Computational Approach to the Adsorption of H_2 on Interstellar Surfaces

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From the work by
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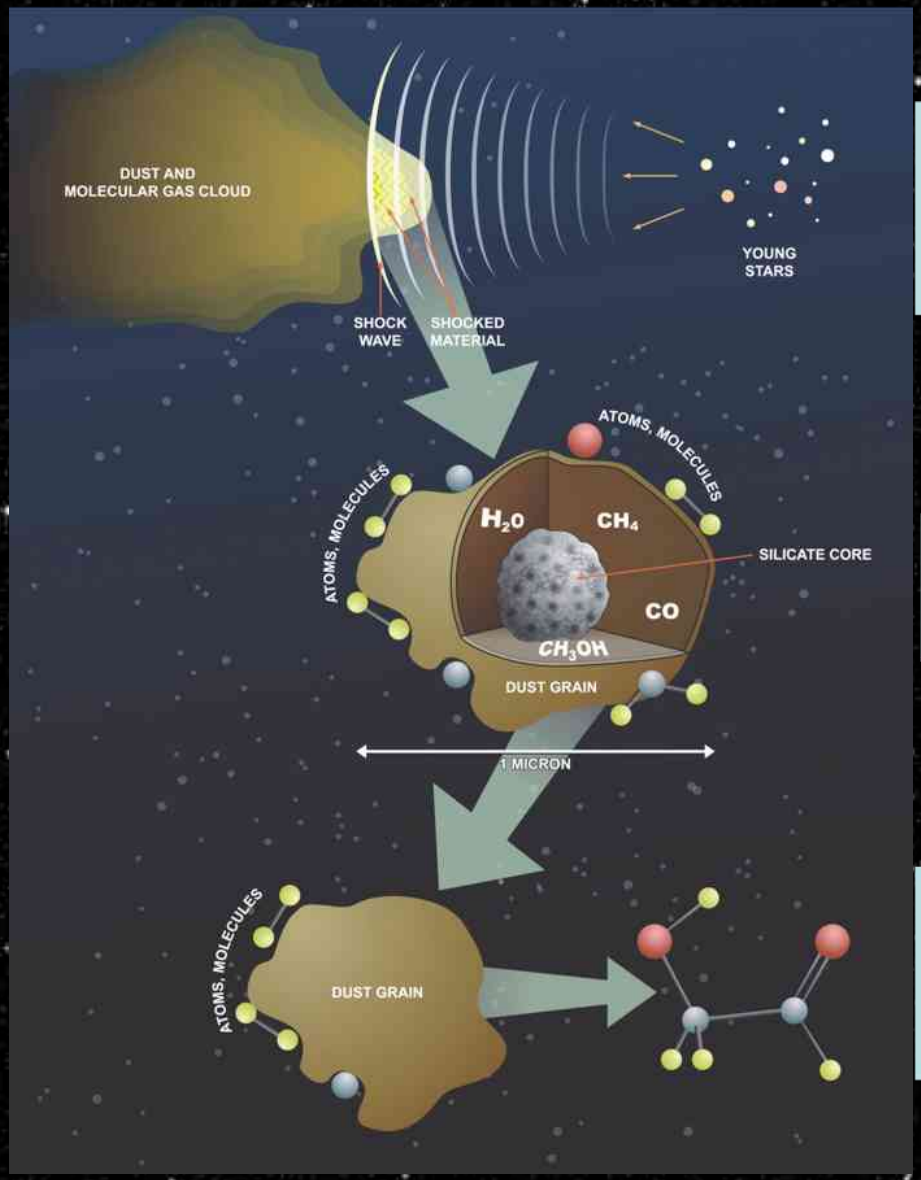
Importance of interstellar dust grains



Typical structure of grains
- Silicates, carbone, glaces
- Accretion

Physisorption/Chemisorption
- Depletion of atoms and molecules

Chemical processes
- Grains as reaction support
- Grains as reactants provider

Adsorption on interstellar grains

Centaurus A Radio Galaxy
(VLT KUEYEN + FORS2)

ESO PR Photo 05b/00 (8 February 2000)

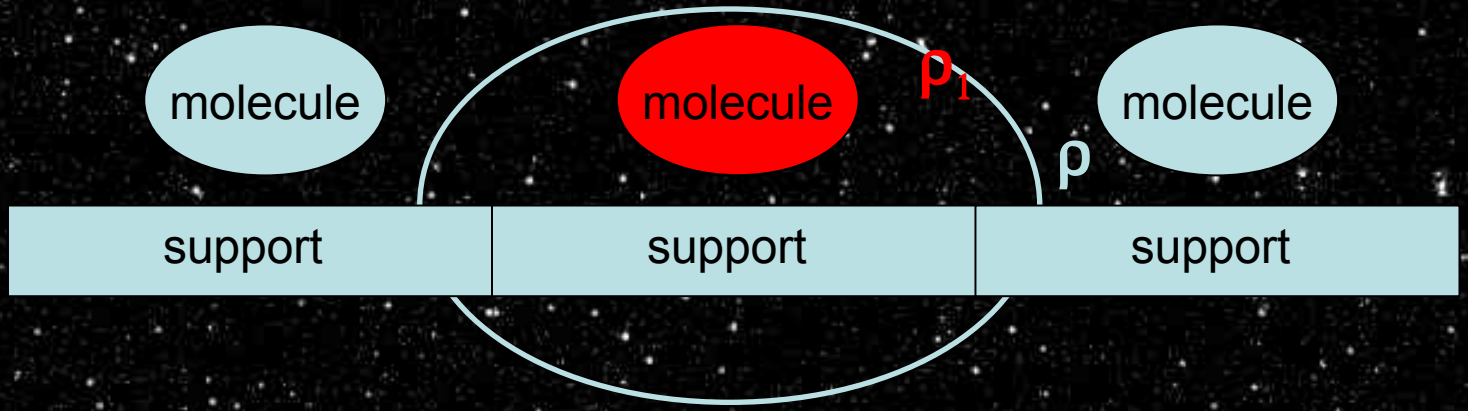
ISOCAM picture of M16, the Eagle nebula

Credit ESA / ISO

Methodologies

weak interactions with systems of large dimension

→ DFT : PW91



- « supermolecule » approach: correction BSSE

  Tran et al. J. Phys. Chem. B (2002); Heine et al. PCCP (2004)

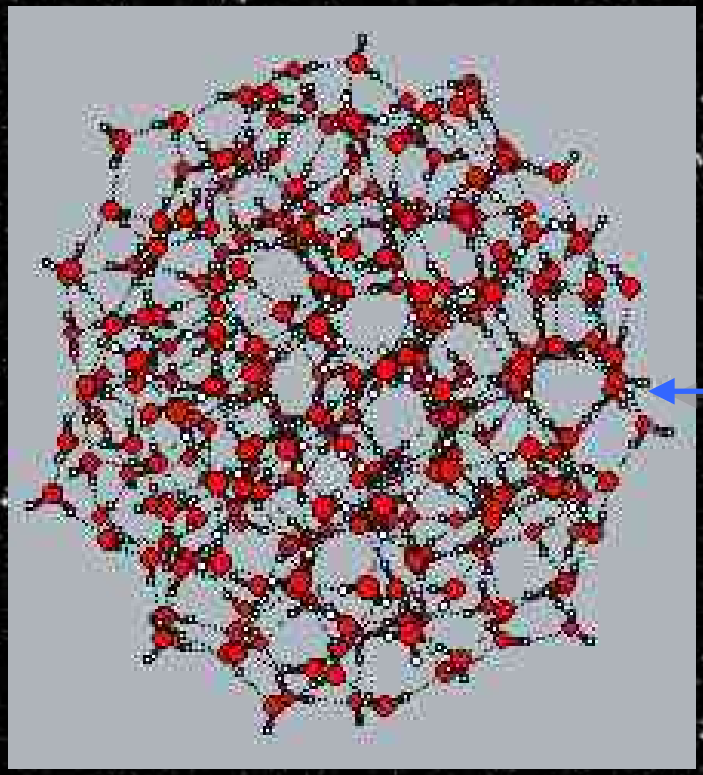
- KSCED approach

  Tran et al. J. Phys. Chem. B (2002)

- Periodic approach: plane waves

Model of solid water surfaces:

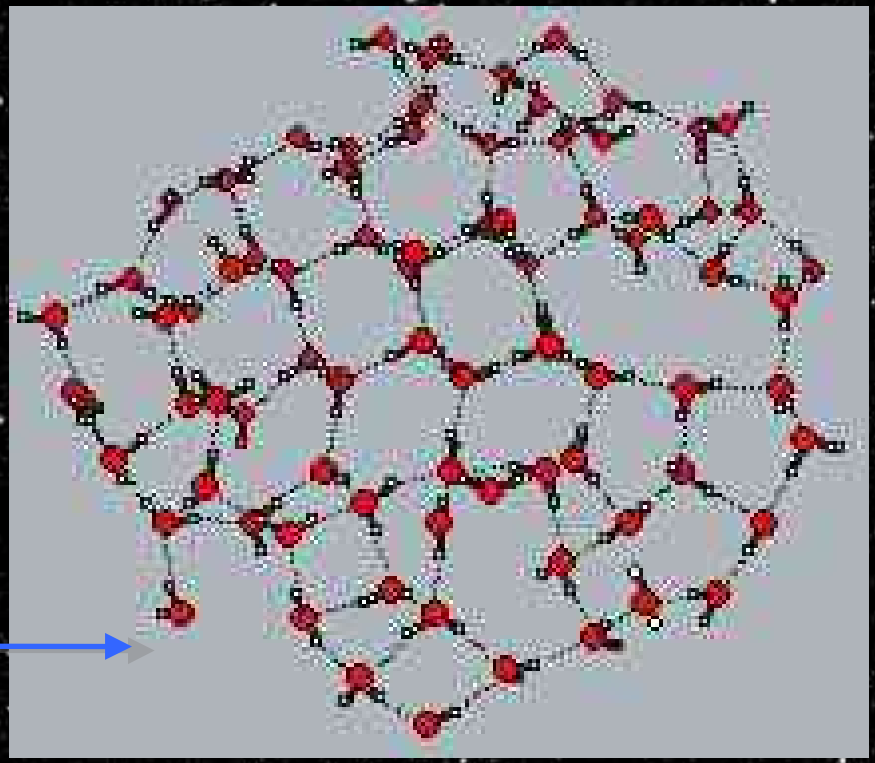
amorphous ice



n=293

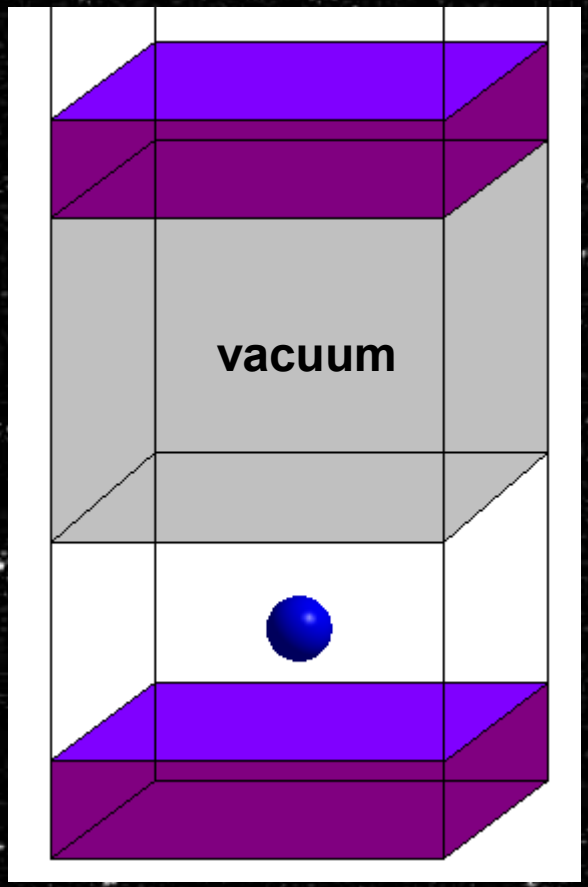
Bulk

Central slice



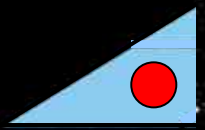
Buch et al. Int. Rev. Phys. Chem. (2004)

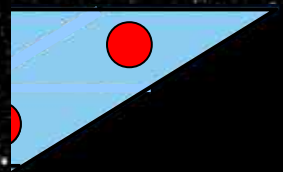
Periodic approach



« super-cell »

Lateral Interactions

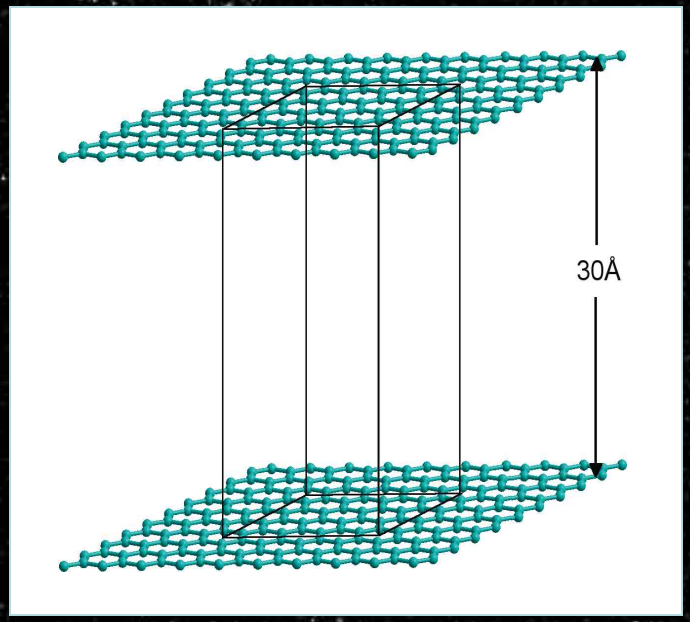




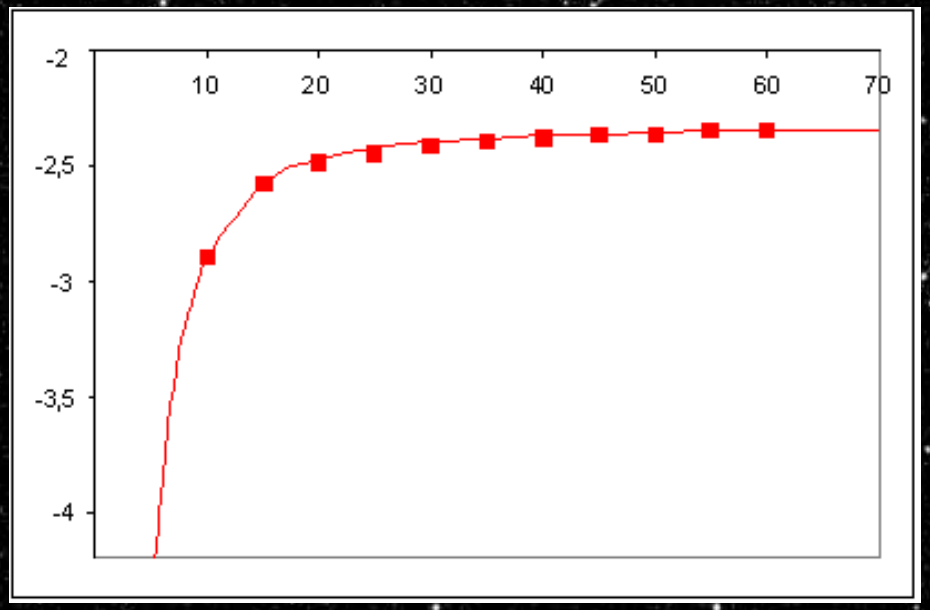
Horizontal replication

Adsorption of H_2 on graphene:

vertical dimension of the cell



hauteur de
la maille (Å)

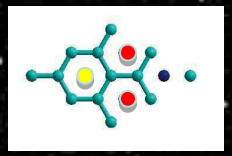


ΔE (kcal/mol)

Test of the adsorption energy of a dipolar system: HCN

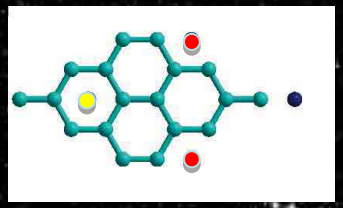
Adsorption of H_2 on graphene:

horizontal dimension of the cell

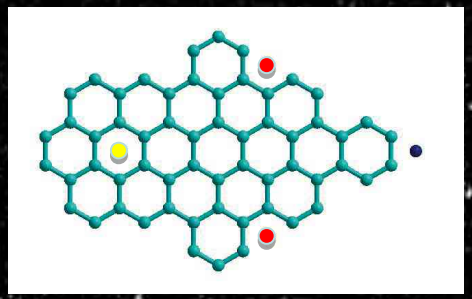


d = 2.46 Å

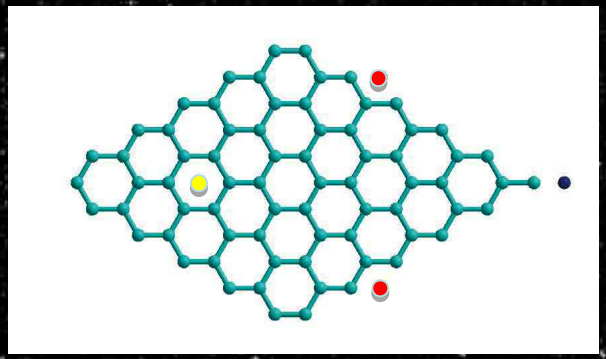
d = 4.26 Å



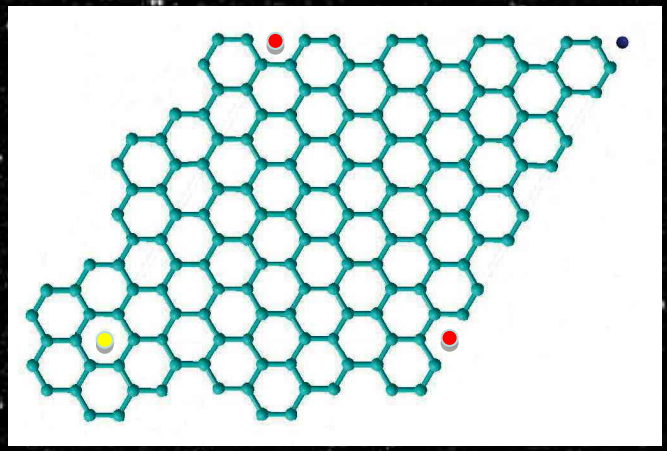
d = 4.92 Å



d = 8.52 Å



d = 9.84 Å



d = 17.04 Å

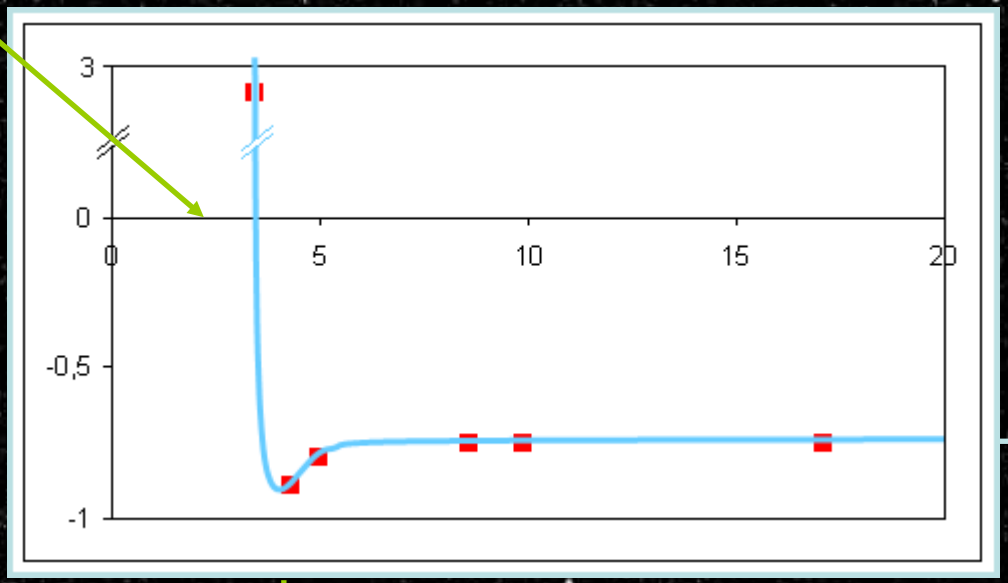
Adsorption of H_2 on graphene

Experimental value: E = 1,1 ~1.2 kcal/mol

Vidali et al. Surf. Sci. Rep. (1991)

repulsive

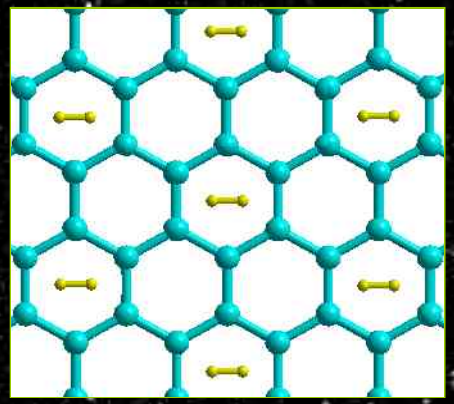
Global interaction energy

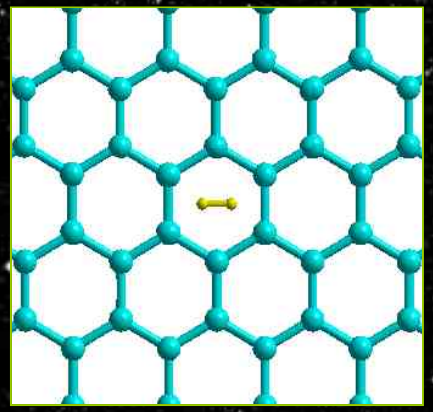


Distance between H_2 molecules

-0.75 kcal/mol

-0.9 kcal/mol





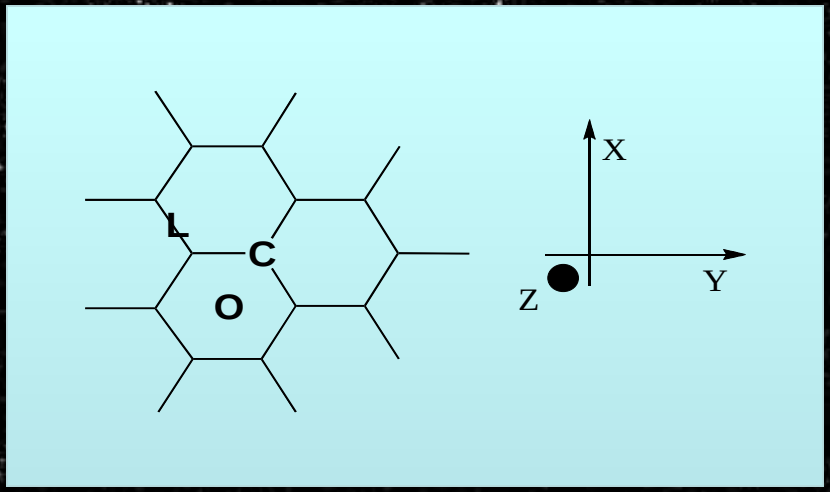
Adsorption of H_2 on graphene

- Position of H_2
- Orientation of H_2

L: middle of a bond

C: carbon atom

O: center of the ring



X: // to plane

Y: // to plane

Z: ⊥ to plane

Table 2. H_2–graphene equilibrium distances, z_m (Å), and corresponding adsorption energies in kcal mol^{-1}; laterally averaged values are given for ∥ to the surface orientations.

Graphene cell	Site	∥ to surface		⊥ to surface	
		z_m	ΔE	z_m	ΔE
Cell **1**	**O**		Rep.		Rep.
	C		Rep.		Rep.
	L		Rep.		Rep.
Cell **2**	**O**	3.26	−0.87	3.40	−0.88
	C	3.60	−0.91	3.56	−0.89
	L	3.52	−0.88	3.47	−0.88
Cell **3**	**O**	3.25	−0.79	3.59	−0.81
	C	3.59	−0.79	3.54	−0.80
	L	3.51	−0.79	3.47	−0.79
Cell **4**	**O**	3.23	−0.74	3.45	−0.77
	C	3.57	−0.72	3.59	−0.76
	L	3.51	−0.73	3.47	−0.76
Cell **5**	**O**	3.24	−0.74	3.38	−0.76
	C	3.52	−0.72	3.41	−0.75
	L	3.50	−0.73	3.53	−0.76
Cell **6**	**O**	3.23	−0.74	3.40	−0.76
	C	3.52	−0.72	3.38	−0.74
	L	3.52	−0.70	3.77	−0.74

Adsorption of H_2 on graphene

Single H_2

Repulsive at short distance

Independent of orientation

→ H_2 able to roll on the surface

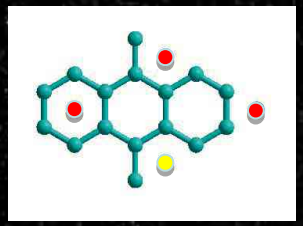
Monolayer of H_2

More stable for inter-H_2 distance close to H_2 dimer

Pauzat, et al. MNRAS. (2011)

Adsorption of H_2 on graphene:

looking for H_2 dimers

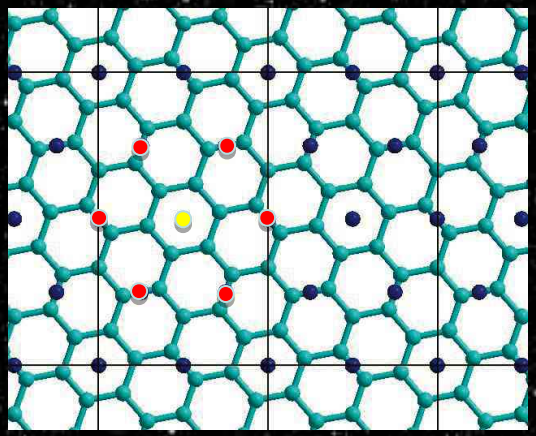


d = 2.46 Å

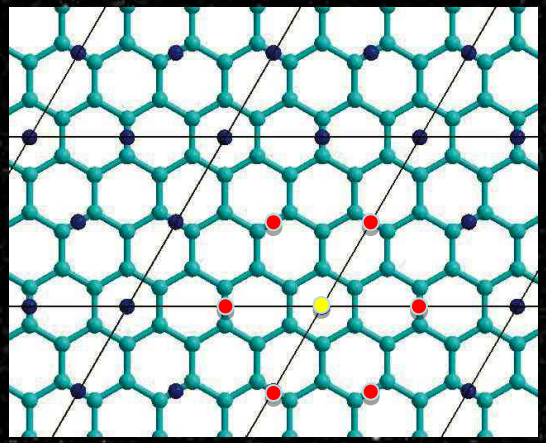
H_2 dimer: d ~ 3.7 Å

Cui & Fain, J. Vac. Sci. Tech., (1987)

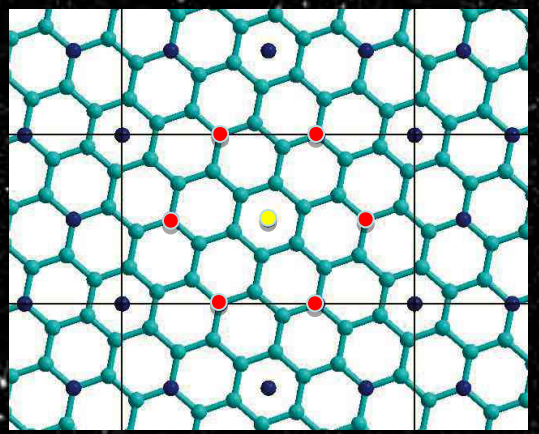
Other arrangements satisfying the hexagonal structure



d = 3.25 Å



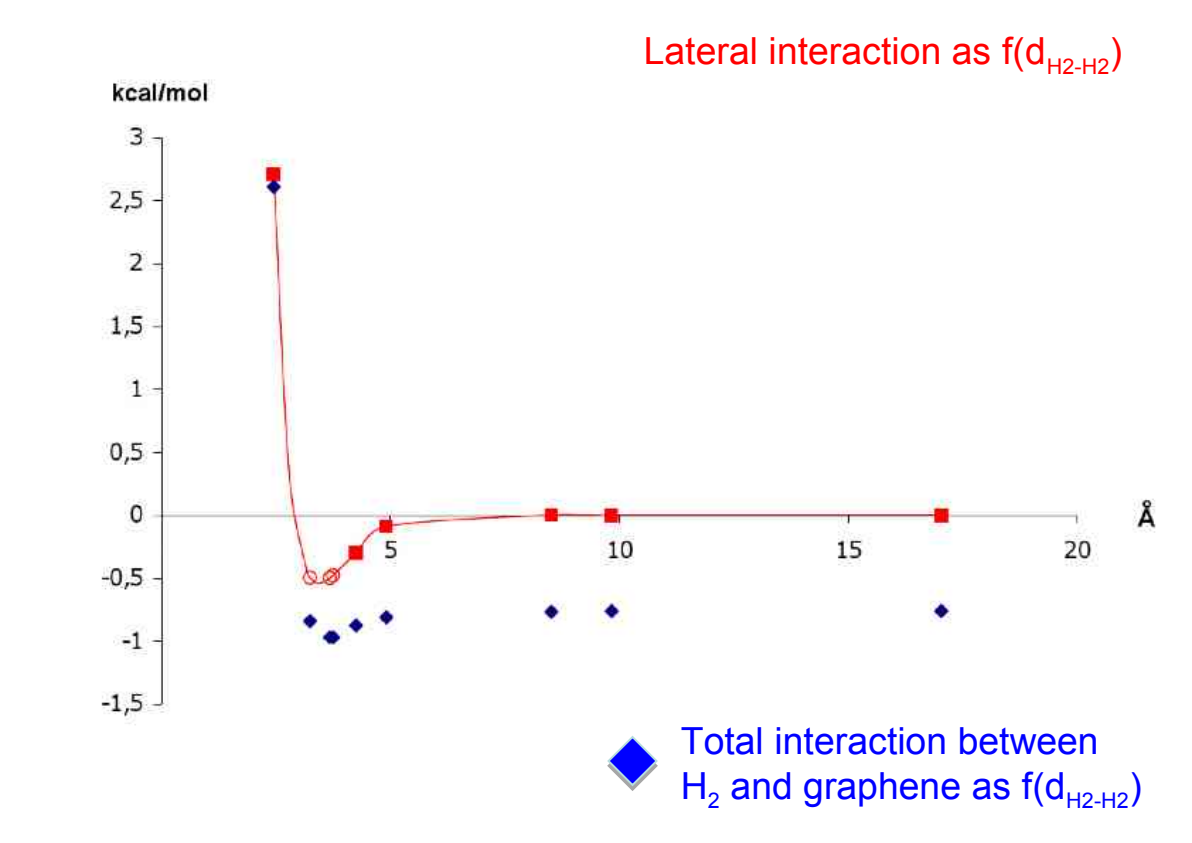
d = 3.69 Å



d = 3.76 Å

Adsorption of H_2 on graphene:

looking for H_2 dimers



Best coverage for inter-H_2 distance close to H_2 dimer

Adsorption of H_2 on graphene

The physisorption energy per molecule in a monolayer is dependent on the distance between adsorbed molecules:

- Physisorption on adjacent rings is not possible
- Best energetical arrangement when $d_{(H2-H2)} \sim d_{(dimer)}$
- Two situations favored: $\Delta E \sim$ 1 kcal/mol
  - H_2 on top of the ring center associated with
    - H_2 on top of a C
    - H_2 on top of the middle of a CC bond

The best coverage by physisorption in a monolayer gives:

- Surface density of one H_2 per 12 $Å^2$ ➡ N ~ 0.8 x 10^{15} H_2/cm^2
- H_2 to C ratio = 1 / 4.6
- Assuming 15-20% of interstellar C locked in aromatic systems
  ➡ 2 x 10^{-5} of H_2 trapped on PAHs

Govers et al., J. Chem. Phys., (1980)

Adsorption of H_2 on graphene

Only a small amount of H_2 can be trapped on PAH-like surfaces but:

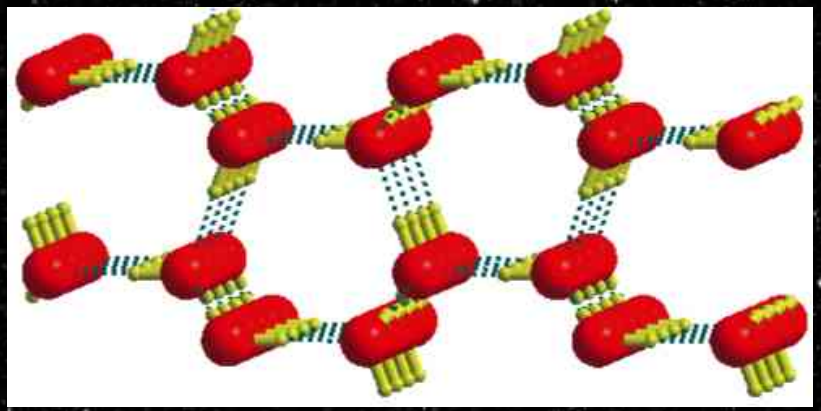
- A mattress of H_2 may play the role of shock absorber
  - Provide a smooth landing ≠ bouncing back to gas phase
  - Help adsorption of incoming species
- A mattress of H_2 may modify the physics of the surface
  - Change vibration frequencies (low energy modes)
- A mattress of H_2 may modify the chemistry of the surface
  - Enhance the formation of H_3^+ where H_2 can be ionized
- A mattress of H_2 may modify the heating rate of the gas
  - Low energy IR radiations often neglected in the evaluation of the gas-grain energy balance could release H_2 with greater energy than when adsorption occured.

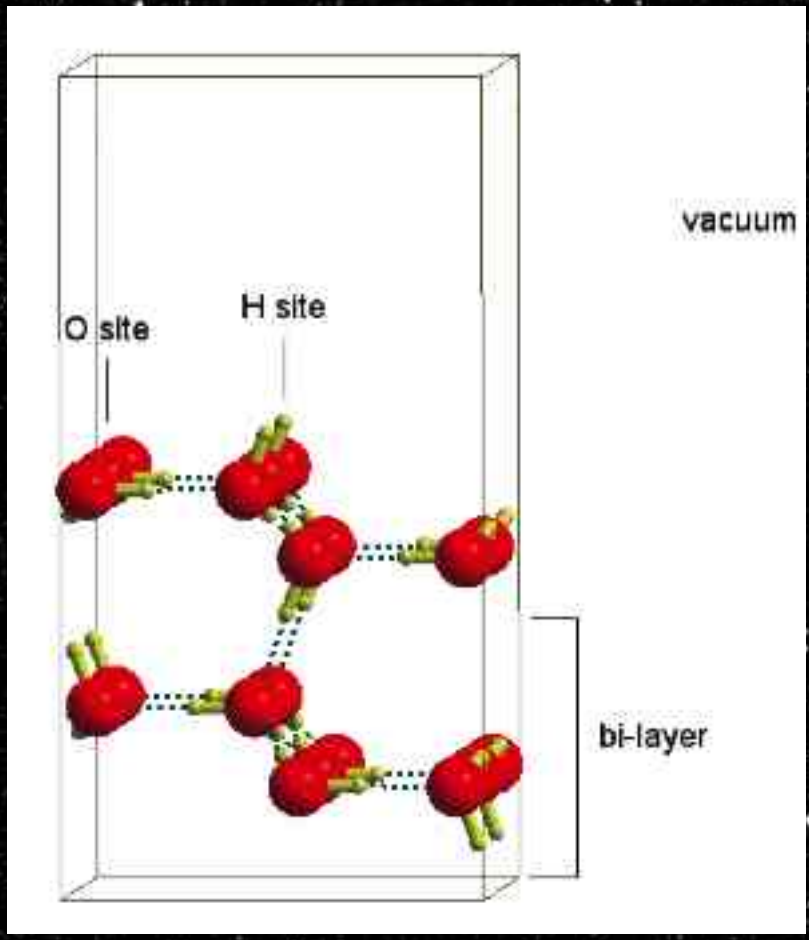
Pauzat et al., MNRAS (2011)

Model of solid water surfaces:

Periodic approach: crystalline ice

- Hexagonal ice
  - Apolar
  - Stable slabs





Adsorption of H_2 on hexagonal ice

Hexagonal mesh of H_2 on top of hexagonal ice

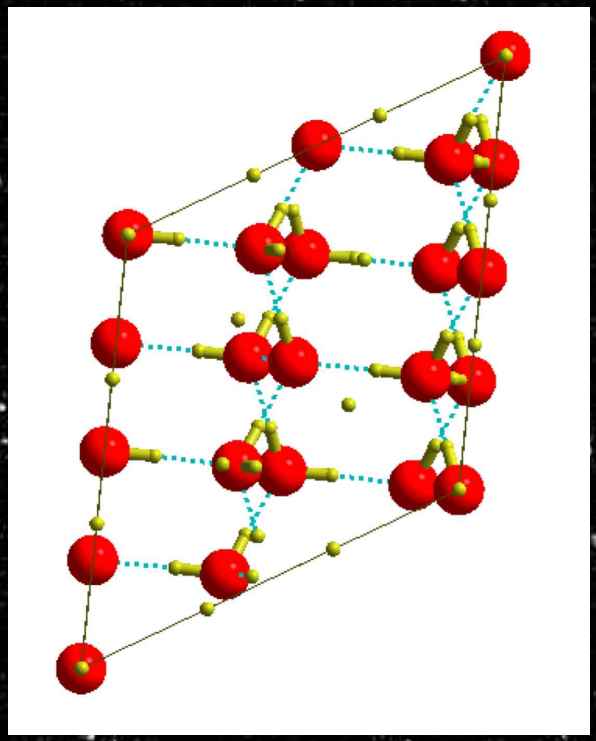
Single H_2

Position: on top of oxygen sites

Orientation: Z favored

$d_{(H2-H2)}$	Zm	ΔE
2.79	3.17	-0.14
3.35	3.15	-1.04
4.19	2.89	-1.30
5.58	3.08	-0.90
8.37	2.93	-1.44
16.74	2.93	-1.45

Distance in Å; ΔE in kcal/mol

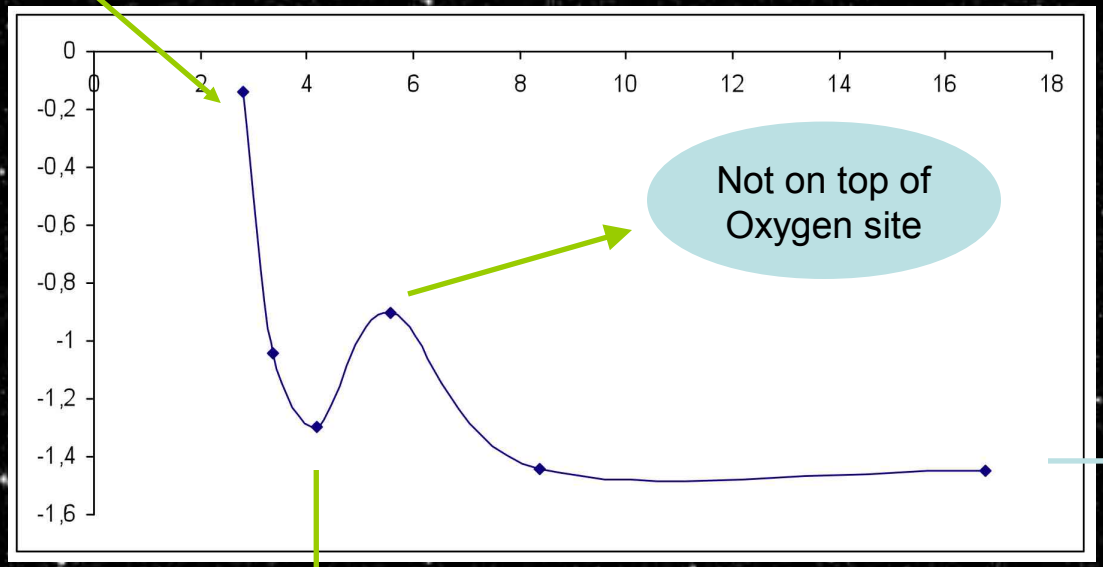


Adsorption of H_2 on hexagonal ice

Hexagonal mesh of H_2 on top of hexagonal ice

Monolayer of H_2

repulsive



Global interaction energy

Distance between H_2 molecules

Not on top of Oxygen site

-1.45 kcal/mol

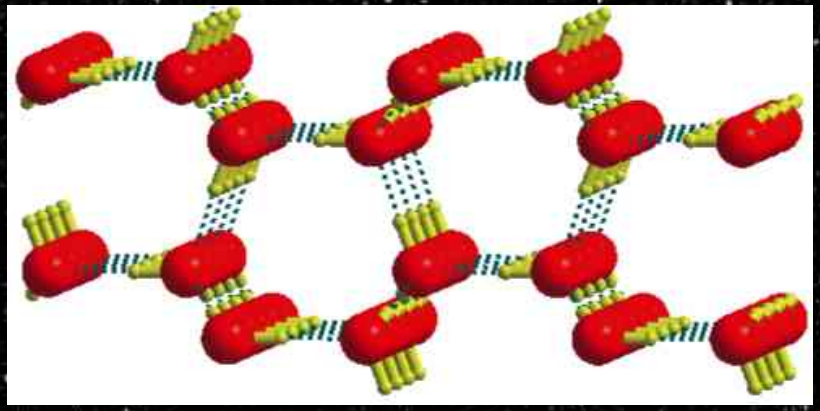
-1.30 kcal/mol

Adsorption of H_2 on hexagonal ice

H_2 on top of oxygen atoms

Rows of H_2

- Nearest neighbours are 2 instead of 6



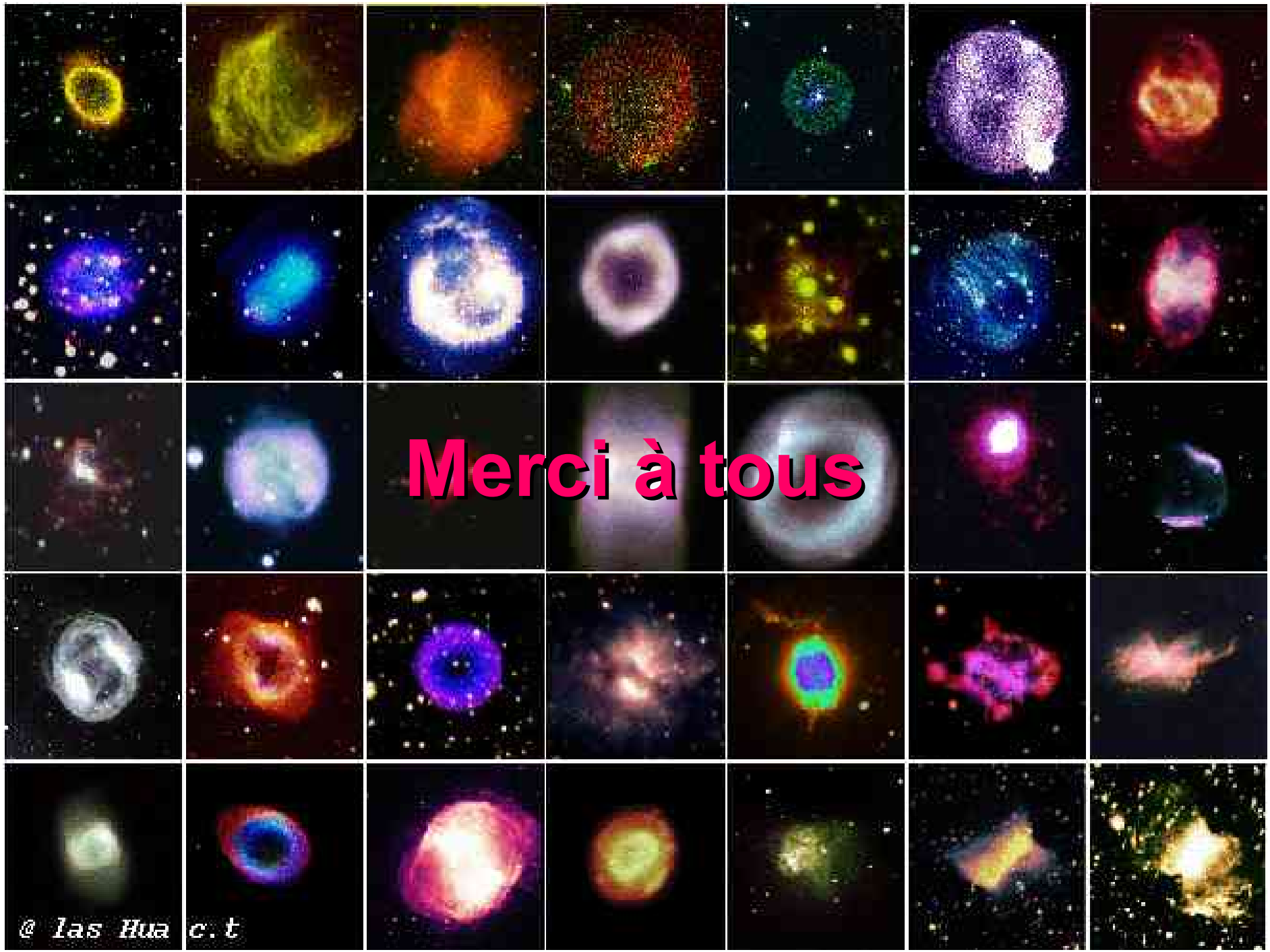
→ d  = 4.37 Å

→ H_2 dimer: d  ~ 3.7 Å

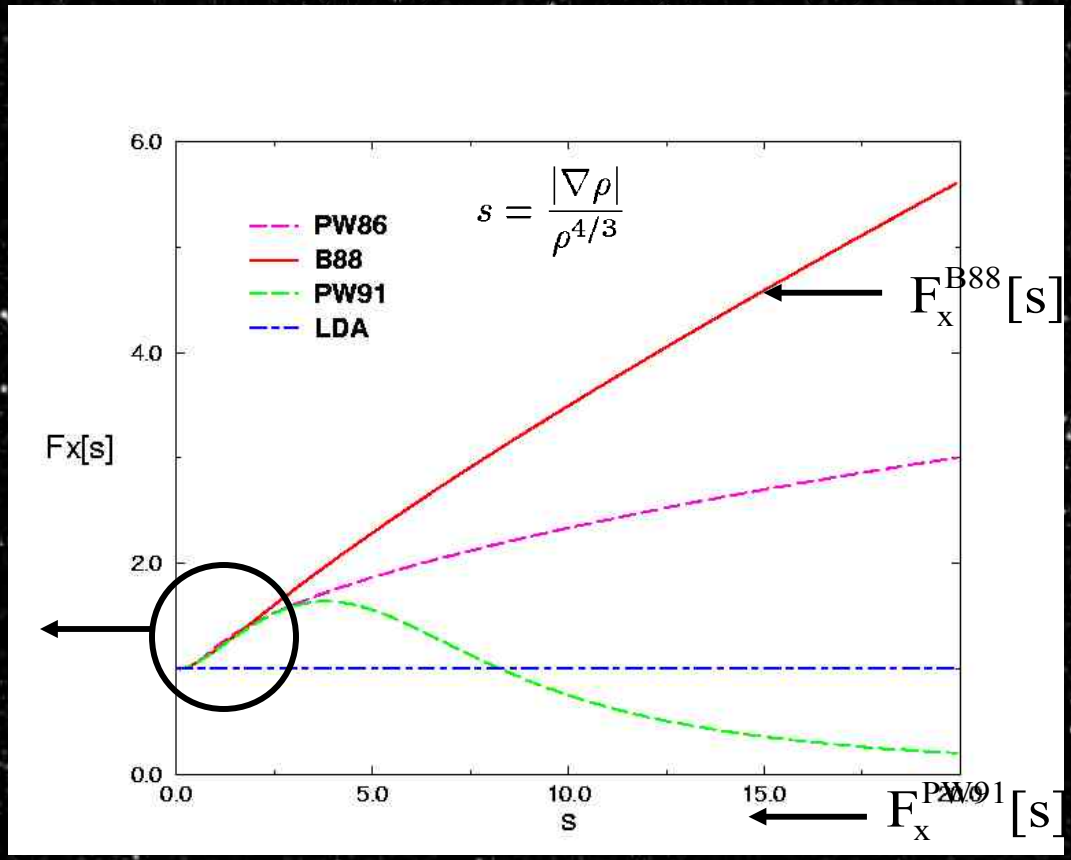
ΔE = 1.47 kcal/mol

The adsorption energy is larger on the ice than on graphene
but
the coverage should be slightly smaller

Lattelais, Pauzat & Ellinger, in preparation (2011)


Merci à tous
@ las Hua c.t

Comportement des fonctionnelles d'échange en fonction du gradient réduit



$F_x^{B88}[s]$ diverge

$F_x^{PW91}[s]$ devient nulle

Comportement « identique » des fonctionnelles d'échange pour les petites valeurs du gradient réduit *s*

Petit gradient réduit = grande densité

Zone van der Waals:
Grand gradient réduit = petite densité