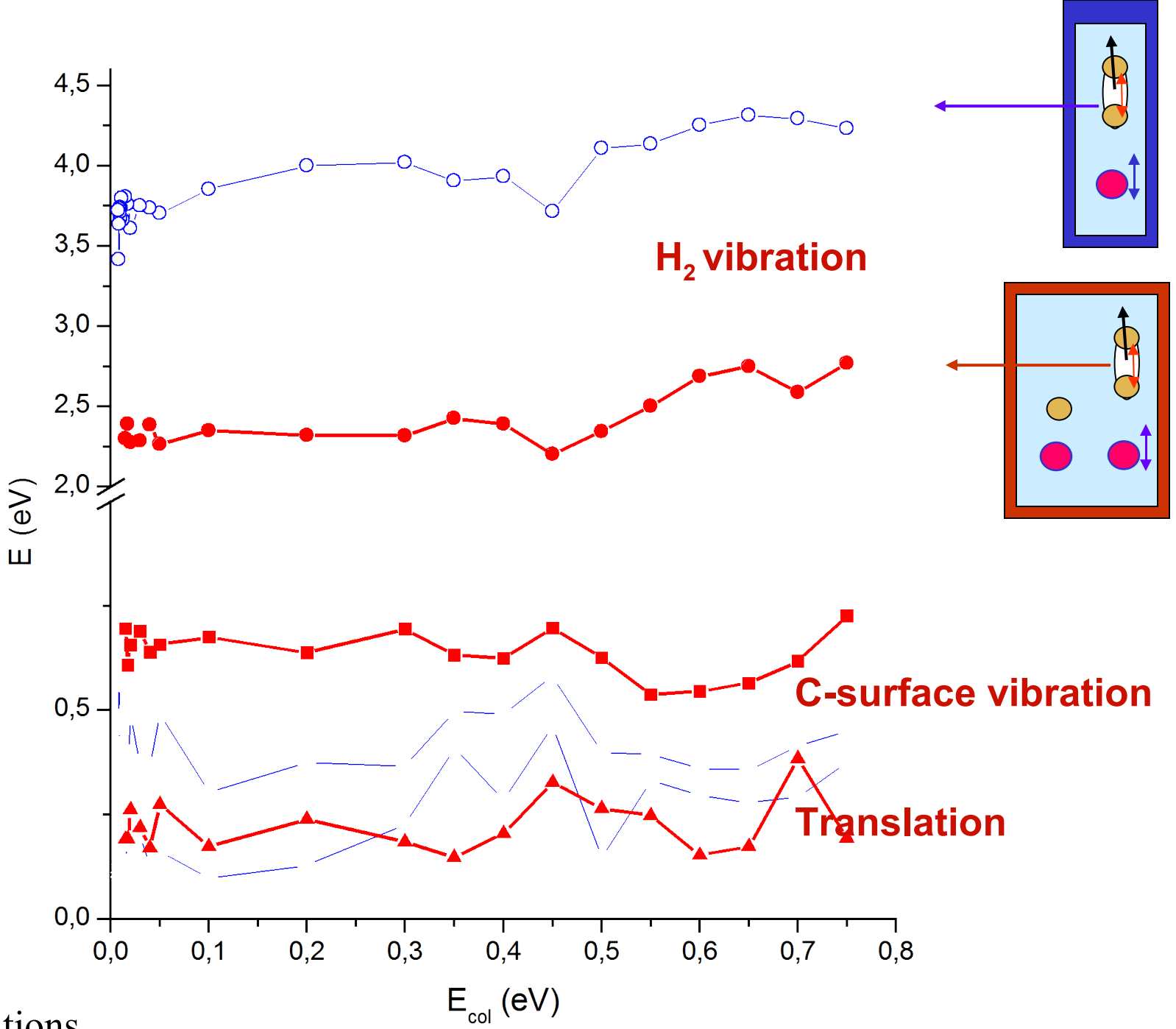


$H_{coll} + H_{\text{chimisorbé /graphite}} \longrightarrow H_2$

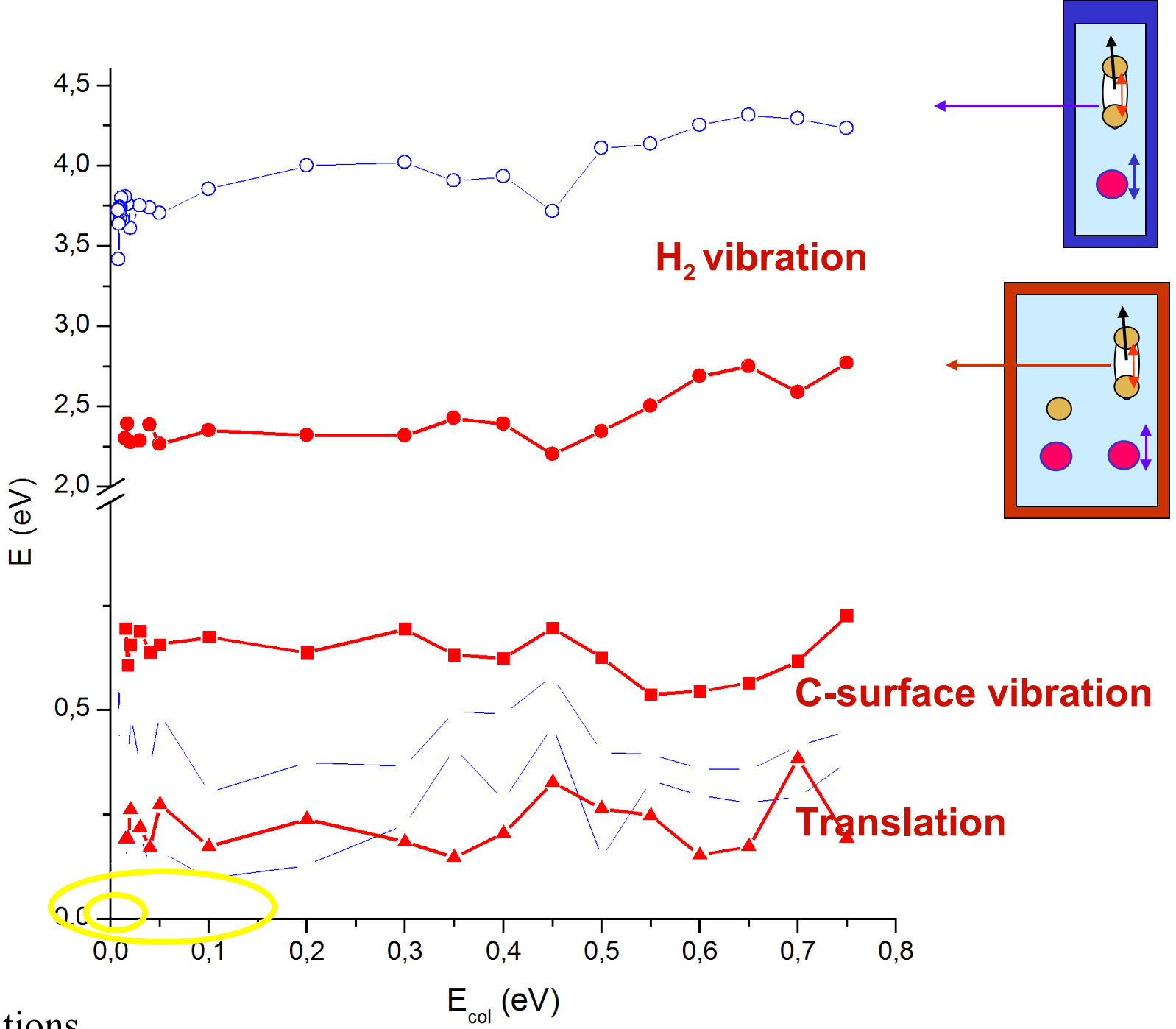
Morisset et al (2003, 2004)
- Quantum Dynamics (QWPP quantal wavepacket propagation)
- Classical Dynamics (QCT quasi classical trajectory)

(3 D calculations : collinear geometry)

Available energy : **4.10eV**+Ecoll+ZPE

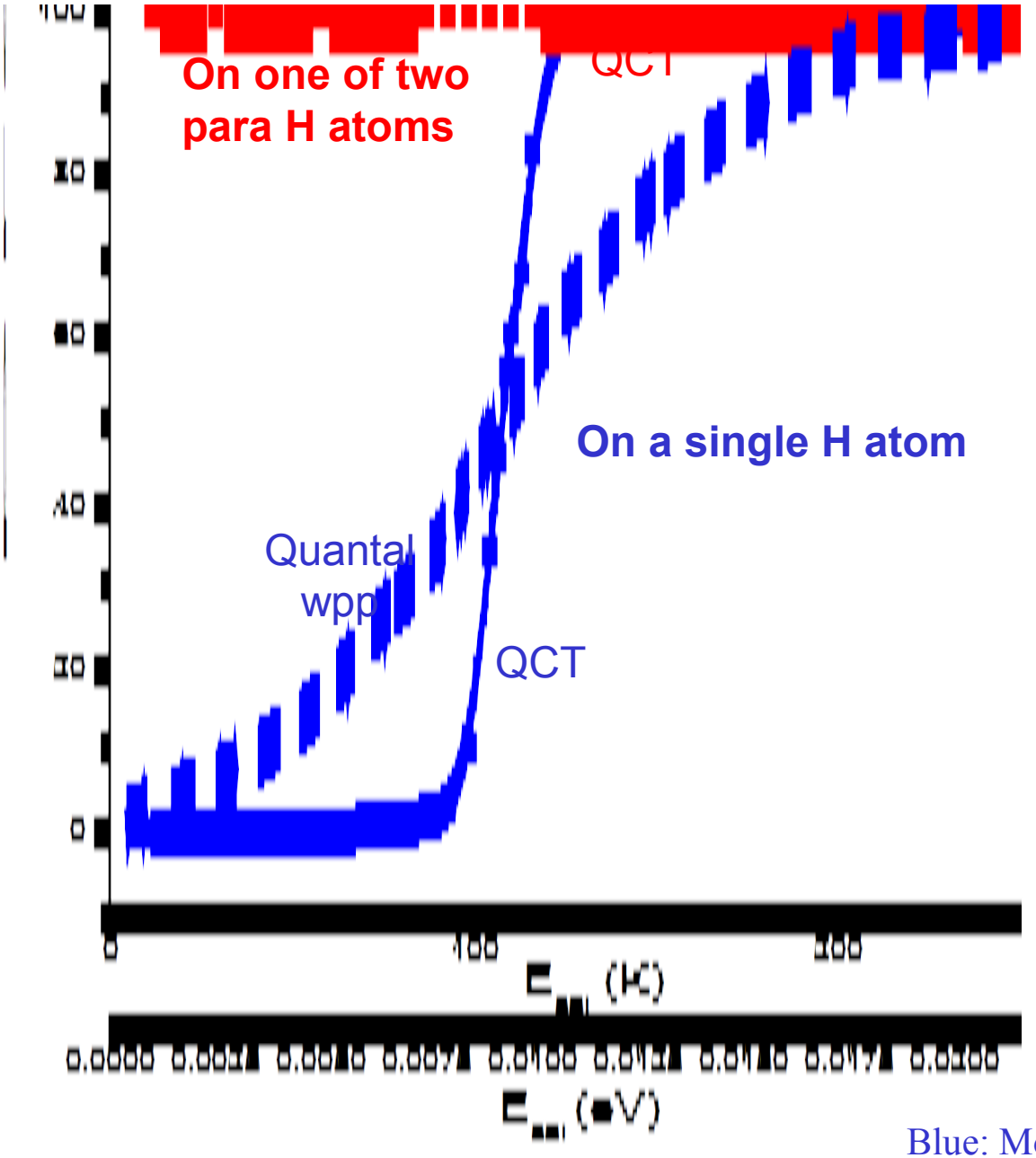


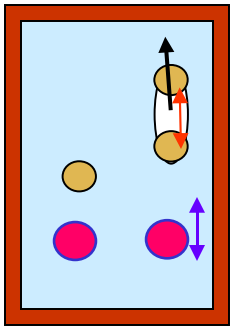
QCT calculations

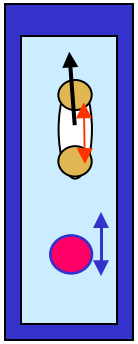


QCT calculations

Eley-Rideal Reaction probability



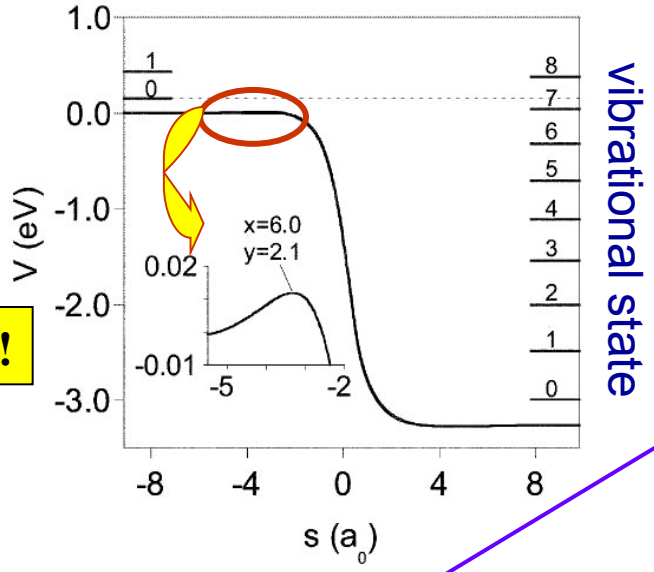




Blue: Morisset et al 2003, 2004

$H_{coll} + H_{\text{chimisorbé /graphite}} \longrightarrow H_2$

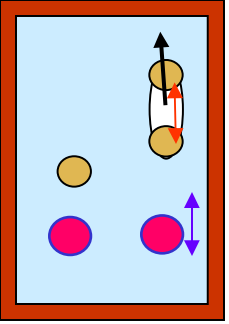
Jeloaica and Sidis 2001
Sha and Jackson 2002
Morisset et al. 2002-2003



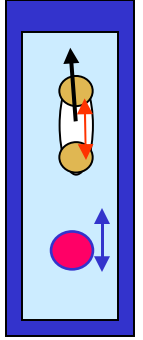
Barrier to reaction !

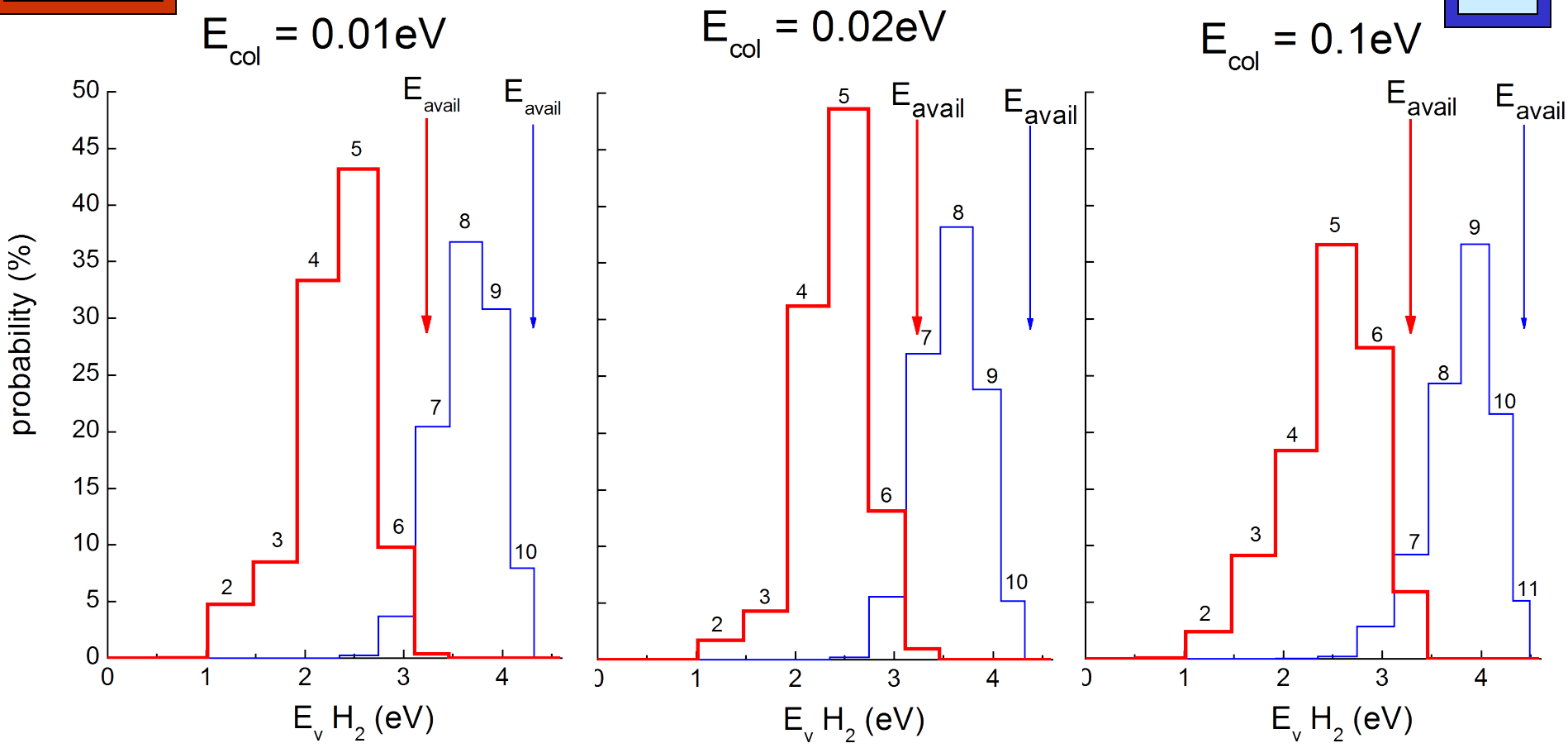
$H_{coll} + H_{\text{chimisorbé /H@graphite}} \longrightarrow H_2$

No Barrier to reaction !



Vibrational distribution of the nascent H_2





Available energy : **4.10eV**+Ecoll+ZPE ; **3.00eV**+Ecoll+ZPE