

# HYDROGENE SUR GRAPHENE

## DFT & DM

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*<sup>3</sup> University of California, Berkeley, CA 94720, USA*

# INSTITUT NÉEL

Recherche fondamentale en physique de la matière condensée, riche d'une importante composante interdisciplinaire aux interfaces avec la chimie, l'ingénierie et la biologie.

**NANO**

**MCBT**

**MCMF**

460 personnes  
20 théoriciens

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Recherche fondamentale en physique de la matière condensée, riche d'une importante composante interdisciplinaire aux interfaces avec la chimie, l'ingénierie et la biologie.

## NANO - Nanosciences

Etude des propriétés physiques d'objets nanométriques, leur utilisation en vue d'applications dans les domaines de l'énergie, des techniques de l'information, et de la biologie



champ proche  
cohérence quantique  
micro- nano magnétisme  
nanophysique et semiconducteurs  
nanospintronique et transport moléculaire  
semi-conducteurs à large bande interdite  
systèmes hybrides de basse dimensionnalité  
théorie et nanosciences

Recherche fondamentale en physique de la matière condensée, riche d'une importante composante interdisciplinaire aux interfaces avec la chimie, l'ingénierie et la biologie.

## MCBT - Matière Condensée - Basses Températures

Etude fondamentale des nouveaux états de la matière condensée, développement des procédés ou des instruments originaux



cristaux électroniques  
hélium : du fondamental aux applications  
matière condensée et physique statistique  
supraconducteurs et matériaux fonctionnels, de l'élaboration aux applications  
systèmes à fortes corrélations électroniques  
thermodynamique et biophysique des petits systèmes  
ultra-basses températures

# INSTITUT NÉEL

Recherche fondamentale en physique de la matière condensée, riche d'une importante composante interdisciplinaire aux interfaces avec la chimie, l'ingénierie et la biologie.

## MCMF - Matière Condensée - Matériaux et Fonctions

Développe l'élaboration, les études cristallographiques ou spectroscopiques et la modélisation de matériaux fonctionnels



intermétalliques & interstitiels – conversion de l'énergie  
matériaux, optique non linéaire et plasmonique  
surfaces, interfaces et nanostructures  
structure et propriétés des matériaux – conditions extrêmes  
théorie et simulation numérique des propriétés électroniques

Recherche fondamentale en physique de la matière condensée, riche d'une importante composante interdisciplinaire aux interfaces avec la chimie, l'ingénierie et la biologie.

**NANO**

**MCBT**

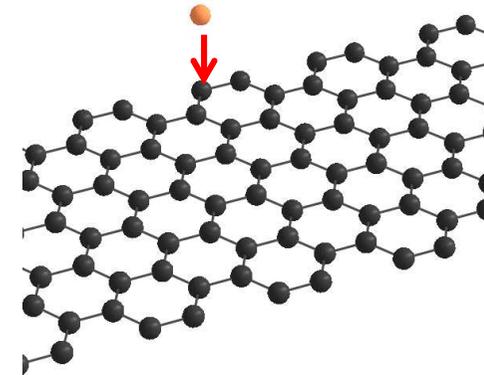
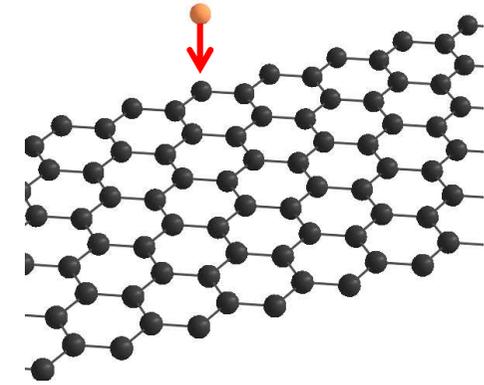
**MCMF**

Yves Joly, Valerio Olevano, Jean-Pierre Julien  
Développement de méthodes et de codes

Xavier Blase, Claudio Attacalite  
Développement de codes et calculs

Marie Bernadette Lepetit, Laurence Magaud  
Calculs

# PLAN



bords de GNR

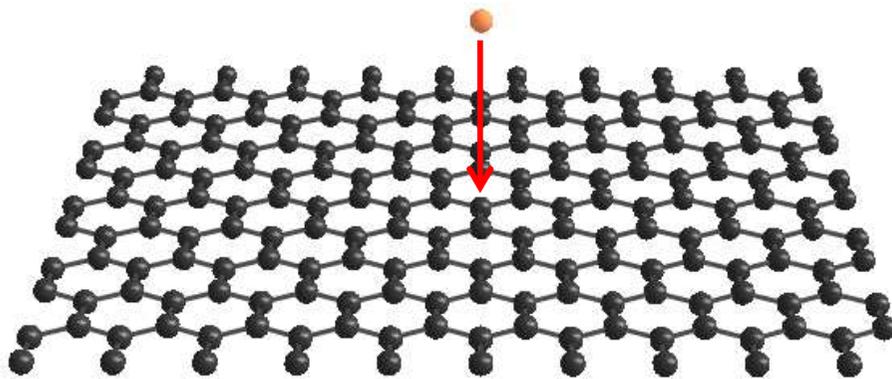
spin

fonctionnelle

Tests sur les paramètres

taille de cellule

relaxation



énergie initiale

DMQ vs DMC

# METHODES

## DFT

VASP

6x6x1

PW91

## DM classique

potentiel C-H REBO 2<sup>e</sup> génération  
(Brenner et al.)

NVE à 0K

Velocity-Verlet

$\Delta t = 0.1$  fs

160 C

# METHODES

## DFT

VASP

6x6x1

PW91

### DM quantique

NVE à 0K

$\Delta t = 0.1$  fs

200 C

## DM classique

potentiel C-H REBO 2<sup>e</sup> génération  
(Brenner et al.)

NVE à 0K

Velocity-Verlet

$\Delta t = 0.1$  fs

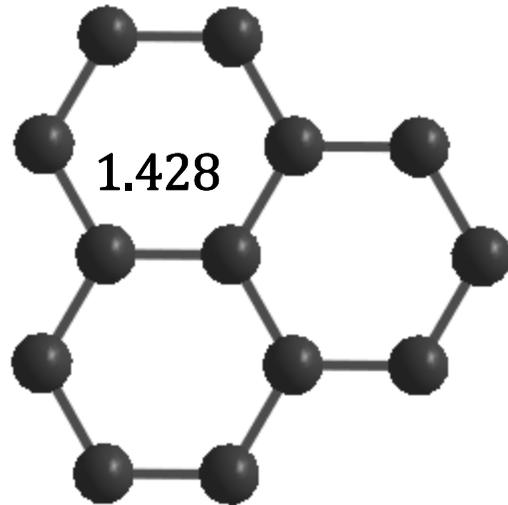
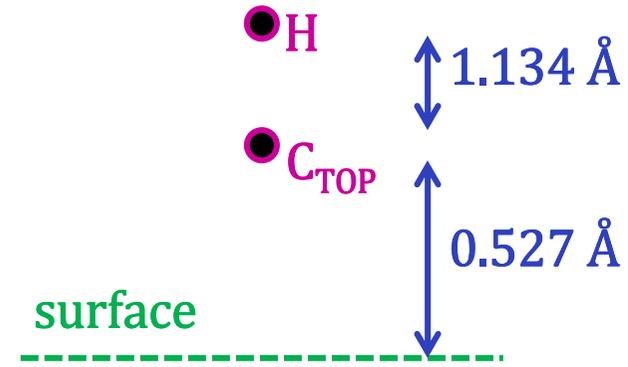
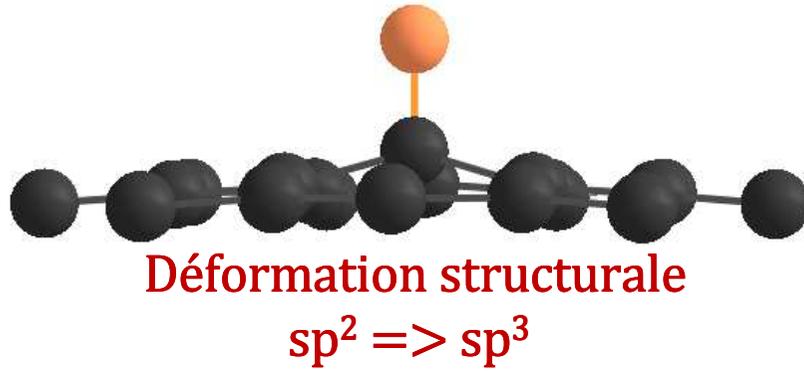
160 C

# DFT

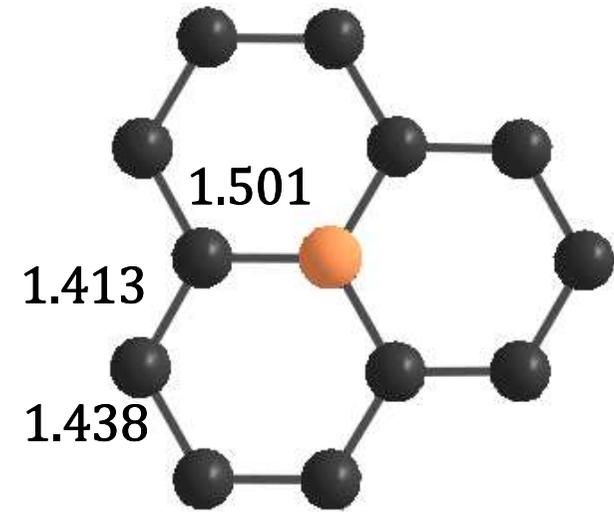
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# TESTS DES PARAMETRES

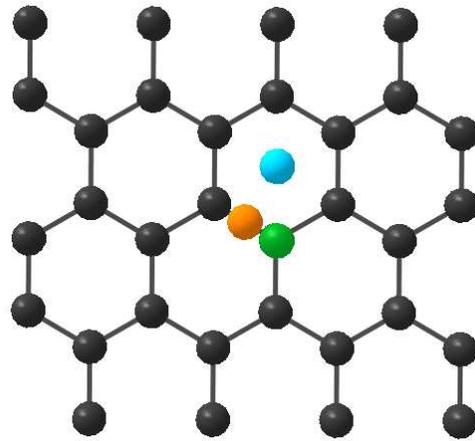
# H ADSORBE



Absorption du H



# H ADSORBE

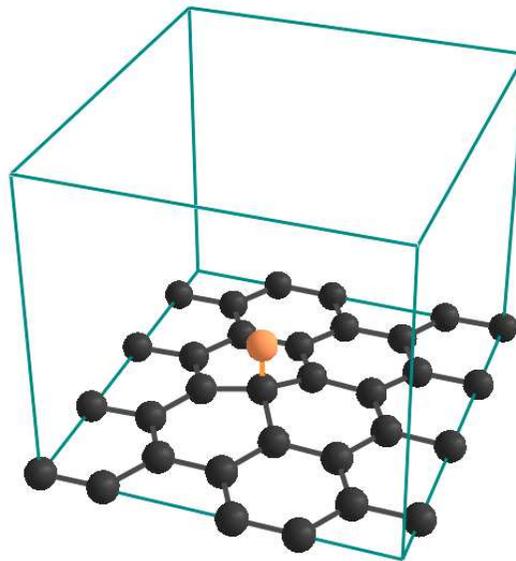


top  
bridge  
hollow

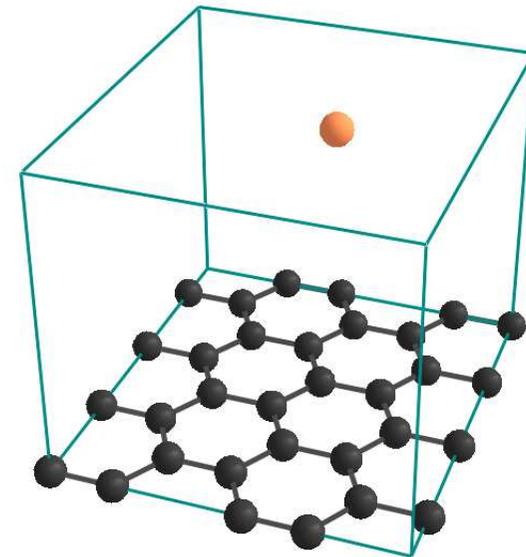


3 sites d'adsorption

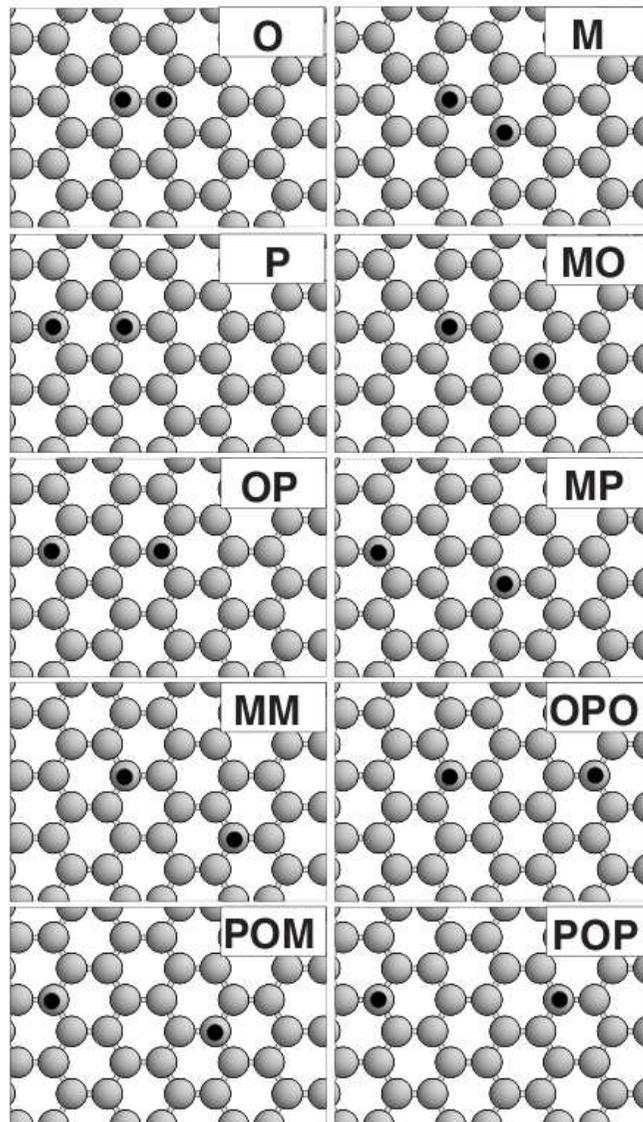
énergie =



moins



# POLARISATION EN SPIN



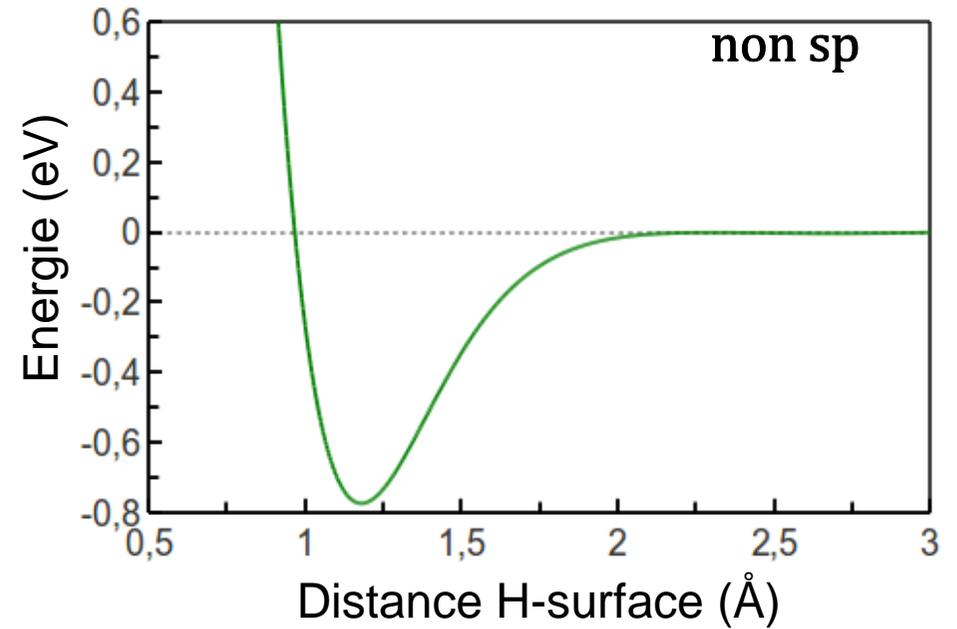
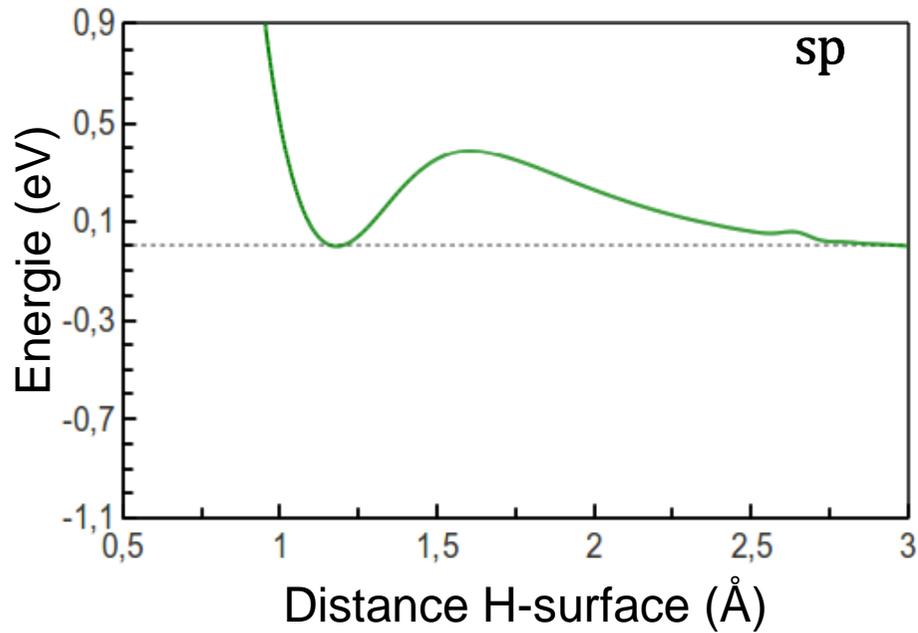
Etude expérimentale et théorique  
de dimères d'hydrogène sur graphite (0001)

la part de sp dans l'énergie de liaison  
des dimères ferromagnétiques  $< 0.12$  eV

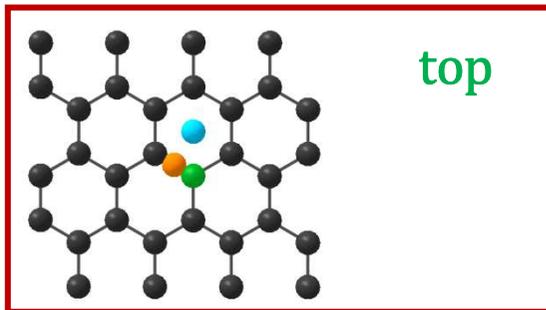
seuls les dimères non-magnétiques  
sont observés expérimentalement

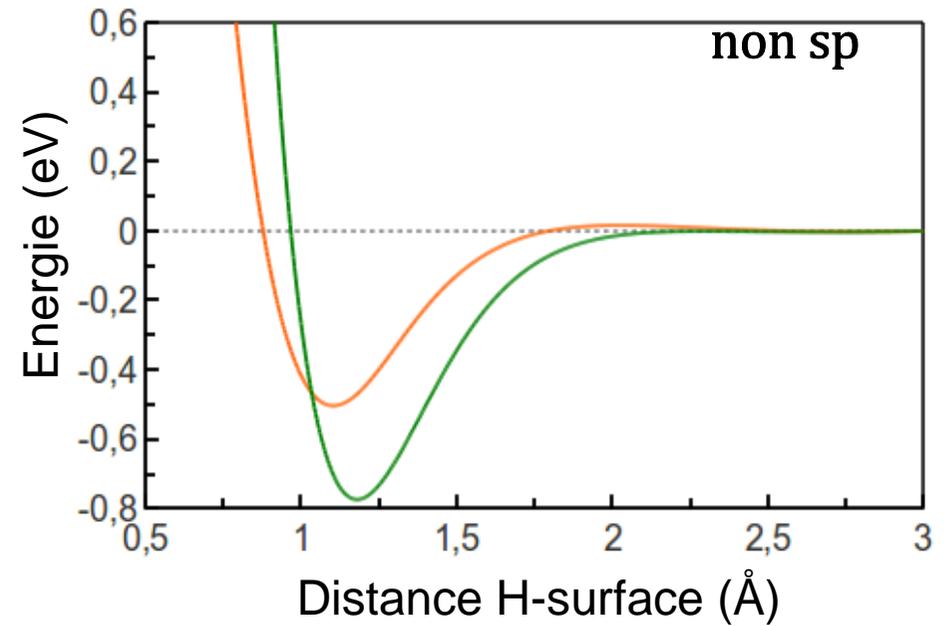
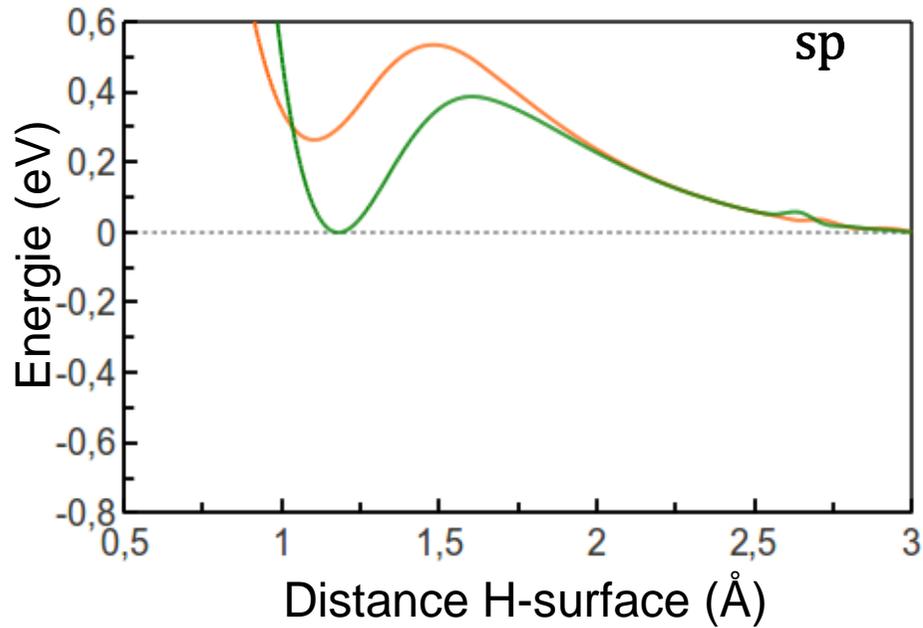
$\Rightarrow$  étude de la stabilité de  $H_2$  sur graphène  
sans sp, qui ralentit les calculs

Ž. Šljivananin et al, J. Chem. Phys. 131, 2009

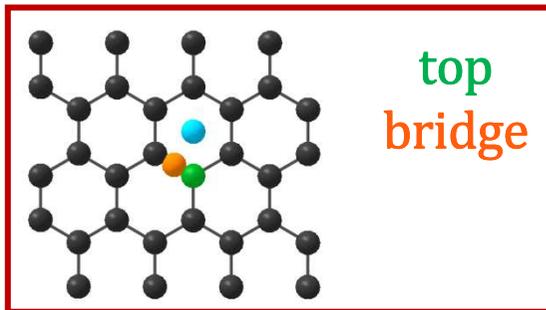


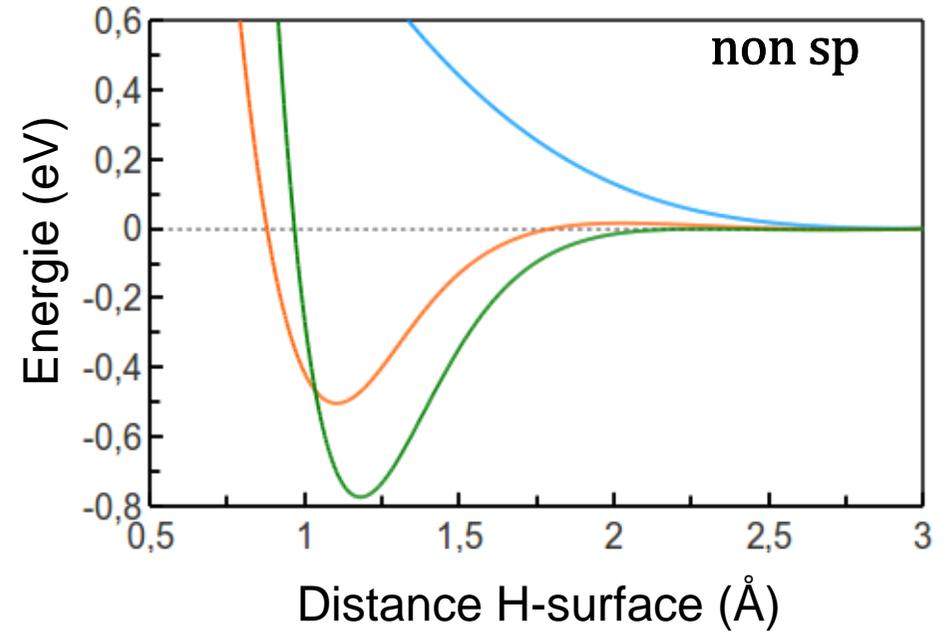
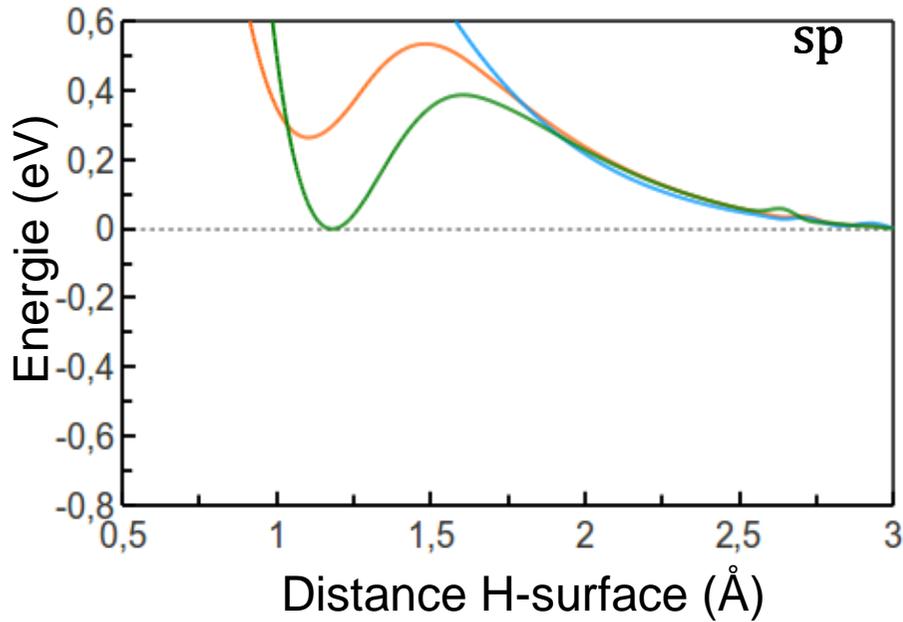
25 eV  
DMQ



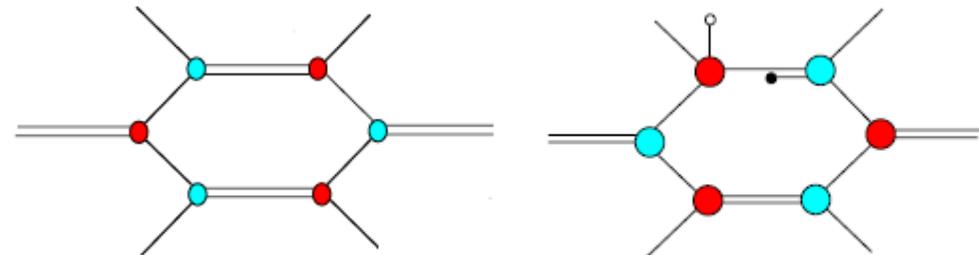
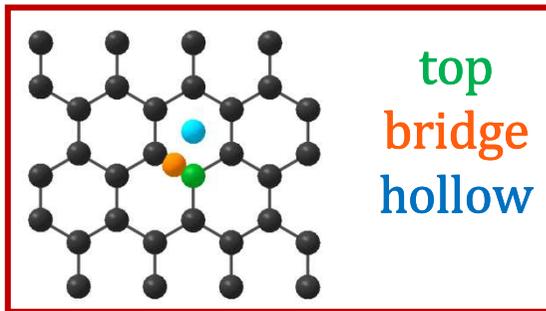


25 eV  
DMQ

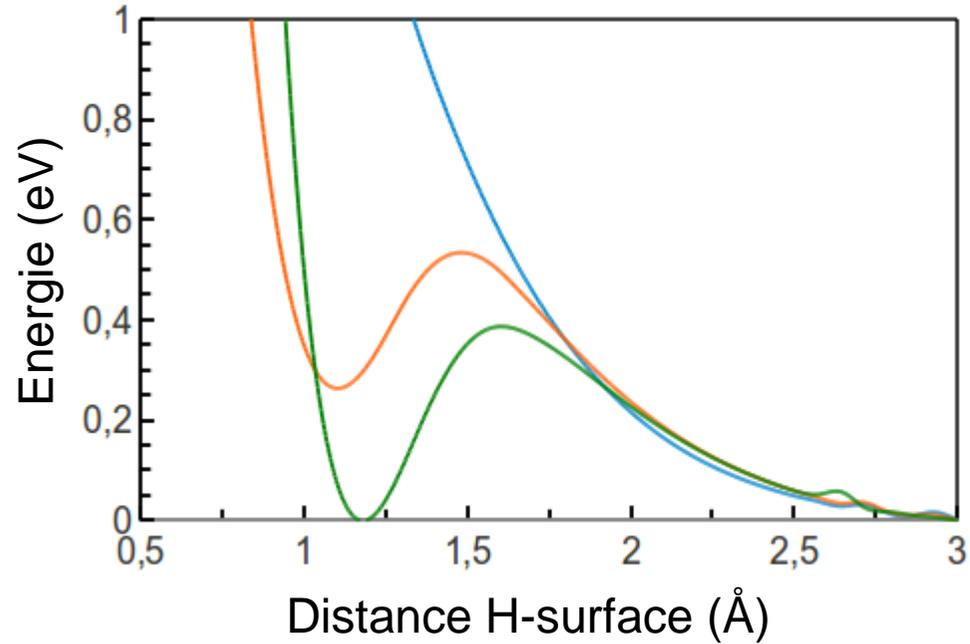




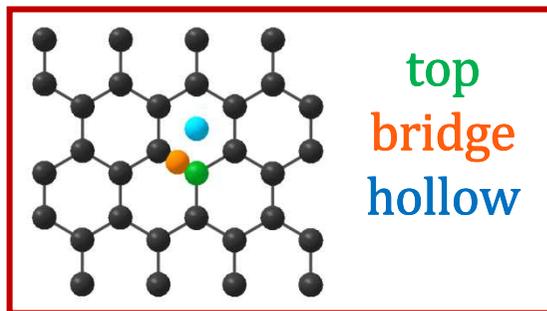
25 eV  
DMQ

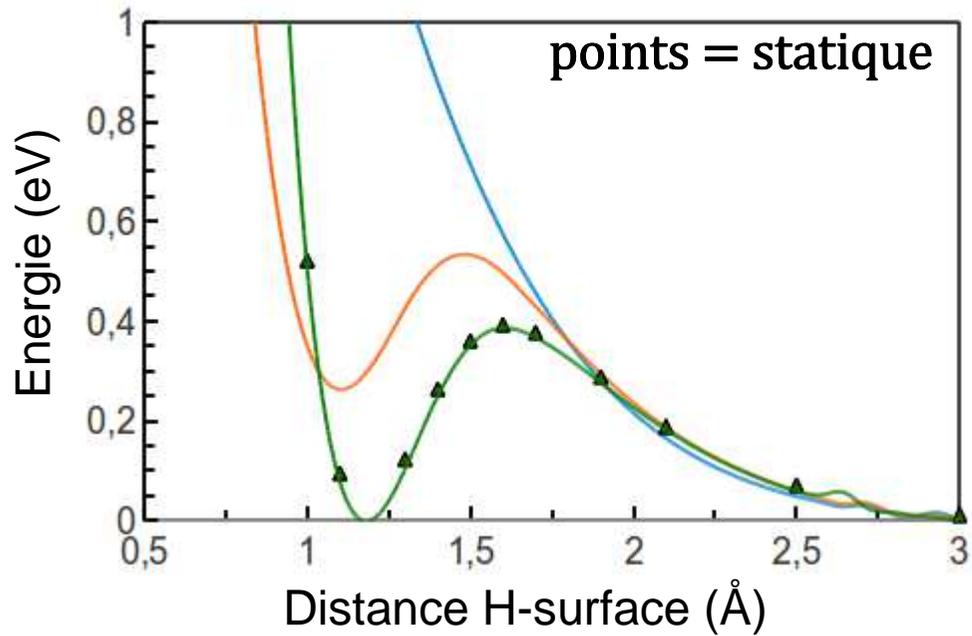


⇒ prendre en compte la polarisation en spin

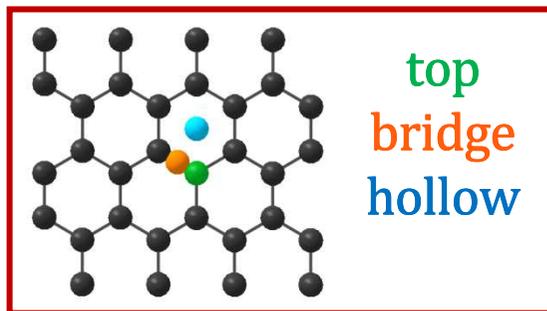


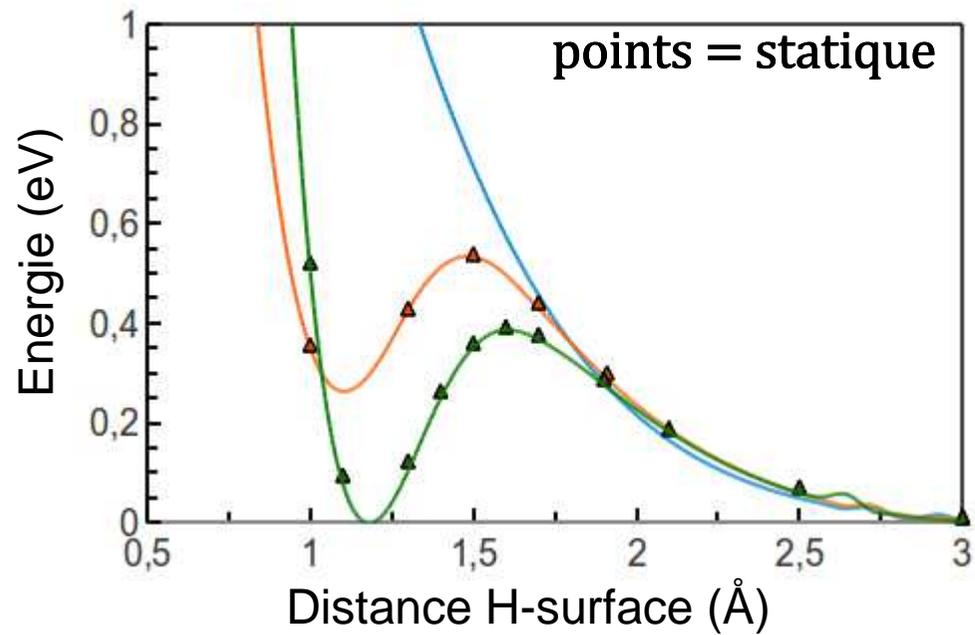
25 eV  
DMQ



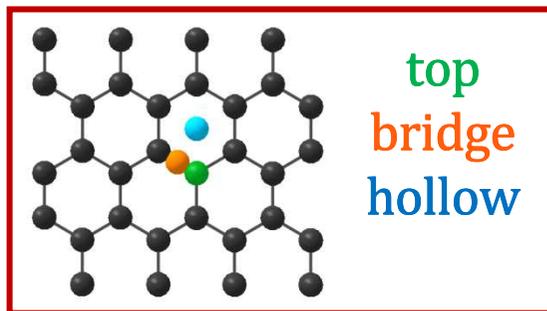


25 eV  
DMQ



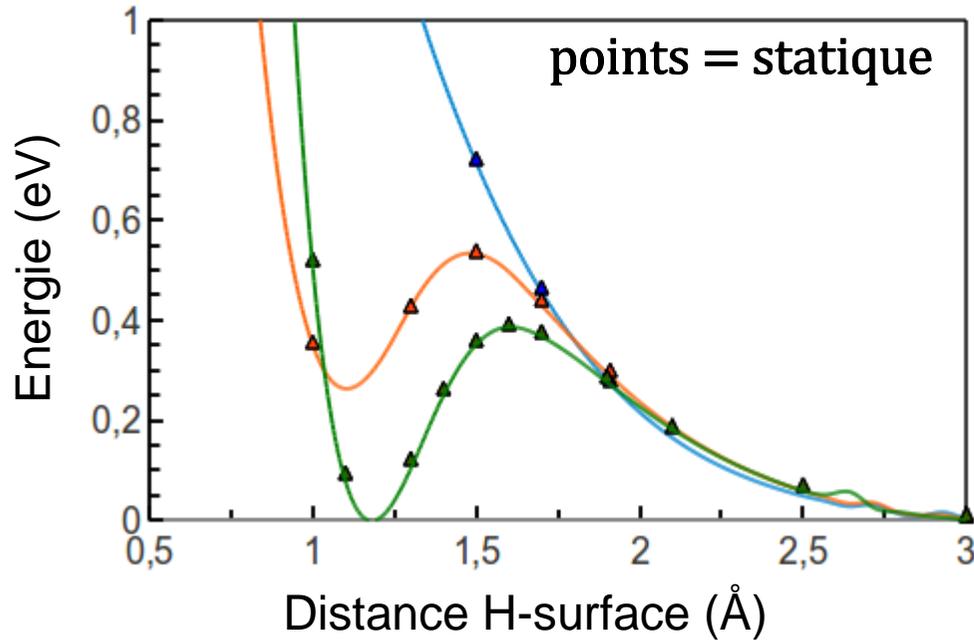


25 eV  
DMQ



top  
bridge  
hollow

# RELAXATION

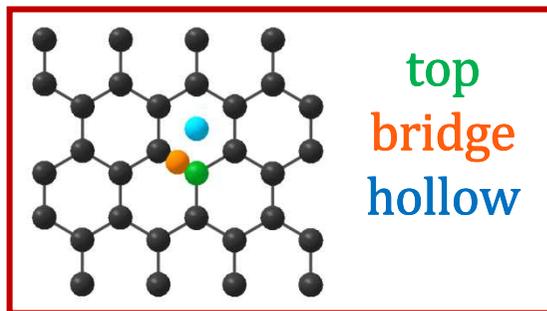


distance > 0.5 Å  
⇒ très bon accord

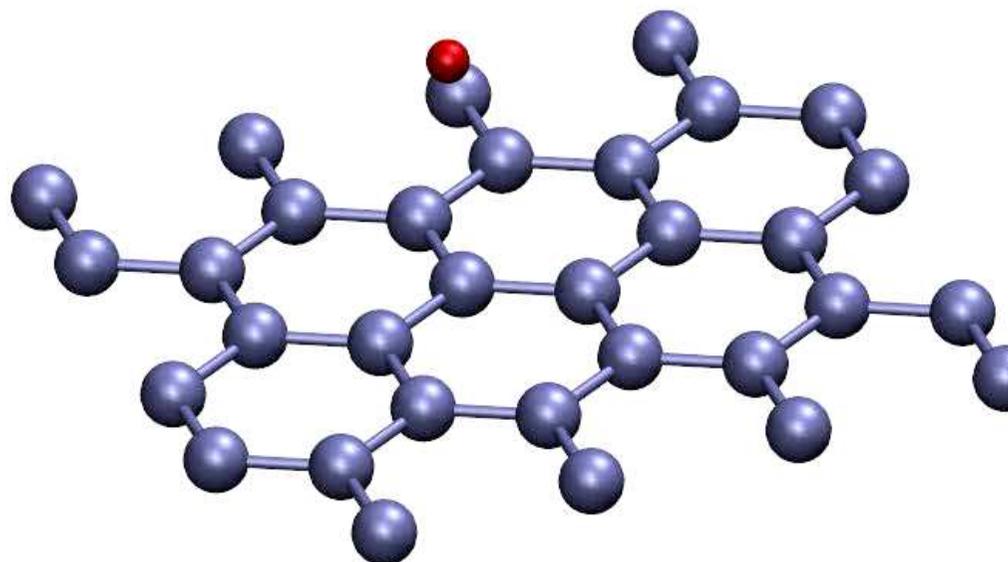
distance < 0.5 Å  
⇒ divergence :

d (Å)	E (eV)
0.5	0.005
0	0.03
0.5	0.1
0	1.87

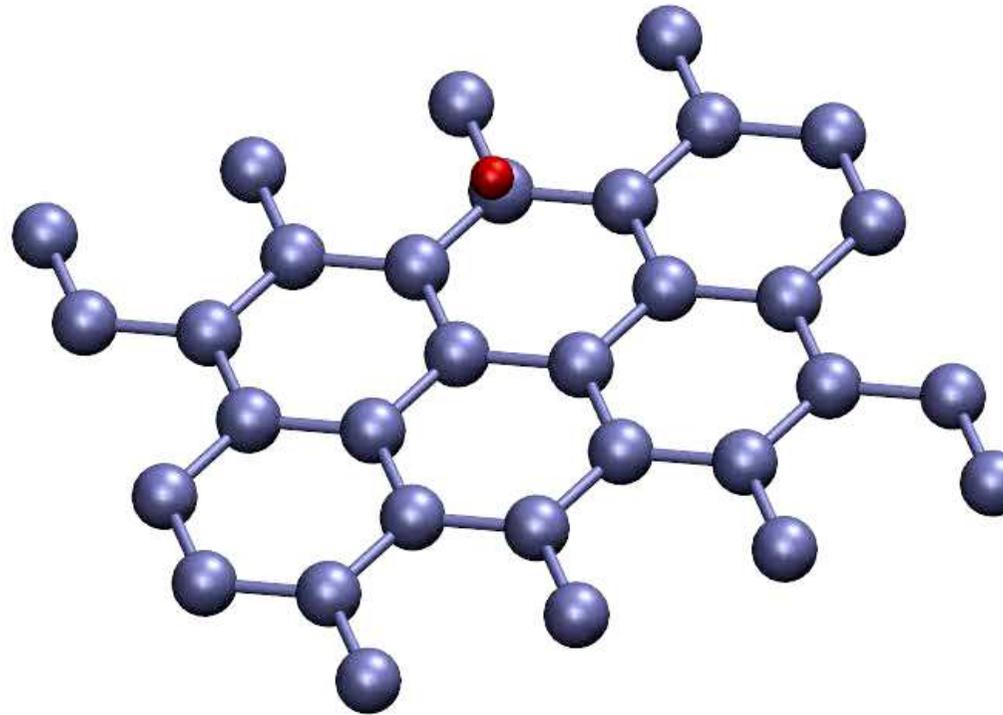
25 eV  
DMQ



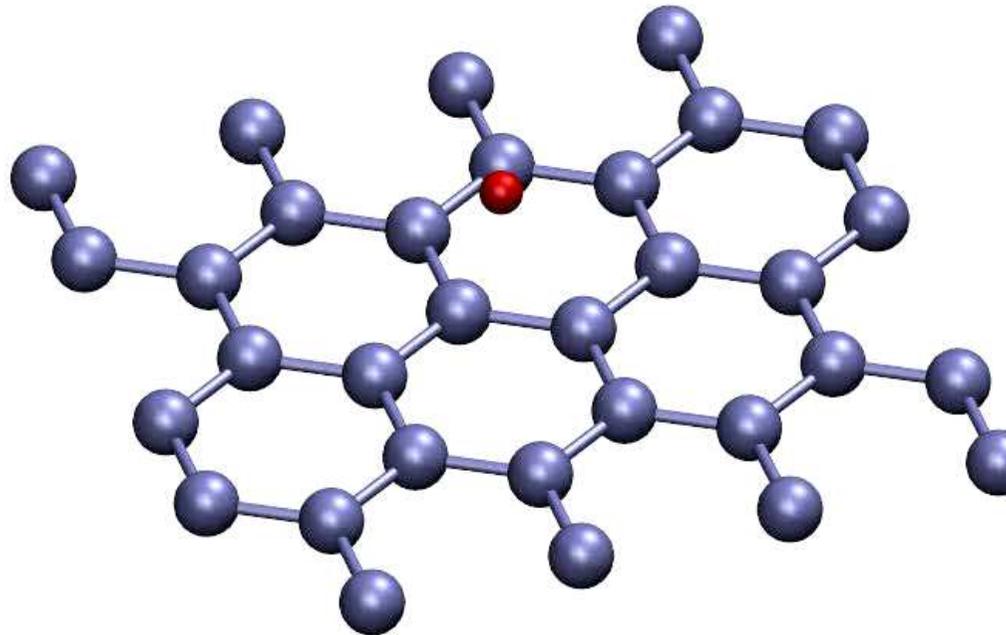
relaxation non négligeable  
à courte distance



top

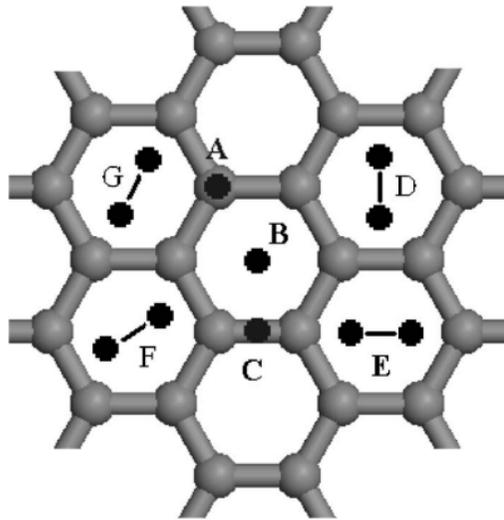


bridge



**hollow**

# FONCTIONNELLE



Longueur de liaison de  $H_2$  obtenue en GGA plus proche que celle obtenue en LDA.

80meV de différence entre LDA et GGA.

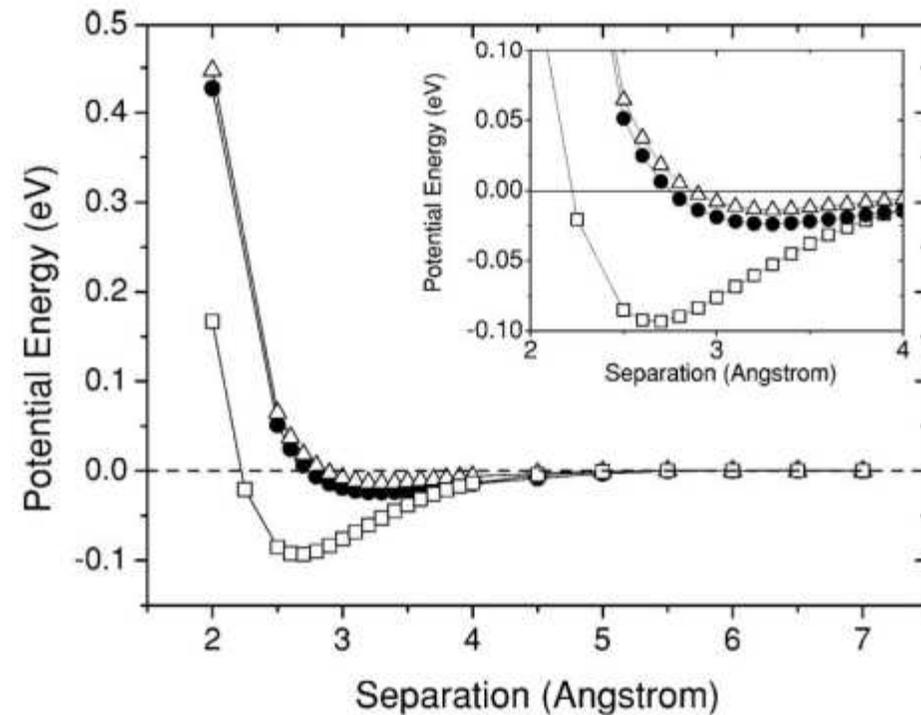
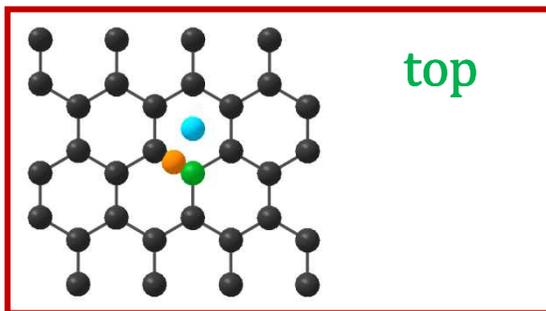
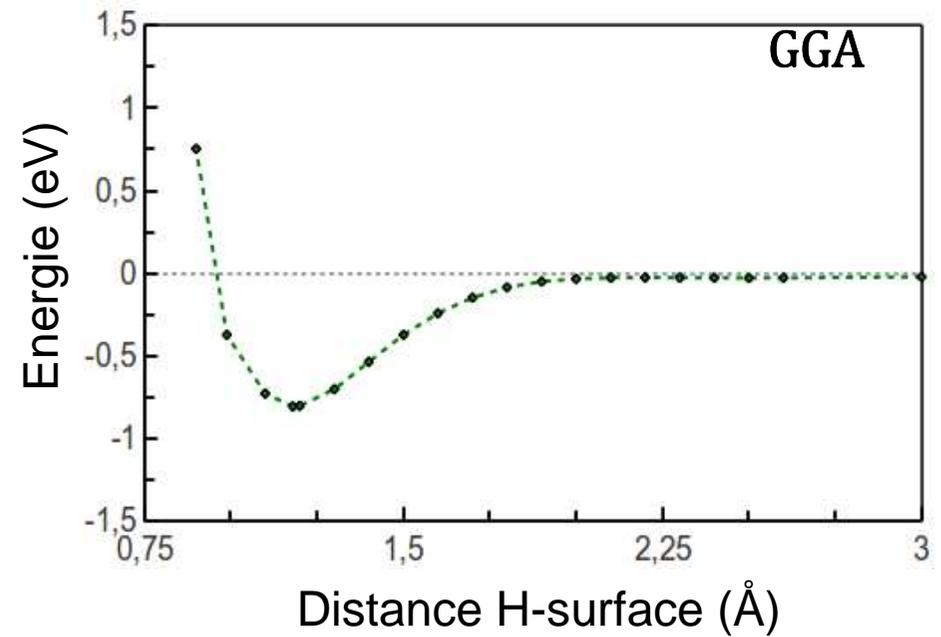
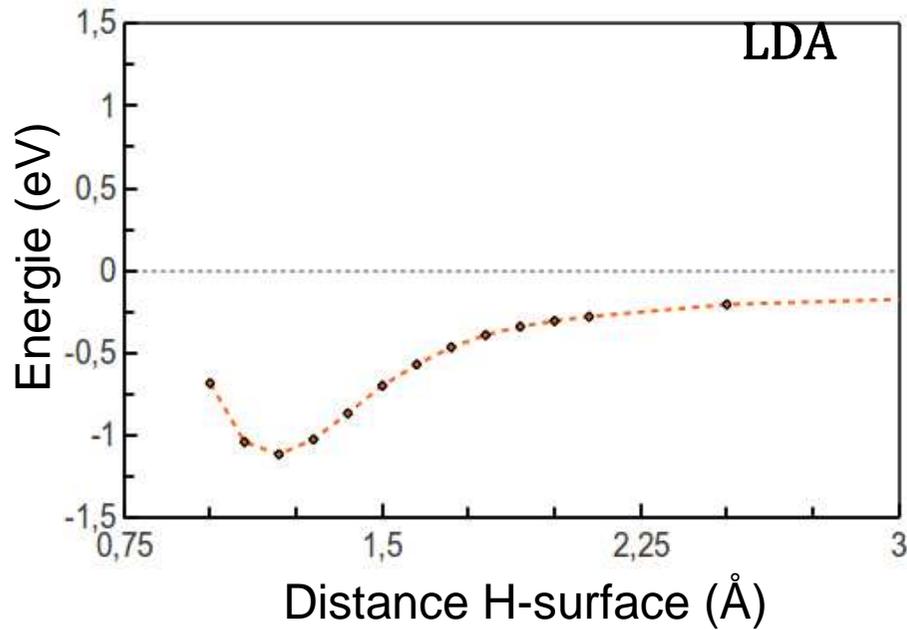


FIG. 3. Variation of potential energy with the separation between the graphene sheet and the center of mass of the hydrogen molecule in site D using the LDA VWN functional ( $\square$ ), the GGA PW91 functional ( $\bullet$ ), and the GGA PBE functional ( $\triangle$ ). Inset: close up of the potential-energy minima.

D.Henwood et al., Phys. Rev. B 75, 2007

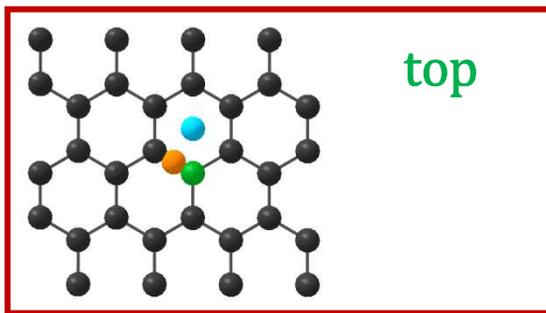
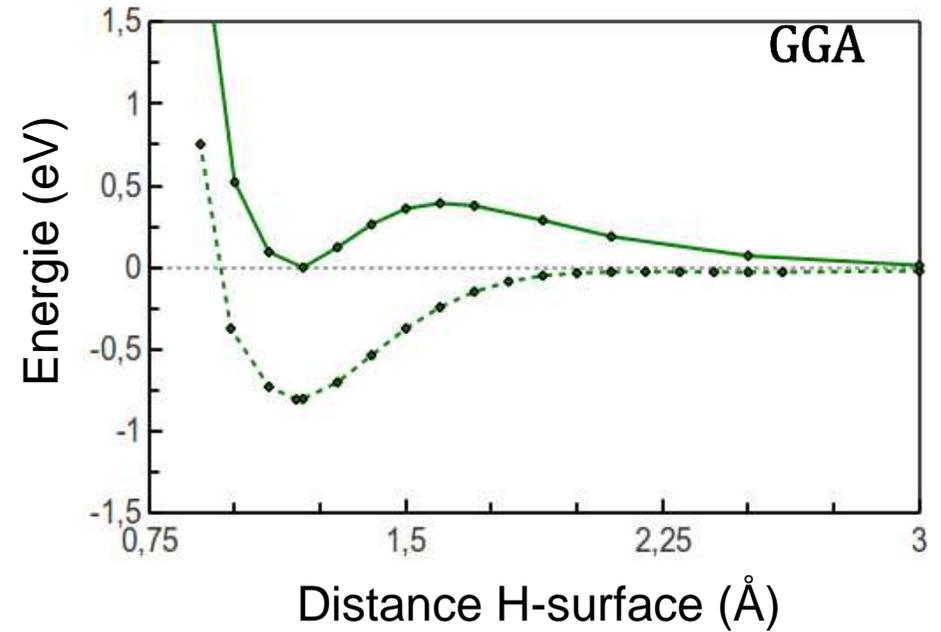
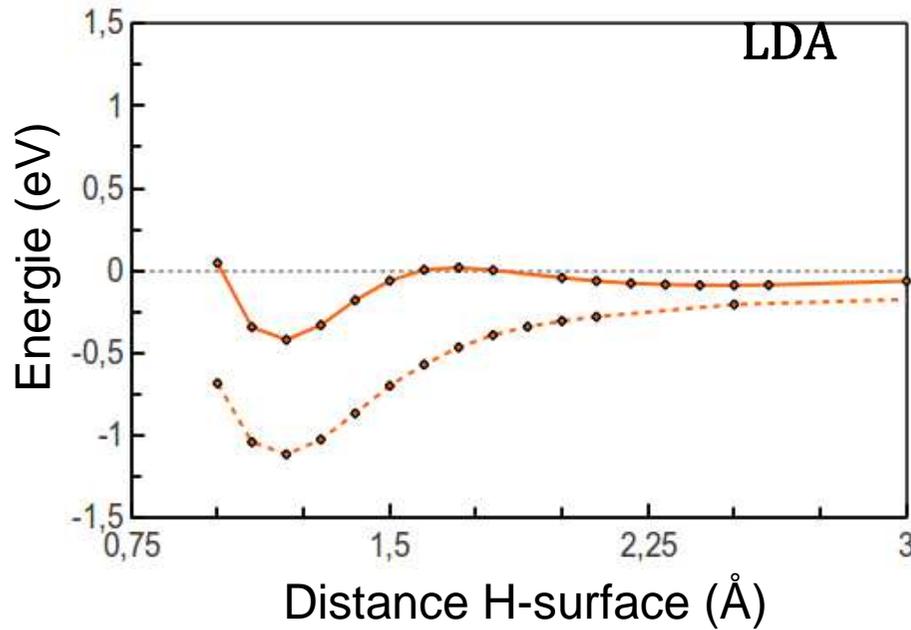
# FONCTIONNELLE



25 eV  
statique

non sp

# FONCTIONNELLE

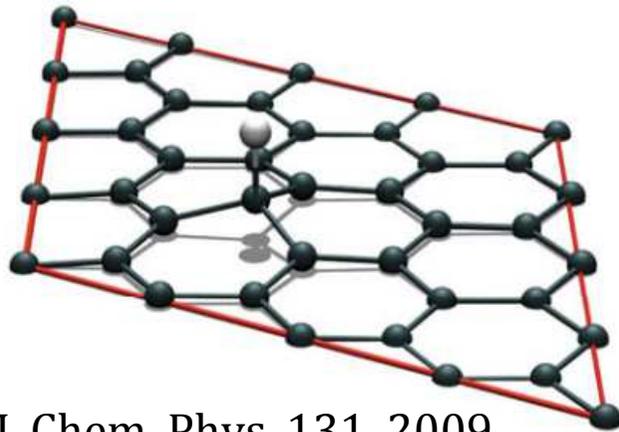


25 eV  
statique

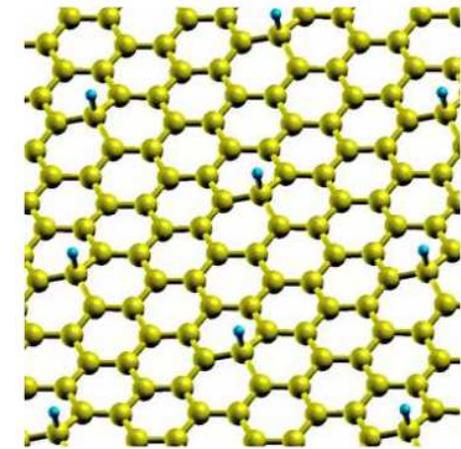
non sp  
avec sp

⇒ Pour ce système, choisir la fonctionnelle GGA

# FONCTIONNELLE

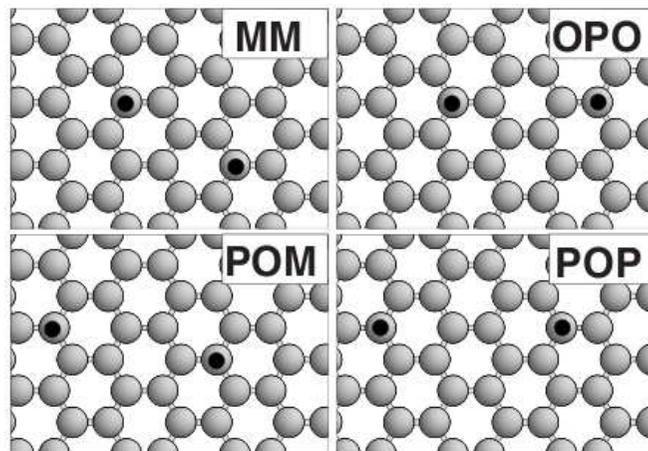


Ž.Šljivananin, J. Chem. Phys. 131, 2009

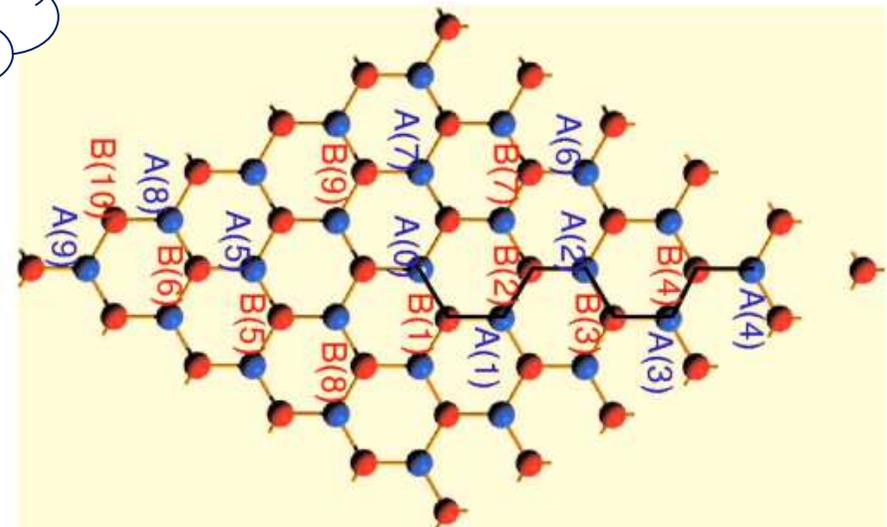


S.Casolo, J Chem Phys 130, 2009

GGA!



M.Mirzadeh, J. Phys.: Condens. Matter 24, 2012

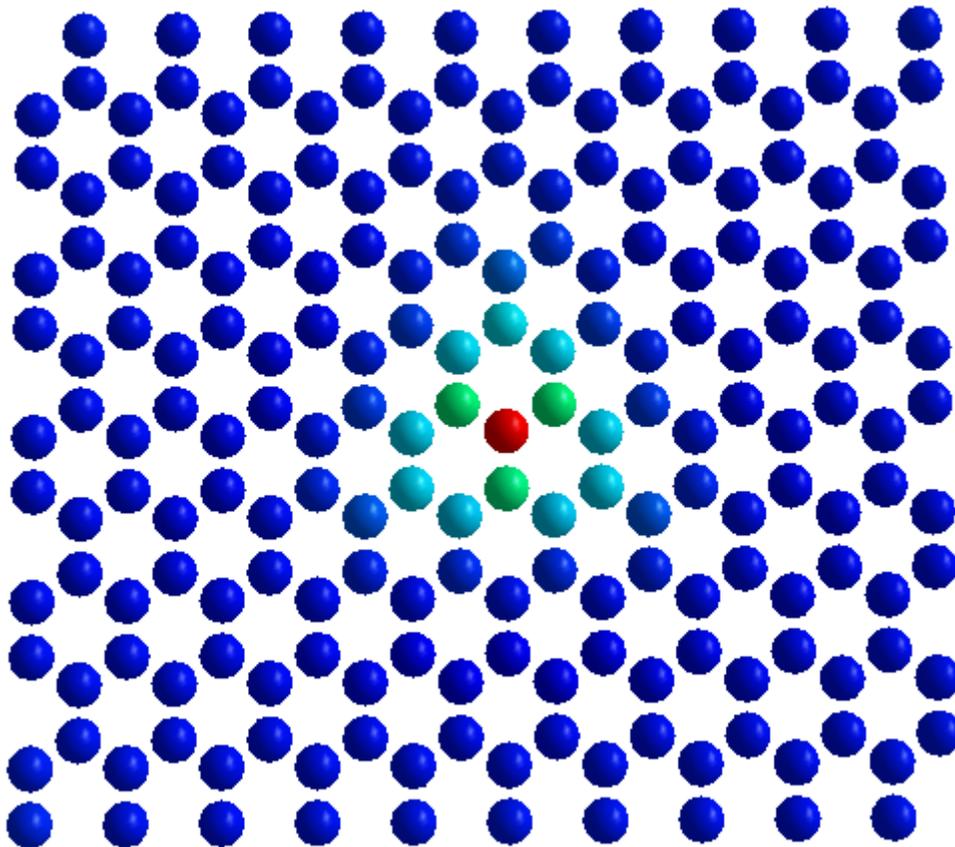


V.V.Ivanovskaya, Eur. Phys. J. B 76, 2010

# CELLULE INITIALE

200 atomes C

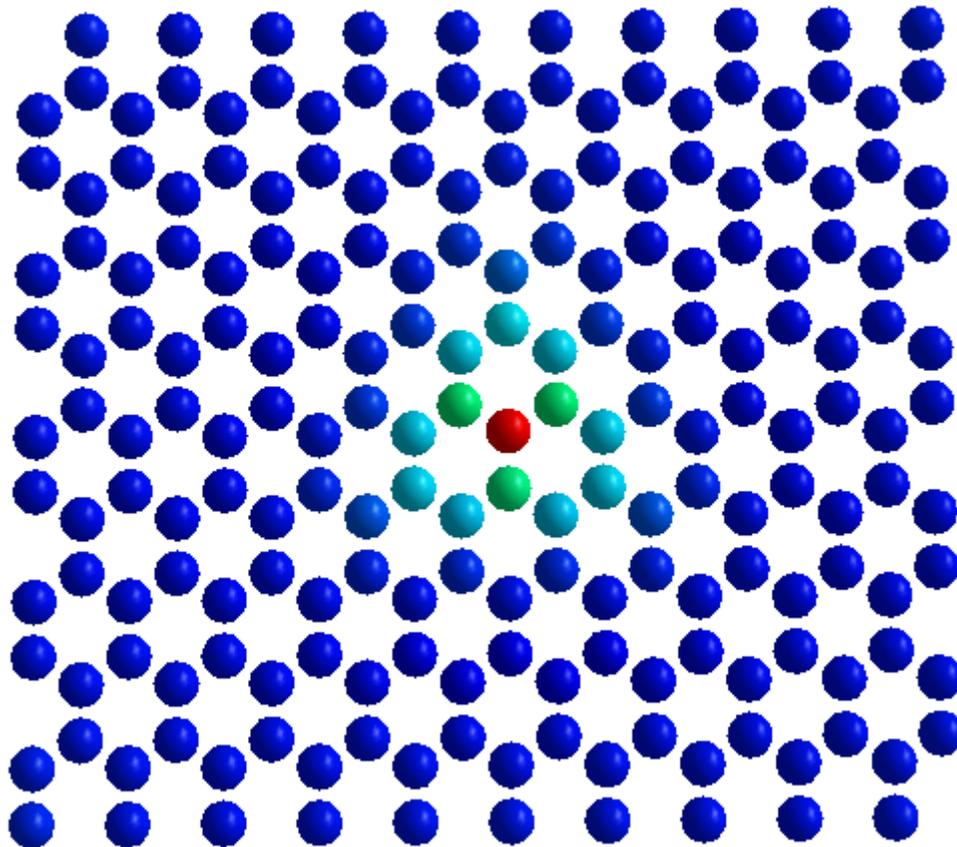
$[-0.02 ; 0.53] \text{ \AA}$



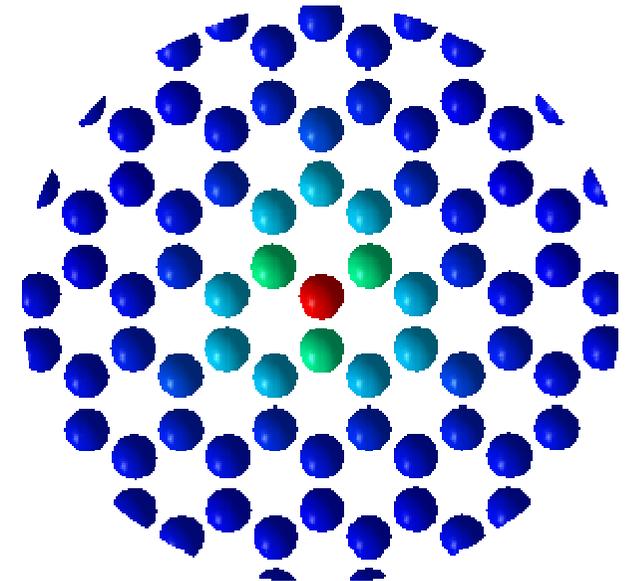
# CELLULE INITIALE

200 atomes C

$[-0.02 ; 0.53] \text{ \AA}$

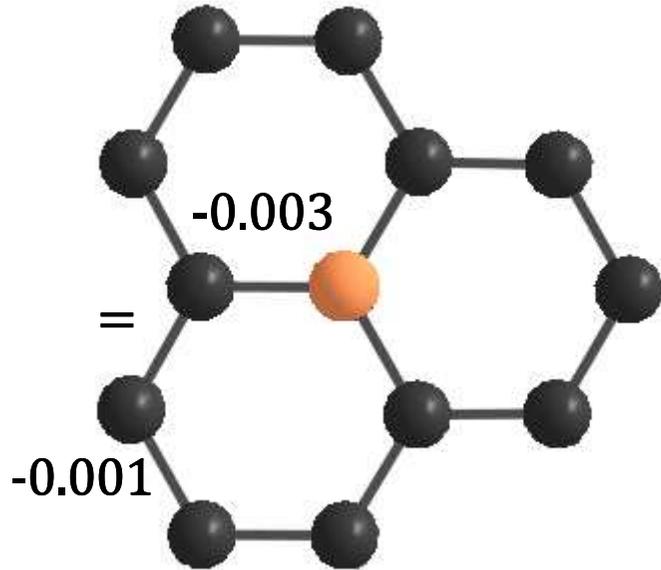


possible ?

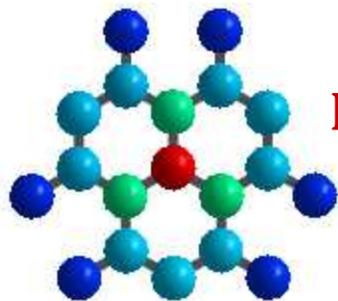
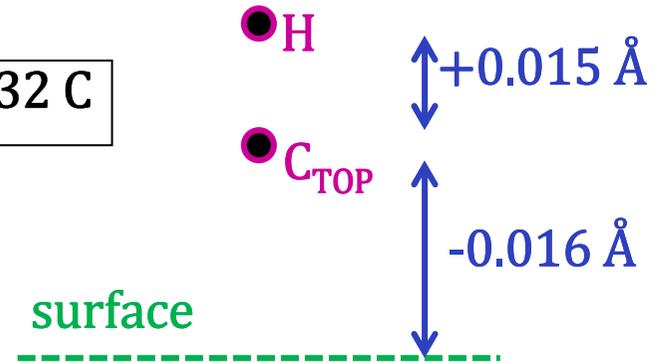


D.W.Boukhvalov et al, Phys. Rev. B 77, 2008

# CELLULE INITIALE

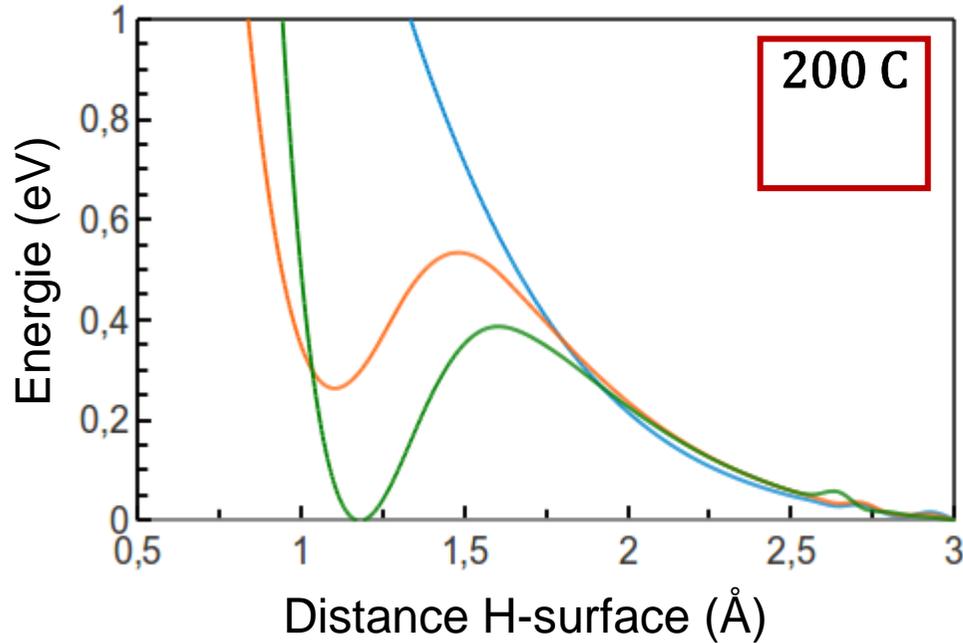


200 C vs 32 C



Déformation de 3.82 Å  
autour du C<sub>TOP</sub>

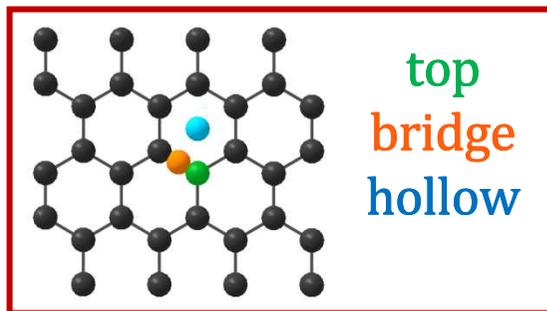
RAYON (Å)	HAUTEUR (Å)
0	1.134
1.501	0.173
2.514	0.088
2.892	0.086
3.820	0.003

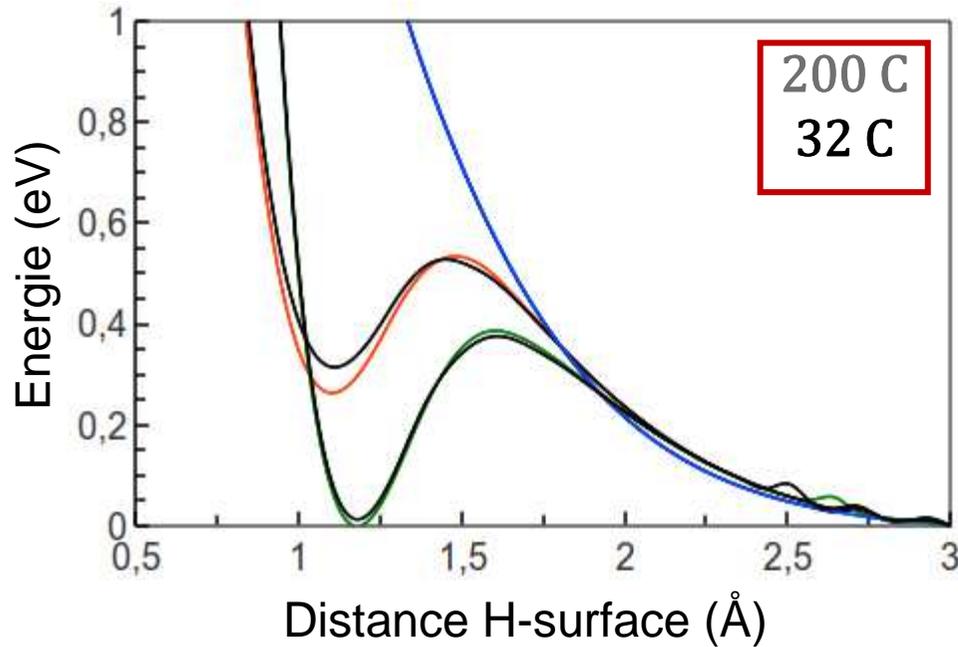


200 C et 32 C  
 ⇒ peu de différences structurales  
 lors de l'adsorption de H

Et pour la structure électronique ?

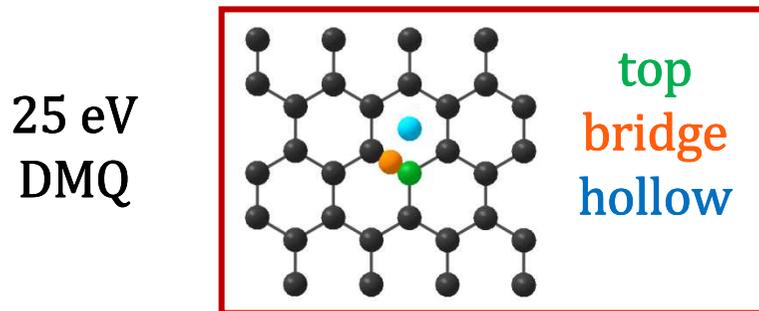
25 eV  
 DMQ





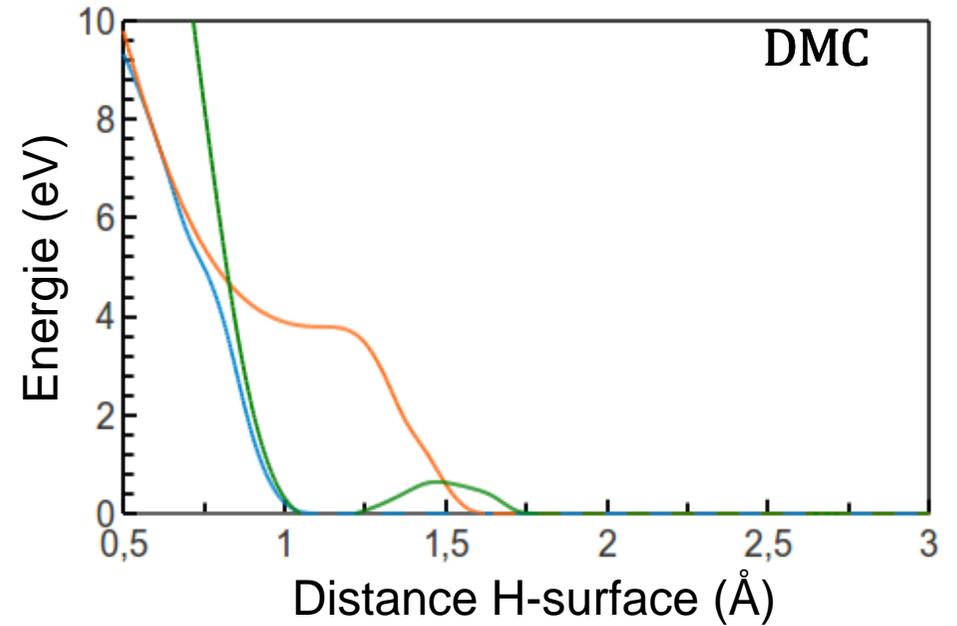
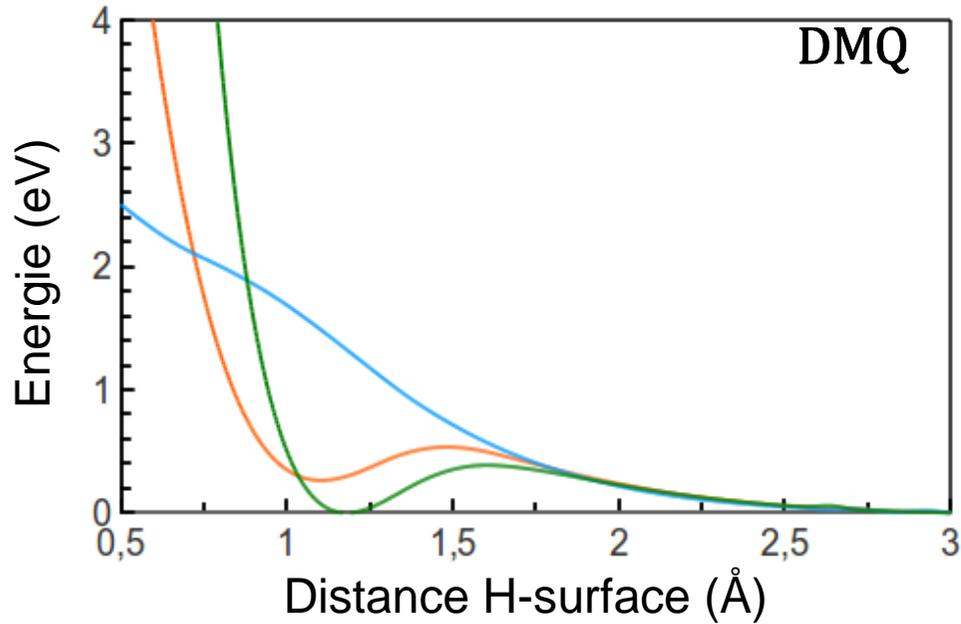
200 C et 32 C  
 => peu de différences structurales  
 lors de l'adsorption de H

pour la structure électronique  
 => interaction entre les défauts

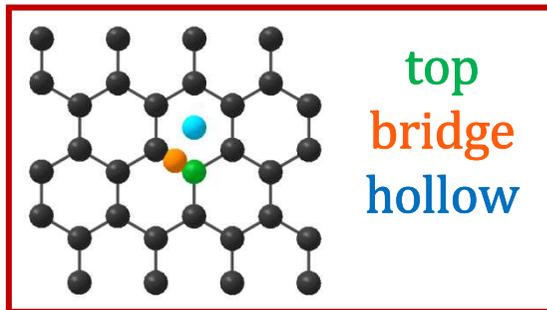


# DFT vs DM

# H ABSORPTION

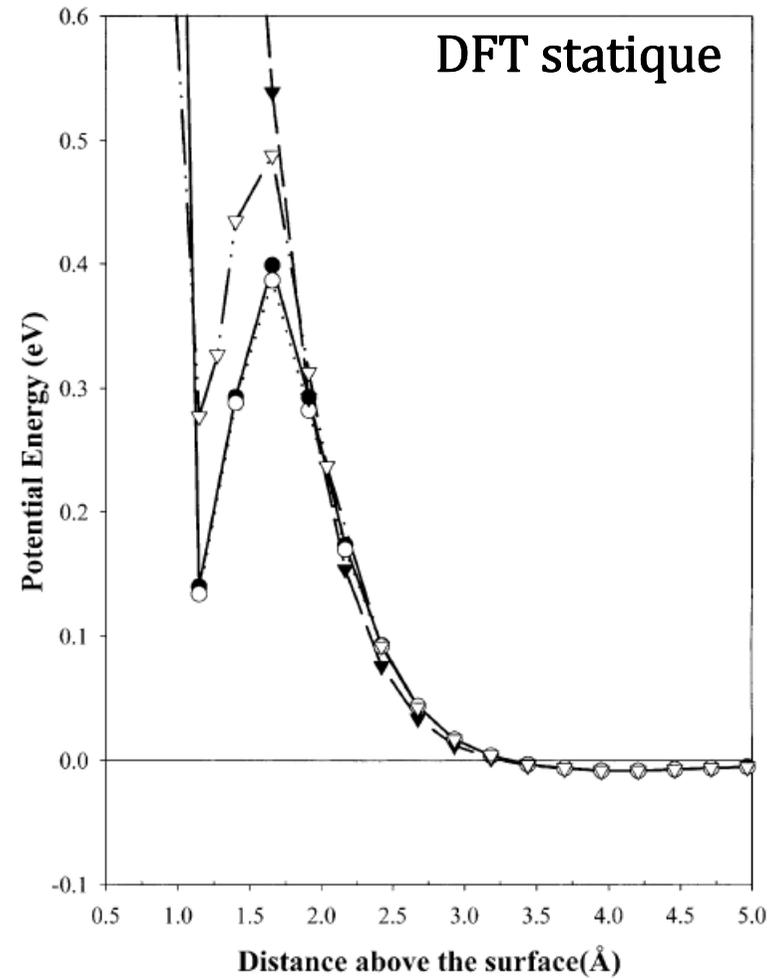
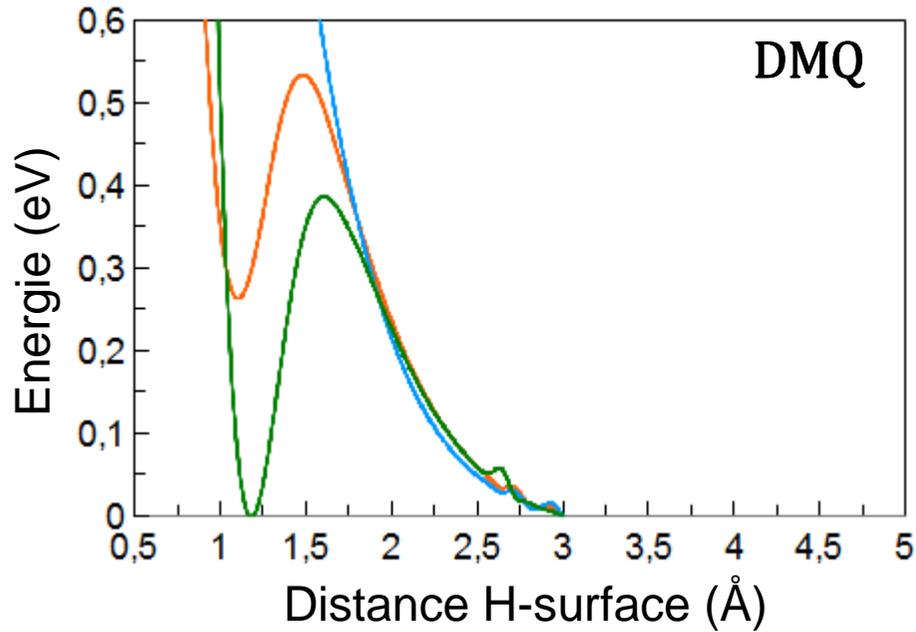


25 eV

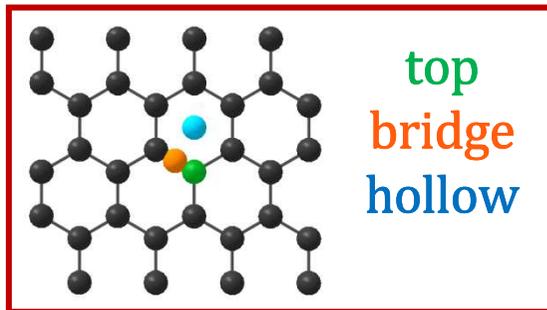


différences : rcut, hauteur de barrière  
comportements quantitativement similaires

# H ABSORPTION

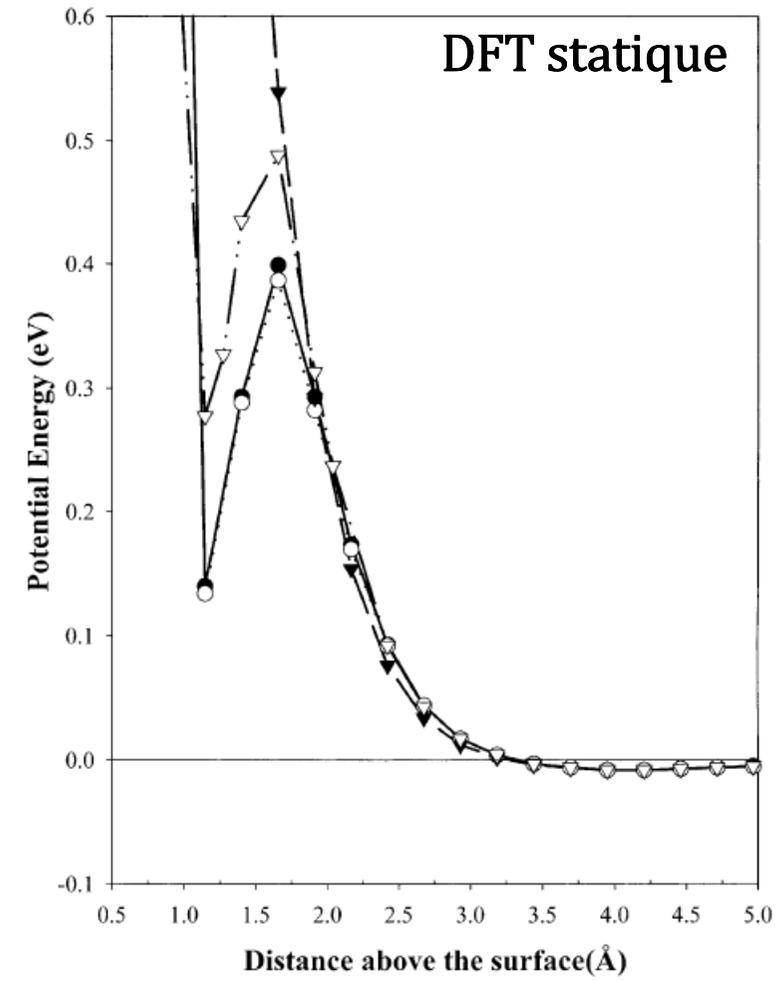
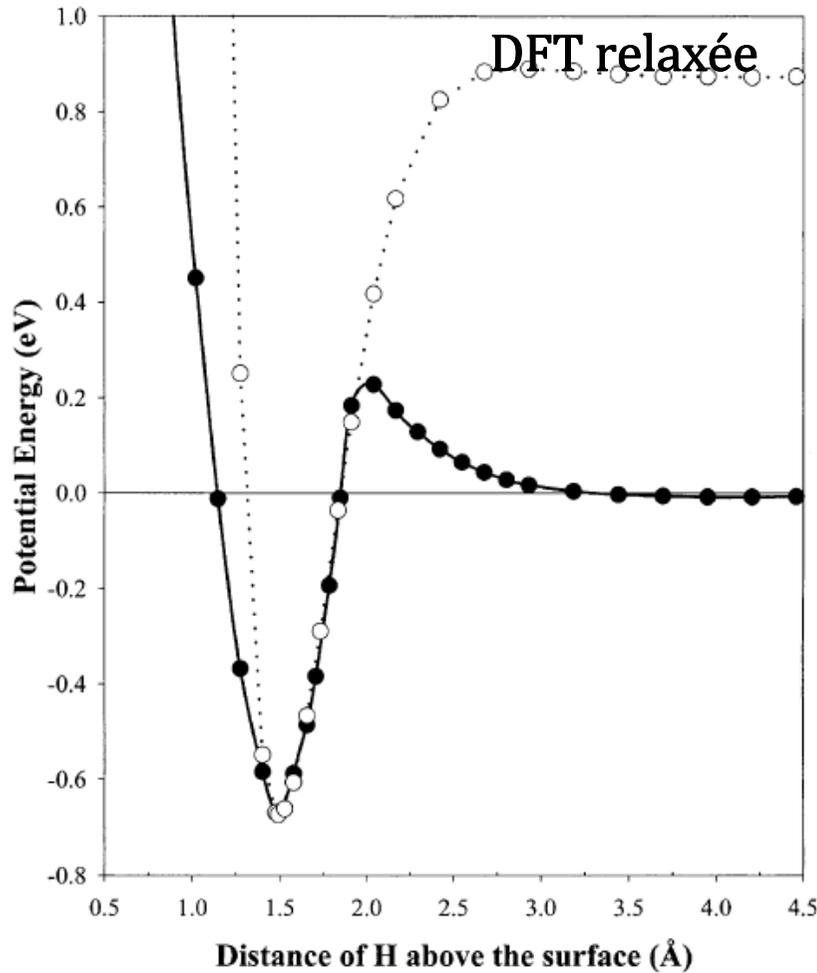


25 eV



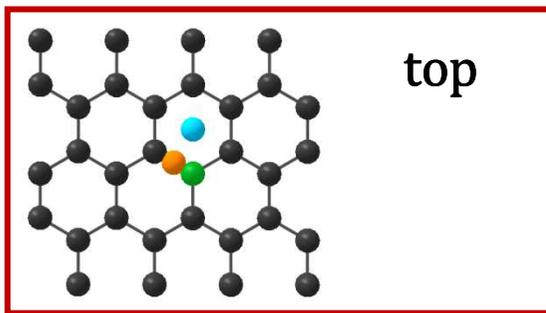
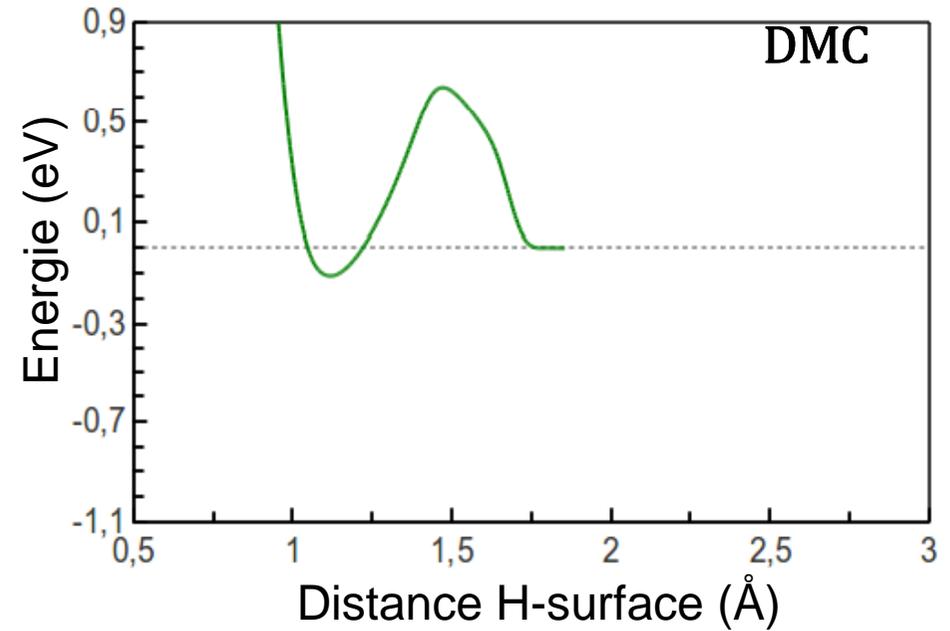
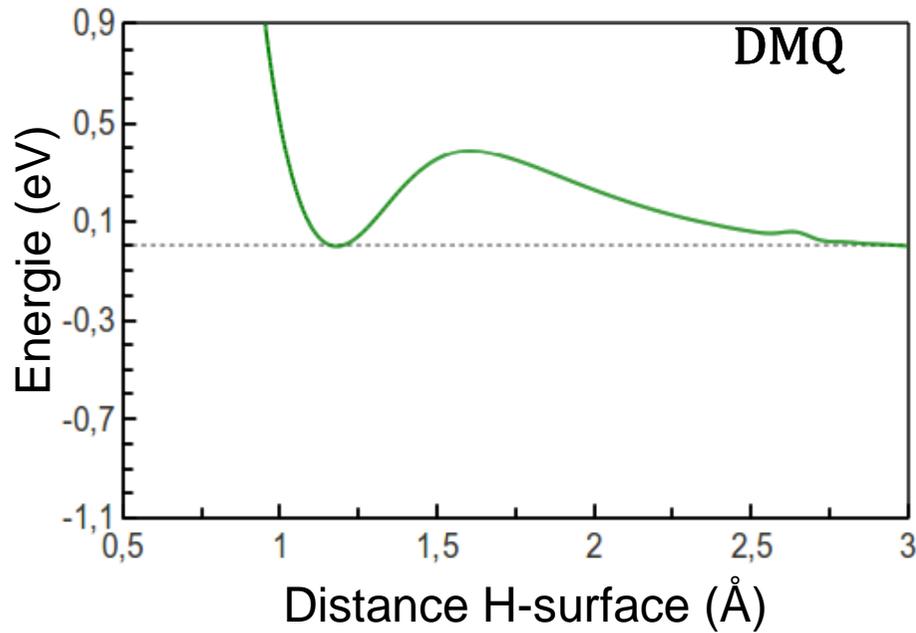
Sha et al., Surface Science 496, 2002

# H ABSORPTION



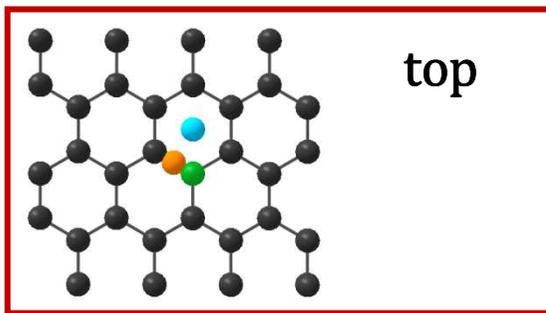
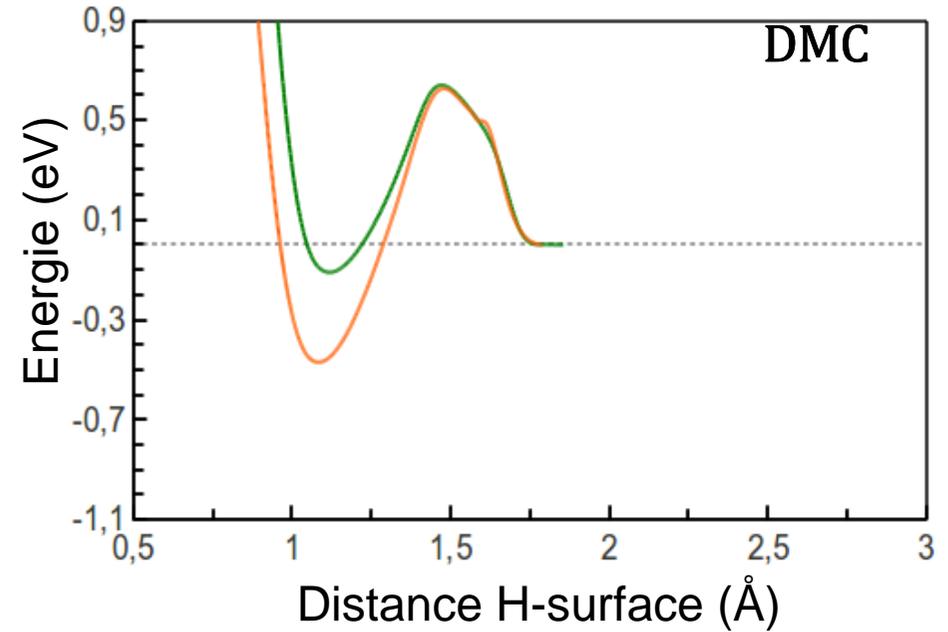
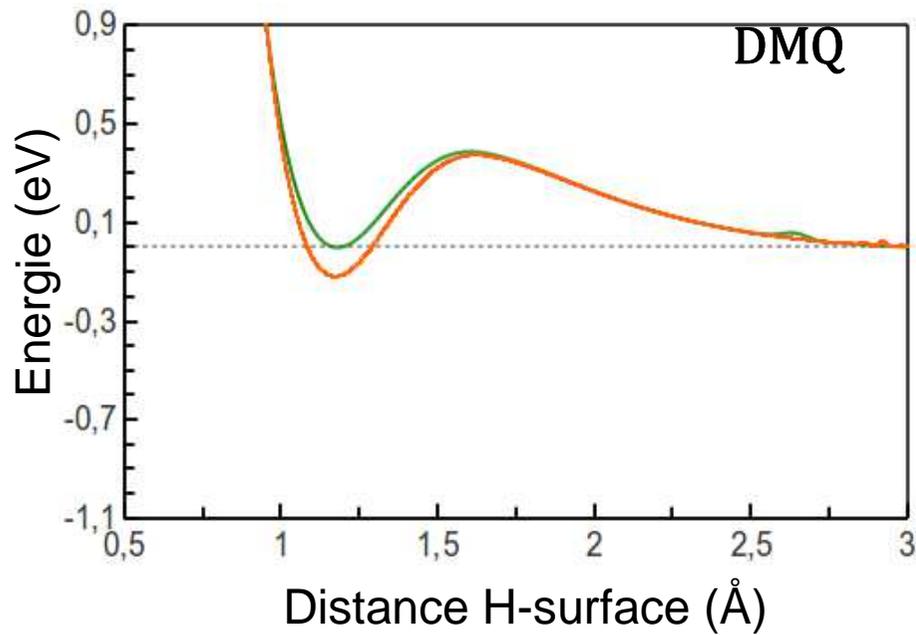
25 eV ~ statique ; réduire la vitesse initiale de H pour voir si nos courbes suivent cette tendance

# VITESSE INITIALE



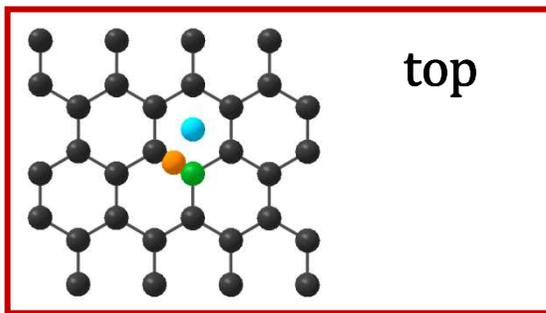
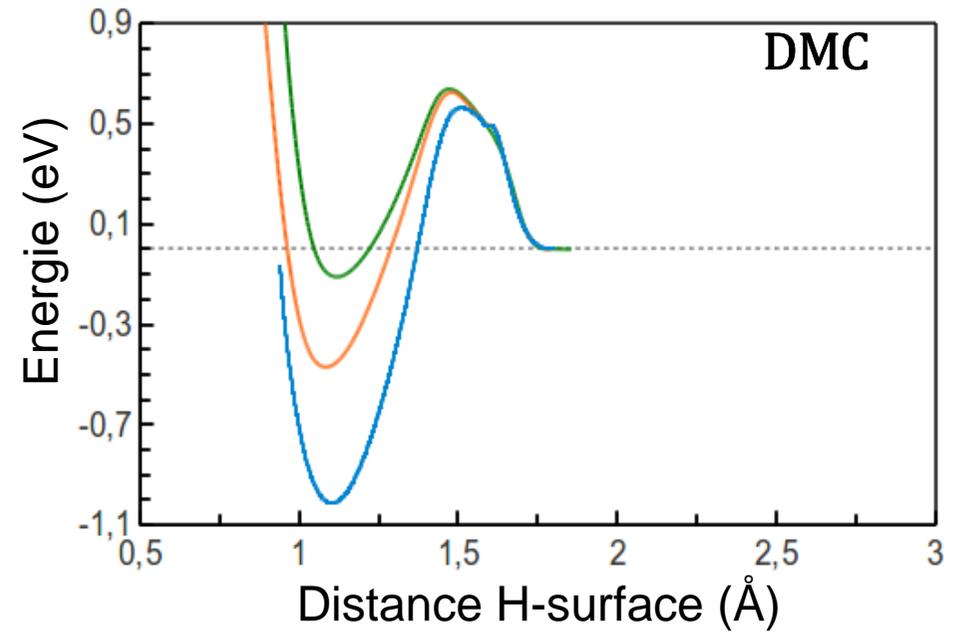
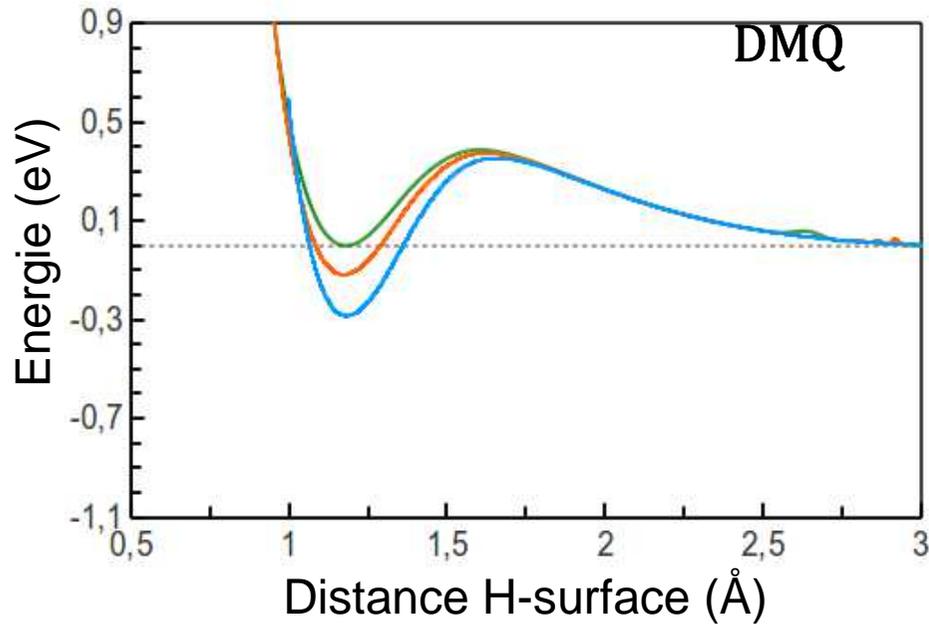
25 eV

# VITESSE INITIALE



25 eV  
2 eV

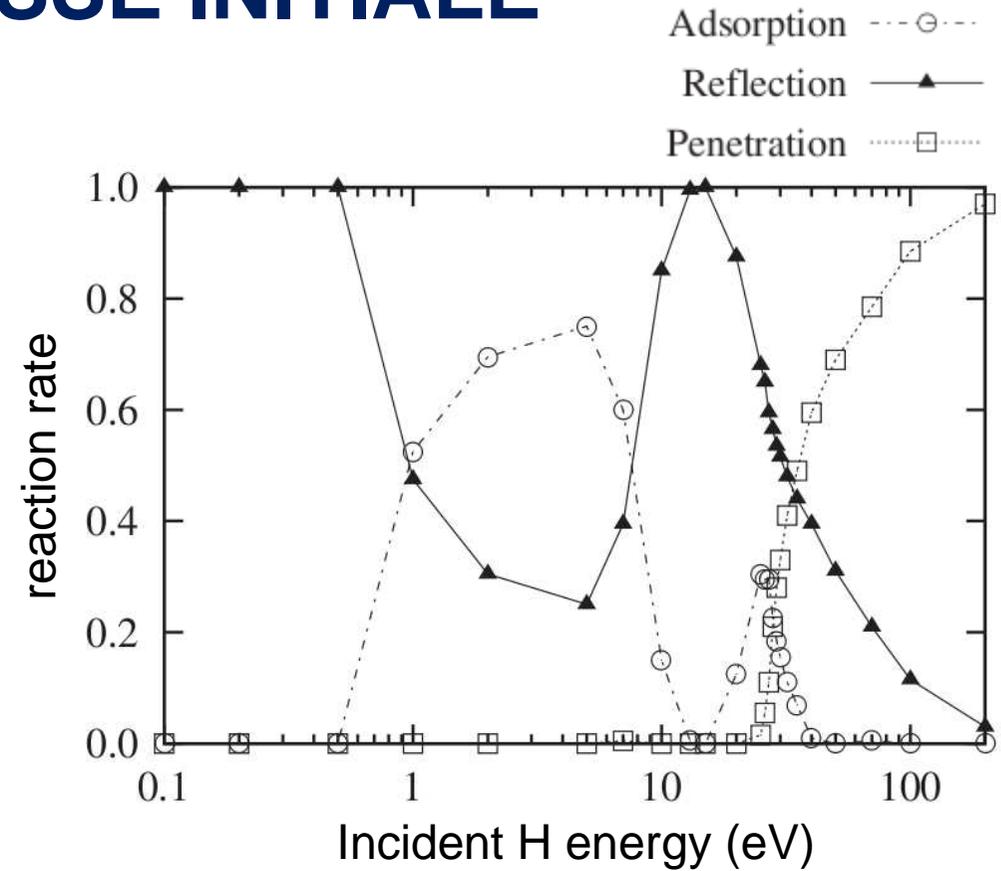
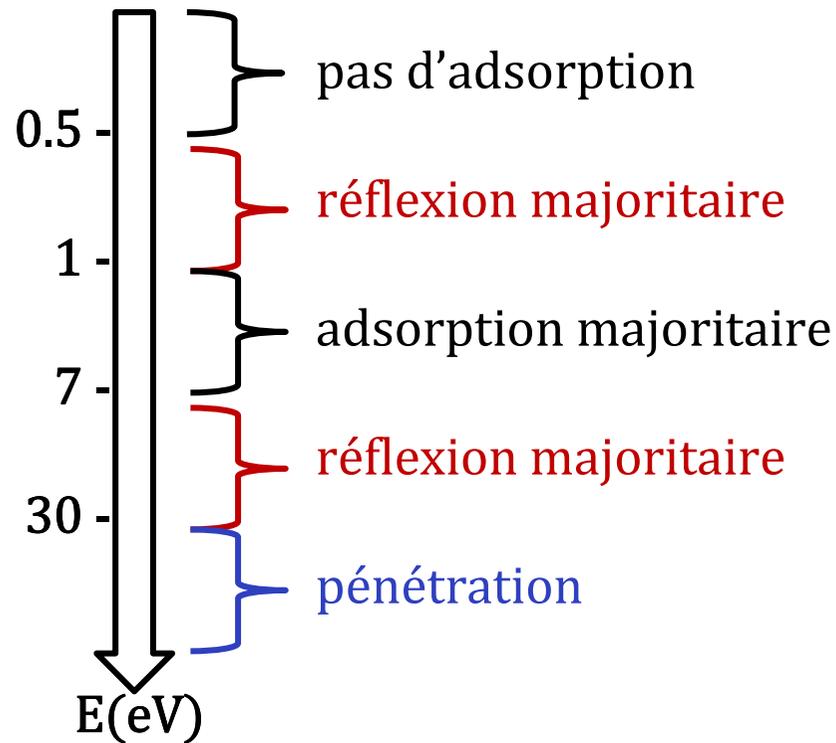
# VITESSE INITIALE



25 eV  
2 eV  
0.8 eV

⇒ toujours quantitativement similaire

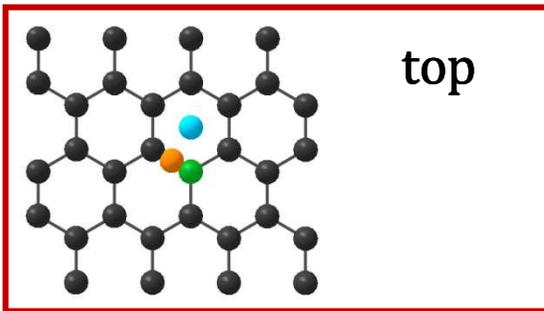
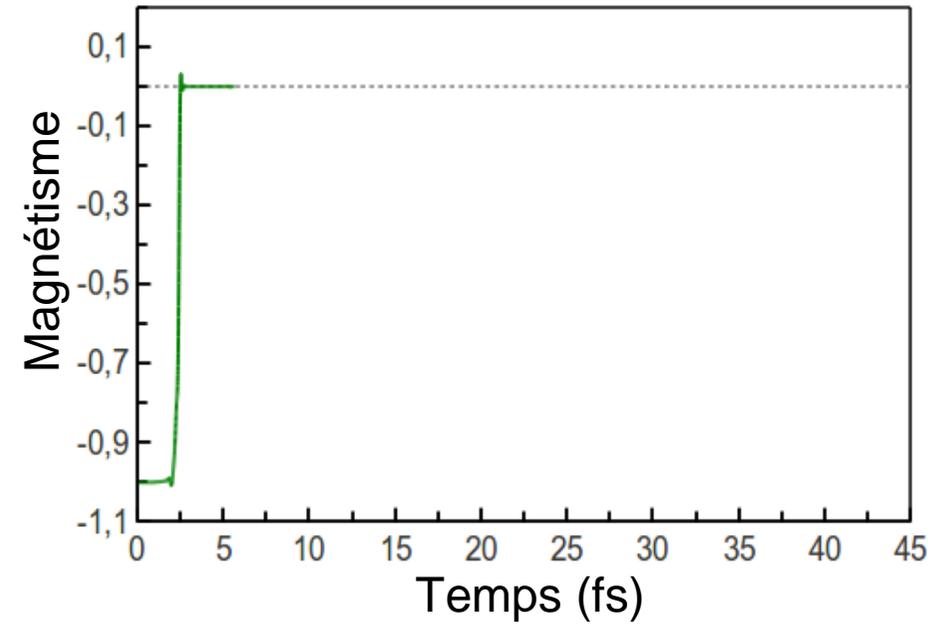
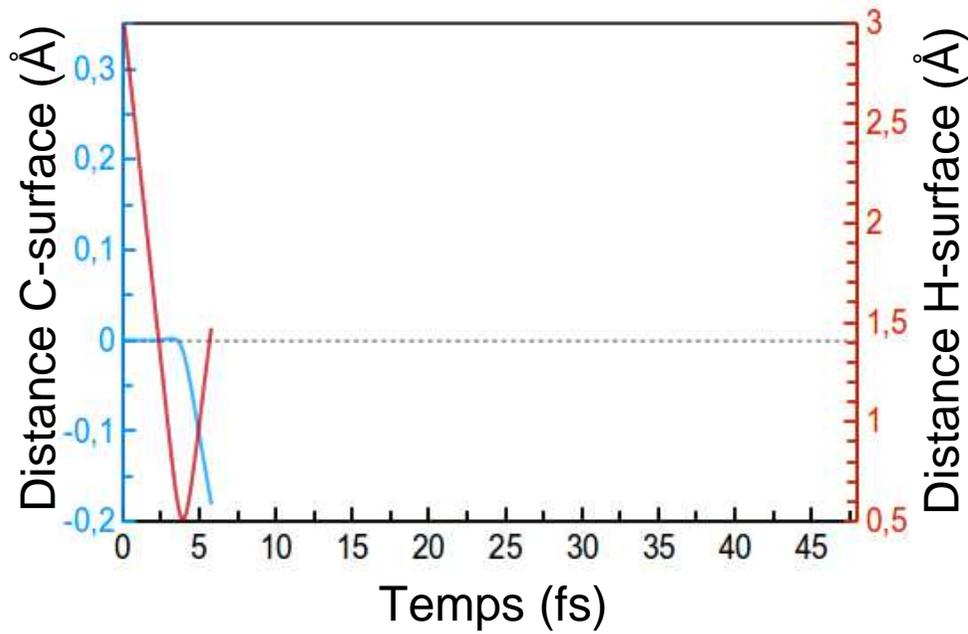
# VITESSE INITIALE



A.Ito et al., J. Phys. Soc. Jpn., Vol. 77, No. 11, 2008

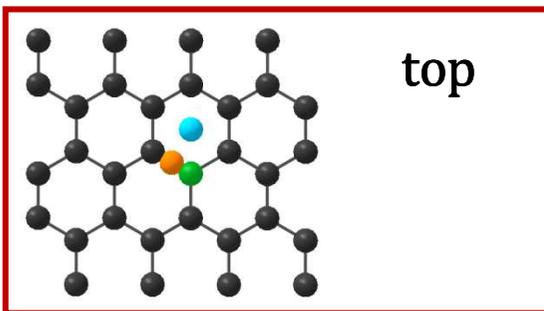
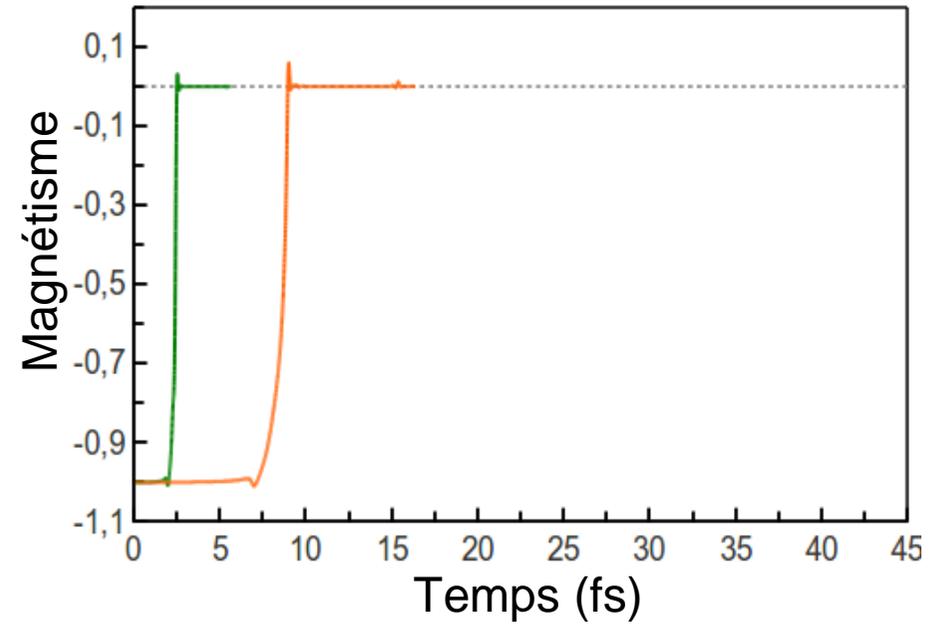
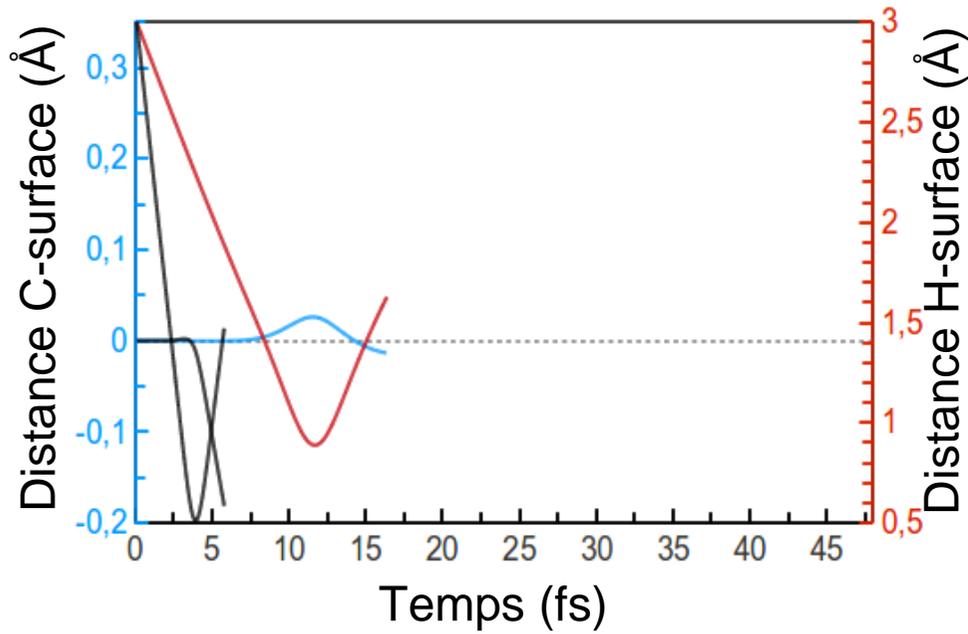
E.Despiau-Pujo et al., soumis à J. Appl. Phys.

# VITESSE INITIALE



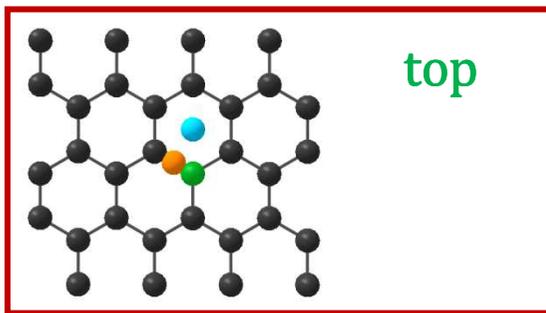
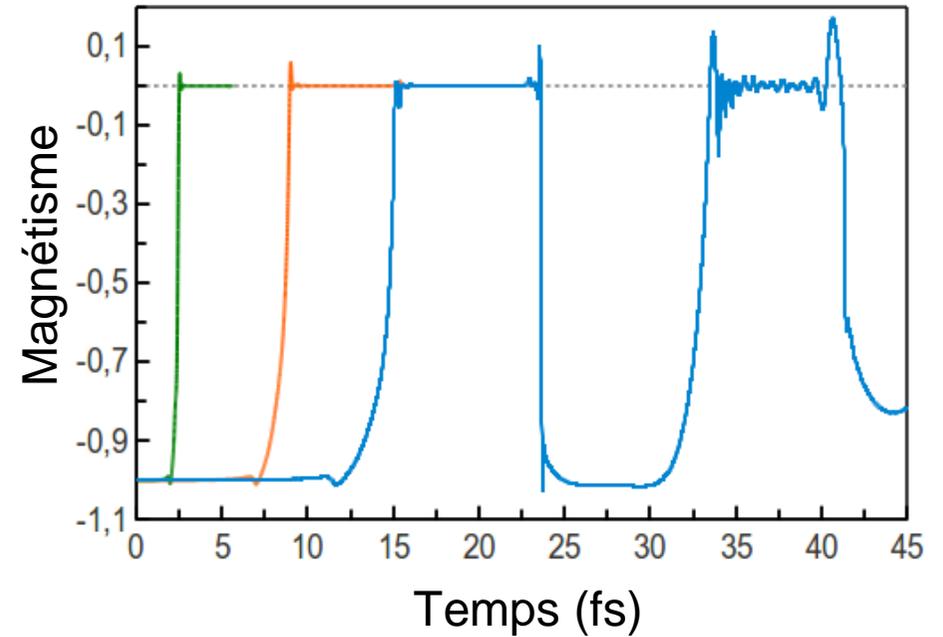
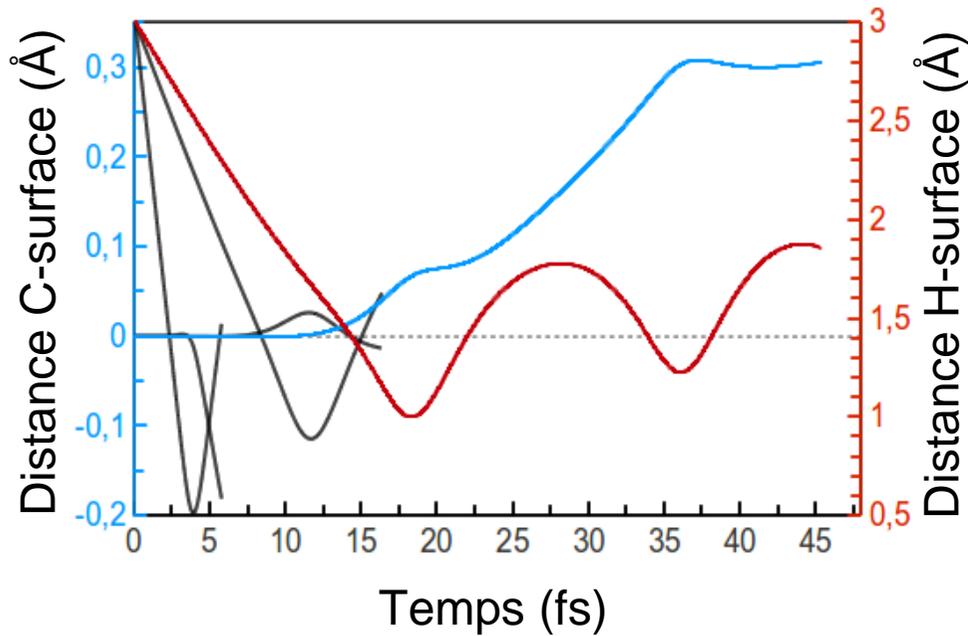
25 eV

# VITESSE INITIALE



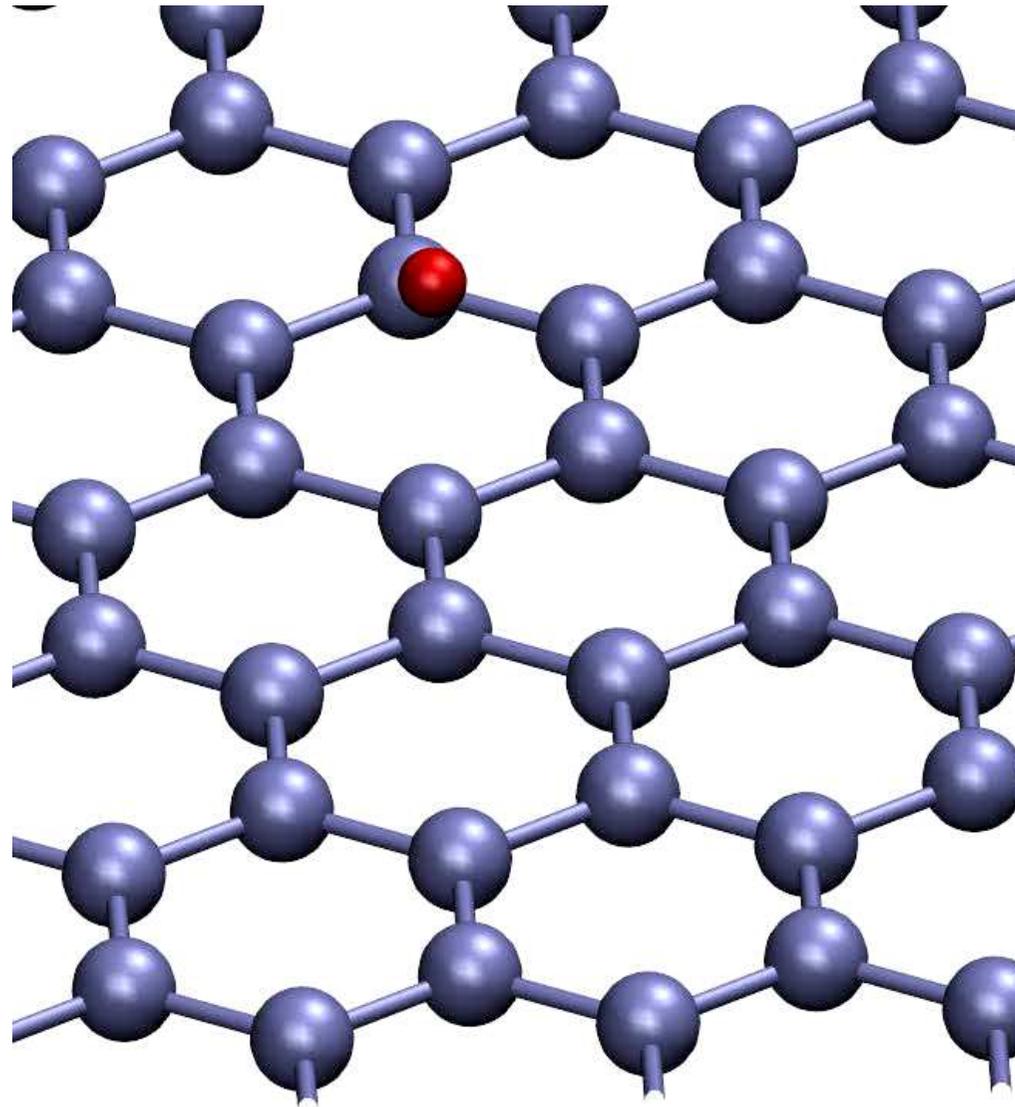
25 eV  
2 eV

# VITESSE INITIALE



25 eV  
2 eV  
0.8 eV

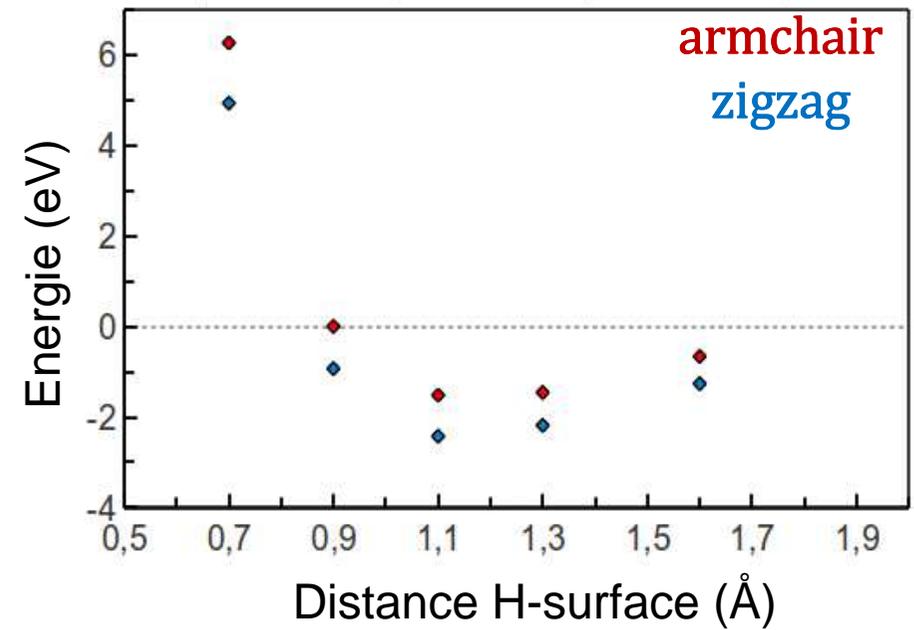
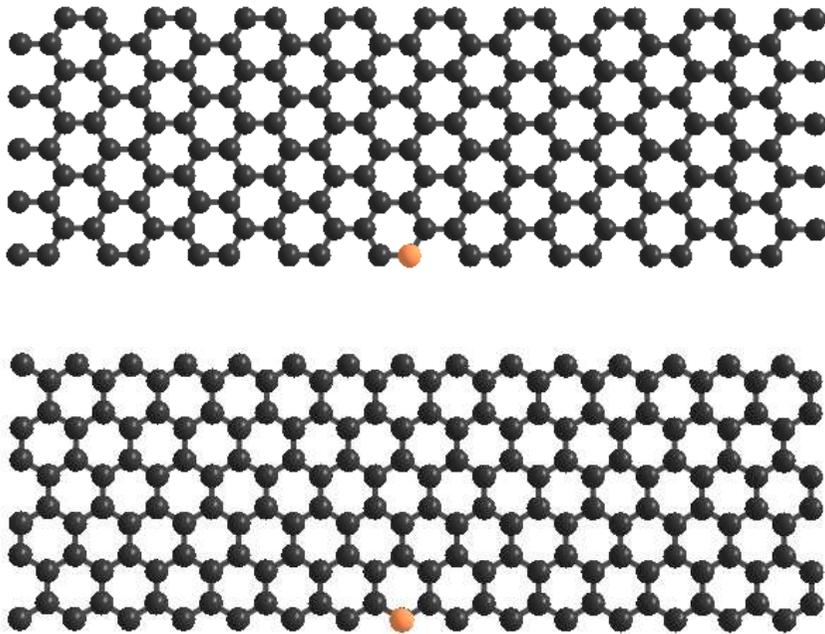
⇒ réflexion pour 25 eV et 2 eV  
adsorption pour 0.8 eV ?



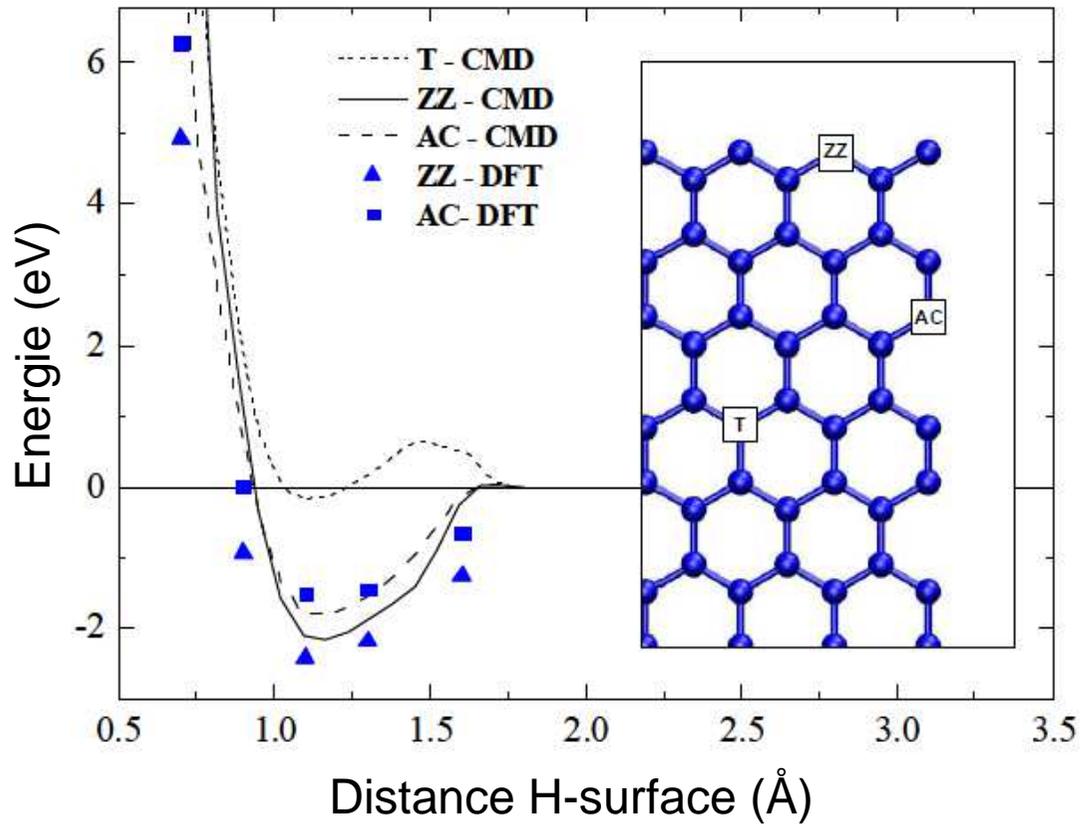
0.8 eV

# EFFET DE BORDS

top - statique



# EFFET DE BORDS



pas de barrière

minimum à 1.1 Å

⇒ accord quantitatif

M.Teraoka et al., Jpn. J. Appl. Phys. 51, 2012

E.Despiau-Pujo et al., soumis à J. Appl. Phys.

# REMERCIEMENTS

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... et vous, pour votre attention !