Hydrogen storage in defective single-wall carbon nanotubes

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Acknowledgments

- ✓ FONDECYT (Grant 1090489)

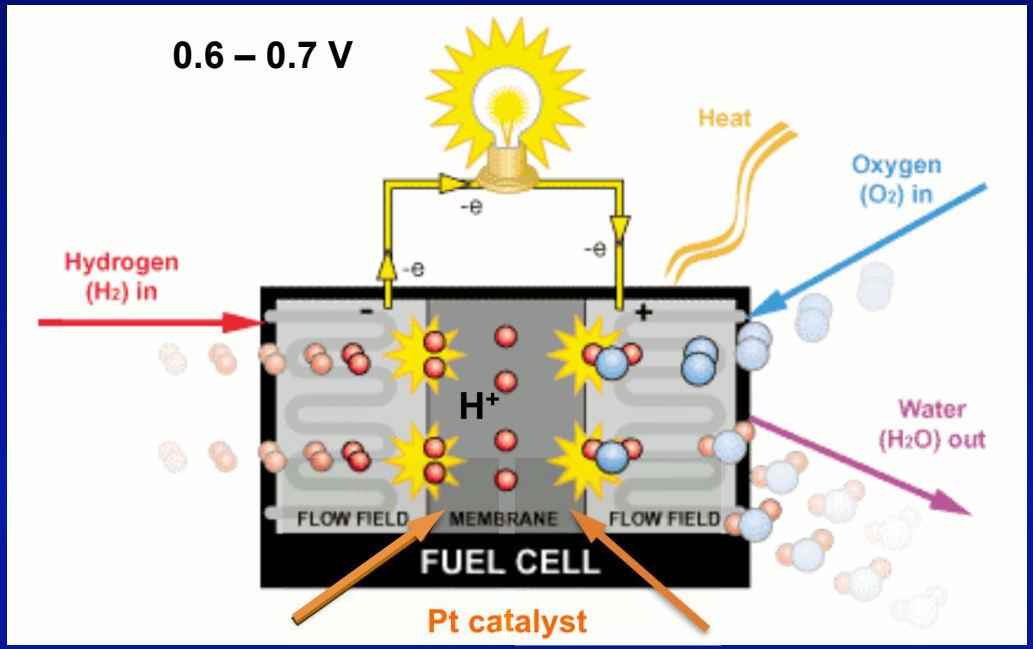
- ✓ PROGRAMA ANILLO BICENTENARIO (Project ACT24/2006)

Outline

- ✓ Motivation: The hydrogen fuel alternative
- ✓ Large-scale vacancy in carbon nanotubes (CNTs)
- ✓ Interaction and incorporation of H_2 molecules inside CNTs
- ✓ H_2 gas storage outside and inside porous CNTs

Motivation

Polymer electrolyte membrane (PEM) hydrogen fuel cell



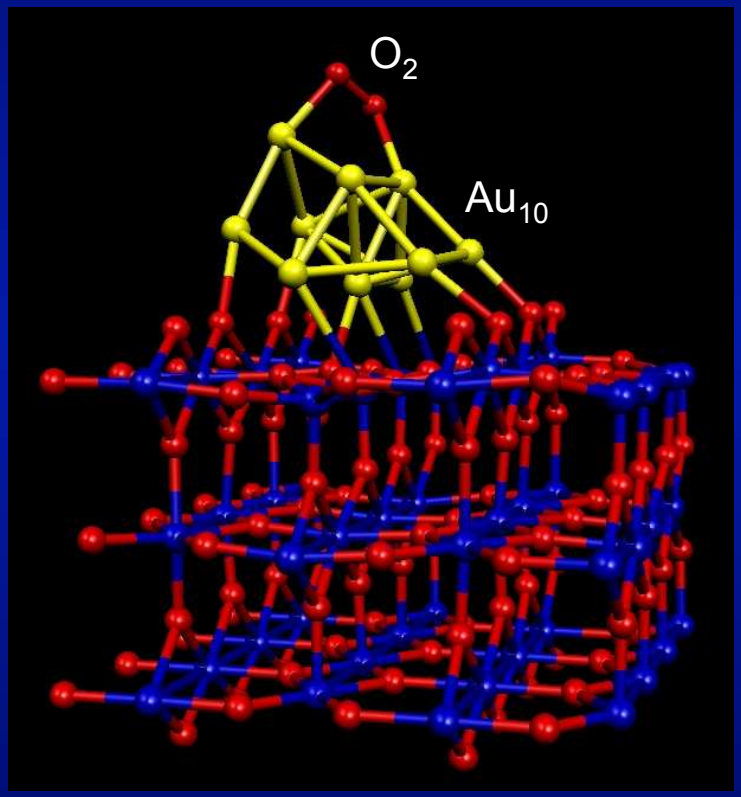
p = 1 – 10 atm
T = 25 – 120 °C

Efficiency 60%

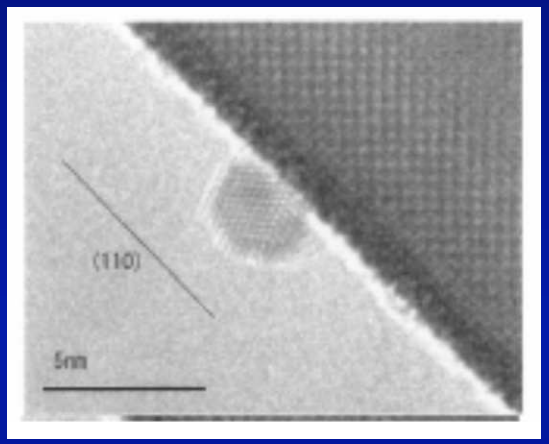
- ✓ The best-known catalysts for PEM fuel cell are Pt nanoparticles supported on carbon substrates, however Pt has an high cost and a relative scarcity in the world.
- ✓ The massive use of PEM fuel cells needs alternative catalysts, active in the acid medium of the membrane, abundant and with low costs.
- ✓ Materials for hydrogen storage need large specific surface area and reversibility for uptake and release hydrogen at nearly ambient conditions.

New catalytic concepts: Metallic nanoparticles

Metallic nanoparticles supported on metal oxide substrate have shown improving catalytic properties for the oxygen reduction reaction (ORR)



O_2 adsorption reaction onto TiO_2(110)–supported Au_{10} cluster (W. Orellana to be published)



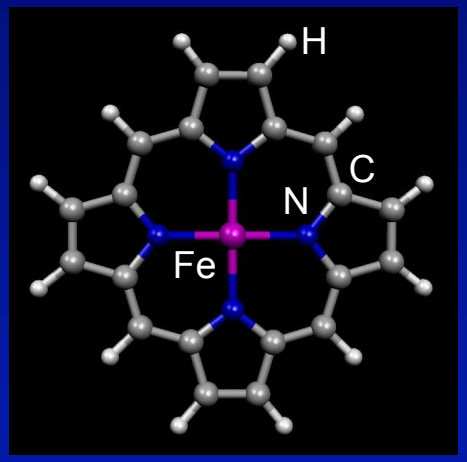
TEM image (profile view) of an Au nanoparticle supported on TiO_2(110)

open issues:

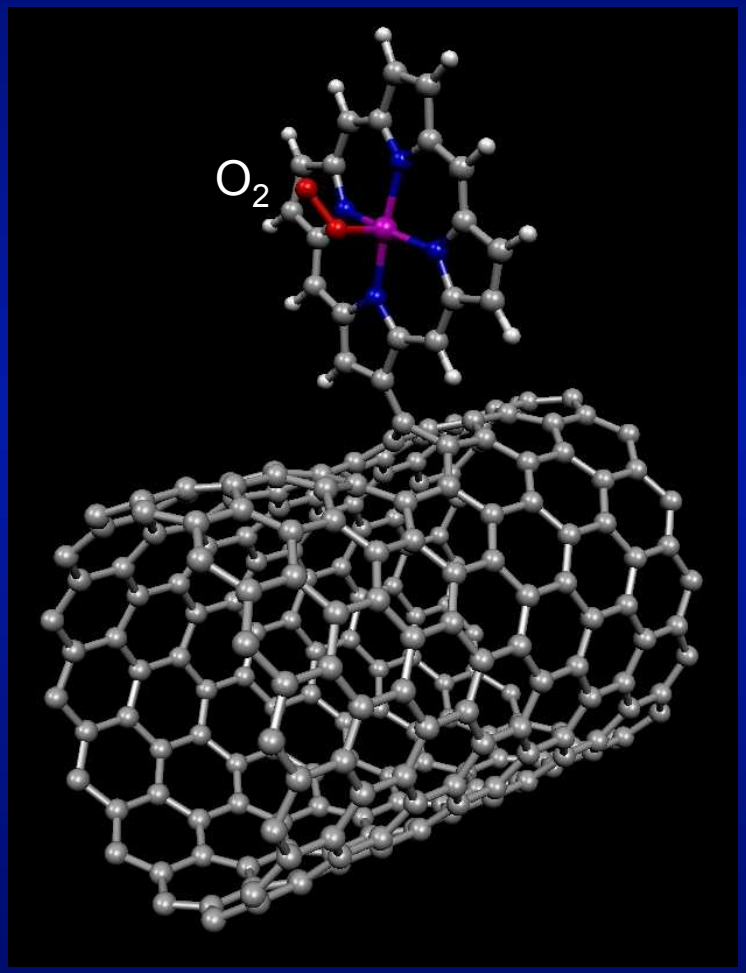
- Metal of the nanoparticles
- Size of nanoparticles
- Substrate characteristic (reduced)
- Surface defect (O vacancies)

New catalytic concepts: Metallomacrocycles

Fe-Porphyrin



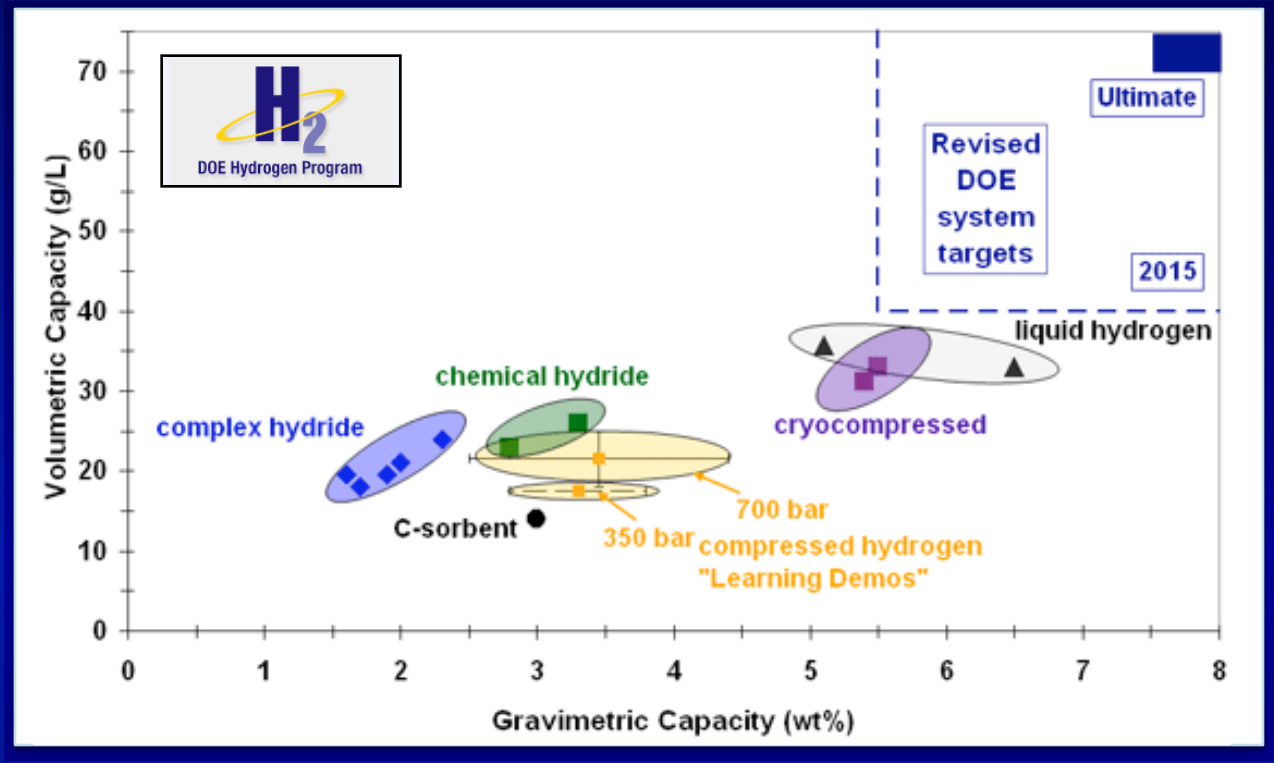
O_2 reaction with a Fe-porphyrin covalently linked to a CNT sidewall (W. Orellana to be published)



open issues:

- Macrocycle type: Porphyrin, Phthalocyanine
- Metal of the macrocycle: Fe, Co, Ni
- Anchoring mechanism
- CNT type: metallic, semiconducting

Hydrogen storage for vehicle applications



- ✓ For transportation, the US Department of Energy (DOE) has stablished a target for gravimetric capacity of 6 wt % and volumetric density of 60 g/L.
- ✓ New complex hydrides: $NaAlH_4$ (4.0 wt %, 1 atm, 33 °C) ,
  Li_2NH (6.5 wt %, 1 atm, 200 °C),
  NH_4BH_4 (6.1 wt %, 1 atm, < 25 °C).
- ✓ Carbono nanostructures (doped fullerenes, functionalized nanotubes and graphene)

H_2 adsorbed on carbon nanotubes

- ✓ An early experiment reported an H storage capacity of 10 wt % on single-wall carbon nanotubes (1.6 – 2.0 nm) at ambient conditions [Nature 386, 377 (1997)].
- ✓ Later experiments and simulations found H storage capacties less than 2 wt % at similar conditions [Science 286, 1127 (1999)].
- ✓ However, DFT calculations have reported H_2 binding energies of about 0.1 eV/H_2 suggesting a very small storage capacity at room temperature.

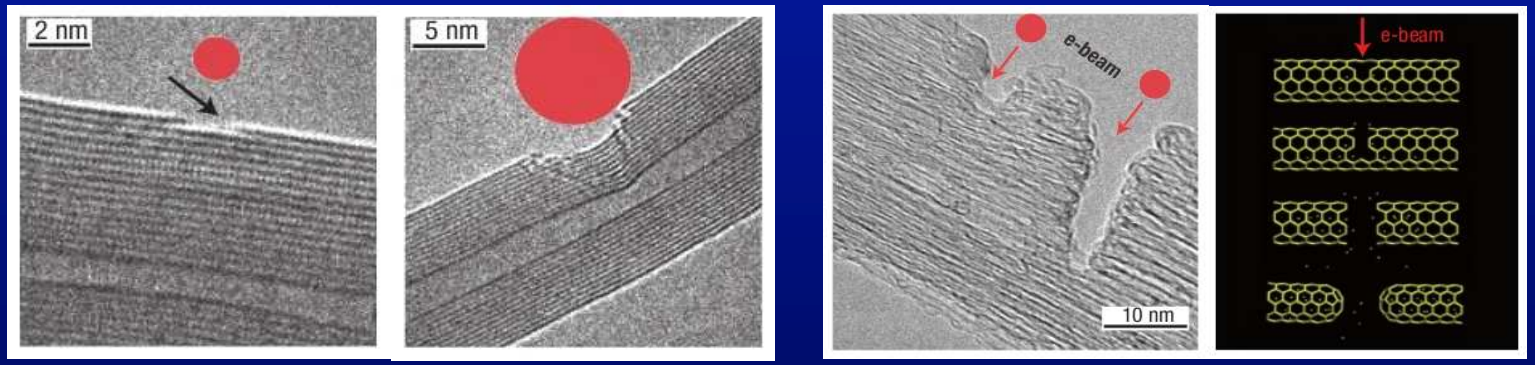
- ✓ The driving force for the adsorption/desorption process at T, is the difference in chemical potential between the free gas and the adsorbed gas:

$$\Delta\mu = \Delta h - T\,\Delta s,$$ where Δh and Δs are the specific enthalpy and entropy.

- ✓ The entropic term at room temperature for the H_2 adsorption on CNTs of ~1 nm in diameter has been calculated of 0.3 – 0.4 eV/H_2 [Langmuir 21, 6282 (2005)].
- ✓ Thus, Δh (gas binding energy) needs to compensate the entropic term to allow the entire adsorption/desorption cycle at ambient conditions.

H_2 adsorbed on porous carbon nanotubes

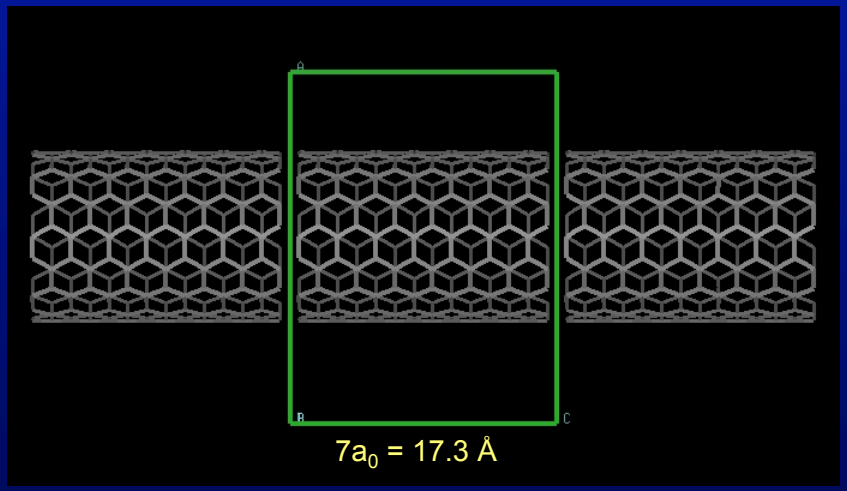
- ✓ In this work we investigate the possibility to incorporate H_2 molecules inside CNTs through large-scale vacancy defects to increase their storage capacity.
- ✓ We study the stability and energetic of different multivacancy structures *nV* with $n = 2 – 16$, and their interaction with a H_2 gas.
- ✓ Vacancies are common irradiation-induced defects in carbon nanostructures. Recent experiments have shown that electron beams can focus onto spots of less than 1 nm desplacing a few atoms permanetly from the CNT structure.



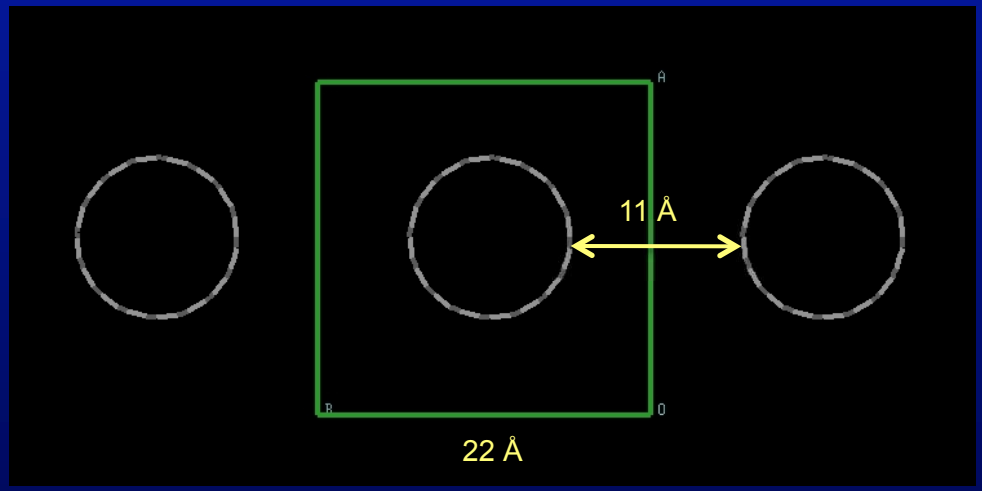
Nature Mater. 6, 723 (2007)

Theoretical approach

- ✓ Density functional theory calculations (SIESTA *ab initio* package).
- ✓ LDA and GGA approaches to the exchange-correlation potential.
- ✓ Molecular dynamic simulations in the canonical ensamble (NVT).
- ✓ Nosé thermostat approach at T = 77, 300, 600 K over 1 ps (time step 1 fs).
- ✓ (8,8) and (10,10) armchair single-wall carbon nanotubes of 11 and 14 Å in diameter.
- ✓ H_2 gas of 32 and 64 molecules adsorbed outside (exohedral) and inside (endohedral) of porous CNTs.
- ✓ Periodic boundary conditions along the tube within the supercells with 5, 6 and 7 CNT unit cells, corresponding to 160, 192 and 224 atoms.



$7a_0$ = 17.3 Å

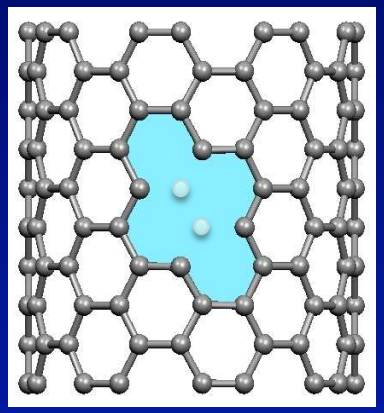
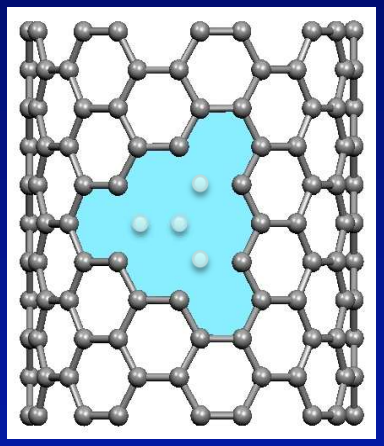
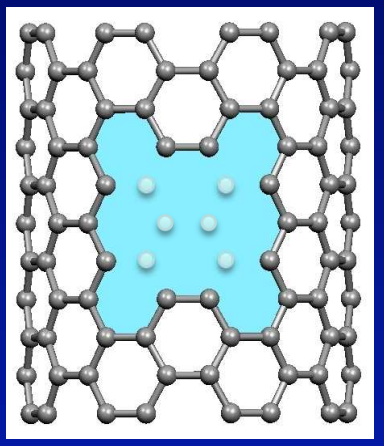
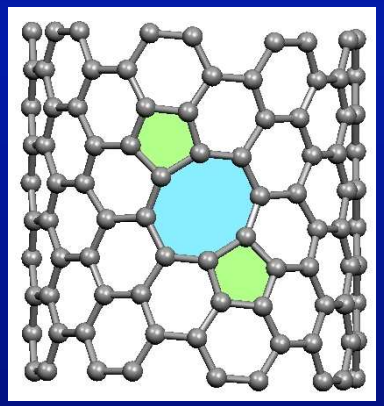
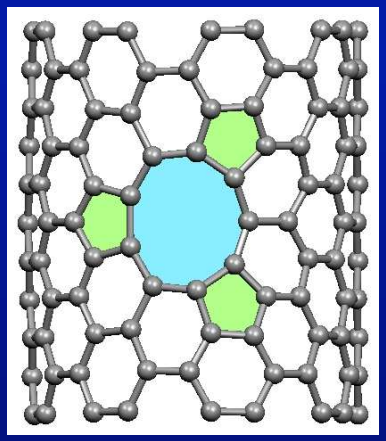
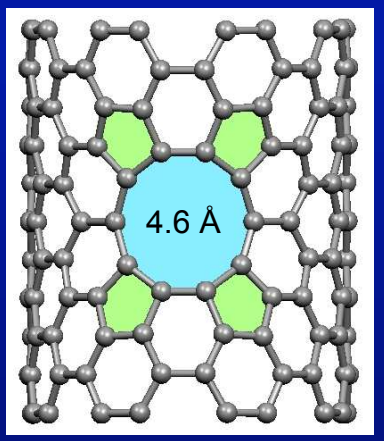


22 Å

Large-scale vacancy defect in CNTs

- ✓ Stability of multivacancies in CNTs (from 2 to 16 missing atoms)
- ✓ The incorporation reaction of H_2 through multivacancies in CNTs

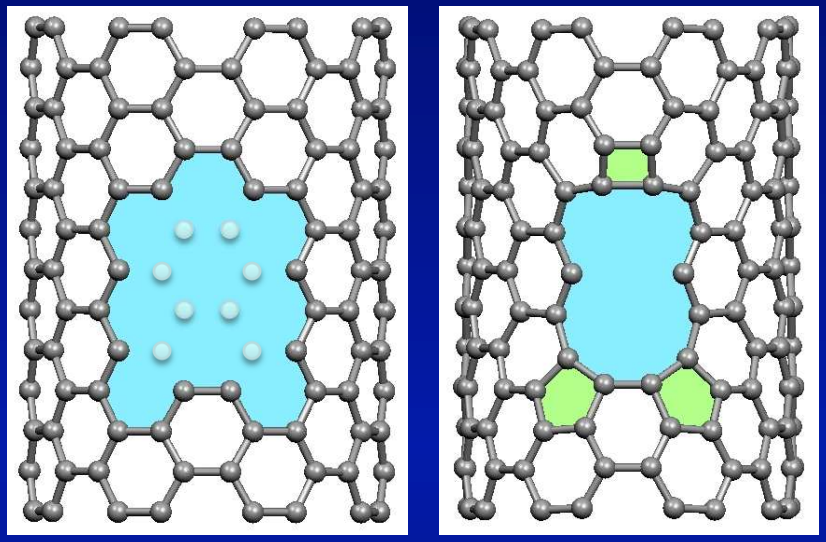
Vacancy structures and energetics

	2V	4V	6V
Initial geo.			
Final geo.			
Formation energy →	E_{form} = 4.5 eV	E_{form} = 8.8 eV	E_{form} = 9.8 eV

The defective CNTs spontaneously reconstruct forming rings with hexagon and pentagon at the defect contour, preserving the three-fold coordination.

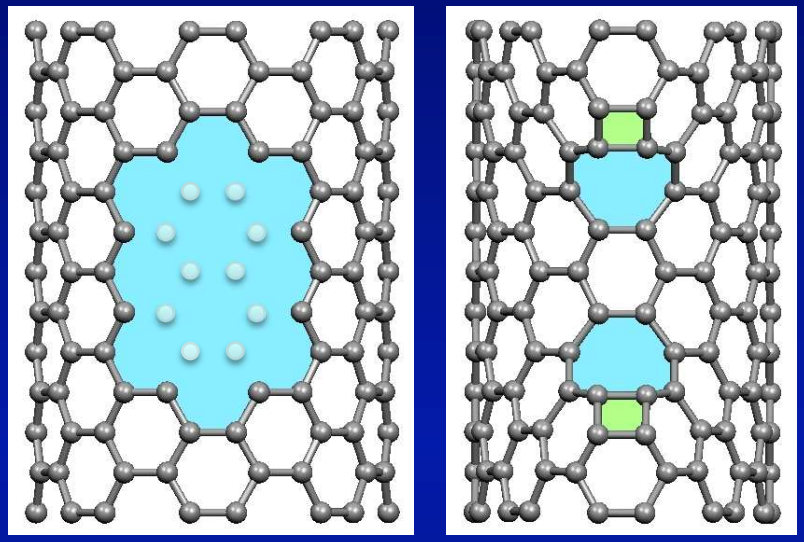
Vacancy structures 8V and 10V

8V

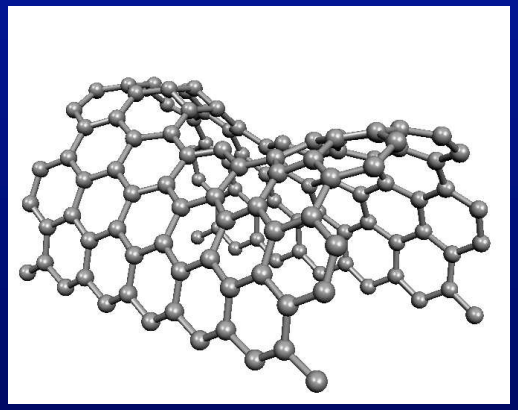


E_{form} = 15.3 eV

10V

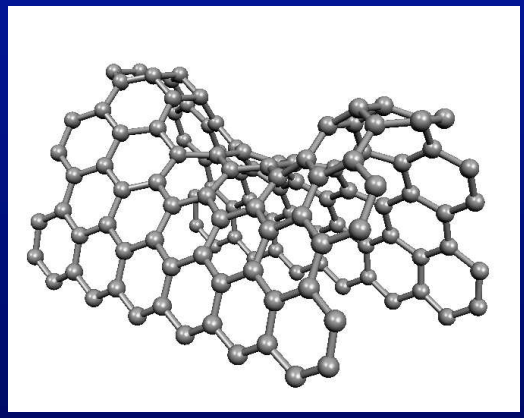


E_{form} = 14.6 eV

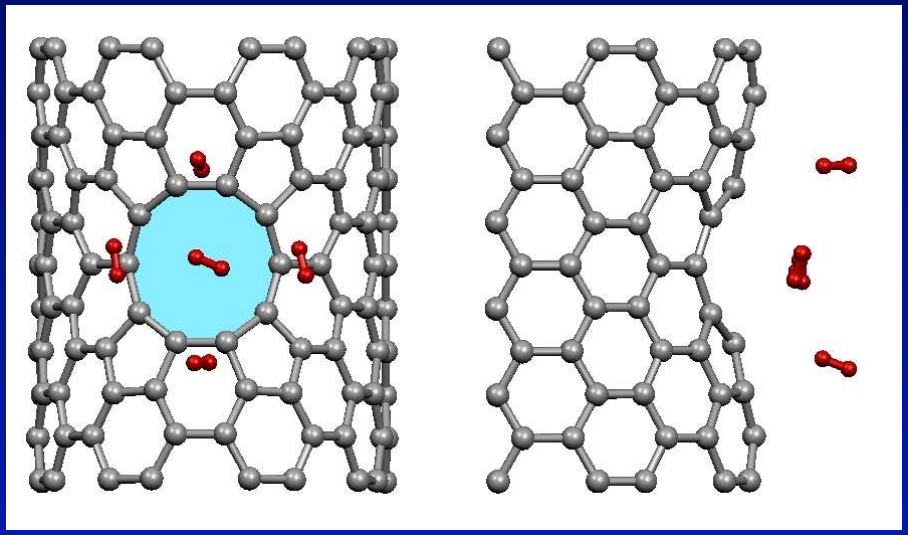


The defect distorts the CNT surface, trying to repair their structure:

The self-healing mechanism

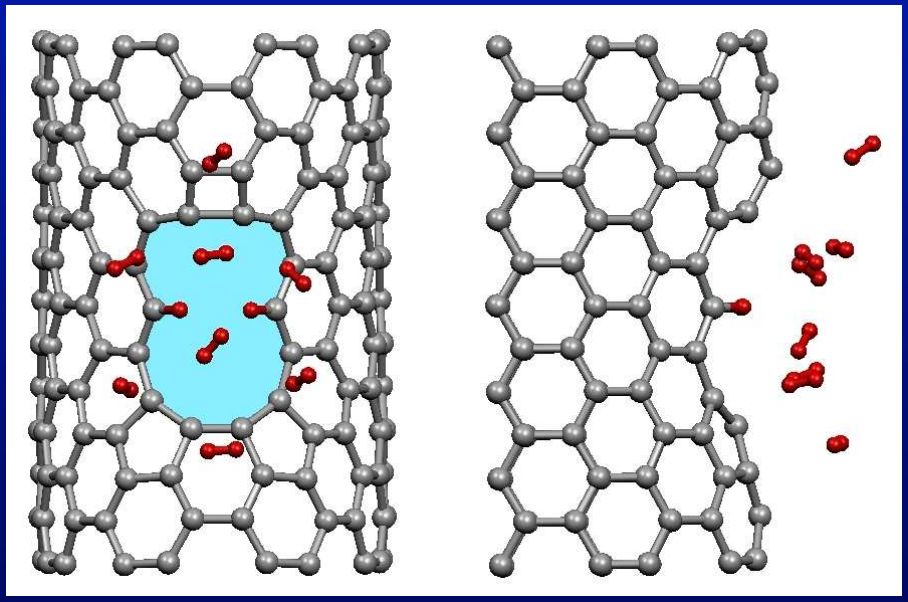


H_2 adsorption on 6V



E_{bind} = 0.26 eV/H_2

The H_2 binding energy on 6V double the value calculated on pristine (8,8) CNT (0.12 eV/H_2)



E_{bind} = 0.22 eV/H_2

The undercoordinated C atoms are passivated by an H_2 molecule which spontaneously dissociates while approaches to the defect with an energy gain of 5.7 eV

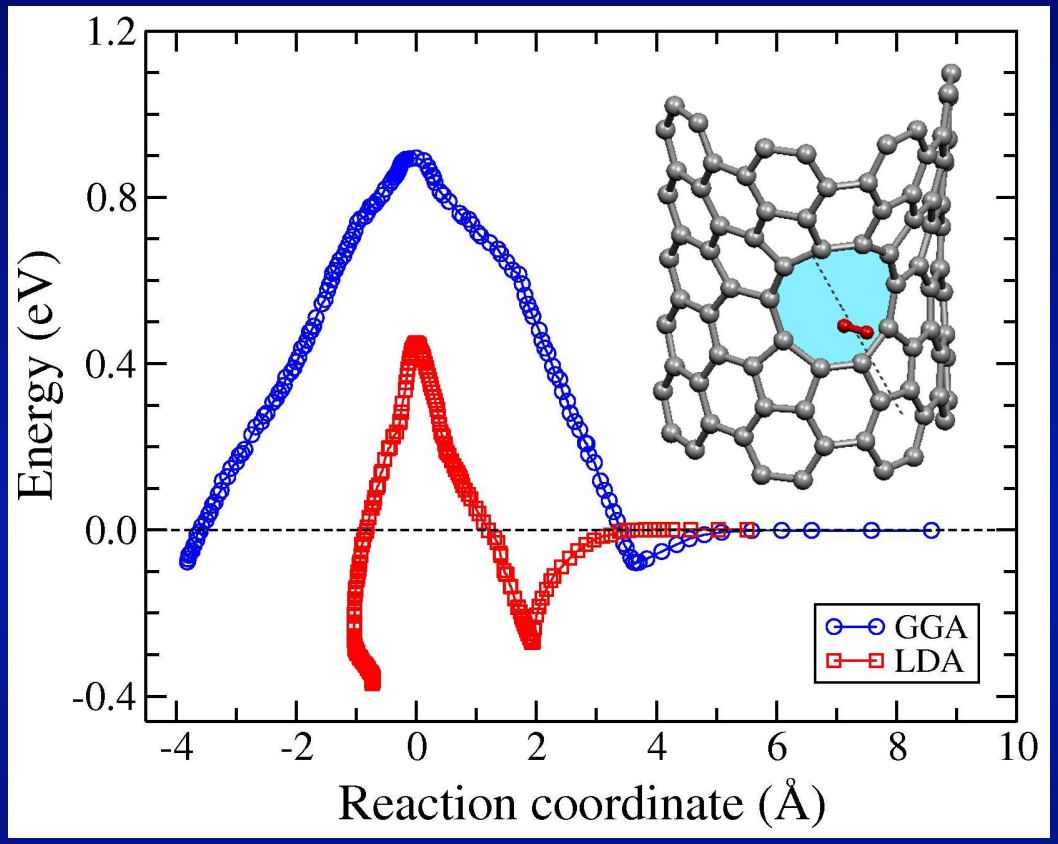
LDA v/s GGA

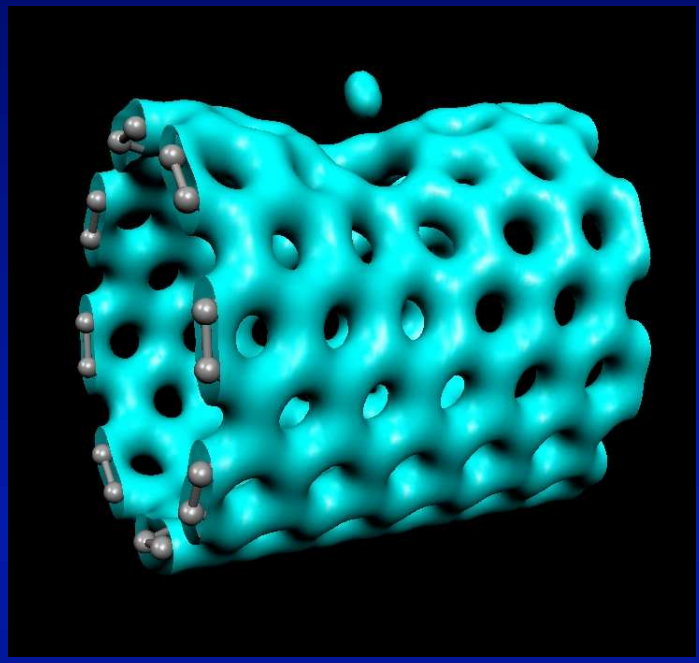
Neither LDA nor GGA can describe precisely the H_2 physisorption on CNTs.
In general, LDA gives stronger binding strengths than GGA.

System	GGA		LDA	
	d(Å)	E_b(eV)	d(Å)	E_b(eV)
(8,8)	3.16	0.076	2.75	0.127
2V	2.84	0.096	2.78	0.186
4V	2.89	0.107	2.66	0.245
6V	3.43	0.102	1.96	0.264
8V-H	–	–	2.45	0.217
10V	–	–	2.77	0.183

LDA must be consider an upper limite while GGA a lower limite
for the H_2 binding energy on CNTs

The H_2 insertion through 6V

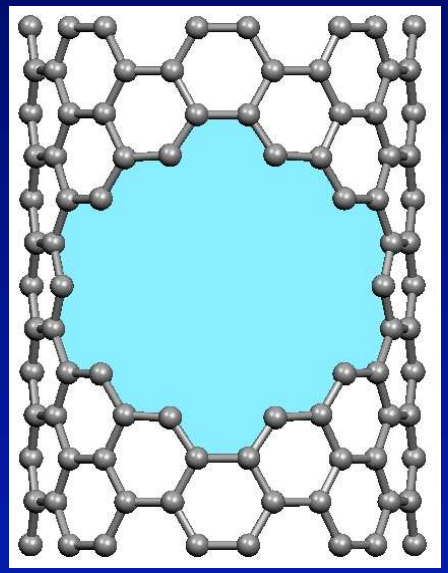




Total charge-density isosurface
(0.05 e/Å^3)

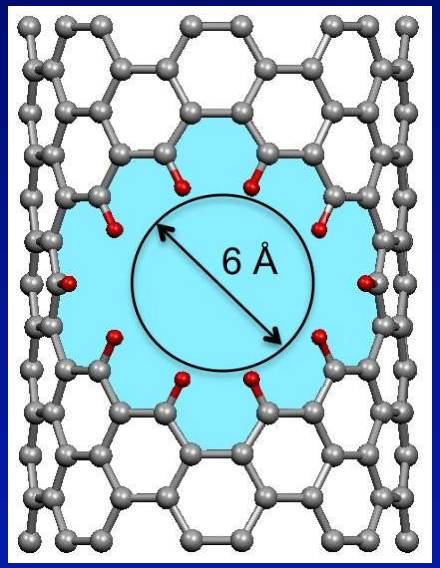
The H_2 molecule has to overcome at least an energy barrier of ~ 0.5 eV to reach the CNT interior, which is impractical for storage purpose.

The stability of 16V and 16V-H



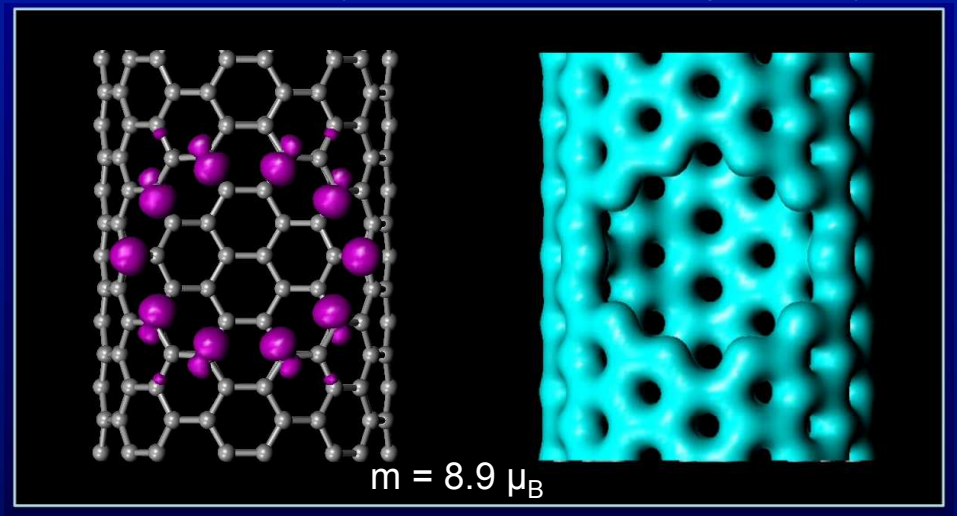
The 16V multivacancy do not reconstruct preserving the CNT defective structure.

After hydrogenation the contour saturates, forming an inert pore where H_2 molecules can transit barrierless inside/outside the CNT

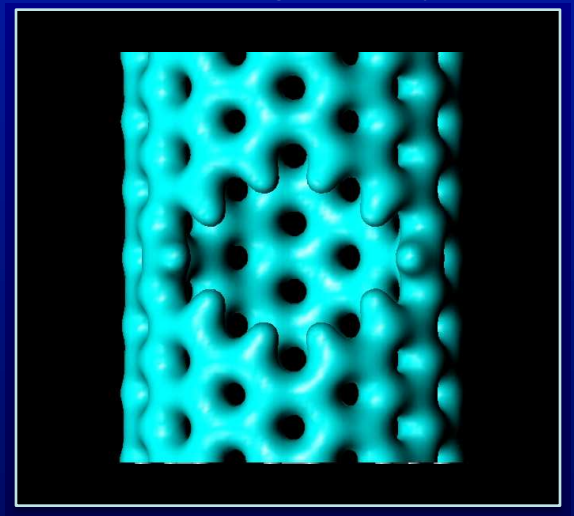


spin density

total charge density



total charge density

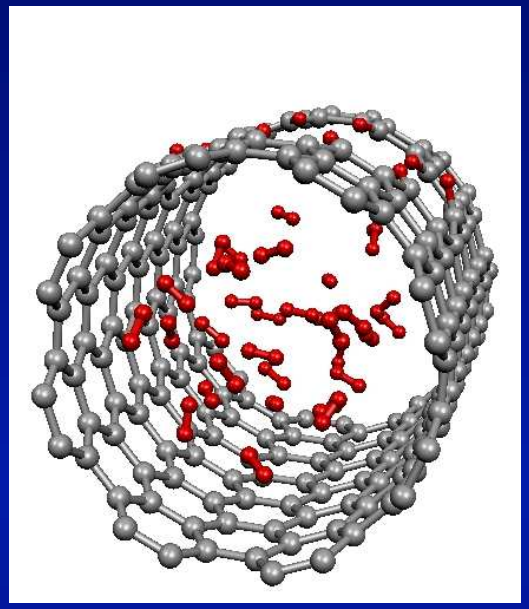


H_2 storage inside and outside porous CNTs

- ✓ 32 H_2 adsorbed on 1.1 nm-diameter CNT
- ✓ 64 H_2 adsorbed on 1.4 nm-diameter CNT

H_2 gas adsorbed on 16V-H at T = 0 K

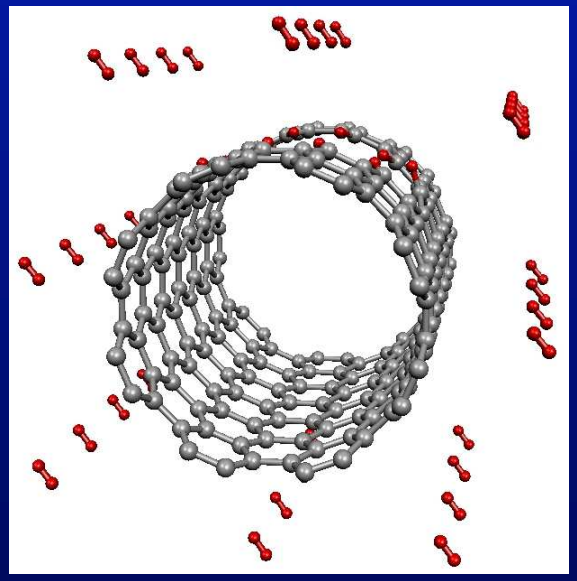
Endohedral



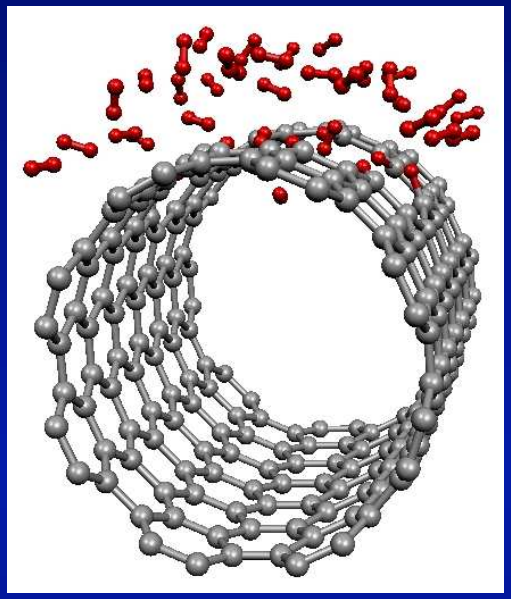
E_{bind} = -0.255 eV/H_2

32 H_2 gas adsorbed inside (endohedral) and outside (exohedral) of the porous CNT.

The gas binding energy is calculated by the difference in energy between the adsorbed and diluted gas



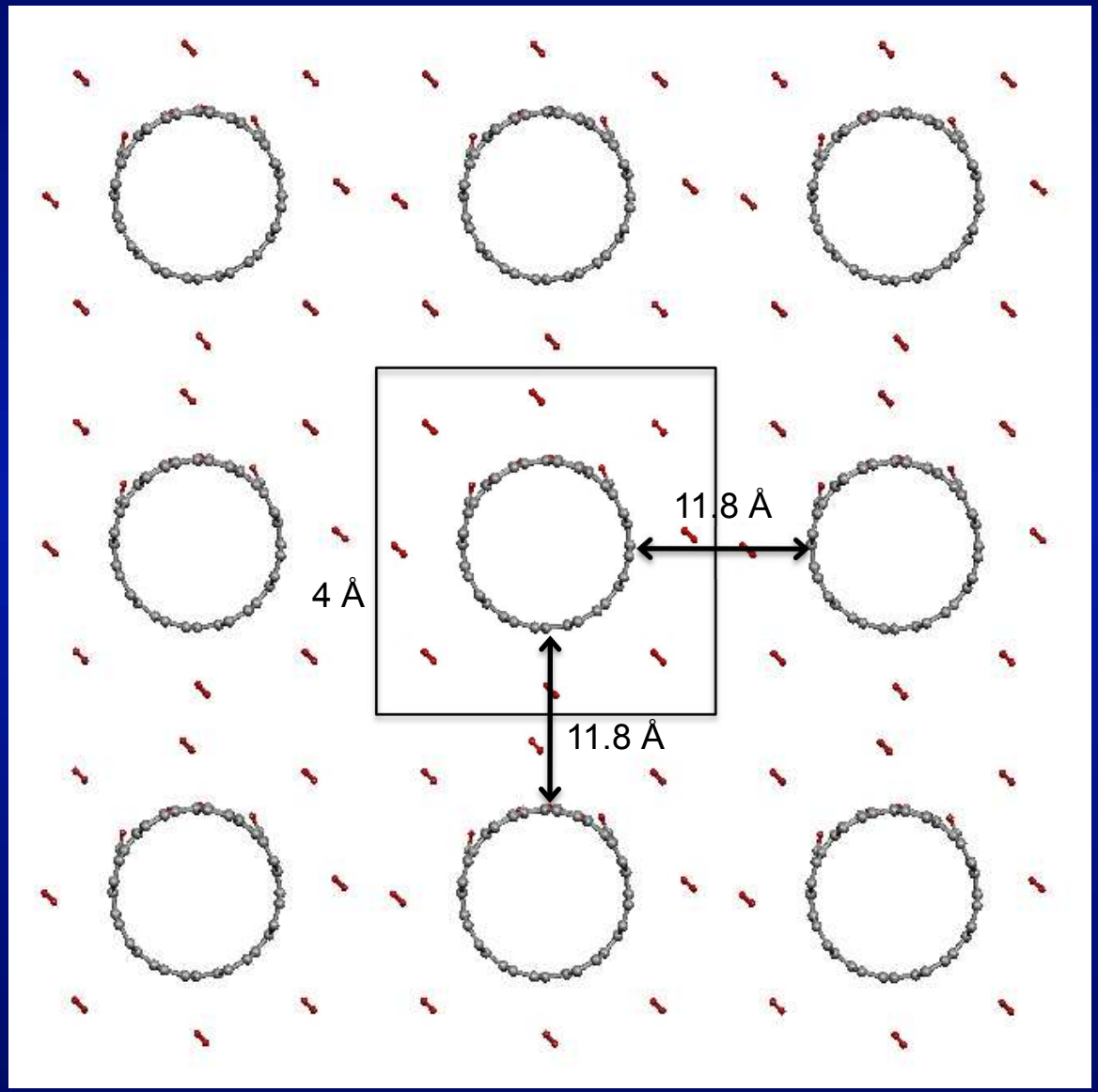
Exohedral



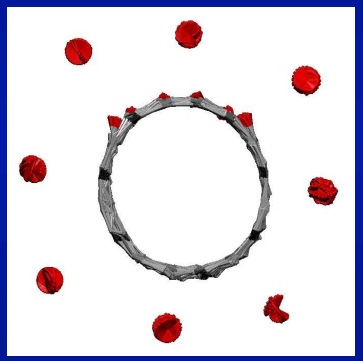
E_{bind} = -0.194 eV/H_2

The diluted gas approach

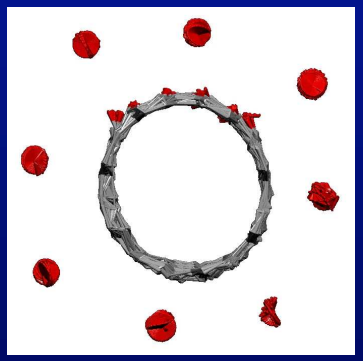
Our approach for the diluted H_2 gas



77 K



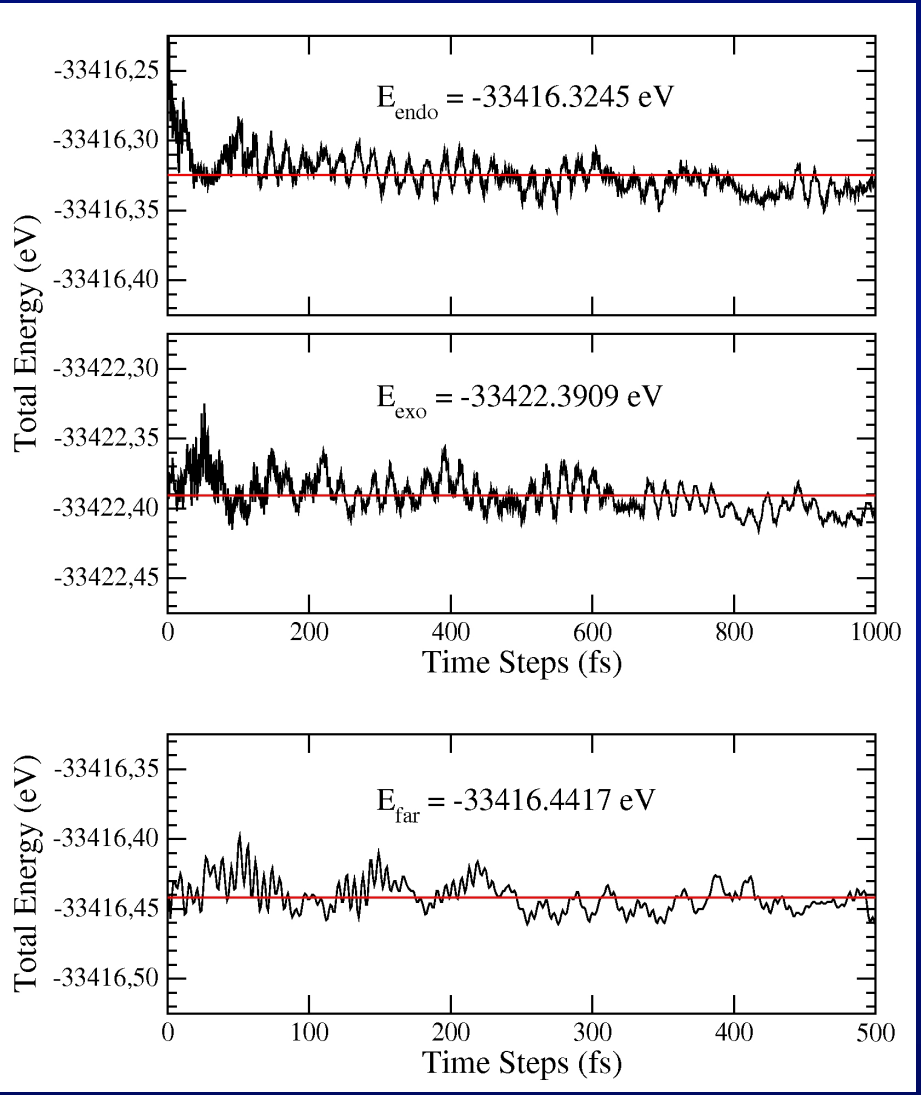
300 K



600 K

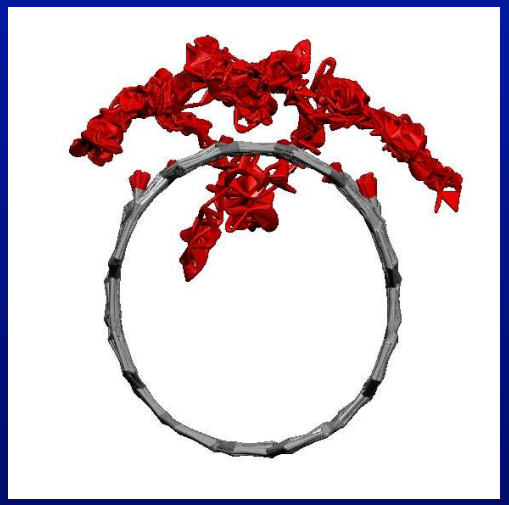
32 H_2 on a porous (8,8) CNT at T = 77 K

Energy of the H_2 gas adsorbed on (8,8):16V-H CNT of 1.1 nm diameter, during a time step of 1 ps



Pathway of H_2 molecules adsorbed on the porous CNT at low temperature

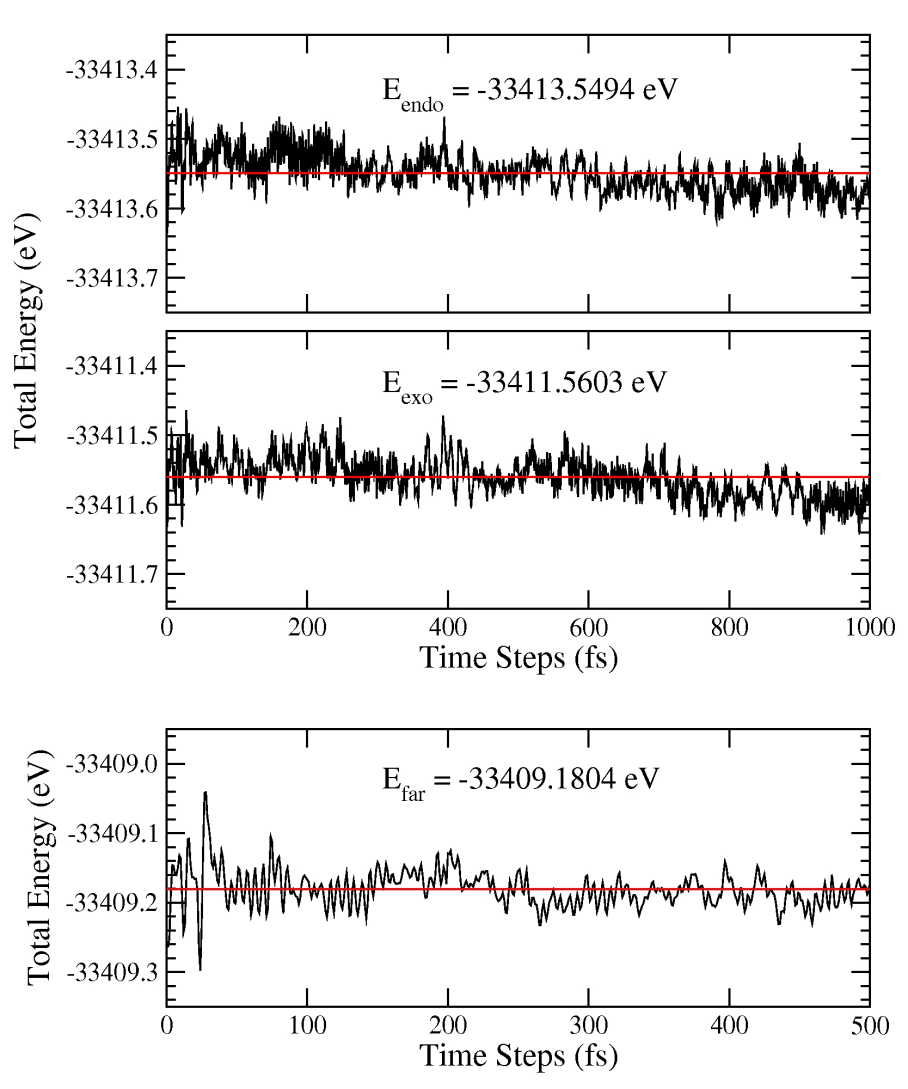
E_{bind} = 0.004 eV/H_2



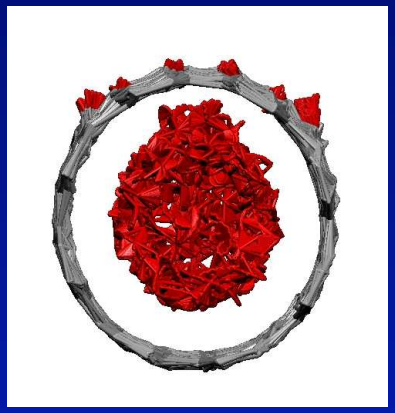
E_{bind} = -0.186 eV/H_2

32 H_2 on a porous (8,8) CNT at T = 300 K

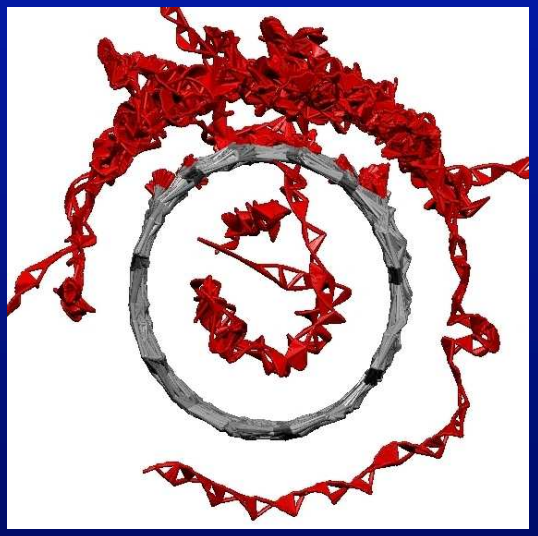
Energy of the H_2 gas adsorbed on (8,8):16V-H CNT of 1.1 nm diameter, during a time step of 1 ps



Pathway of H_2 molecules adsorbed on the porous CNT at room temperature



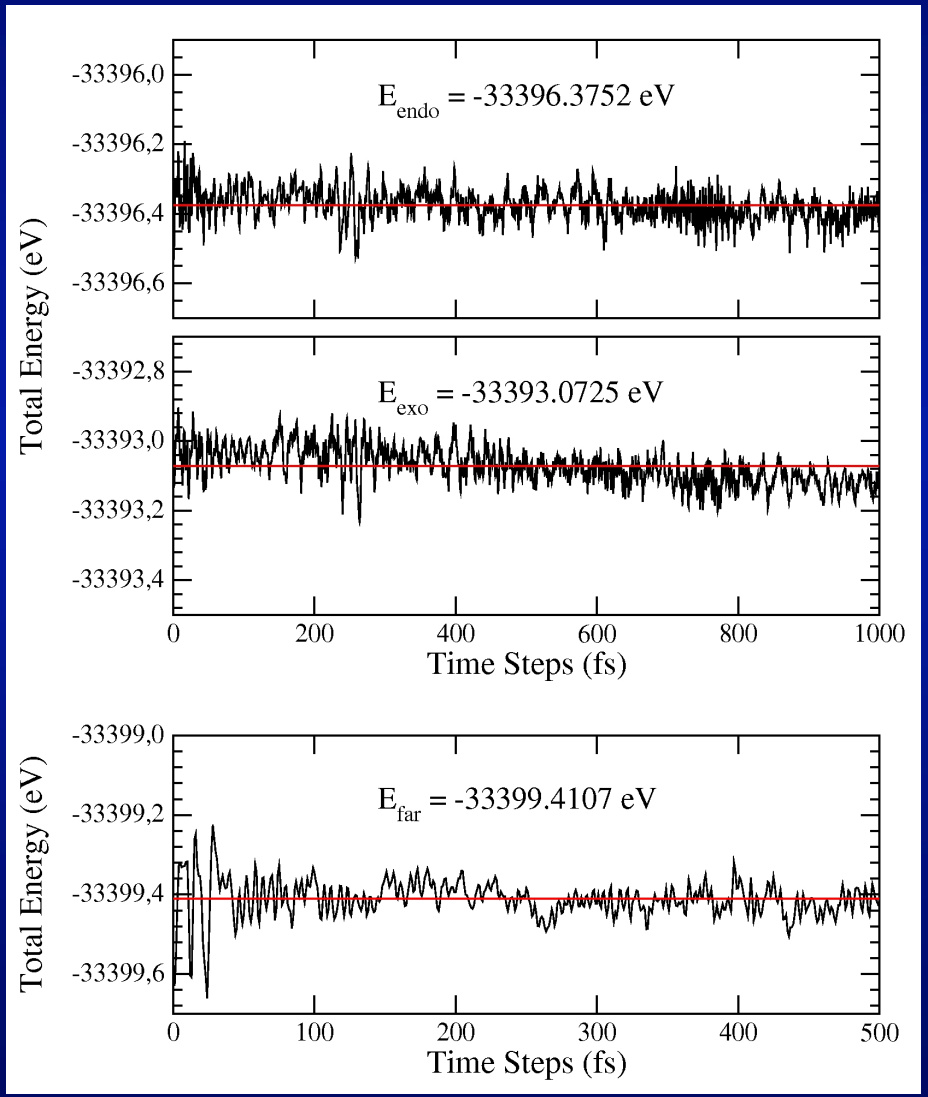
E_{bind} = -0.136 eV/H_2



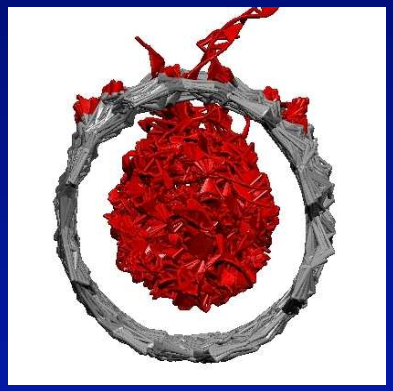
E_{bind} = -0.074 eV/H_2

32 H_2 on a porous (8,8) CNT at T = 600 K

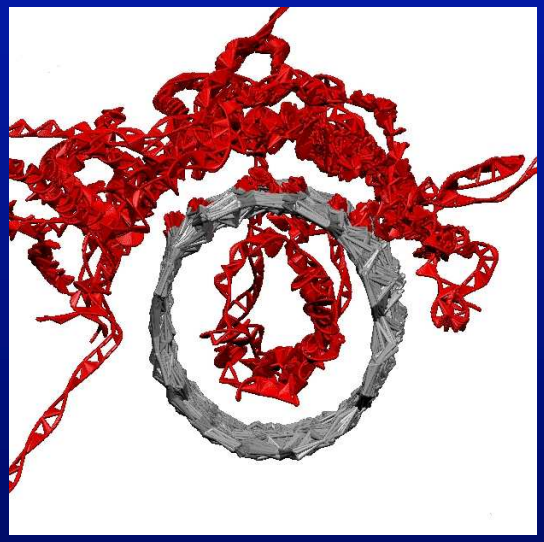
Energy of the H_2 gas adsorbed on (8,8):16V-H CNT of 1.1 nm diameter, during a time step of 1 ps



Pathway of H_2 molecules adsorbed on the porous CNT at room temperature



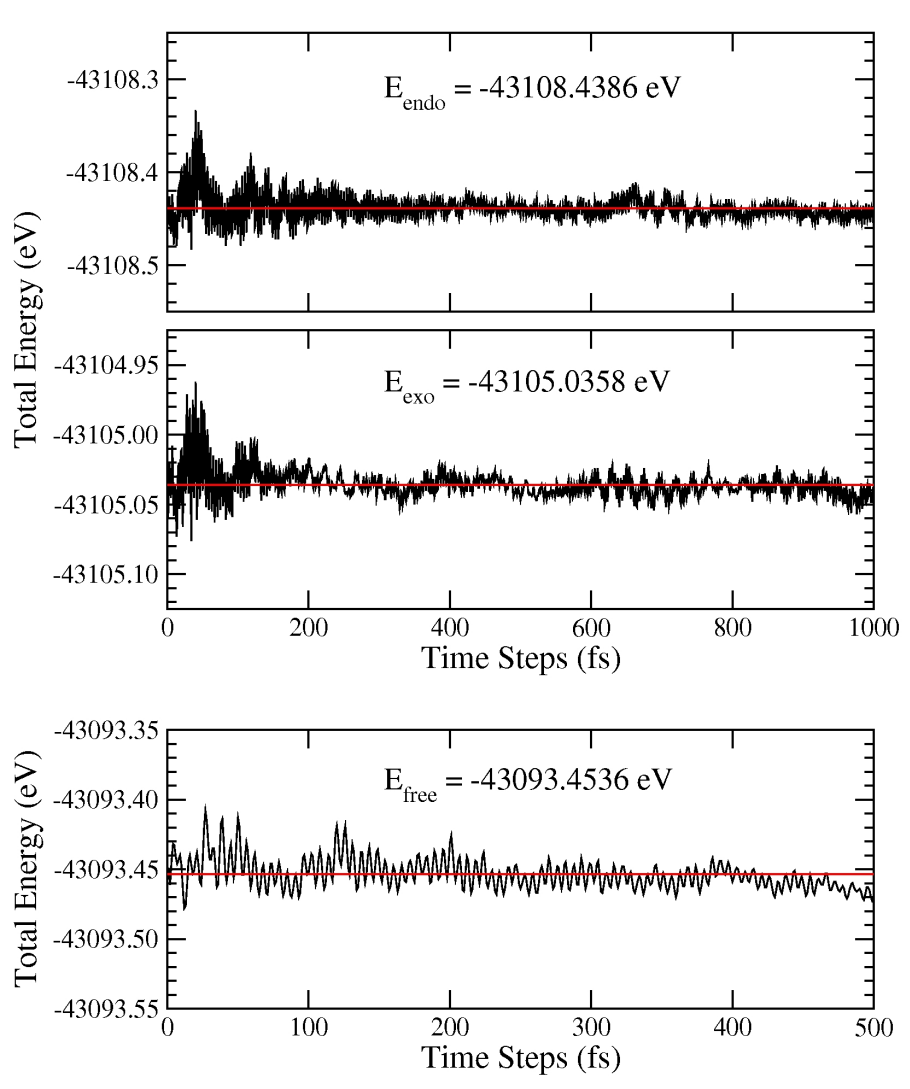
E_{bind} = 0.096 eV/H_2



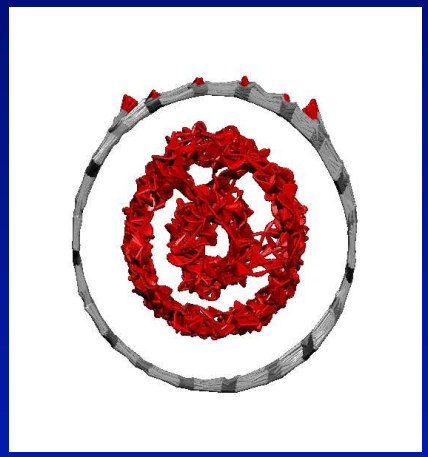
E_{bind} = 0.198 eV/H_2

64 H_2 on a porous (10,10) CNT at T = 77 K

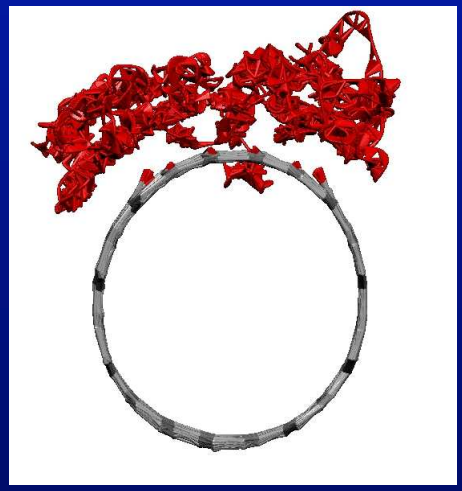
Energy of the H_2 gas adsorbed on (10,10):16V-H CNT of 1.4 nm diameter, during a time step of 1 ps



Pathway of H_2 molecules adsorbed on the porous CNT at low temperature



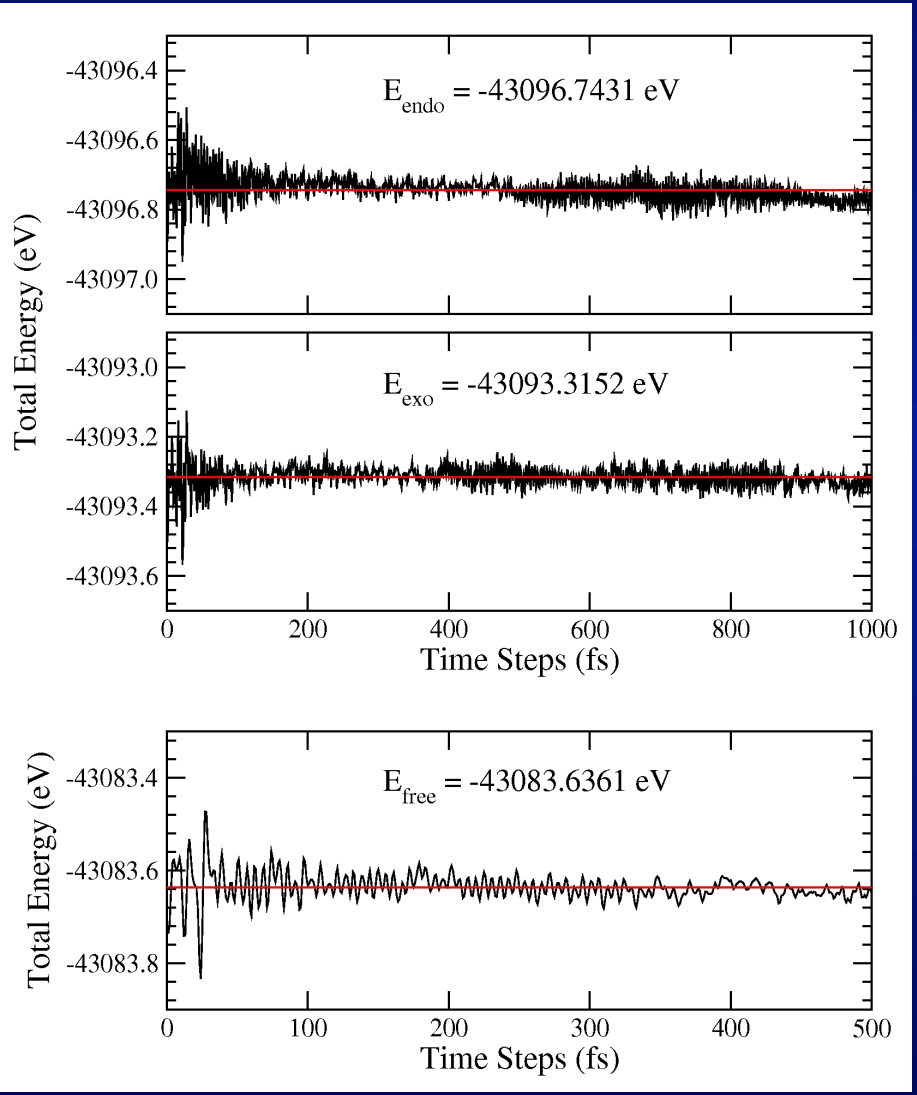
E_{bind} = -0.234 eV/H_2



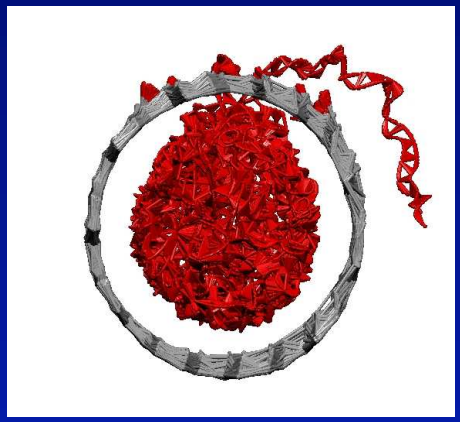
E_{bind} = -0.181 eV/H_2

64 H_2 on porous (10,10) CNT at T = 300 K

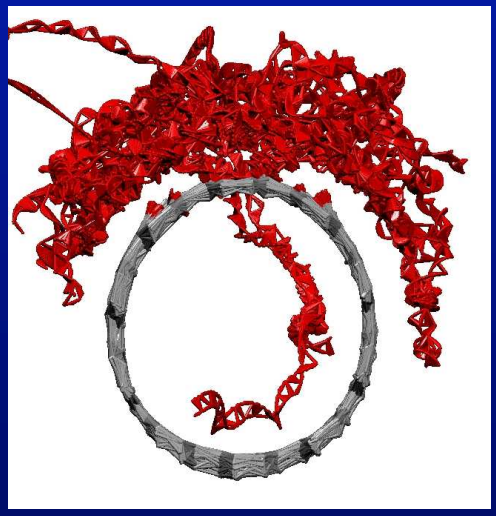
Energy of the H_2 gas adsorbed on (10,10):16V-H CNT of 1.4 nm diameter, during a time step of 1 ps



Pathway of H_2 molecules adsorbed on the porous CNT at room temperature



E_{bind} = -0.205 eV/H_2



E_{bind} = -0.151 eV/H_2

Summary

porous CNT of 1.1 nm in diameter + 32 H_2

H_2 storage capacity: 2.6 wt% and 66 g/L

Temp. (K)	E_{bind} endo (eV/H_2)	E_{bind} exo (eV/H_2)
0	-0.255	-0.194
77	0.004	-0.186
300	-0.136	-0.074
600	0.095	0.198

porous CNT of 1.4 nm in diameter + 64 H_2

H_2 storage capacity: 4.0 wt% and 80 g/L

0	-0.249	-0.191
77	-0.234	-0.181
300	-0.205	-0.151

- ✓ CNTs of 1.4 nm have an endohedral storage capacity of 4.0 wt %, suggesting that larger SWCNTs can increase this value.
- ✓ Nanoporous CNTs with a hydrogen gas inside are very stable, preserving their structure up to 600 K.
- ✓ The endohedral binding strength of an H_2 gas is higher than the exohedral one at different temperatures, suggesting favorable conditions for the H_2 incorporation

Conclusions

- ✓ Our results suggest that porous CNTs can be formed by passivated multivacancies. These pores could be created by electron irradiation in a H_2 atmosphere.
- ✓ The 16V-H pores in CNTs are very stable at high temperatures and have the proper diameter to incorporate H_2 molecules inside (~ 6 Å) .
- ✓ The H_2 endohedral adsorption energy at room temperature tends to increase with the CNT diameter (0.14 - 0.21 eV/H_2), approaching to those estimated optimal for the entire adsorption-desorption cycle (~ 0.3 eV/H_2).

Phys. Rev. B 80, 075421 (2009)