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**Chemical Reactions on Graphitic Surfaces: Combined  
Stationary States - Molecular Dynamics Approaches**

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CNRS – Université de Provence

# Goals

Quantum modeling of the fundamental chemical processes implicated on **plasma facing graphite surfaces:**

Hydrogen retention and restitution (de-tritiation)

Chemical erosion and radicals (re)deposition on graphite

# Quantum Methods applied to chemical reaction on surfaces

-First step:

Potential Energy Surfaces (PES) calculation:

Stationary states: transition states and minimum, energy barriers, charge transfers...

Electronic structures, DOS...

-Next step (if any): Quantum Molecular Dynamics (QMD) simulations: temperature, impinging energy..

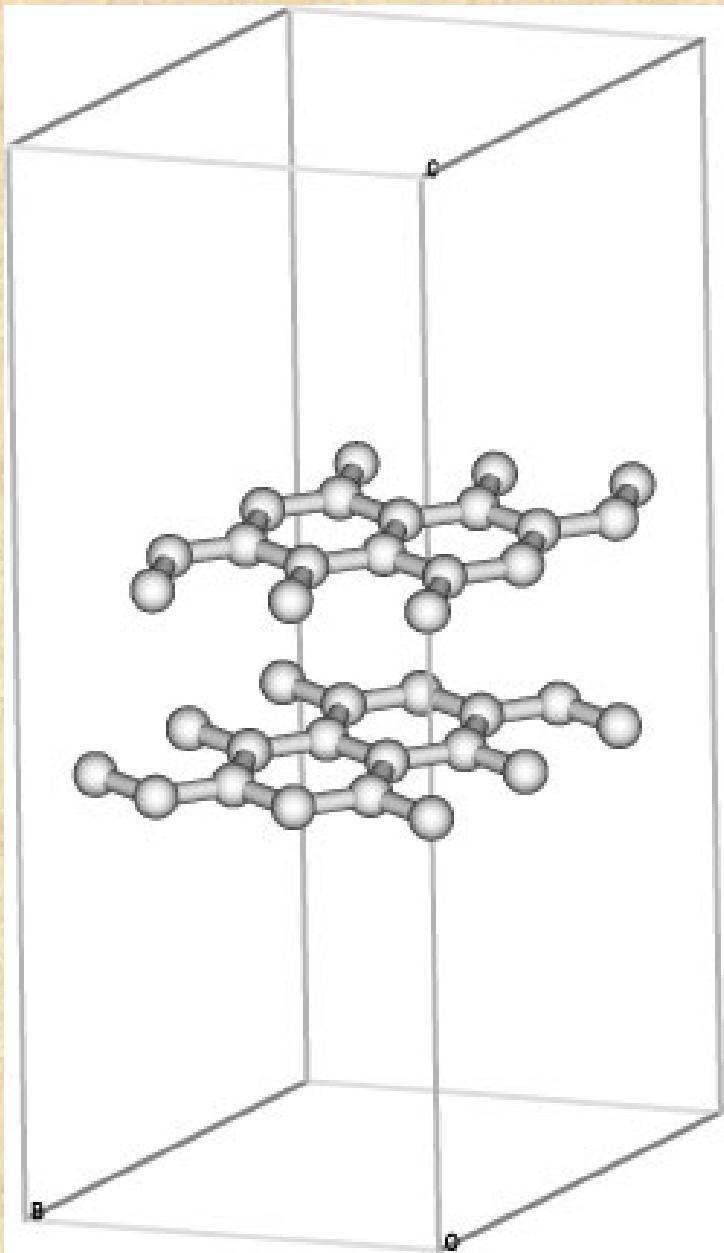
# Tools

Density Functional Theory:

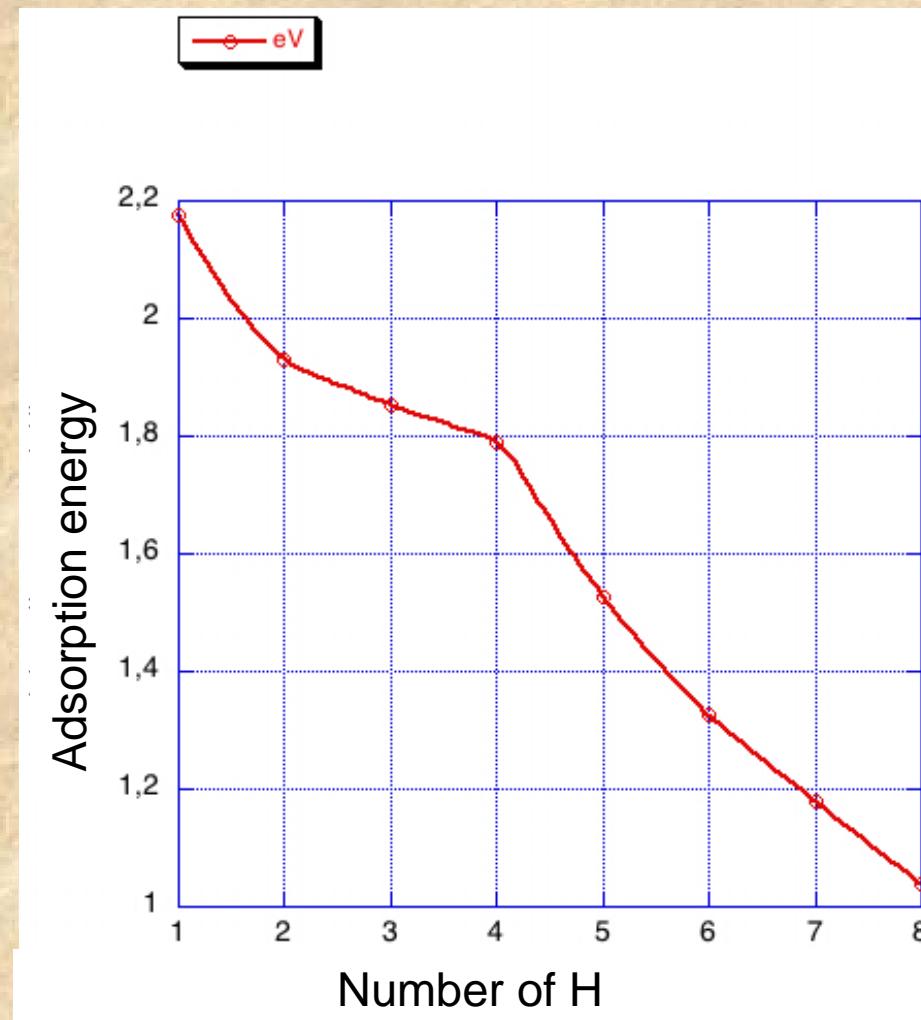
- Periodic 3D models (PBE + numerical orbitals or PW)
- ONIOM (B3LYP + 6-31G/UFF)
- Born-Oppenheimer or Car-Parrinello QMD

# Hydrogen Interaction with (0001) graphite surface

# Working cells: $3 \times 3 \times 2$ or $3 \times 3 \times 1$

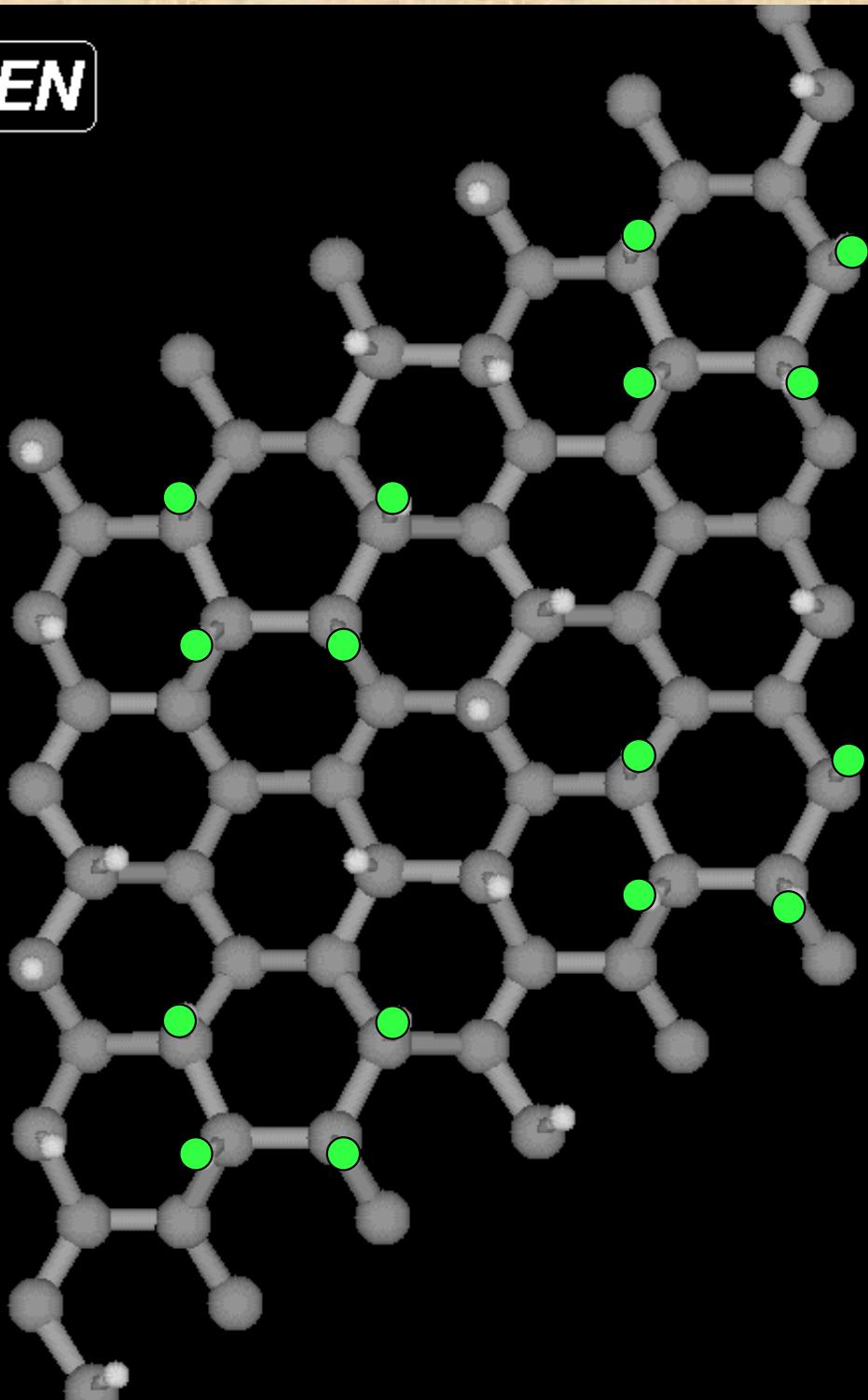


# Surface coverage at saturation : $8H/18C = 44\%$



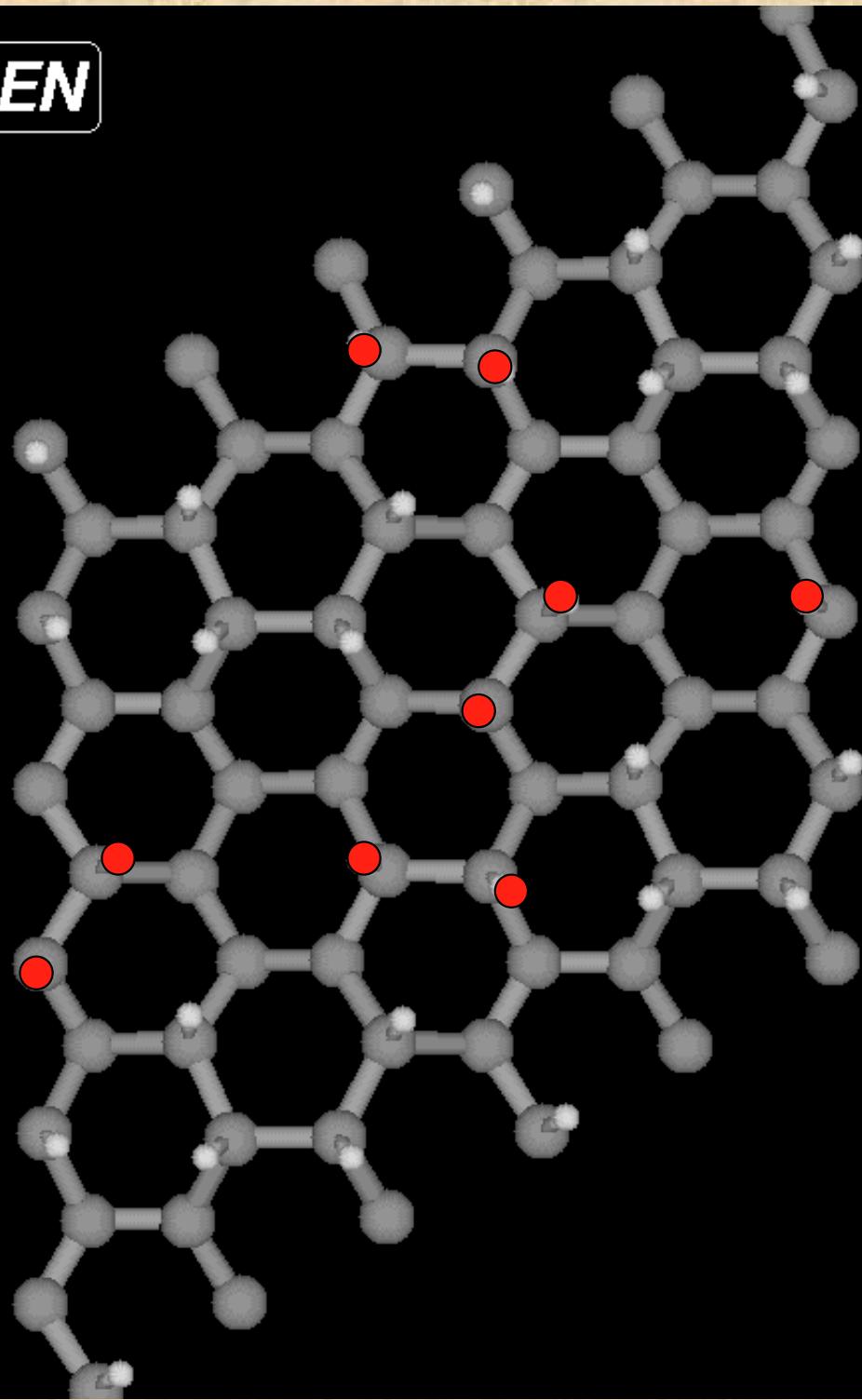
**MOLDEN**

Quartet



**MOLDEN**

Doublets



# Discussion

The calculated saturation coverage is in good agreement with experiment (~40%)

TDS shows that at least 2 types of adsorbed H co-exist

The TDS desorption energies are respectively of 1.1 to 1.2 eV and 1.7 eV

The Nosé-Hoover thermostat QMD simulation shown that desorption starts at 400K and is achieved at 600K.

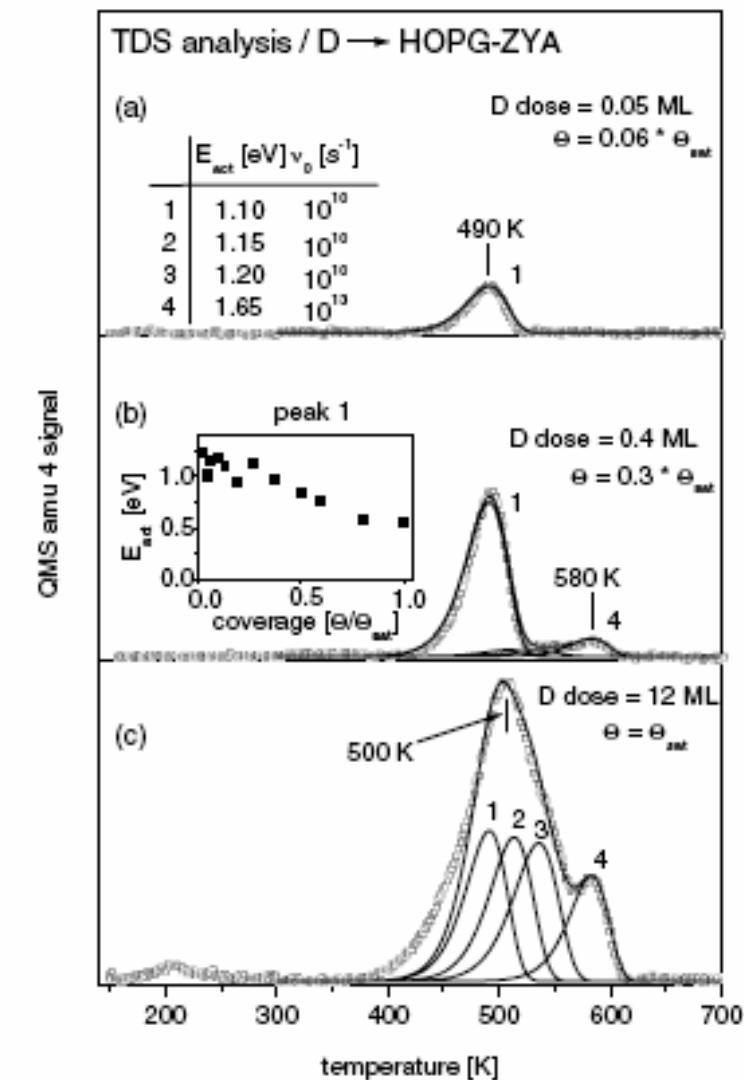


Fig. 8.  $D_2$  desorption from terraces measured (symbols) and numerical simulated (lines) with first order desorption kinetics after admitting 0.05 ML (a), 0.4 ML (b) and 12 ML (c) D atoms ( $1 \text{ ML} = 3.8 \times 10^{15} \text{ cm}^{-2}$ ) to a HOPG-ZYA at 150 K. The inset in (a) shows the activation energies ( $E_{act}$ ) and frequency factors ( $v_0$ ) for the desorption peaks (1–4) used in the calculation. The inset in (b) shows activation energies obtained from a leading edge analysis of the measured spectra with respect to D coverage.

# Methyl adsorption on saturated graphite surface

# Motivation

The  $\text{CH}_3$  sticking probability is very dependent on the chemical environment

Methyl is always supposed to adsorb on non-hydrogenated carbon dangling bonds

MD simulations on diamond shown that even with impinging energy of 10 eV  $\text{CH}_3$  cannot substitute H [D.R.Alfonso et al, PRB 48(1993)12235]

**Graphite ≠ diamond**  
**Methyl is a radical and radicals cannot be described by MM**

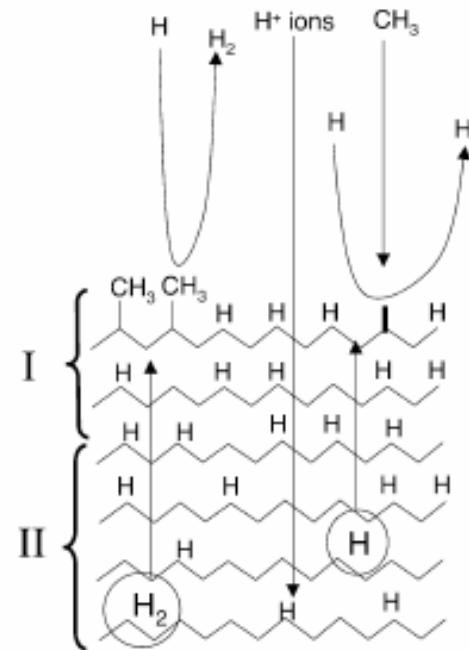


Fig. 4. Schematic of the growing film surface. I: Chemistry dominated growth zone. Incident atomic hydrogen eliminates surface bonded hydrogen via abstraction and creates chemisorption sites for incoming saturated hydrocarbon radicals. II: Ion dominated growth zone. Penetrating ions displace bonded hydrogen within the collision cascade. Displaced hydrogen might recombine to form  $\text{H}_2$  molecules or it might re-saturate dangling bonds in the film or at the physical surface.

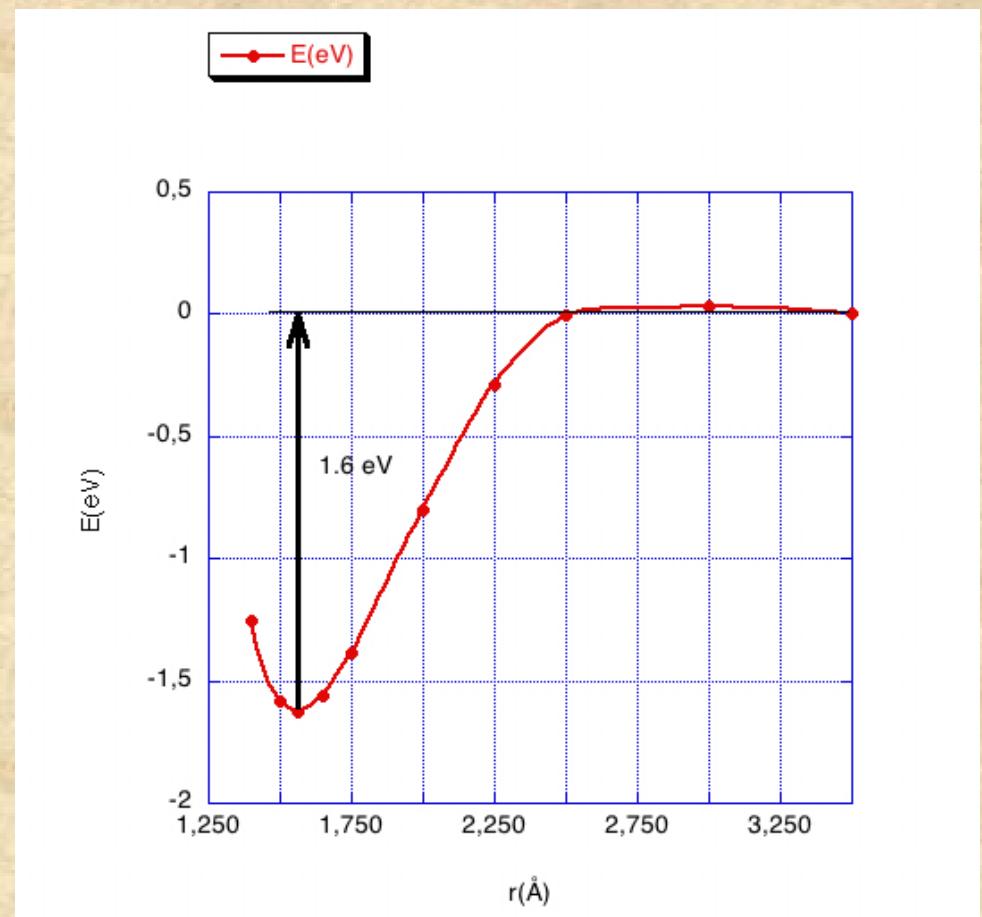
# Questions

What are the conditions for methyl adsorption ?

Can methyl substitute an adsorbed hydrogen ?

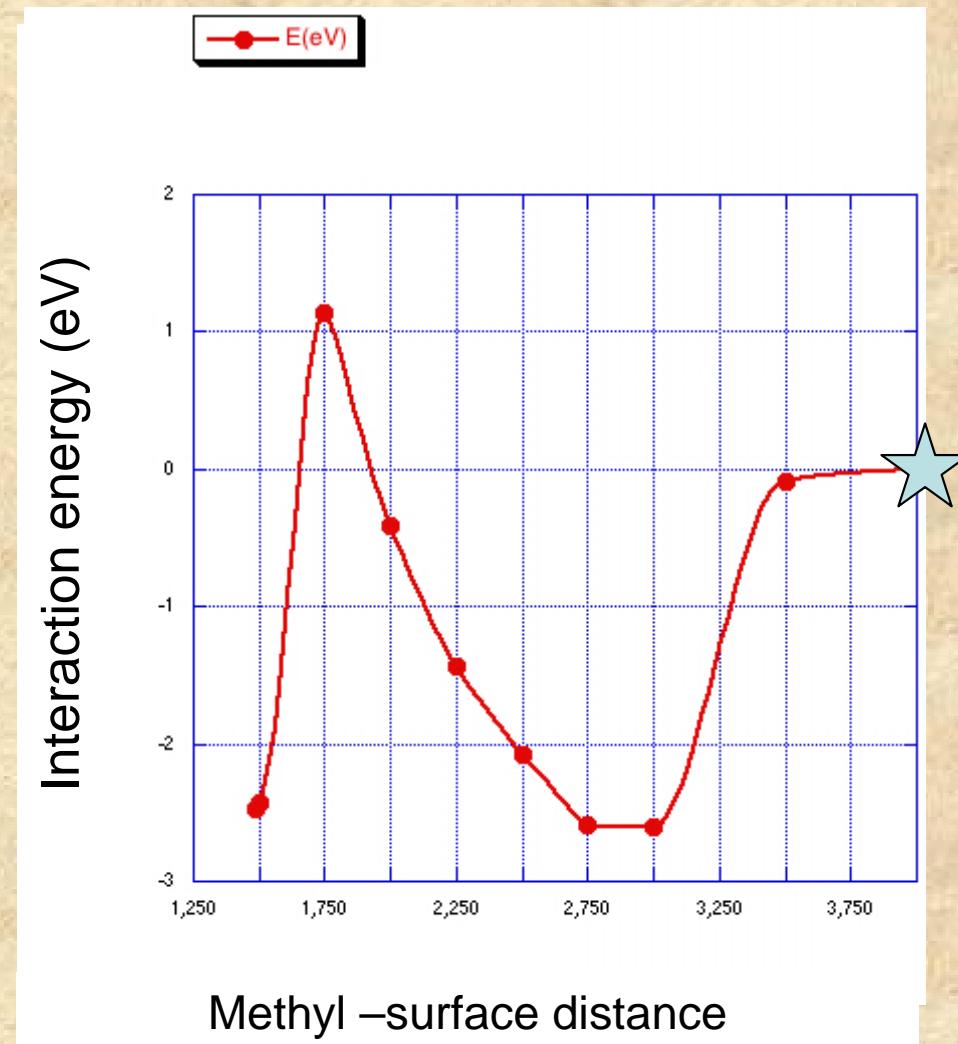
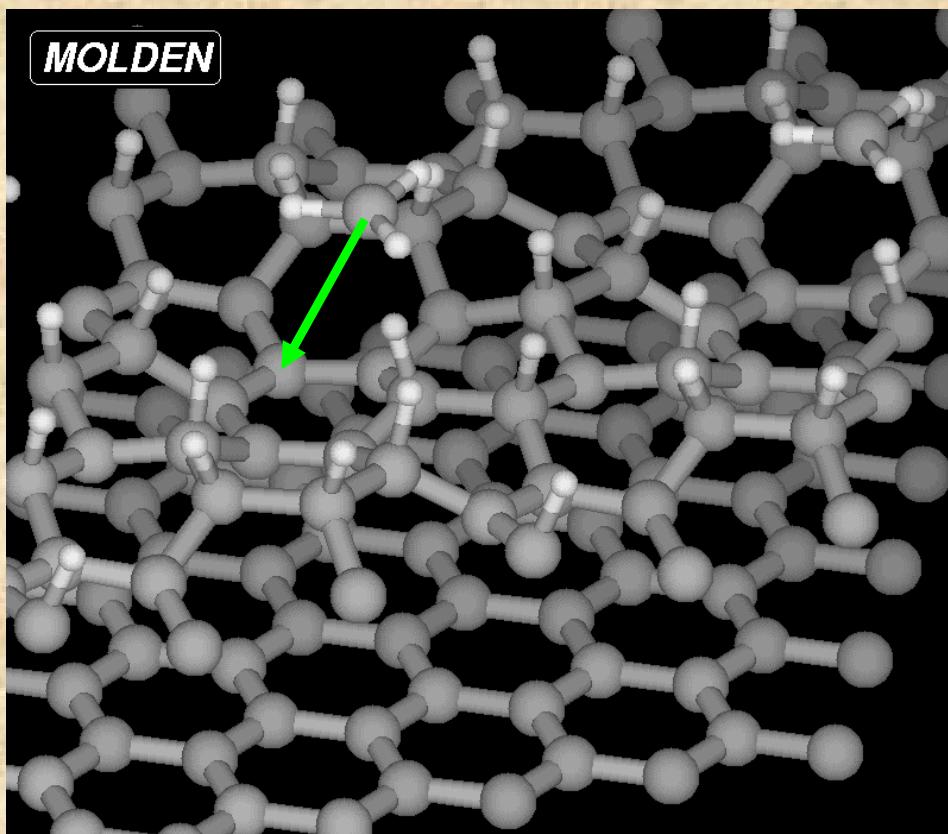
# Adsorption on bare surface

C-CH<sub>3</sub> and C-H bonds on graphite  
are of similar energies

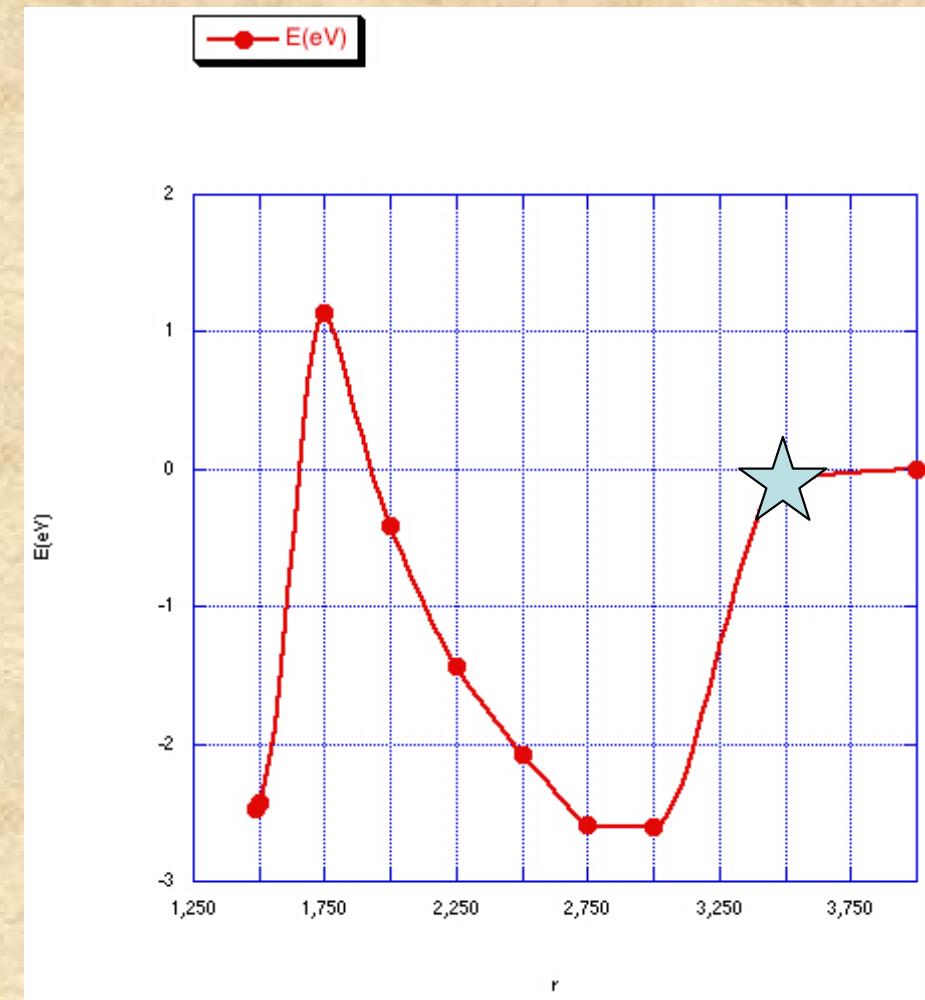
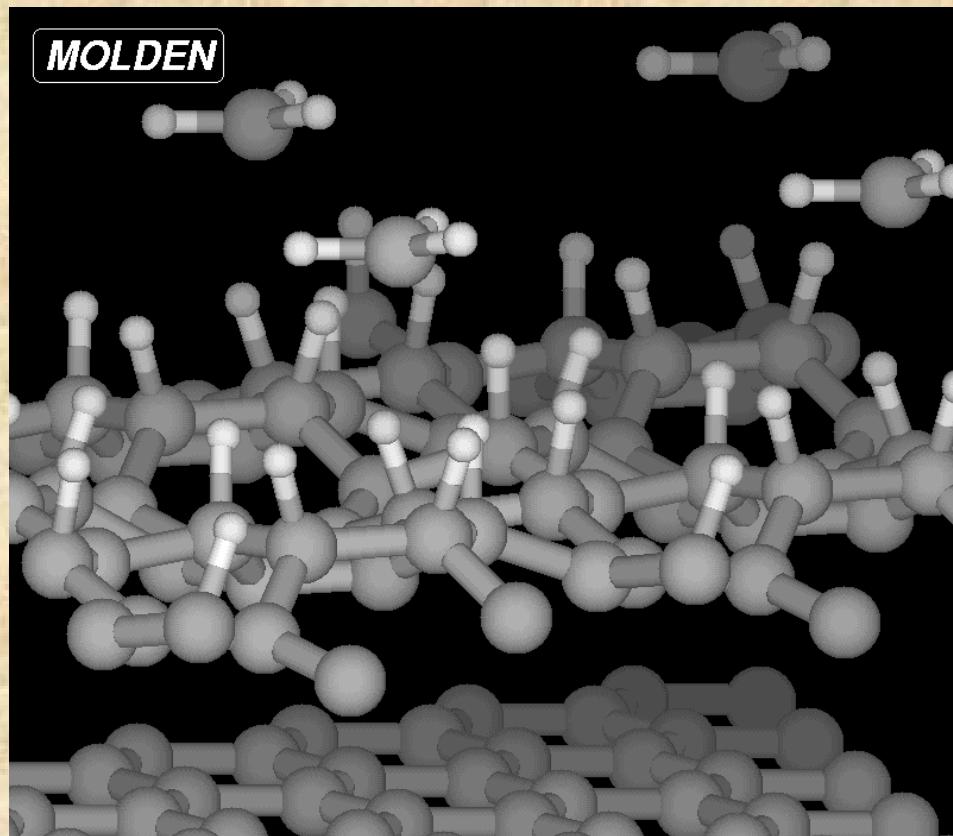


# **Adsorption on saturated surface:H-free site**

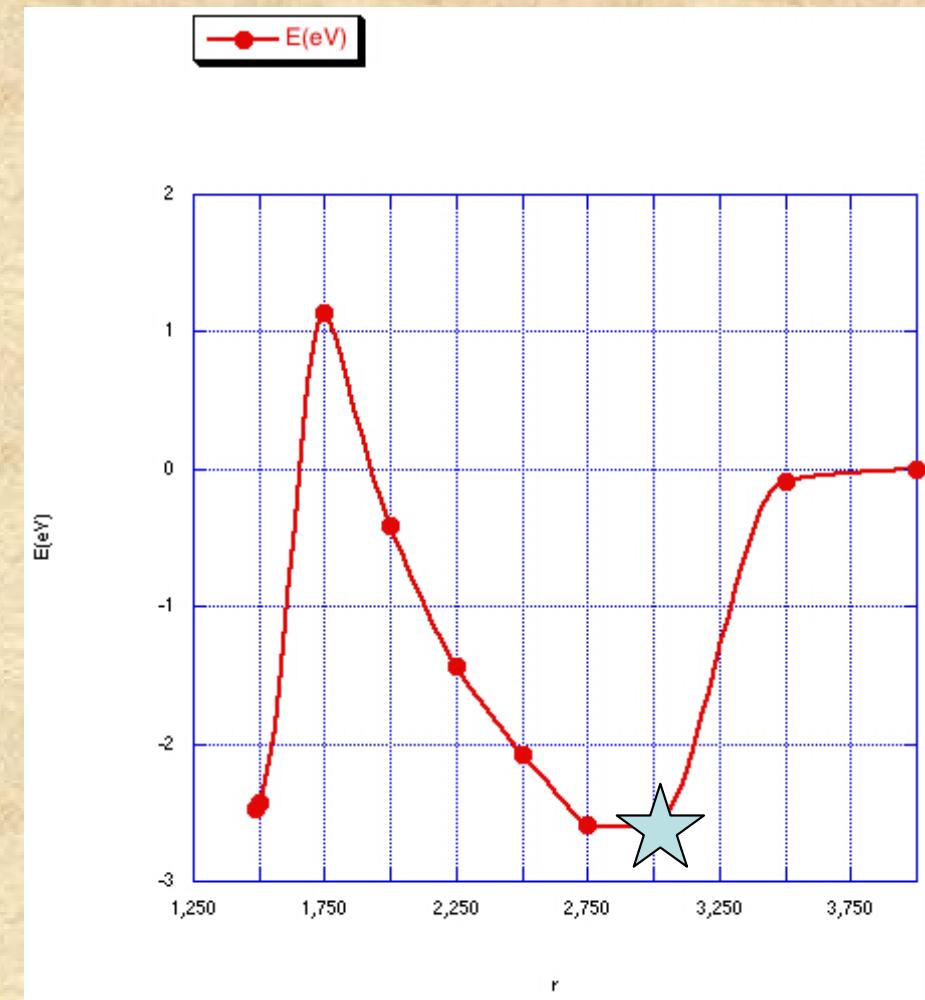
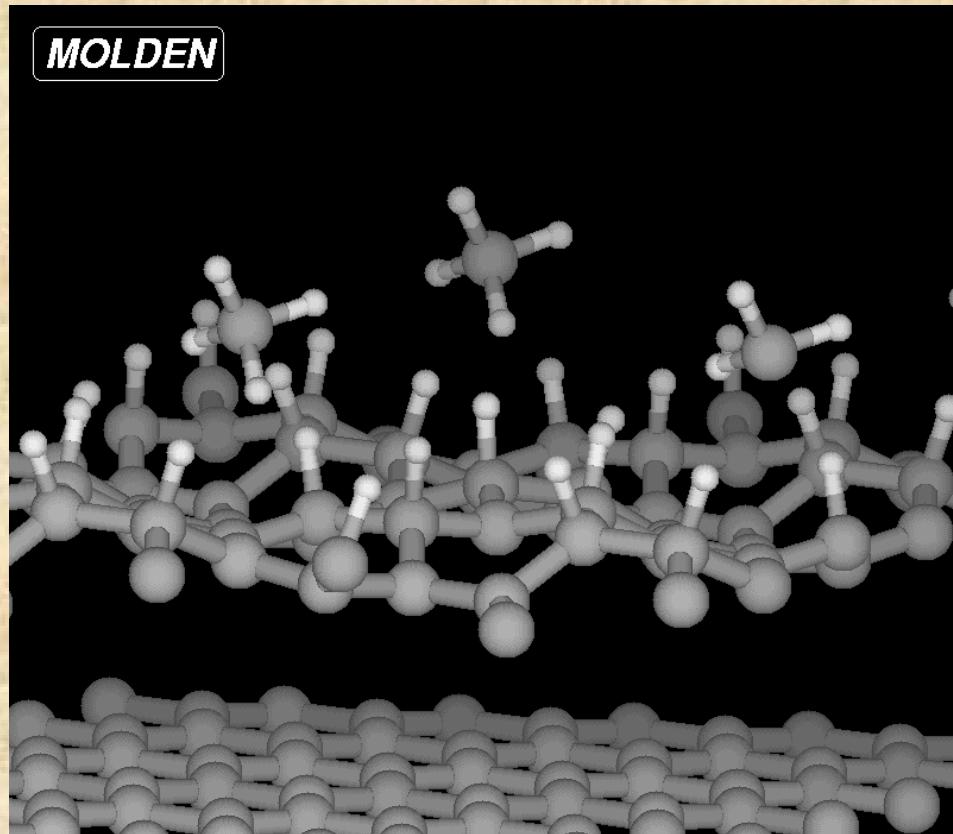
4.0 Å



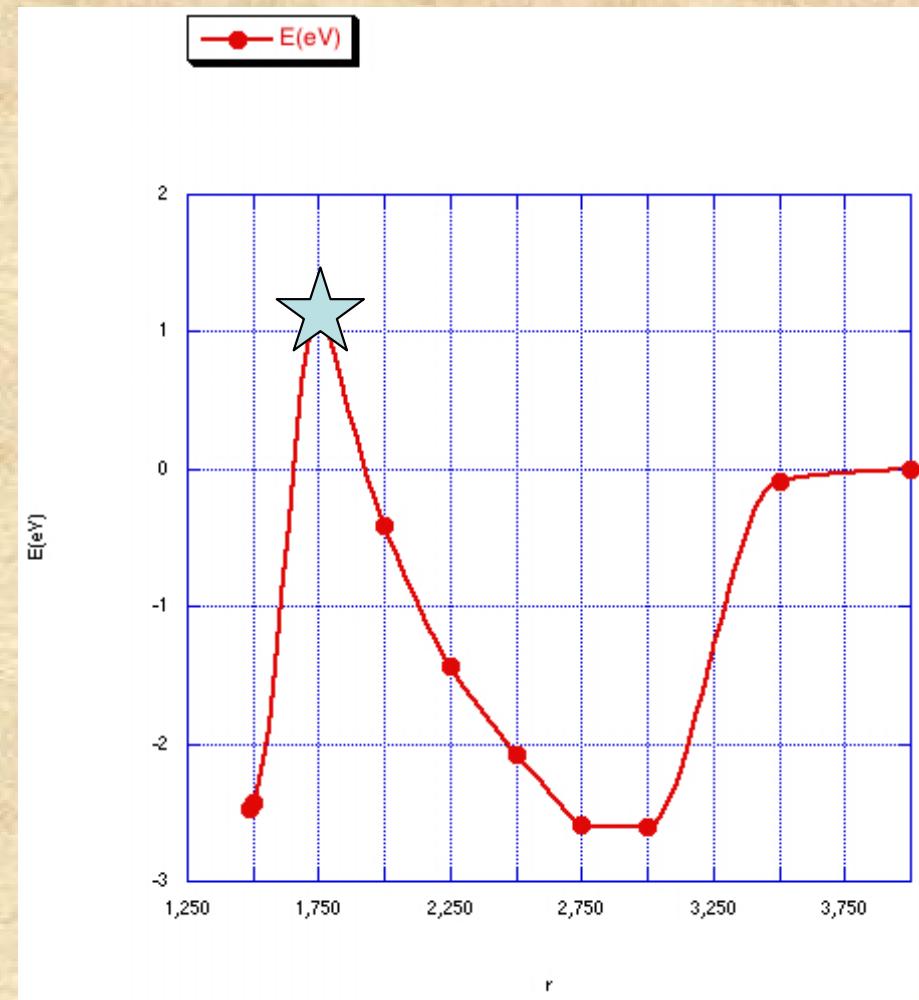
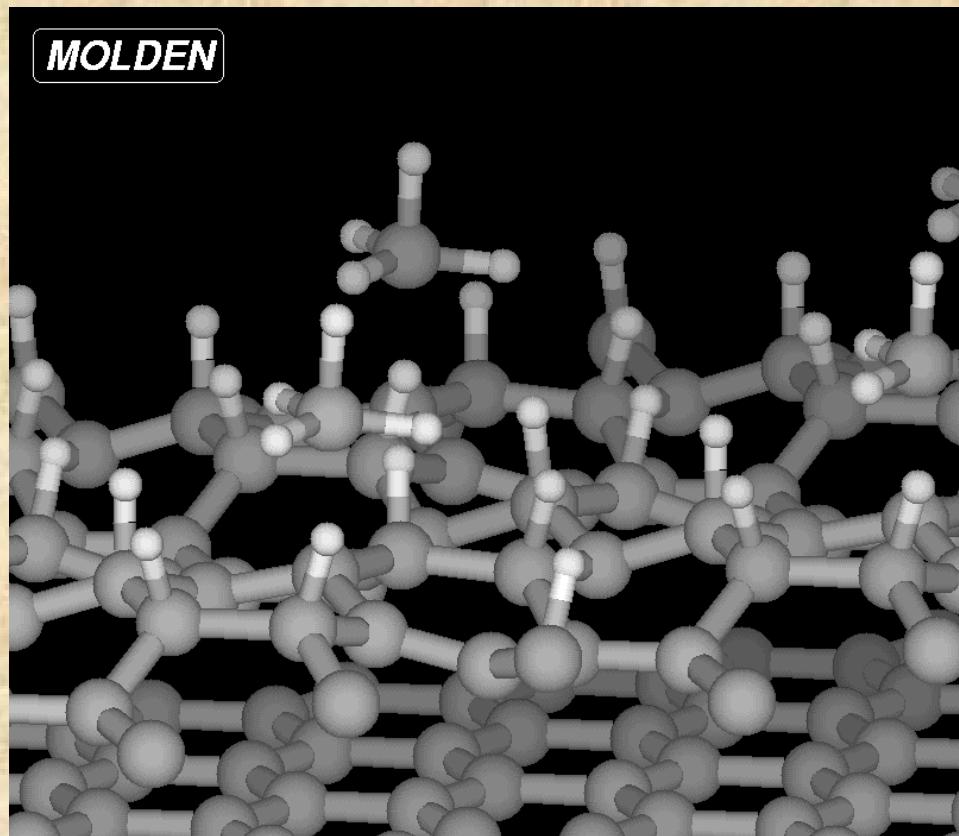
3.5 Å



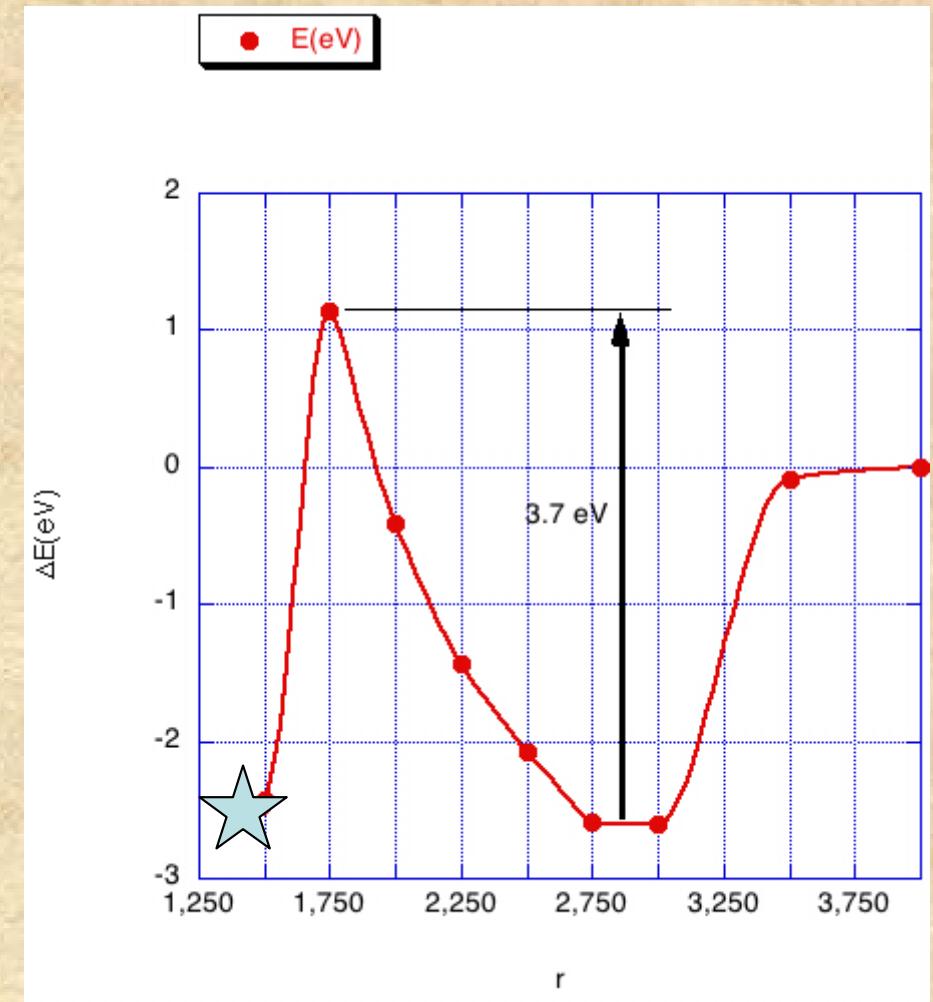
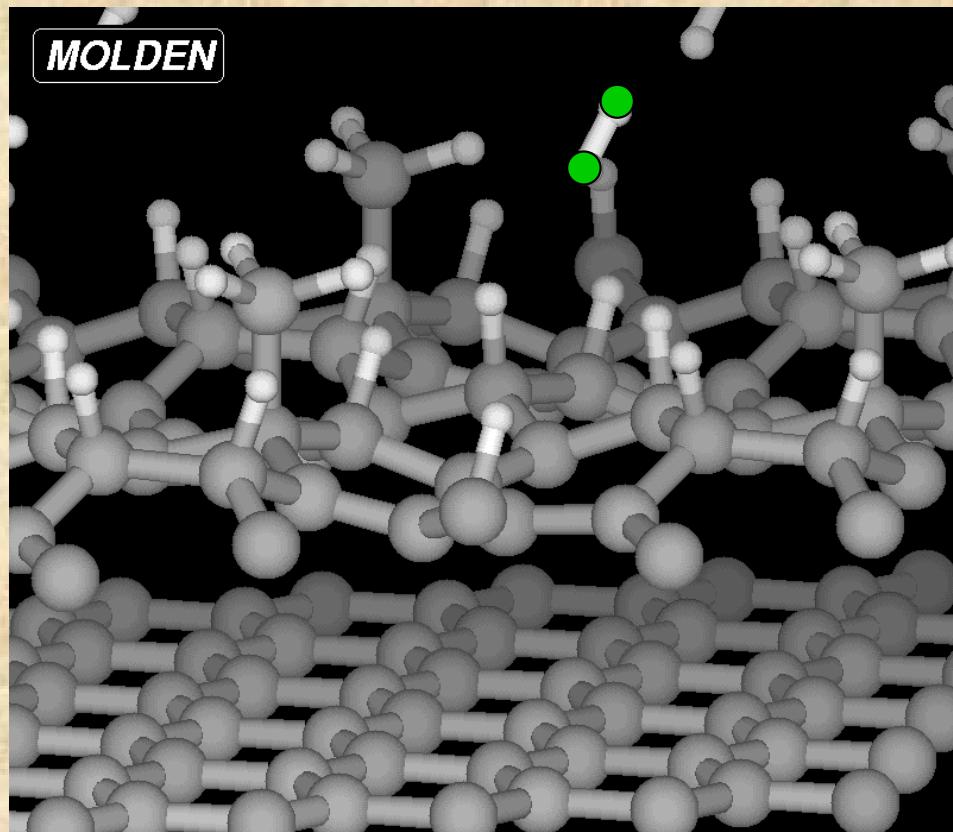
3.0 Å



1.75 Å



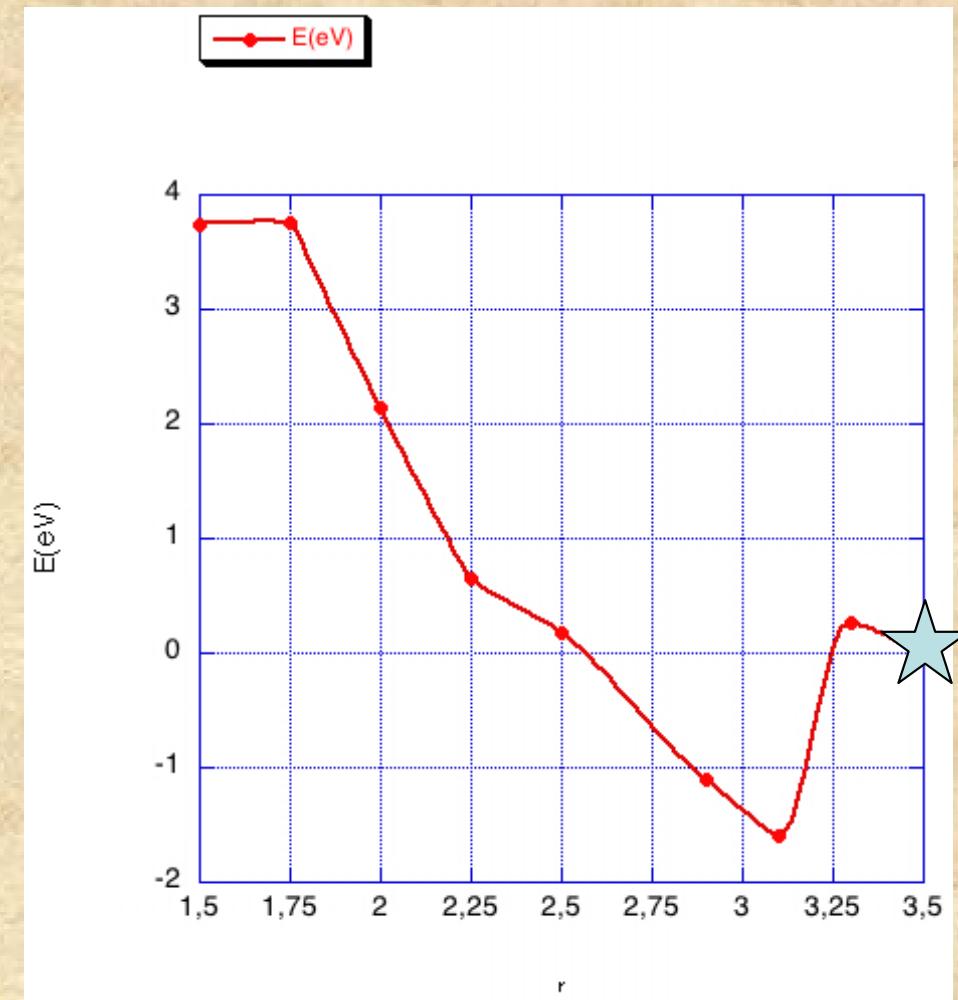
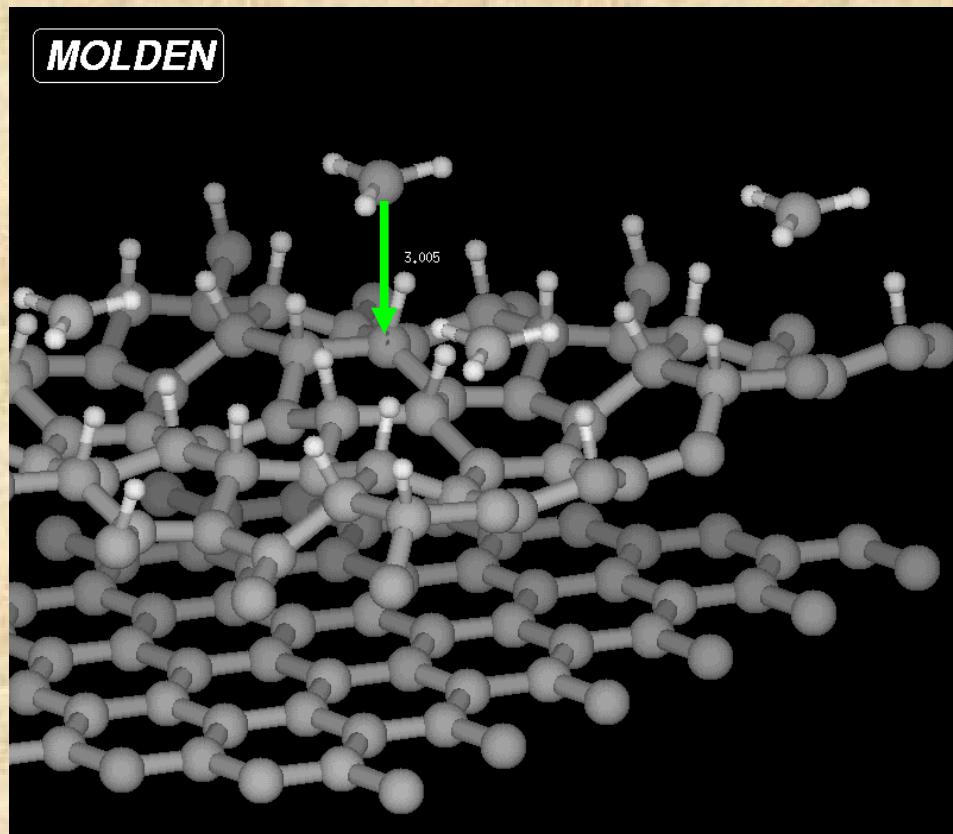
# minimum 1.48 Å



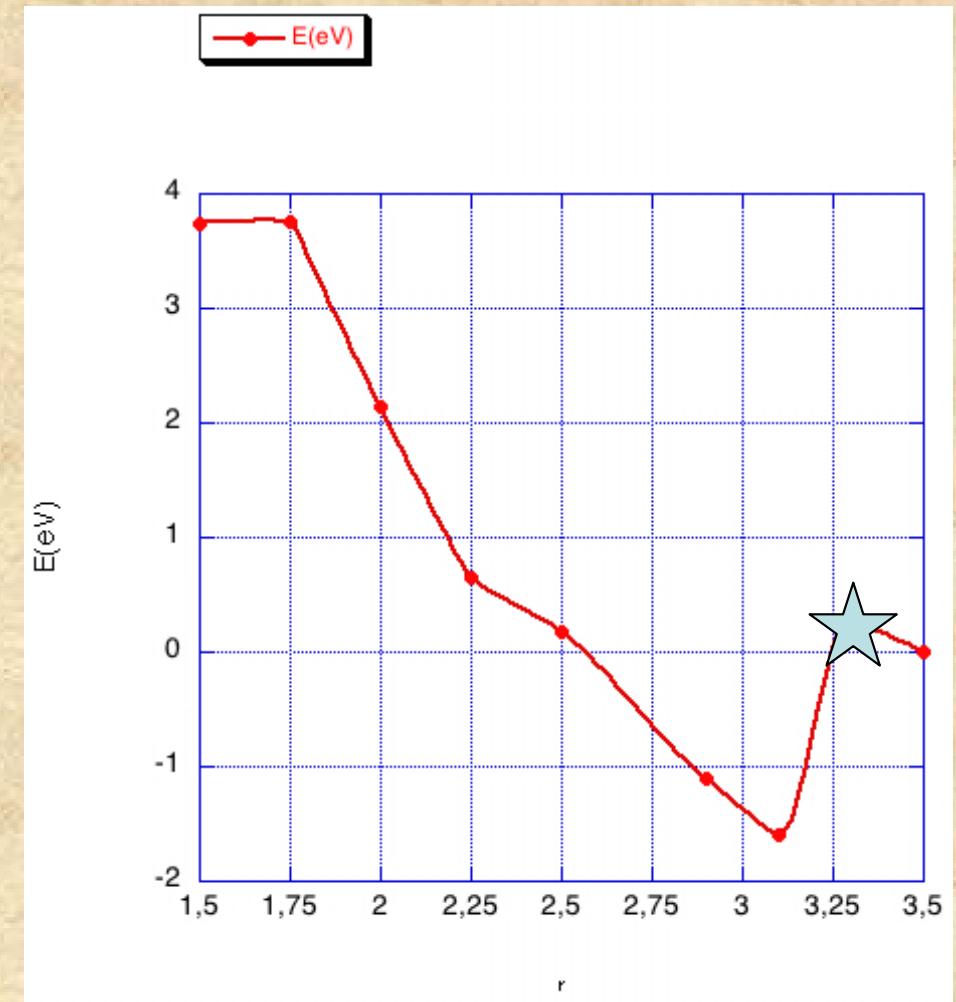
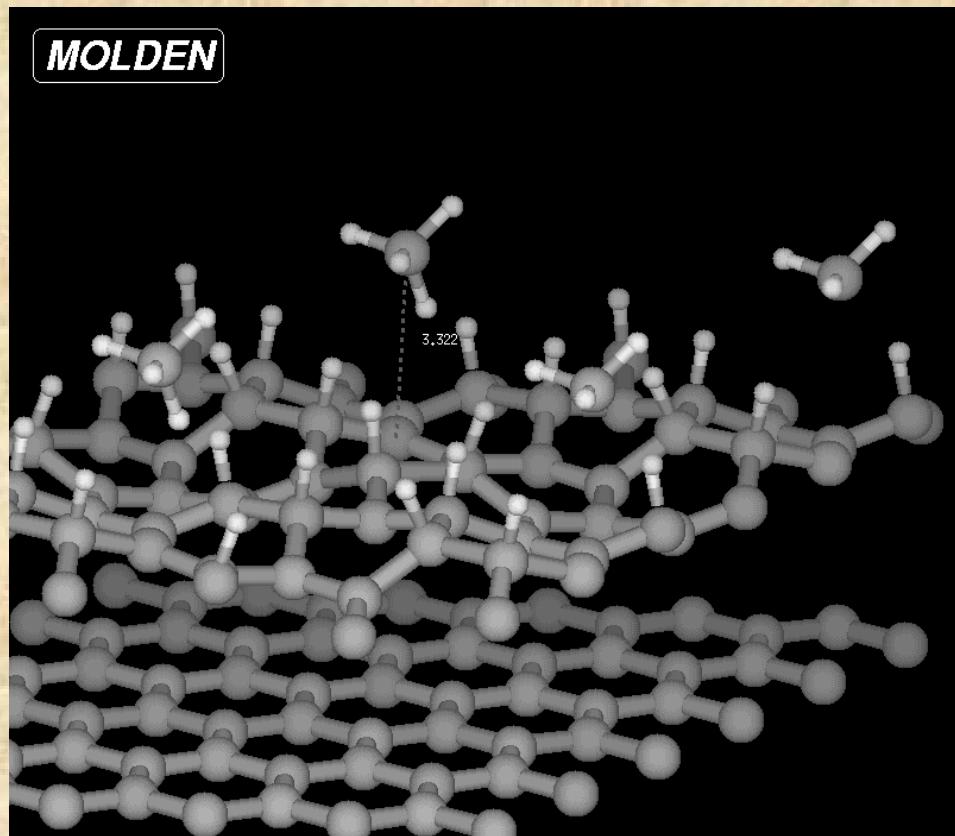
The gain in energy is due to H – H recombination

# **H substitution on saturated surface: first position in the quartet**

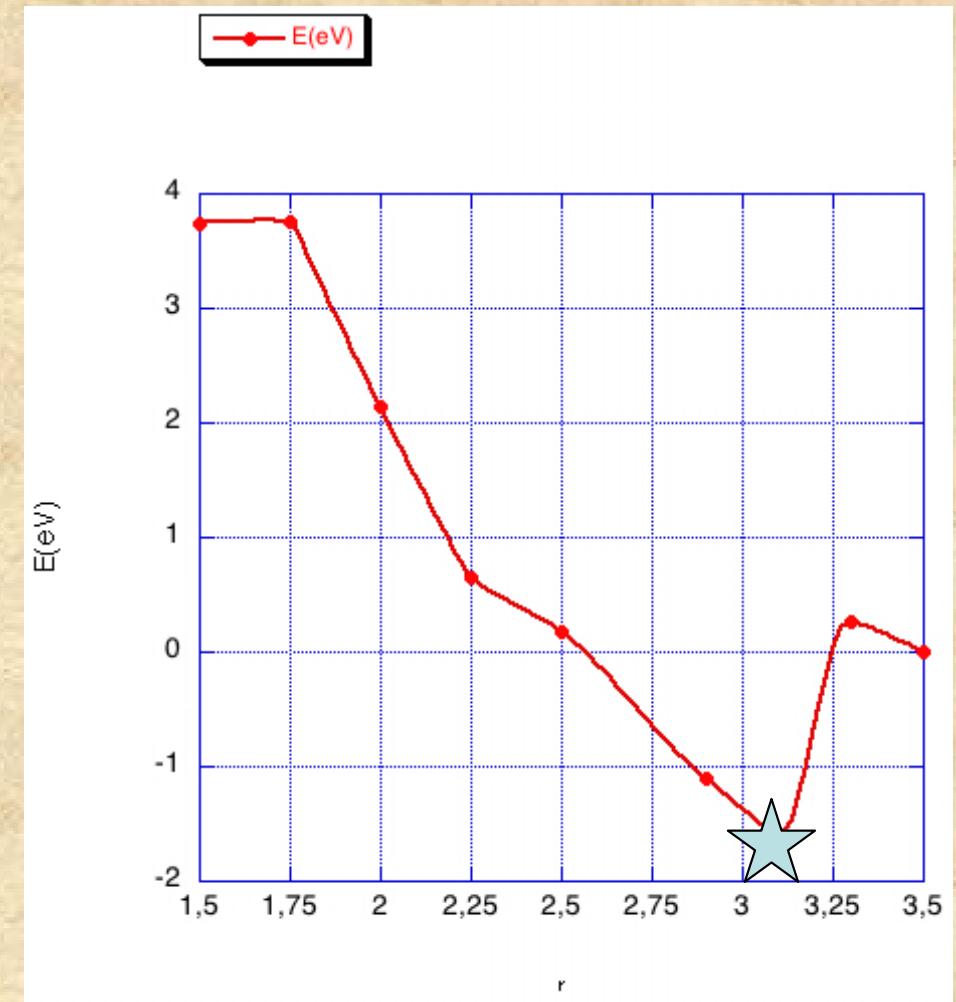
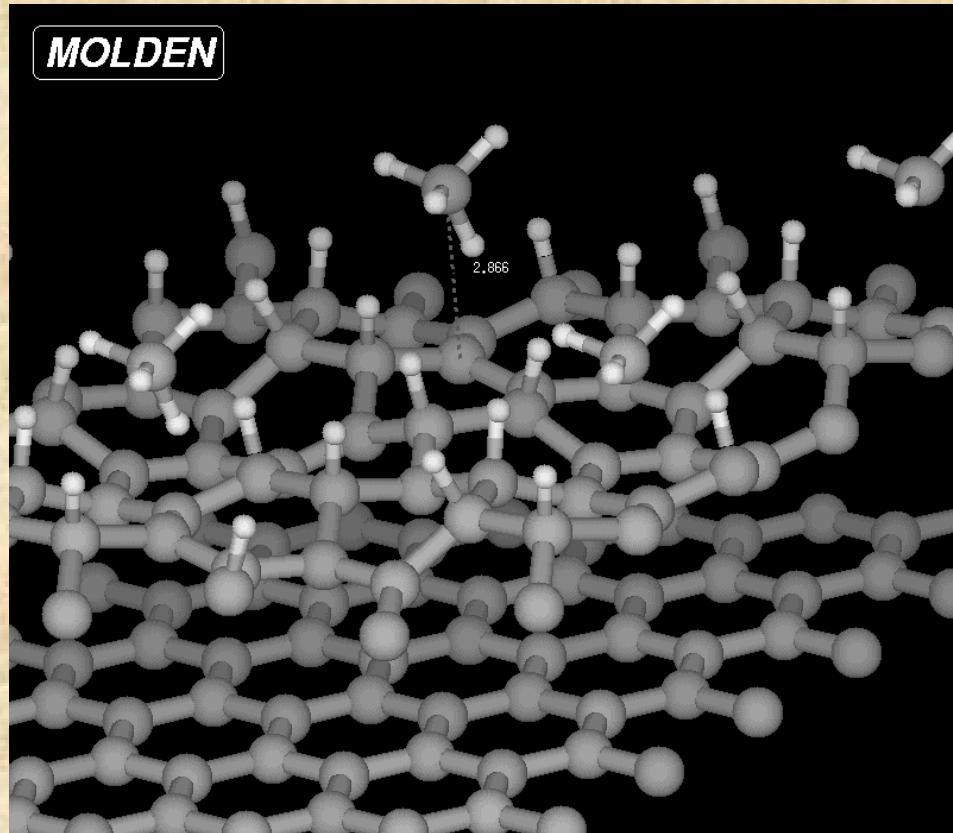
3.5 Å



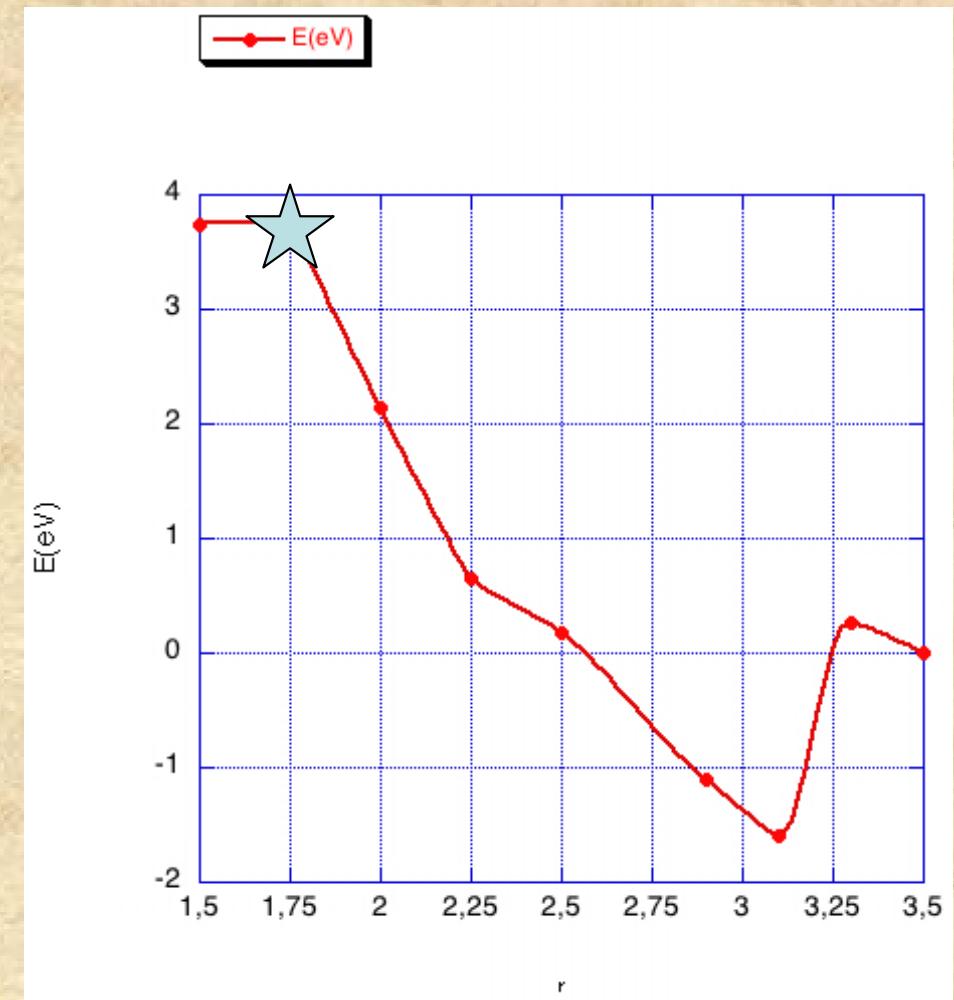
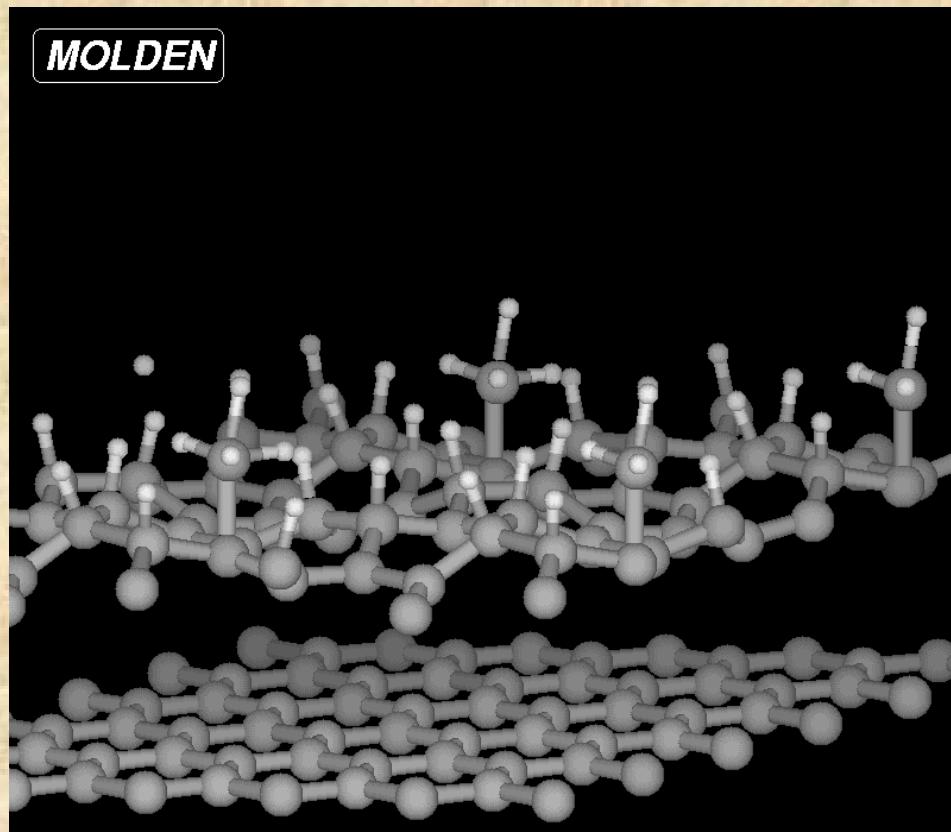
3.3 Å



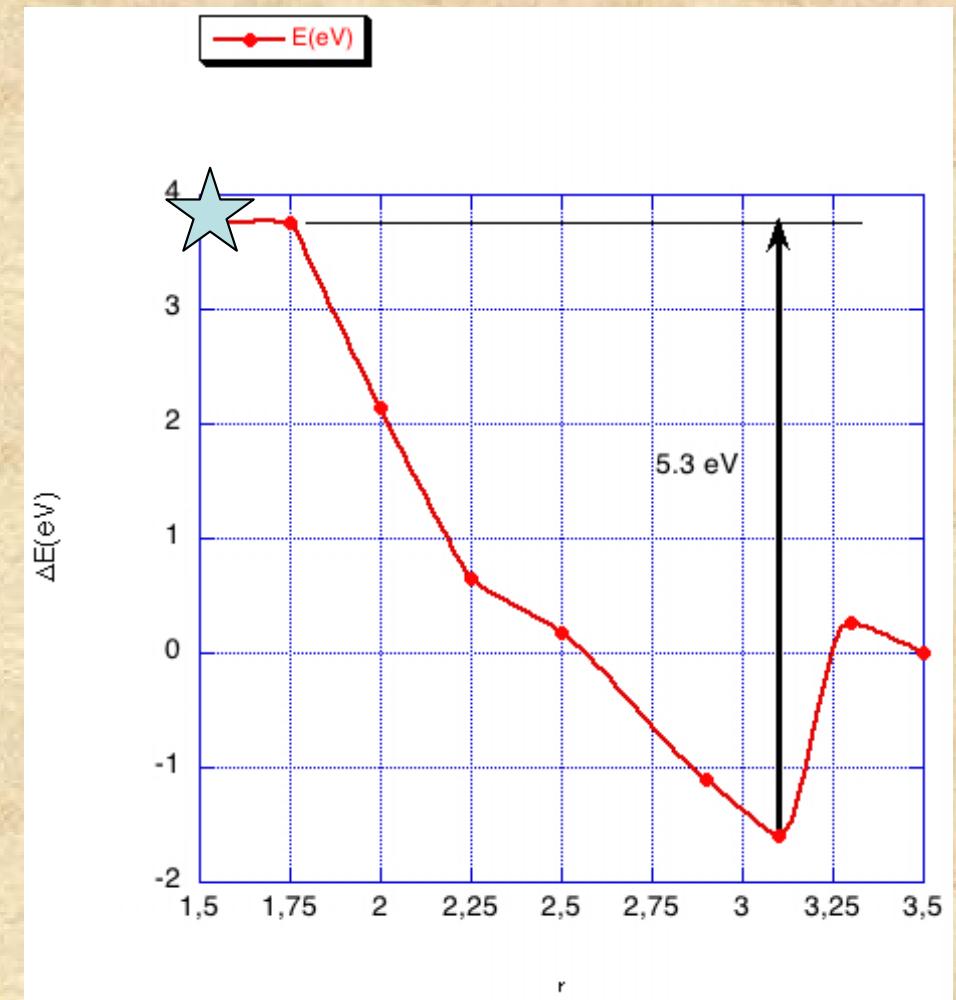
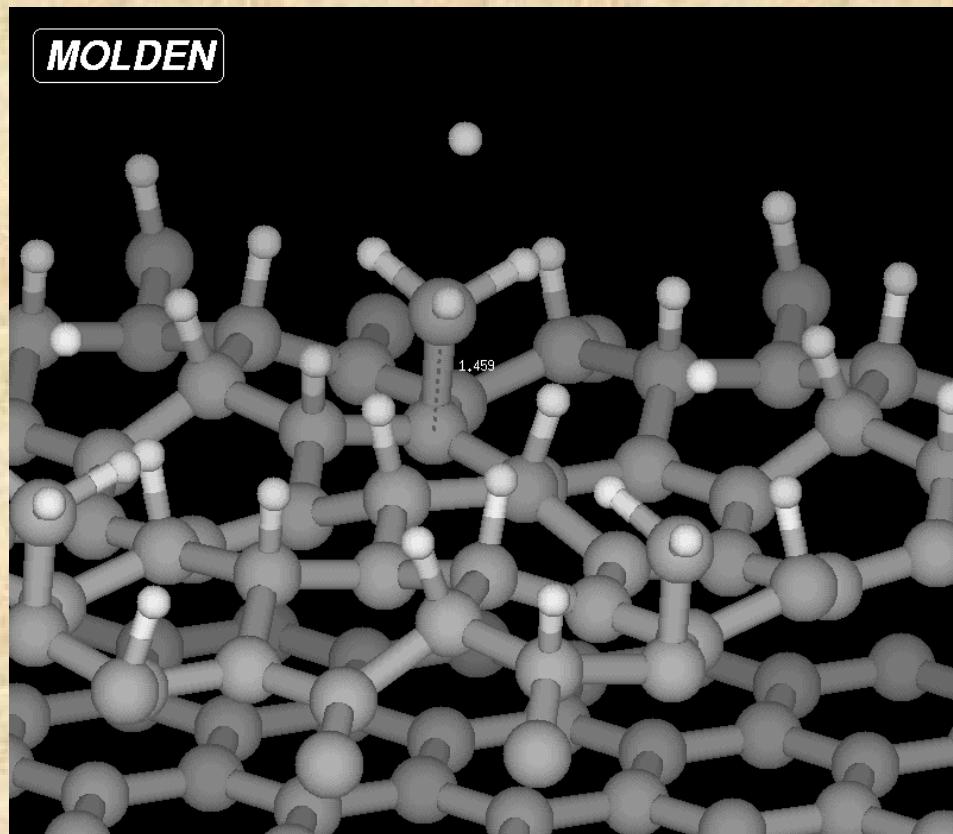
3.1 Å



1.75 Å

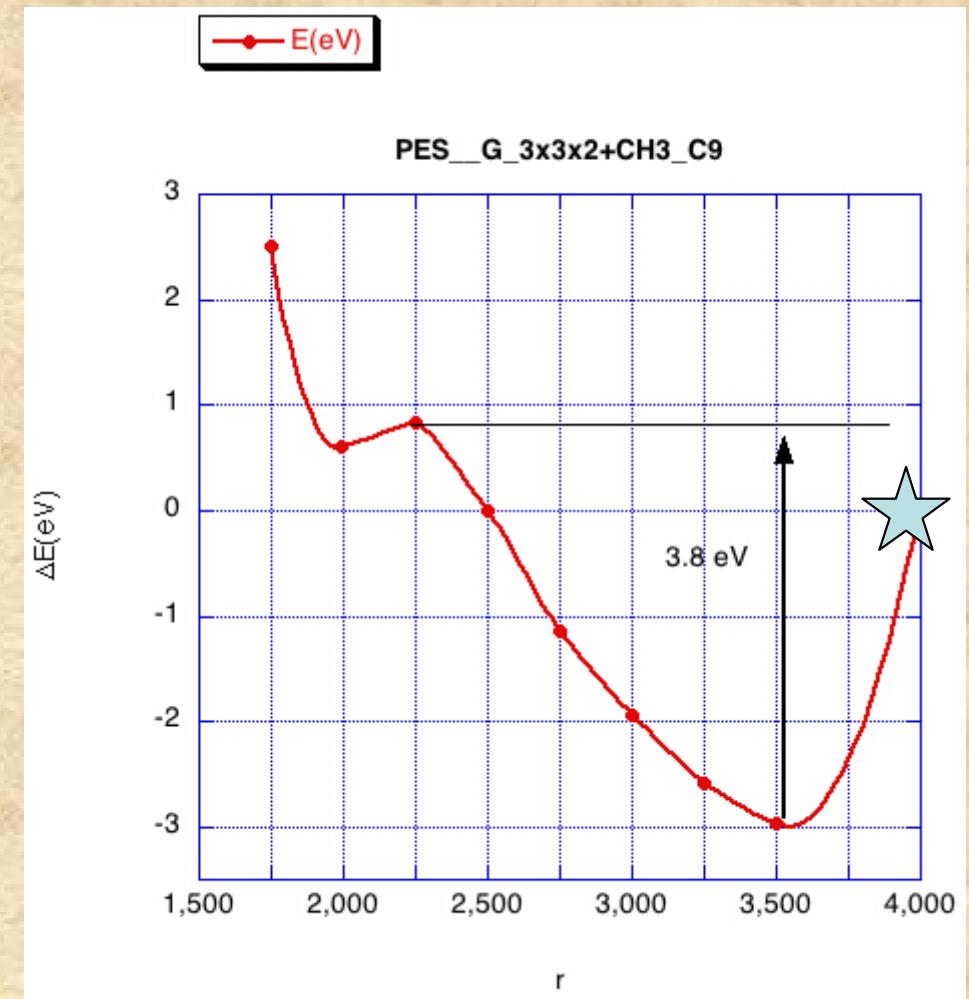
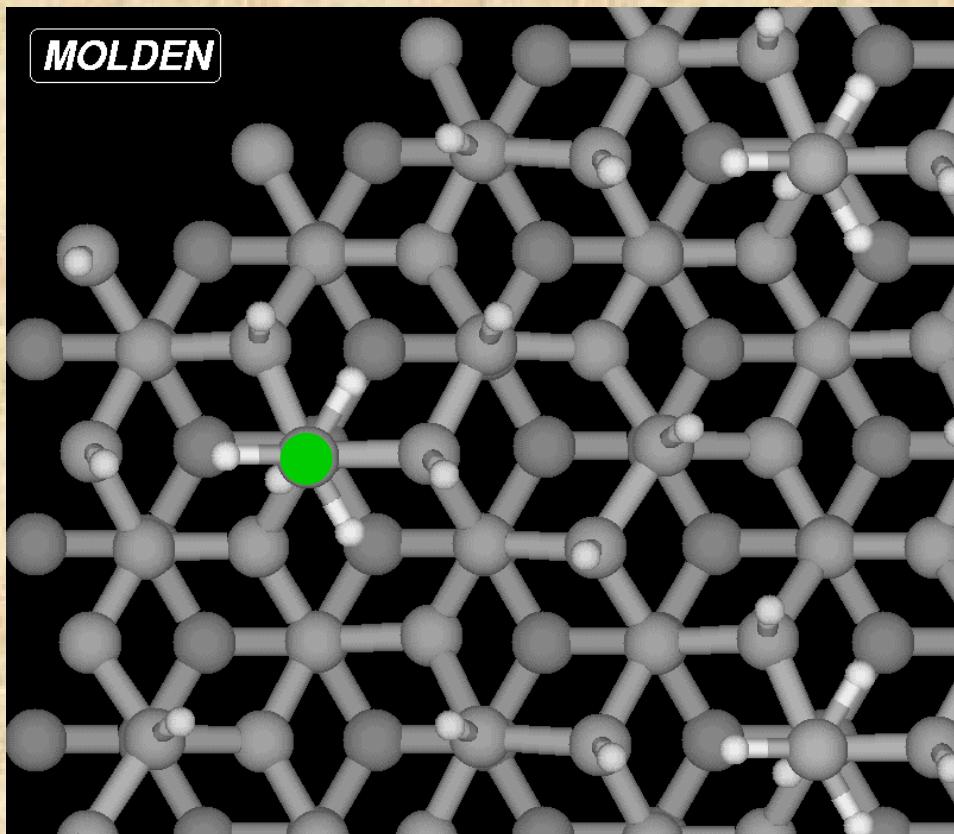


1.5 Å

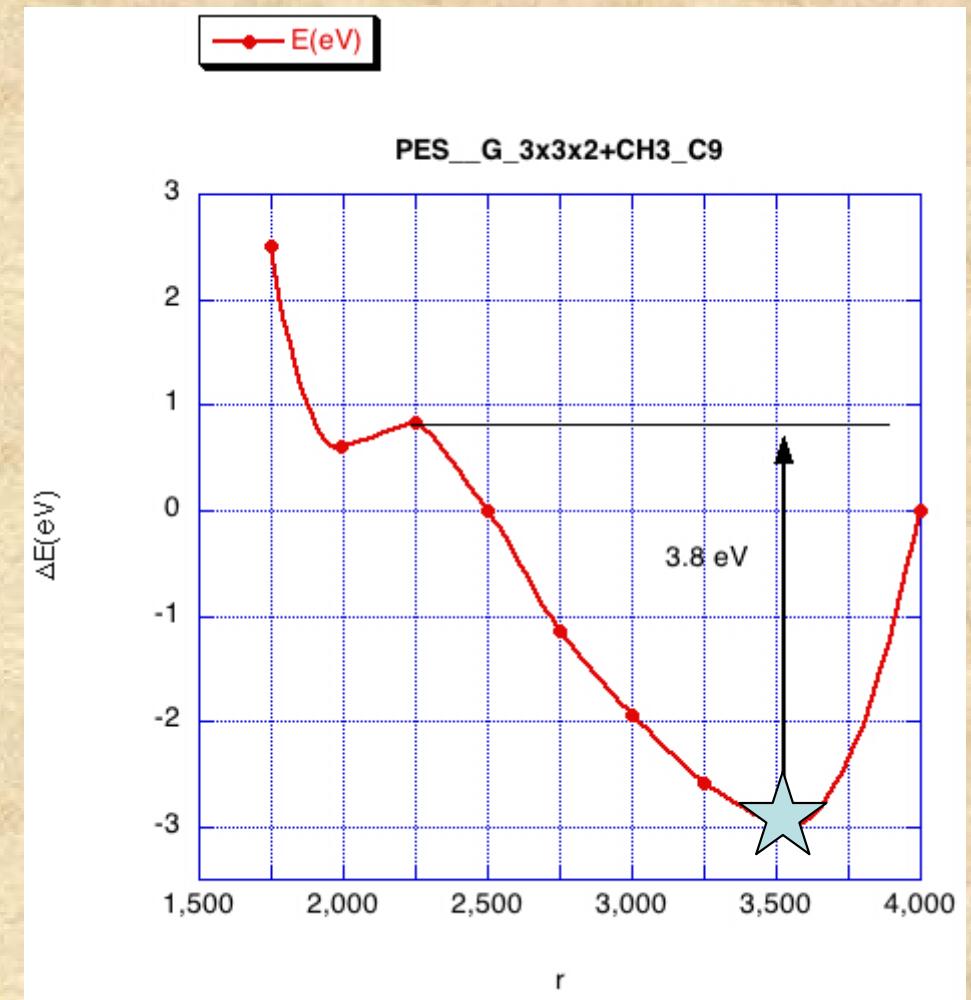
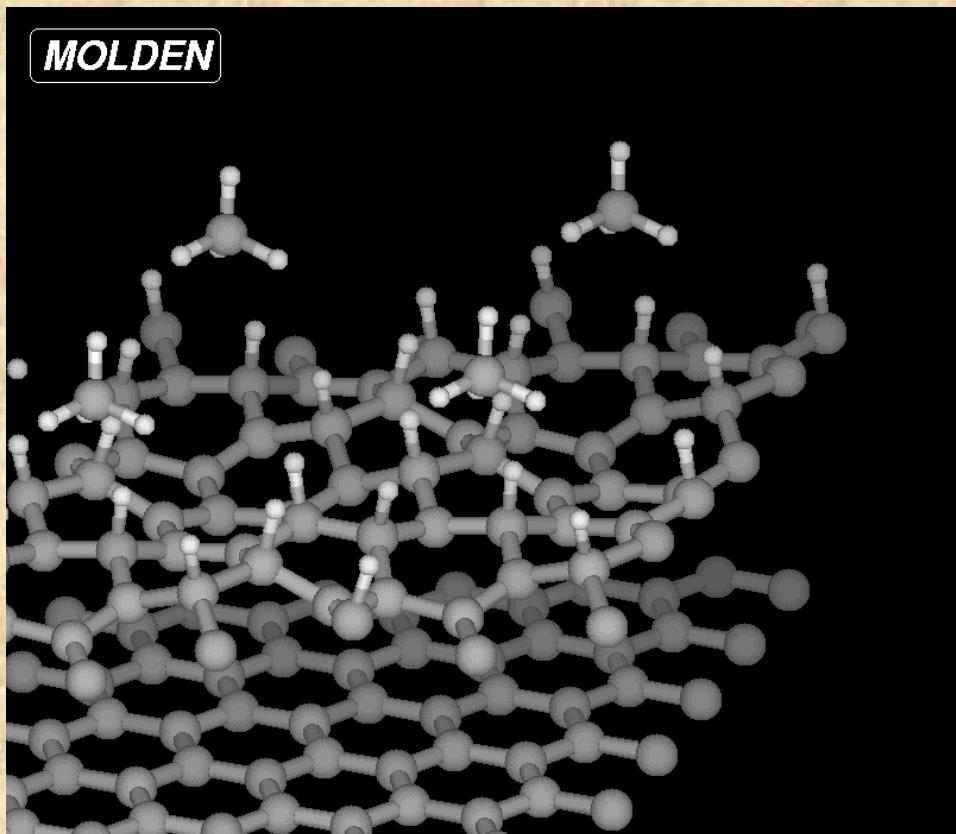


# **Adsorption on saturated surface: in a middle site in the quartet**

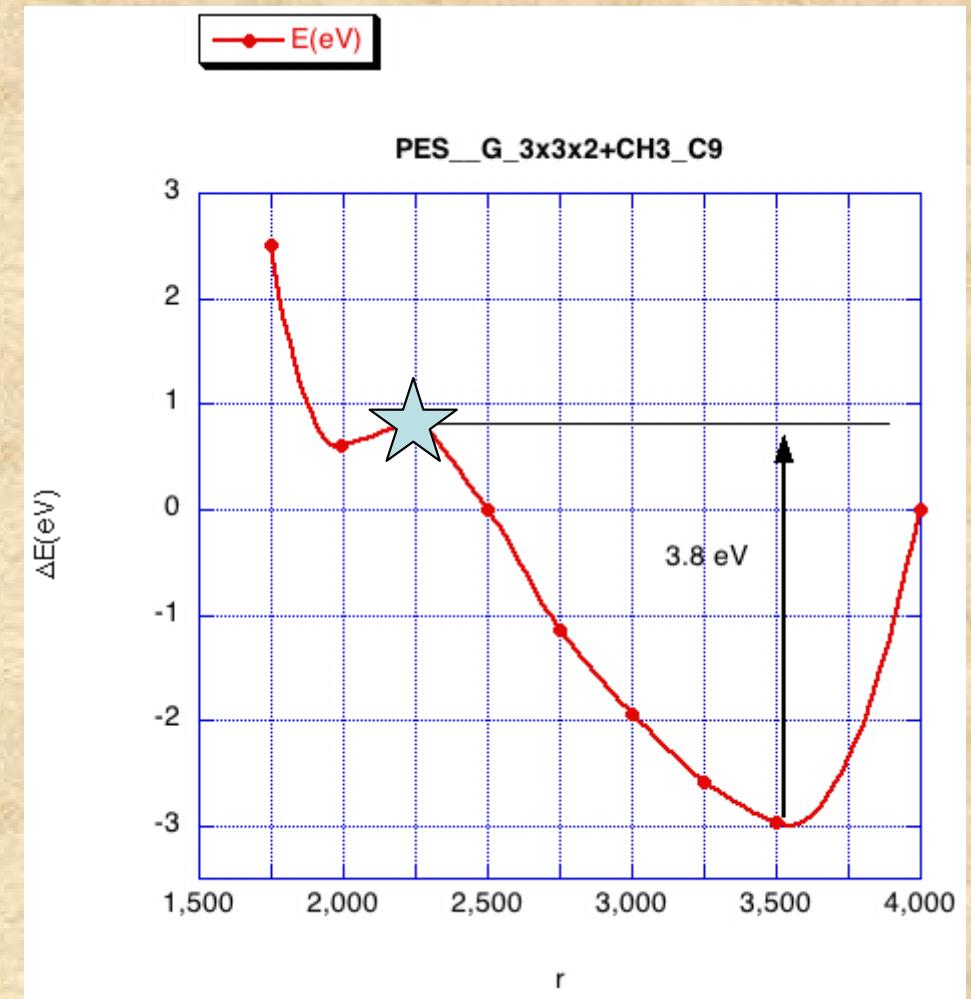
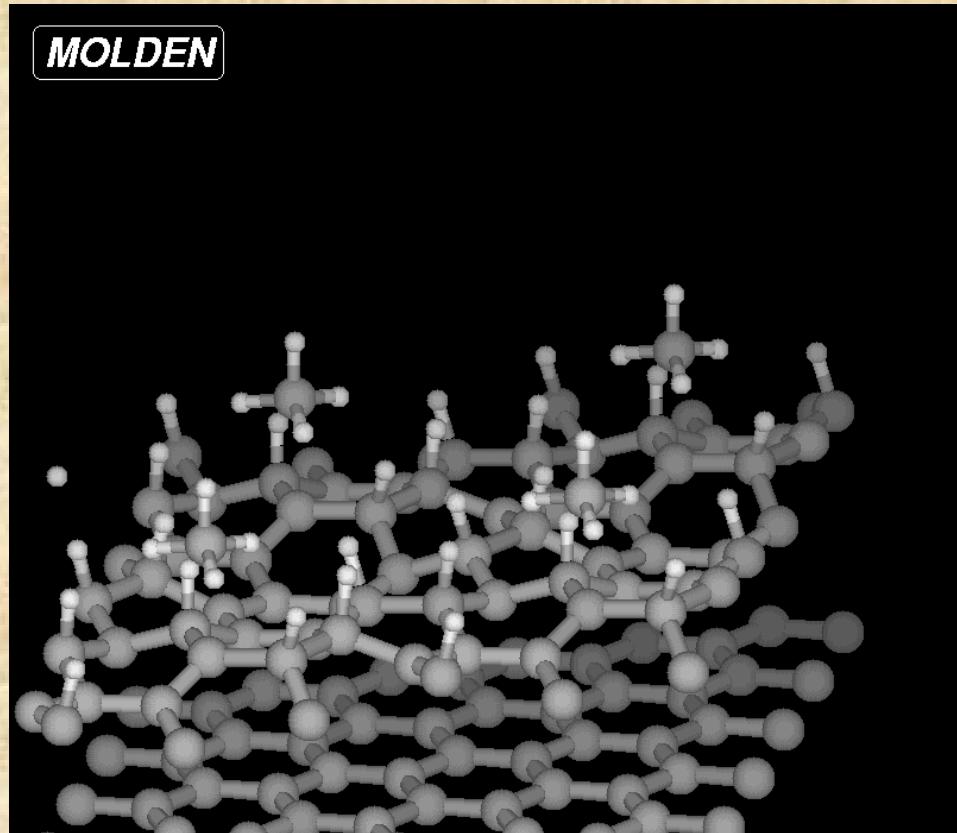
4.0 Å



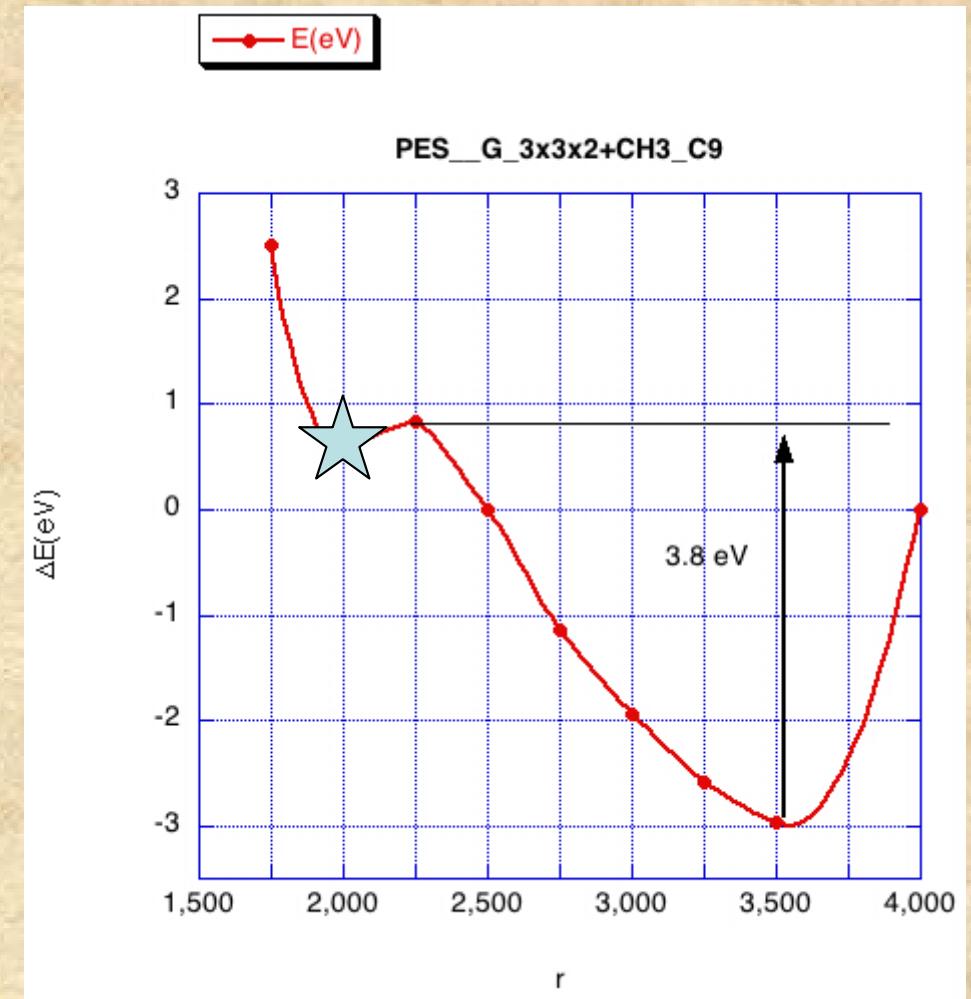
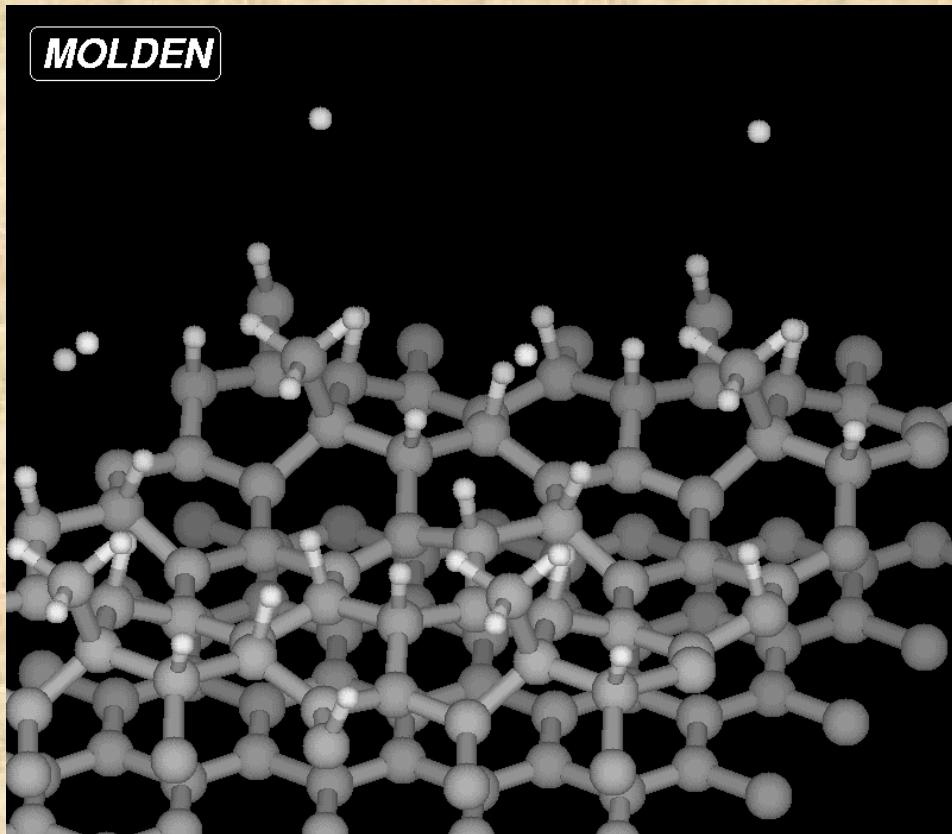
# First minimum



# TS



# Second minimum



# First conclusions

**Those barriers of energy are high  
compared to methyl deposition in PSI  
but:**



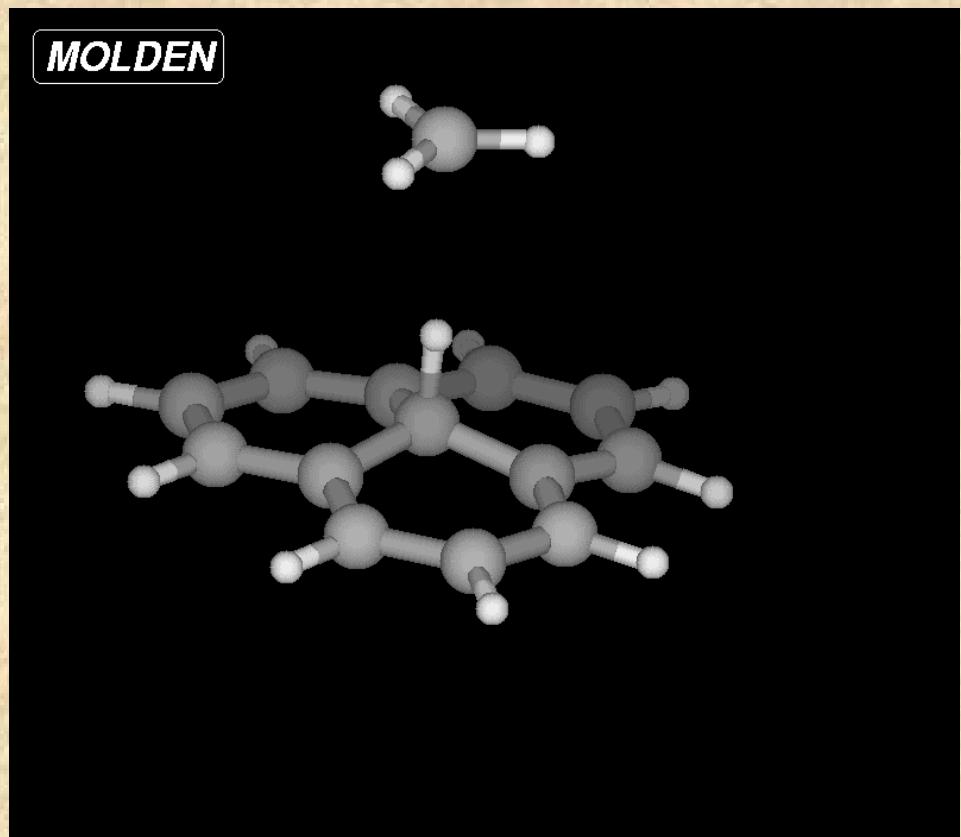
- The first calculation are performed at the  $\Gamma$  point of the Brillouin zone, they have to be refined.
- Only one approach of  $\text{CH}_3$  to the surface (perpendicular) has been considered

### Qualitatively:

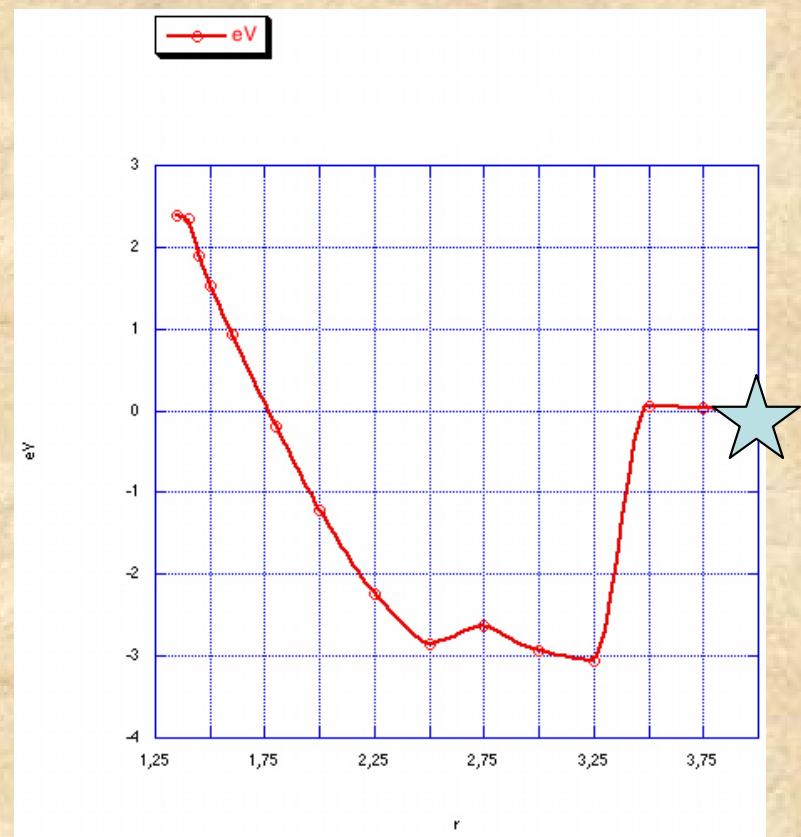
- The processes are very dependent on local structure of the surface.
- The energy barriers are equivalent for adsorption and substitution ( 3.7 compared to 3.8 eV)
- Extra H atoms could modify the energy profile and the barriers: PES graphite +  $\text{CH}_3$  + H(s) ?

**Is graphite the best model ? Molecules as representative of reactive site in a-C:H**

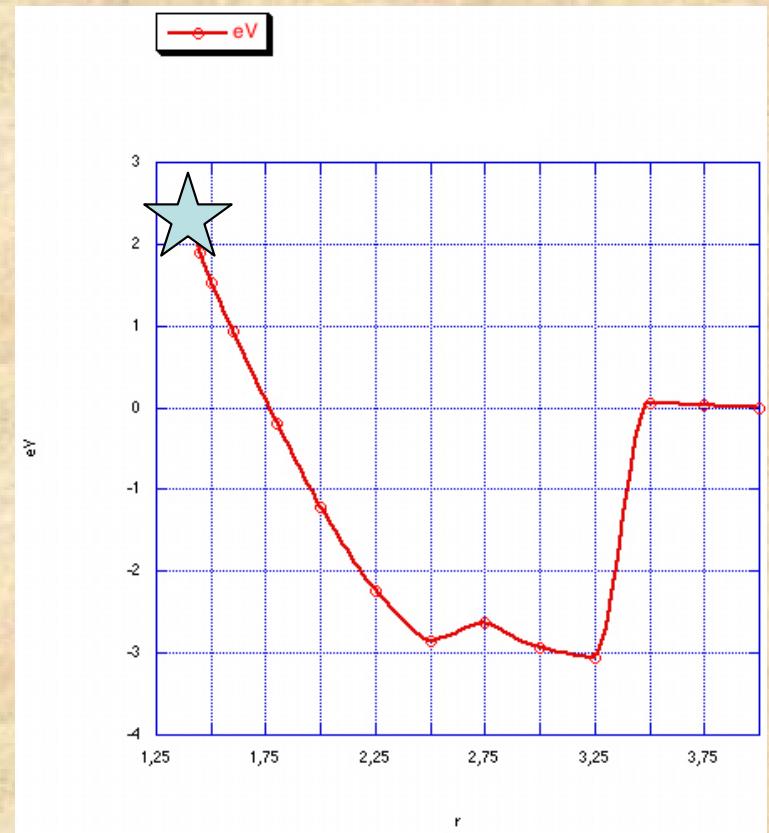
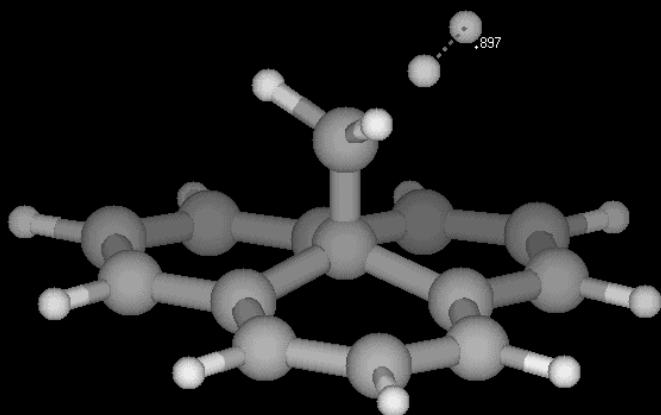
# **H/methyl substitution in molecules: a first attempt**



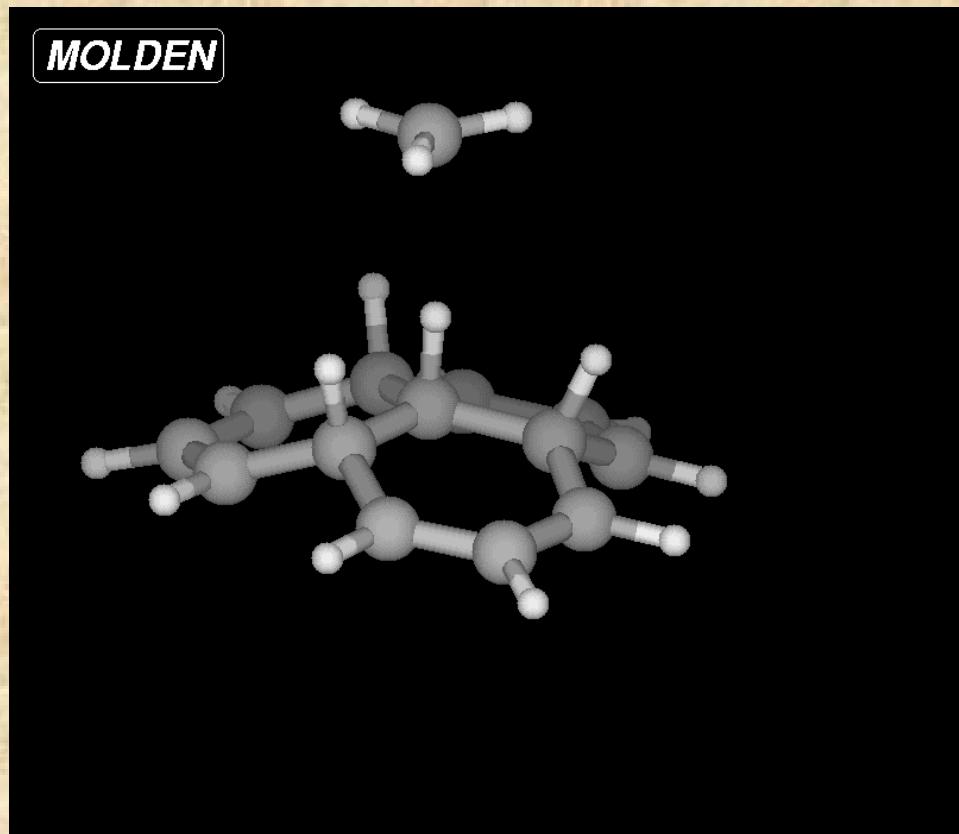
$$\nu_{\text{CH}} = 2592 \text{ cm}^{-1}$$



**MOLDEN**

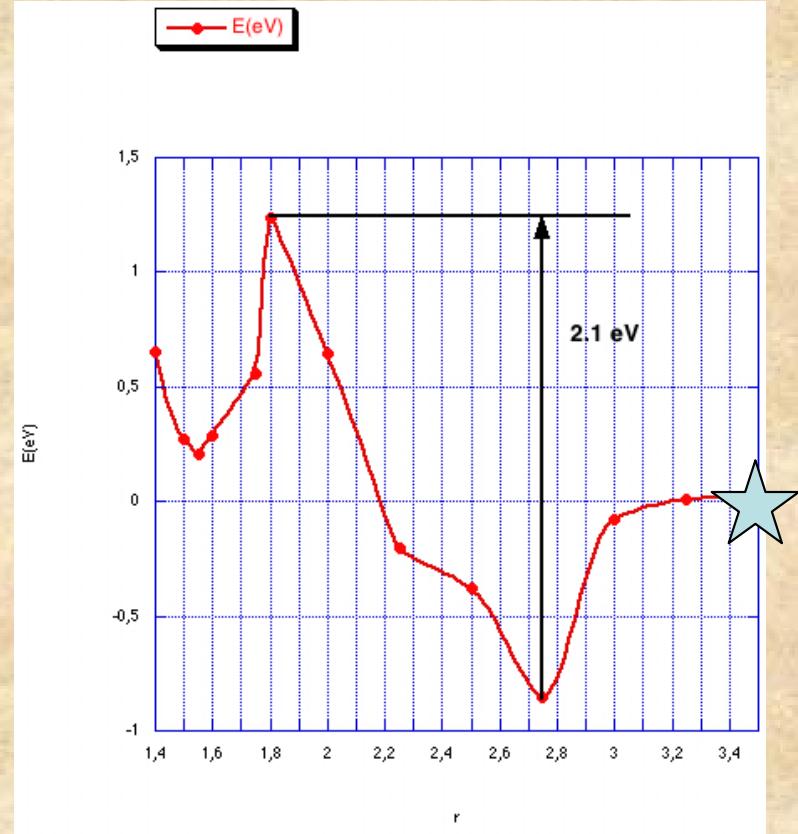


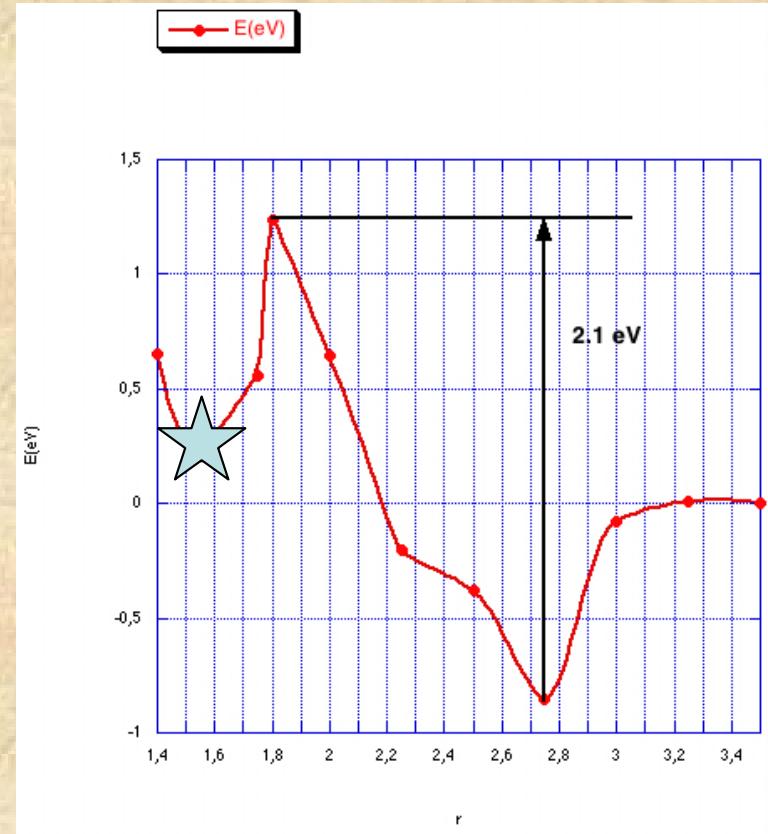
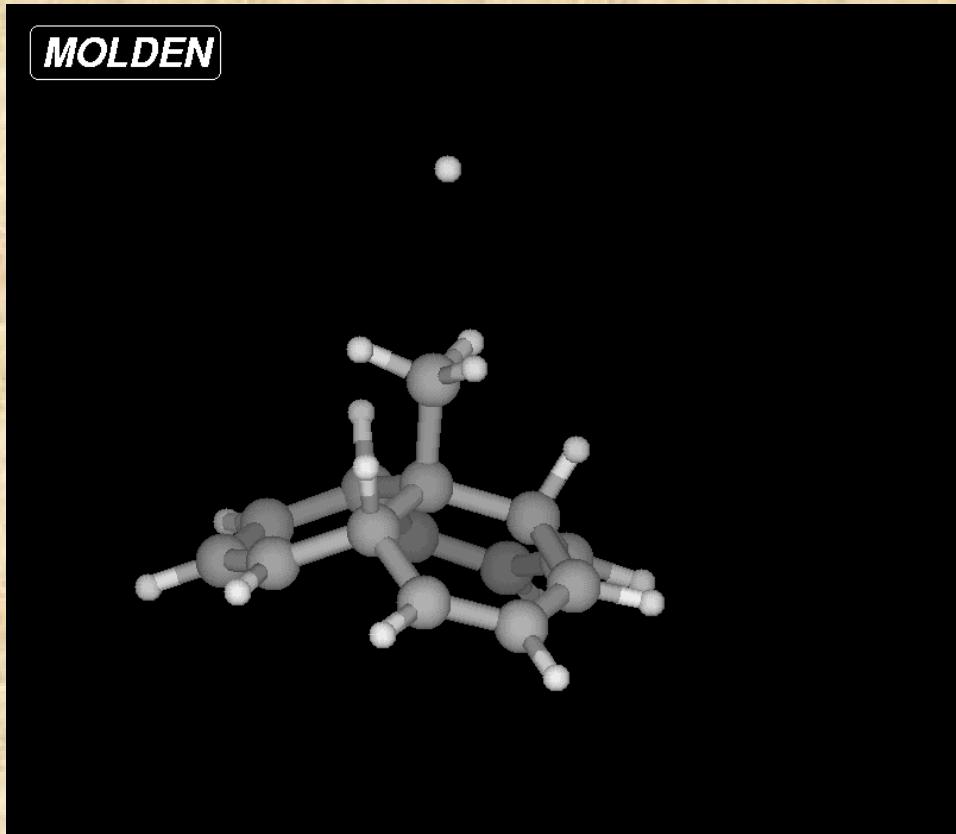
# H saturated site



$$\nu_{\text{CH}} = 2636 - 2928 \text{ cm}^{-1}$$

- C(sp<sub>2</sub>)-H  
Ethylene 3022–3124 cm<sup>-1</sup>,  
Benzene 3057–3096 cm<sup>-1</sup>,  
Pyrene 3055–3087 cm<sup>-1</sup>,  
Coronene 3058–3080 cm<sup>-1</sup>,





# **Not for ever-final conclusions**

- 1) In the molecular case, the barrier is reduced of ~50% comparing to the lowest barrier on graphite**
- 2) The chemical bond strength is not the only parameter**
- 3) Other typical situations have to be imagined**
- 4) Again interaction with other reactive H is to consider: energy and/or H transfer between reactants → (2 reaction coordinates PES ?)**

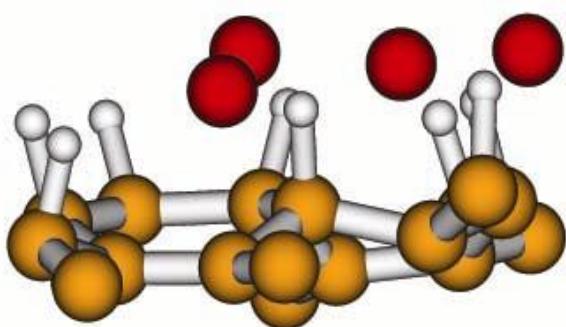
# *Dehydrogenation of hydrogen saturated graphite surfaces*

# Motivations

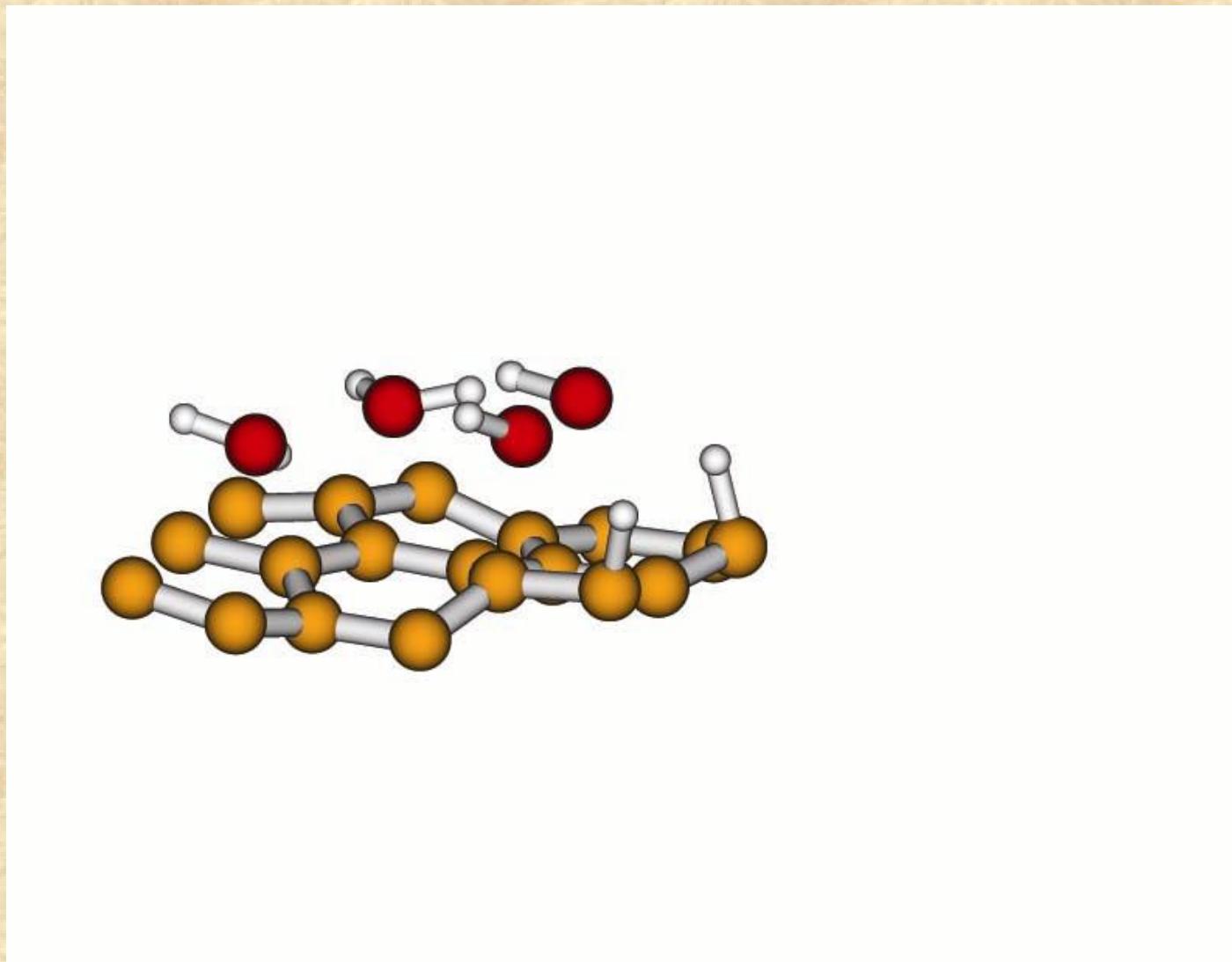
**Can oxygen be an help in graphite dehydrogenation ? Water formation**

*Formation of water molecules by reaction between  
oxygen atoms and adsorbed hydrogen atoms:  
Nosé-Hoover simulation*

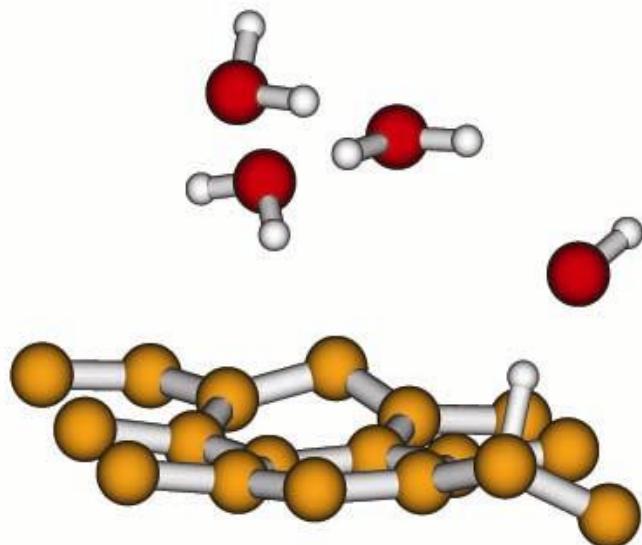
0 fs , T = 300K



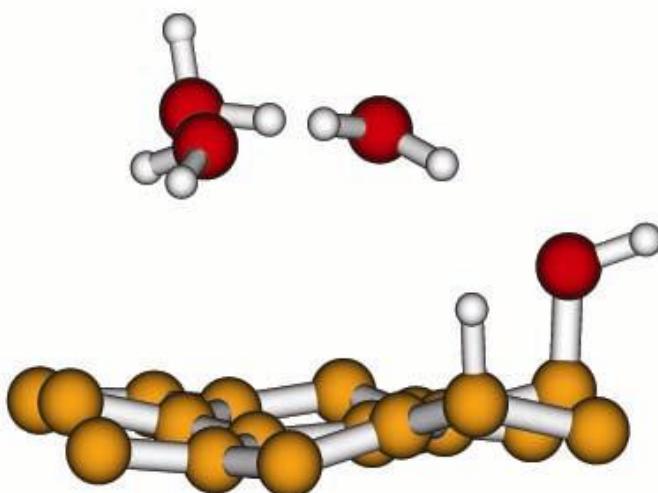
25 fs



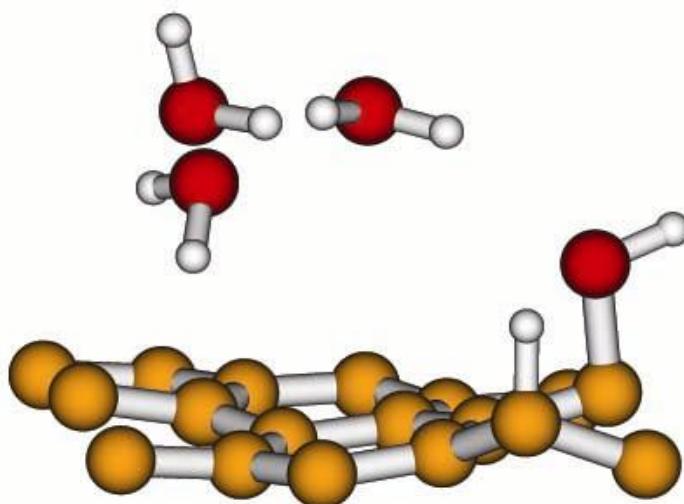
180 fs



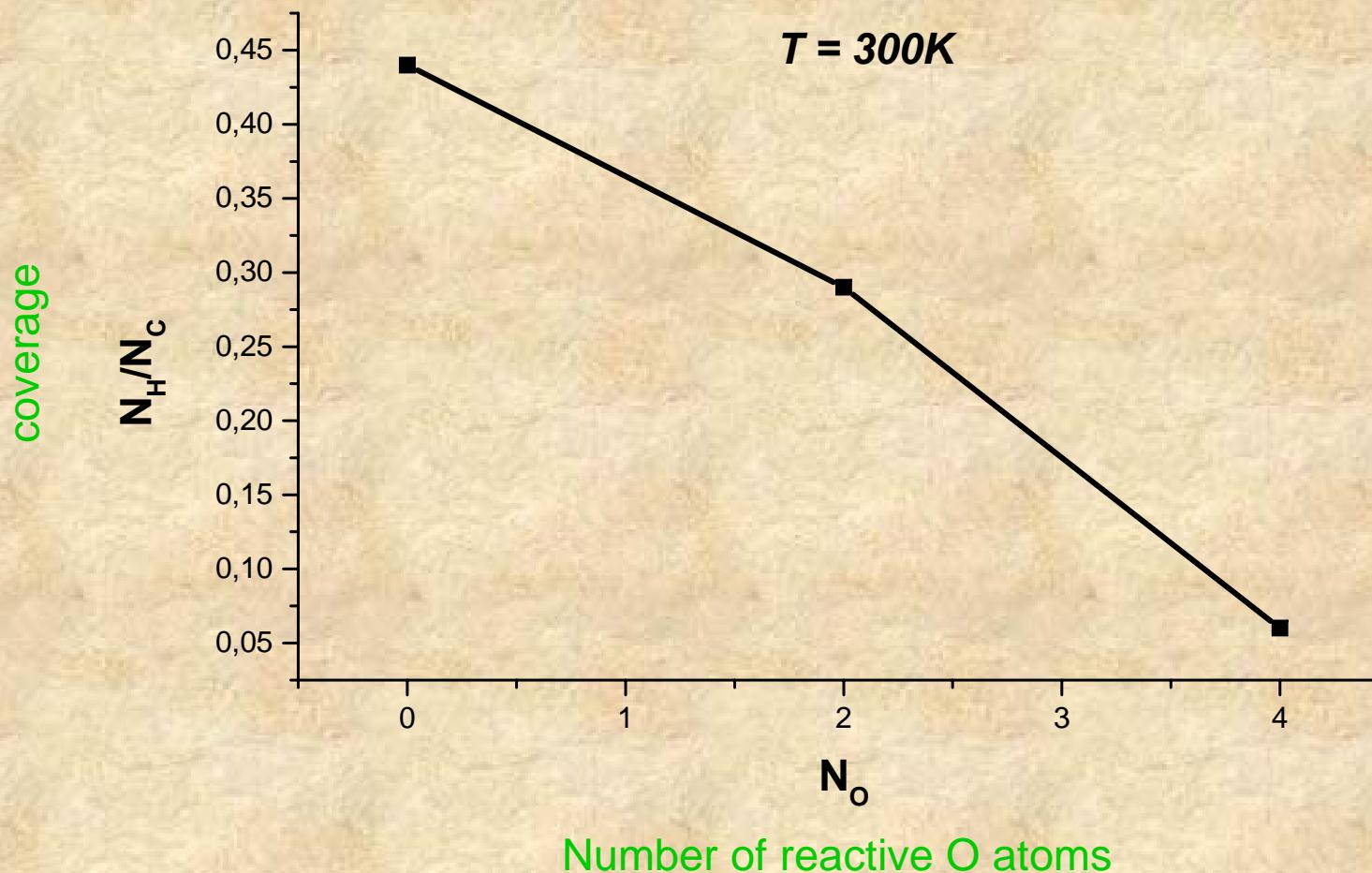
300 fs



500 fs

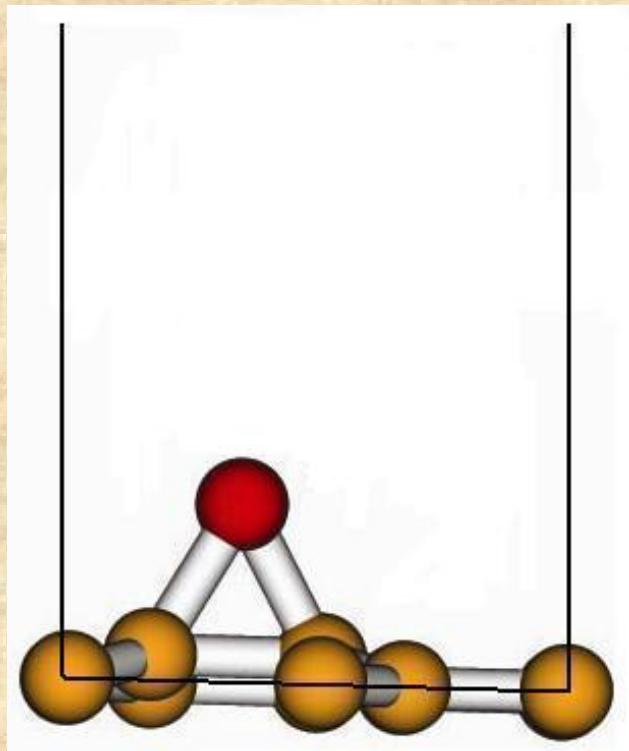


## *Dehydrogenation of graphite surfaces using oxygen atoms at 300K*



# Adsorption of oxygen atoms

*The atomic oxygen can adsorb on the graphite basal plane with formation of graphite oxide (epoxide like structure):*



$$E_{ads} = 1.8 \text{ eV (ref. } {}^3O\text{)}$$

$$E_{ads} = 2.5 \text{ eV (ref. } {}^1O\text{)}$$

# Formation of hydroxyl radicals (PES)

*The adsorbed oxygen atom can react with hydrogen atoms*

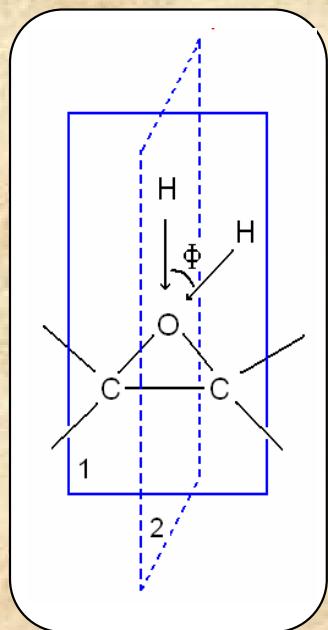
*Mechanisms*

*Eley – Rideal*

*Langmuir – Hinshelwood*

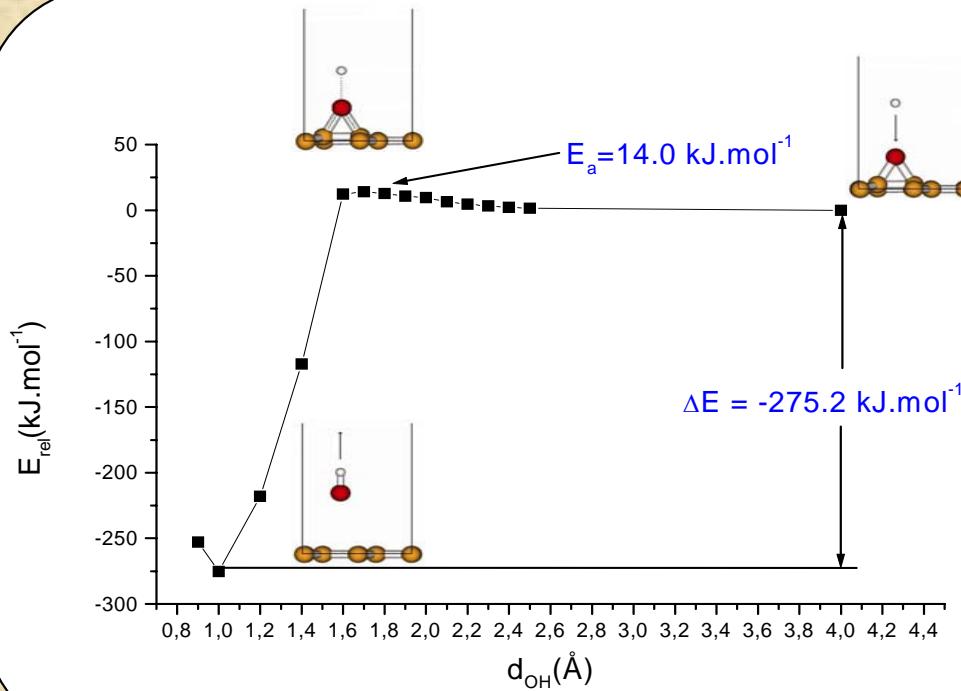
*Symmetric  
Attack*

*Asymmetric  
Attack*

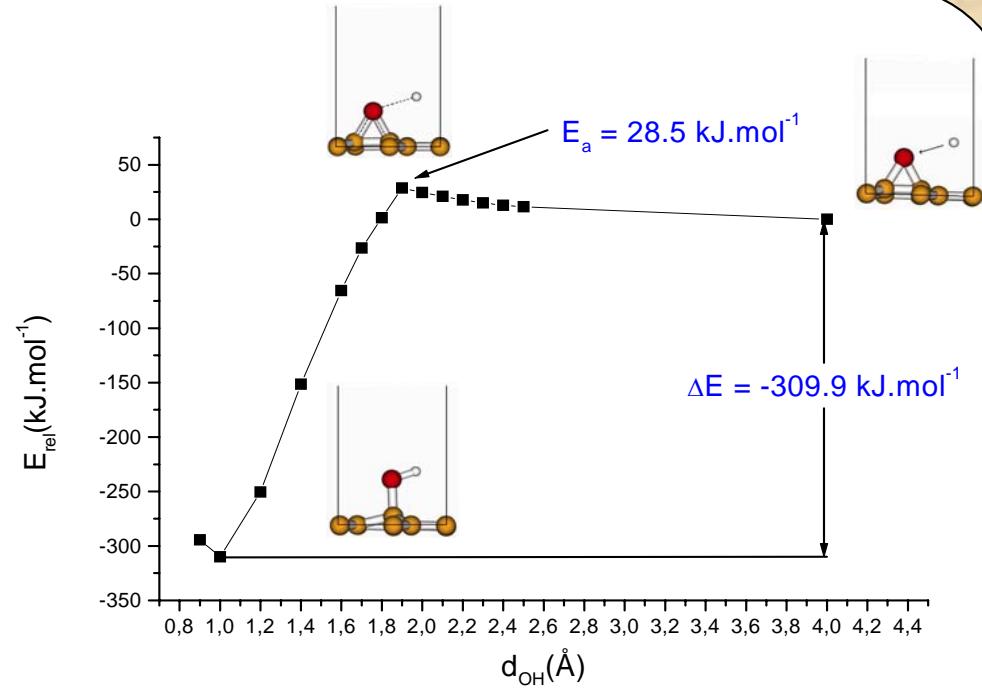


# Eley-Rideal mechanism

## Symmetric Attack (SA)



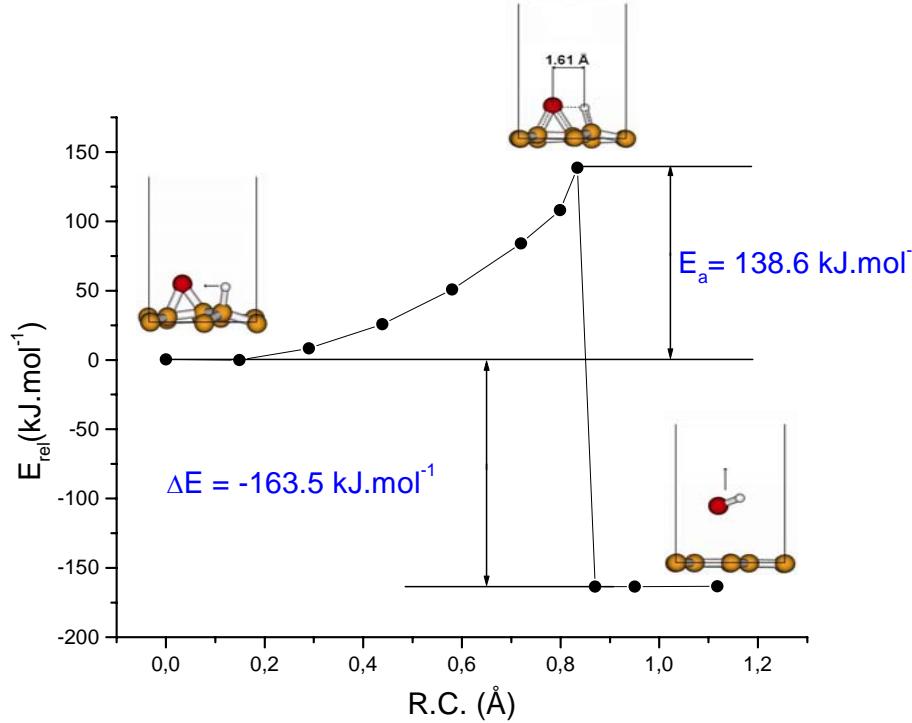
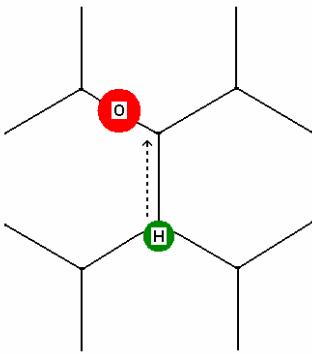
## Asymmetric Attack (AA)



**SA:** formation of free OH radicals, small activation energy, strong exothermic effect

**AA:** formation of bound OH radicals, activation energy increases with attack angle

# The Langmuir – Hishelwood mechanism



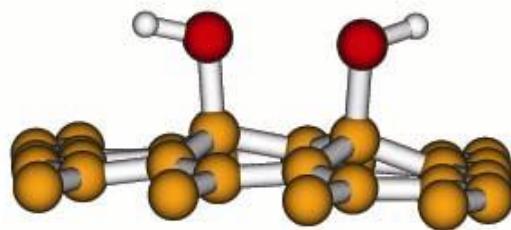
*The activation energy is more important for this mechanism than for Eley – Rideal => Eley – Rideal is kinetically favored*

*The exothermic effect is smaller than for Eley – Rideal (the H – gr – O system is more stable)*

*Formation of water molecules by  
reaction between  
hydroxyl radicals*

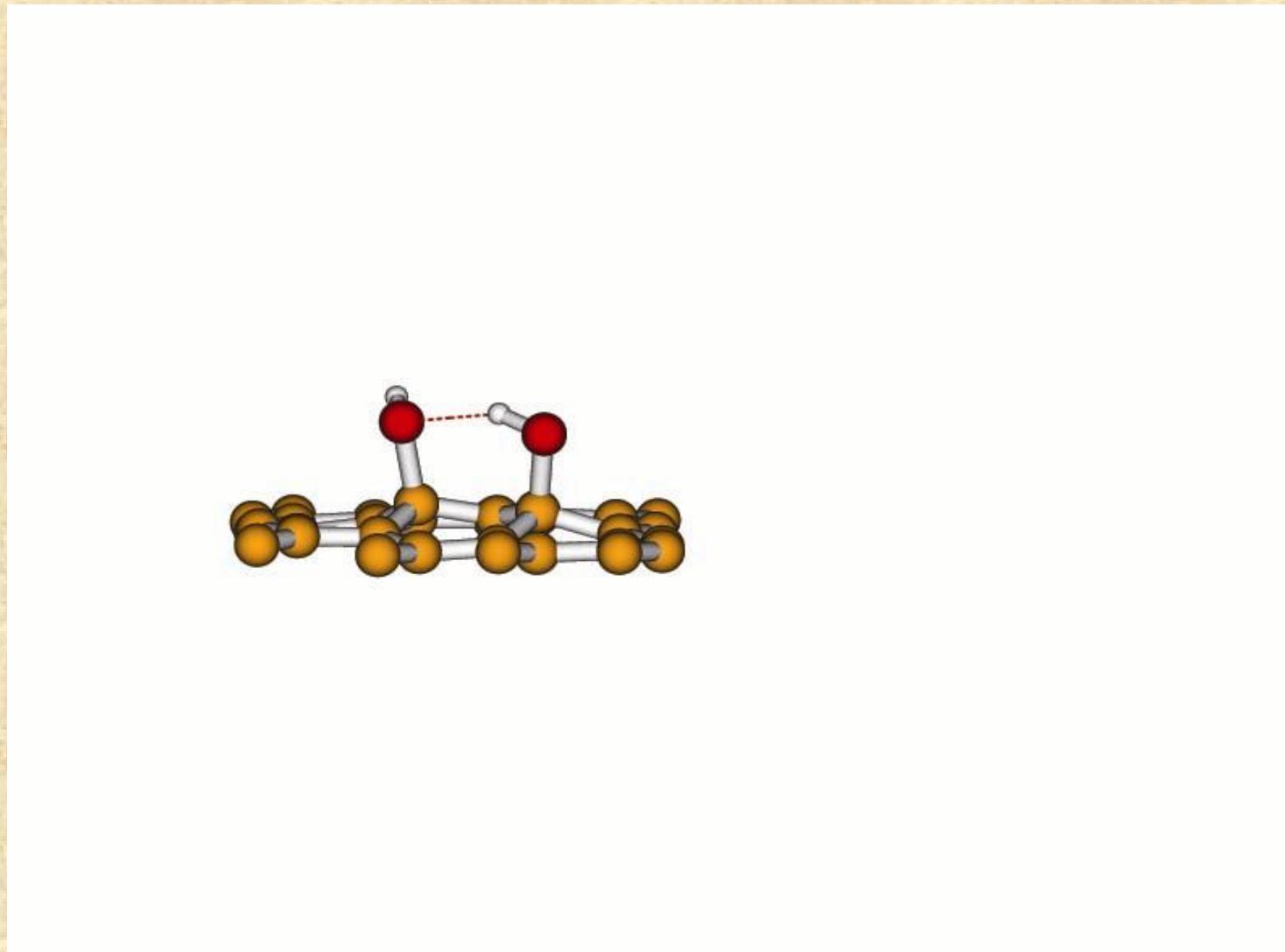
$t = 0 \text{ fs}$

$T = 500 \text{ K}$



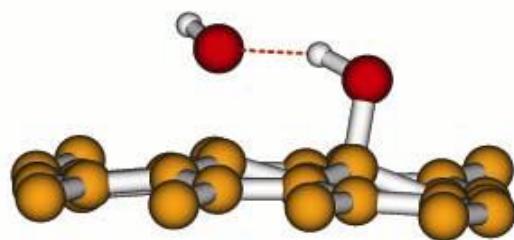
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$T = 500 \text{ K}$



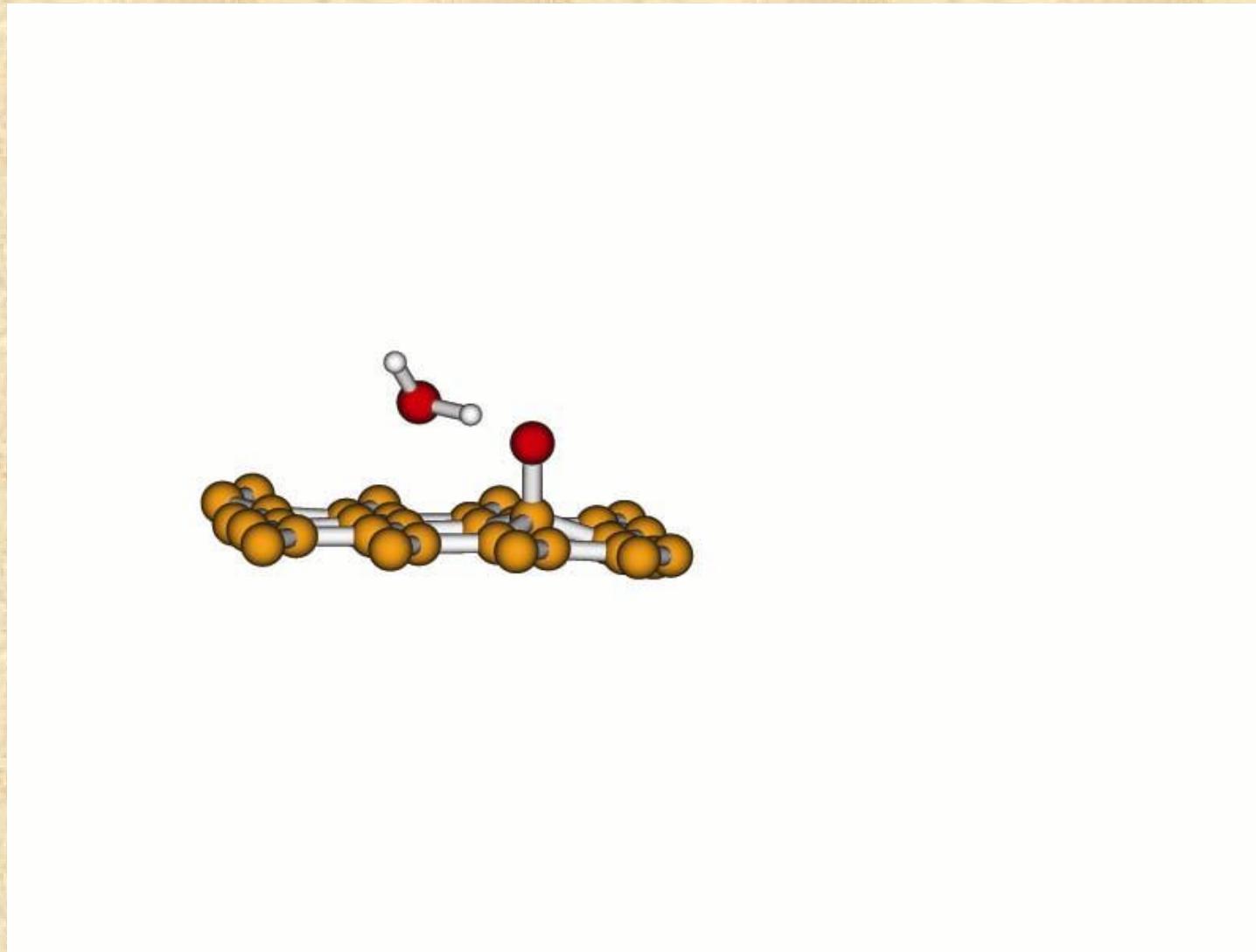
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$T = 500 \text{ K}$



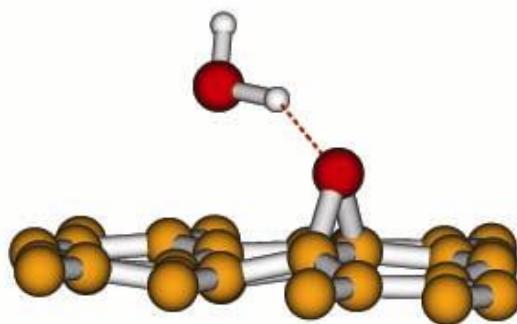
$t = 420 \text{ fs}$

$T = 500 \text{ K}$



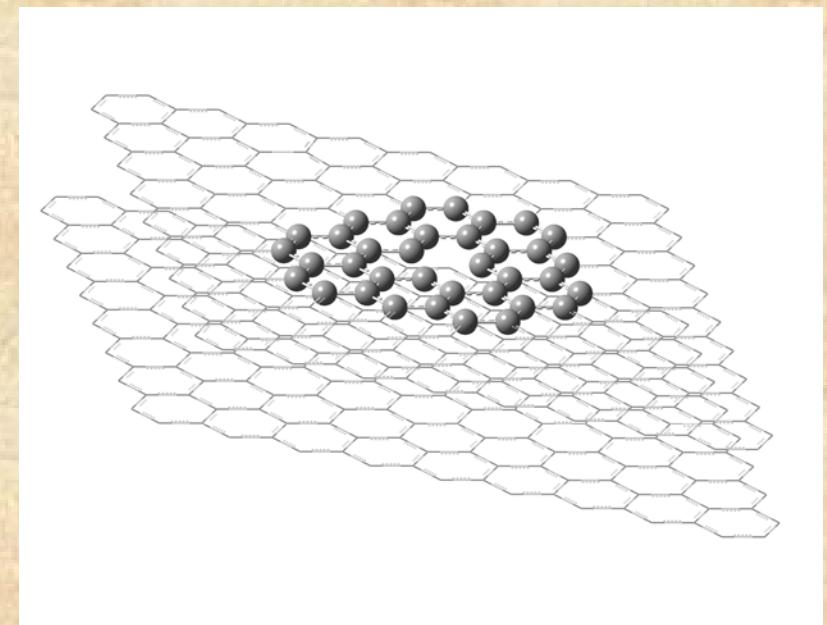
$t = 450$  fs

$T = 500$  K



# In development..

- 1) Reactivity of graphite surface vacancy
- 2) Influence of boron doping on oxygen/hydrogen reactivity
- 3) Hydrogen retention in beryllium
- 4) Hydrogen interaction with mixed materials: C/W



An aerial photograph of the city of Marseille, France, showing a dense urban area with numerous buildings and a large marina filled with boats. In the background, several small islands are visible in the Mediterranean Sea.

*Thank you for your attention*