Modulating tritium binding on graphene related materials

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Outline

- ✓ The problem
  - ✓ designing the potential for Tritium: how do we want it to be?

- ✓ The interaction of hydrogen with "graphene"
  - ✓ Which graphene?
  - ✓ Covalent binding vs van der Waals interaction, desorption vs hopping
  - ✓ Curvature and cooperative effect

- ✓ Possible architectures
  - ✓ Nanotubes
  - ✓ Fullerites
  - ✓ Epitaxial and layered
  - ✓ Others

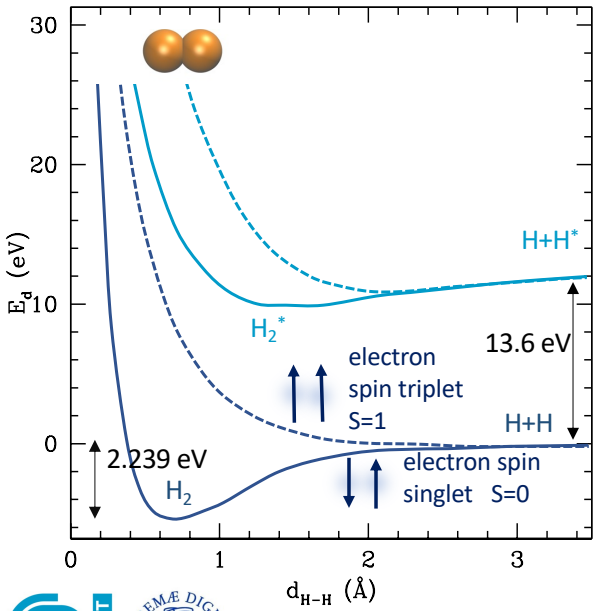
- ✓ Summary and perspectives

The problem: designing the potential for Tritium: how do we want it to be?

Dissociation/association profile of H_2 (T_2) in vacuo (tons of literature!)

- ✓ The dissociation energy of H_2 is 4.478 eV (**ε=2.239 eV/atom**, T_2 value little larger)
- ✓ The dissociation curve is narrow (**λ~0.5 Å**) → the **stiffness $\kappa = \varepsilon/\lambda^2 \sim 9$ eV/Å^2 is large!**
- ✓ The curve flattens in the excited states

	Bond length (Å)	E_d(eV)	notes
H_2	0.7414	4.478	Ground state, spin singlet (expt)
H_2	1.5	2.72	First electronic excited state (Theory)
D_2	0.742	4.556	Expt
T_2		4.591	Theory (accuracy 10^{-4})
HD		4.514	experimental
HT		4.527	Theory (accuracy 10^{-4})
DT		4.573	Theory (accuracy 10^{-4})



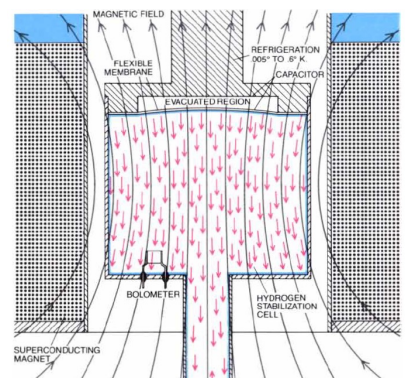
- ➢ We want T very weakly bound (i.e. a binding potential with low stiffness)

Ideally,

- ➢ We want T in atomic form

- ✓ The ground state of the H_2 (T_2) molecule is an electron spin singlet ↓↑ with null total spin
- ✓ The energy profile for the spin triplet couple ↑↑ has a barrier to dimerization

- ➢ Atomic hydrogen can be stabilized as a gas in vacuo at high magnetic fields and low temperatures (kept for minutes at the density of $10^{23}/m^3$ at T=0.3K with B=10T)



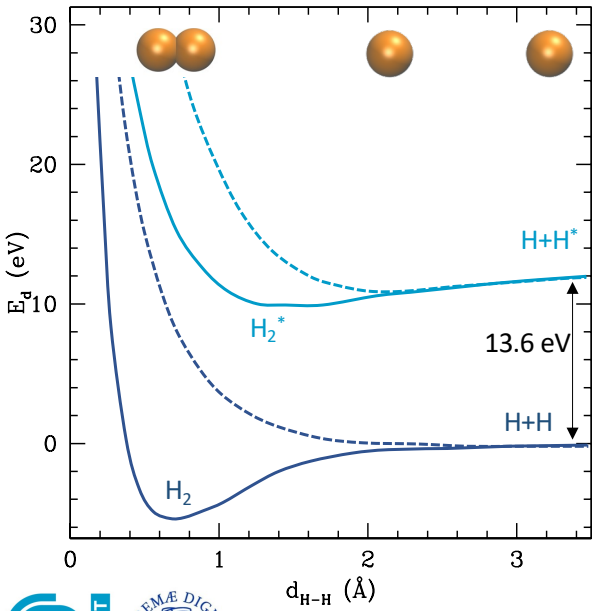
L Lehtonen et al 2018 New J. Phys. 20 055010; Gillaspy PRB 1988; Silvera PRL 1980

The problem: designing the potential for Tritium: how do we want it to be?

- ✓ We want T very weakly bound (i.e. a binding potential with low stiffness)
- ✓ We want T in atomic form

AND

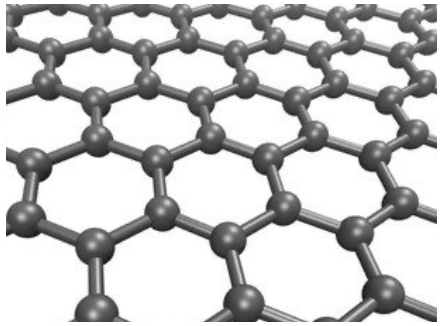
- ✓ We want T in high concentration



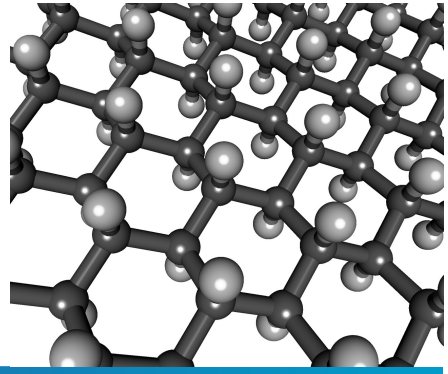
One possibility to reconcile these conditions:

Chemisorption on graphene

Upon full hydrogenation of graphene sheet, one gets graphAne, the material which can store T at the closest distance (~2 Å, σ~0.17 mg/m³))



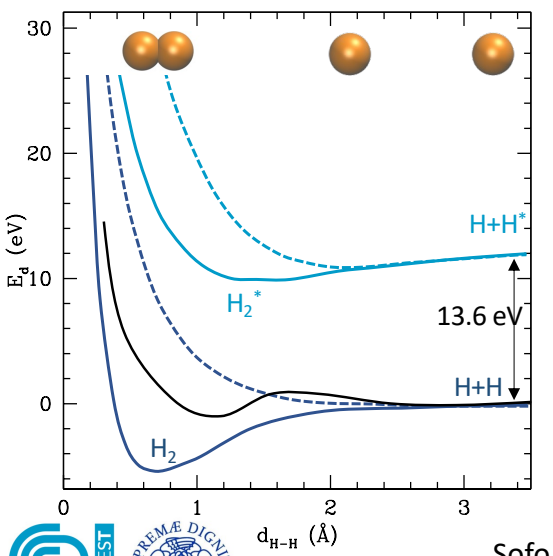
+H



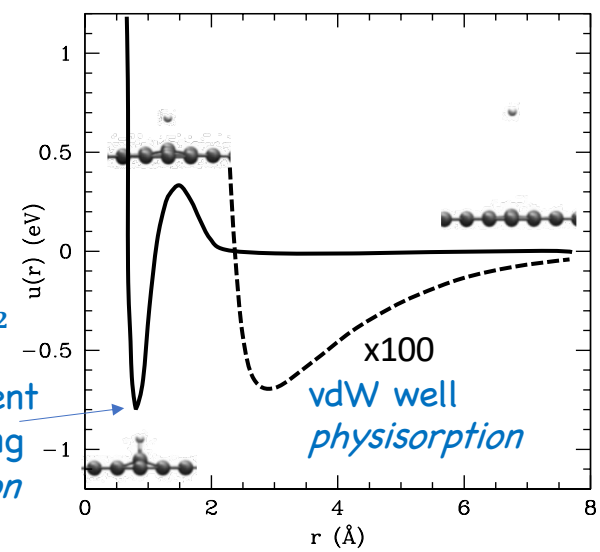
Chemisorption on graphene

Upon full hydrogenation of graphene sheet, one gets graphAne, the material which can store T at the closest distance (~2 Å, σ~0.17 mg/m³))

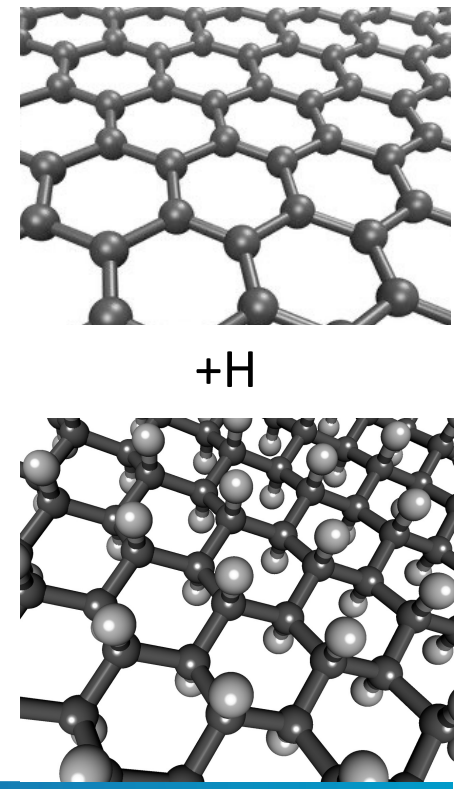
- ✓ H on graphane was predicted to be stable enough (avg binding energy of H ~ 2.38 eV/atom, with respect to atomic H)
- ✓ Binding energy of isolated H on graphene ~0.8 eV/atom
- ✓ The chemisorption well is as large as H_2 pot, but 1/6 softer → $\kappa = \varepsilon/\lambda^2 \sim 1.5\ \mathrm{eV/Å^2}$



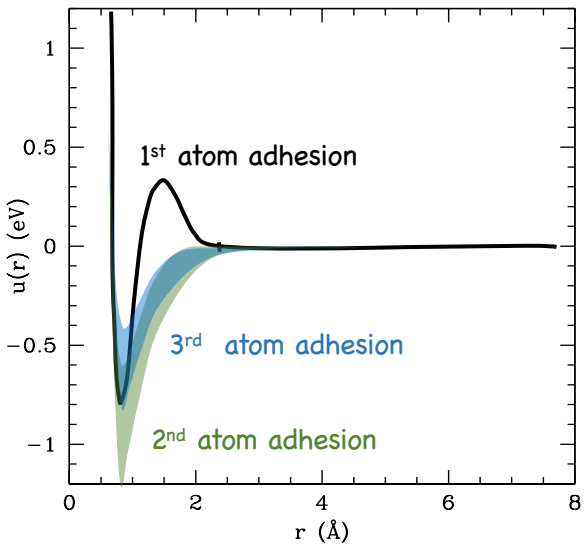
- ✓ In addition, there is an extremely weak physisorption well, stabilized by vdW force $\kappa \sim 0.001\ \mathrm{eV/Å^2}$



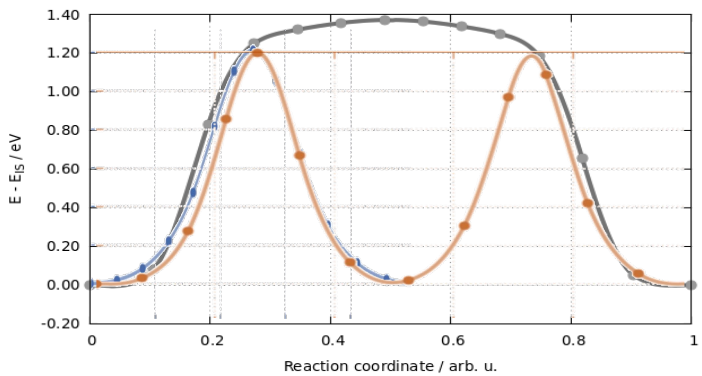
Sofo et al, PRB 75 (2007)

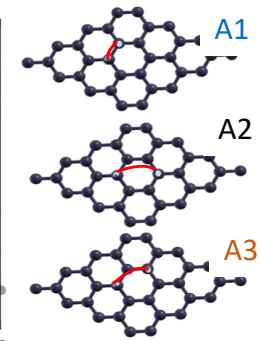


Chemisorption on graphene - hopping and cooperative binding



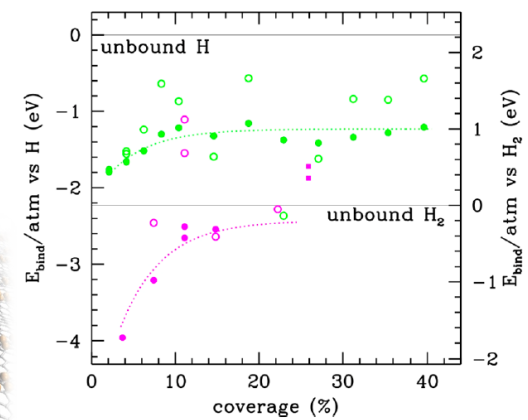
✓ Hopping energy of H(T) on graphene is 1.2–1.4 eV (depending on the path)
(Curtesy of T Mamo)





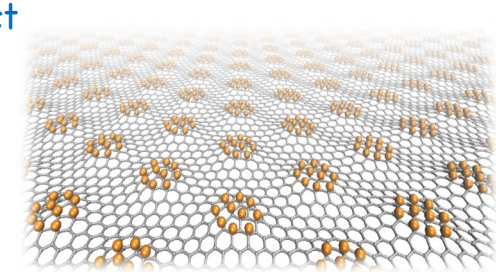
➢ The equivalent stiffness is $\kappa \sim 3.5\ eV/Å^2$

✓ Binding energy of isolated H on graphene ~0.8 eV/atom, dimers binding energy is up to 2eV/atom and graphAne average binding energy is ~ 2.38 eV/atom → cooperative effect



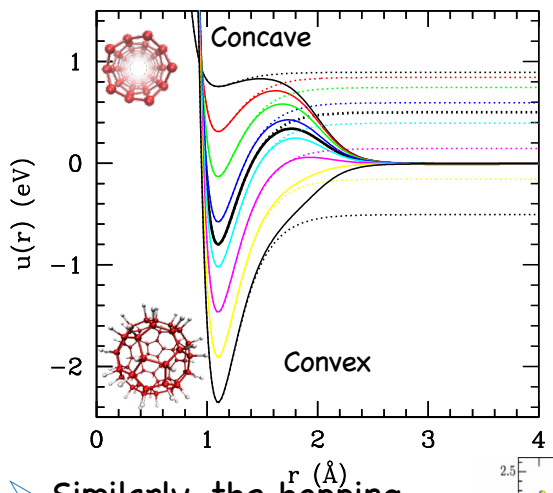
✓ H binds in clusters on graphene up to the nano-size, then the deformation of the sheet hinders further adsorption

Goler et al Jpcc 2013,
Rossi et al JPCC 2015,
Tozzini et al PCCP 2013

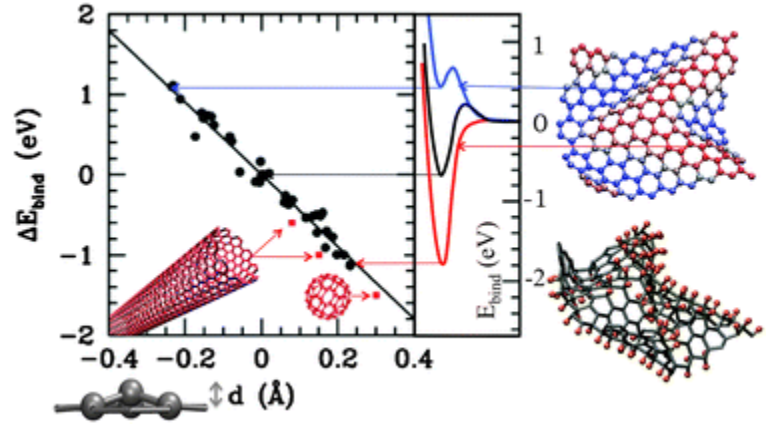


Chemisorption on graphene - effect of curvature

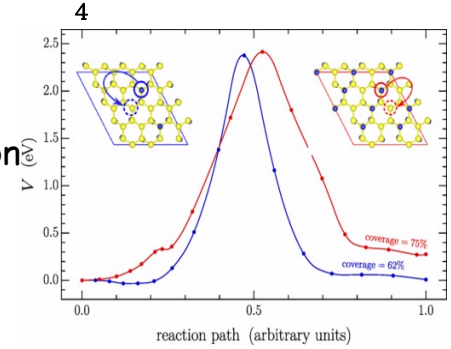
Tozzini et al JPCC 2011,
Tozzini et al PCCP 2013
Apponi et al PRD 2022

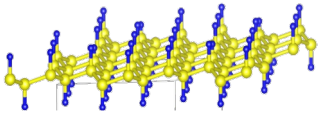


- ✓ The chemisorption profile of single H(T) on graphene depends on the local curvature of the sheet
- ➢ convex sites have stronger binding potential while concave sites can have it very weak!

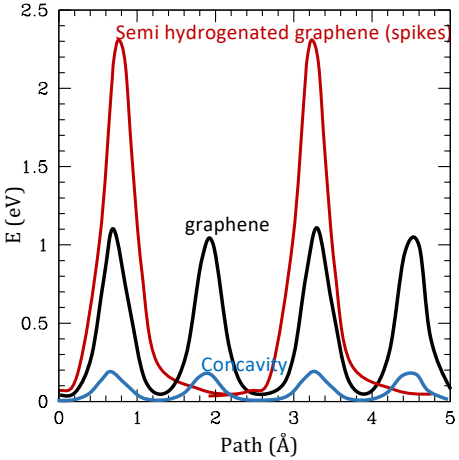


- ➢ Similarly, the hopping barriers are larger on convexities and smaller on flat or concavities (on graphAne, with spikes, ~2eV, on graphEne, flat, ~1.2eV)





Effective stiffness and hopping can be made small or vanishing in concavities



Partial summary & conclusions

system	Potential (equivalent stiffness)	Env conditions	density
Vacuum, T_2	Very strong ($\kappa \sim 9$ eV/Å^2)	Any	Up to 0.21 g/cm^3 (molecular liquid)
Vacuum, T_2^*	Less strong ($\kappa \sim 2$ eV/Å^2)	Electronic excited state	
Vacuum, T	null ($\kappa \sim 0$ eV/Å^2)	T ~0.3 K, B ~10 T	~0.5 g/m^3=0.5μg/cm^3 (for minutes)
T:graphene	Less strong ($\kappa \sim 1.5$-4 eV/Å^2)	Any	Up to 1.7 μg/cm^2 ~0.17g/cm^3 (graphAne)

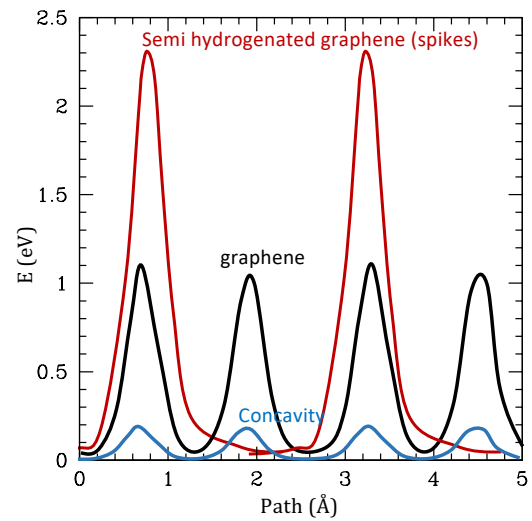
- ✓ Using graphene would hugely increase the tritium concentration with respect to gaseous form…

  But

- ✓ The binding potential is still too stiff

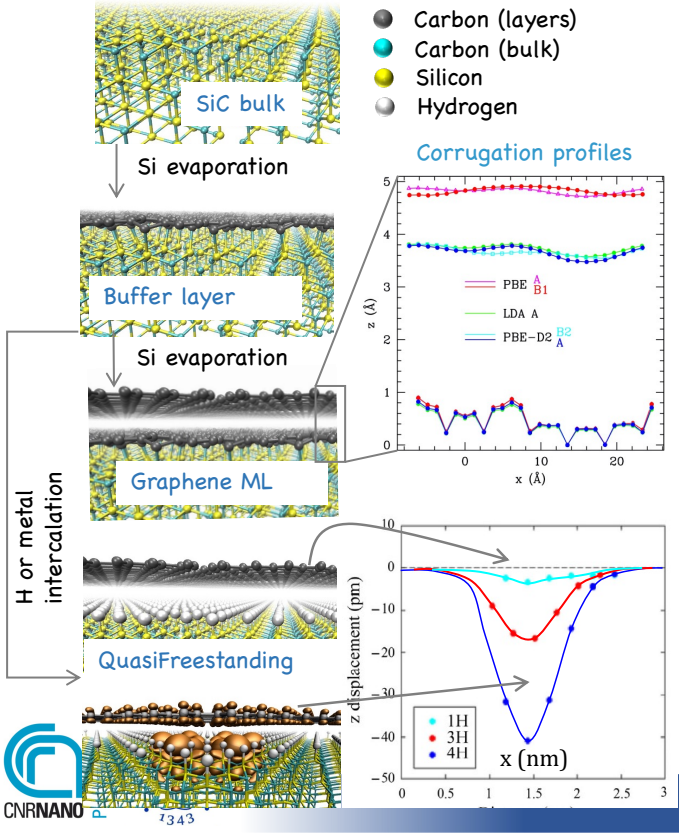
  However

- ✓ Concavities could help solving the problem

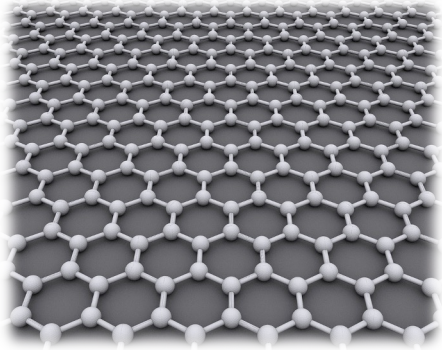


A step backward… which graphene?

- ✓ Ideal = flat, infinite, suspended, 2D hexagonal crystal → a dream (almost)
- ✓ Epitaxial = real, robust, different structures (C Coletti, S Heun)

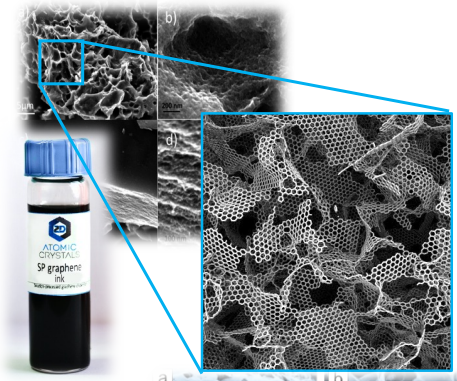


STM



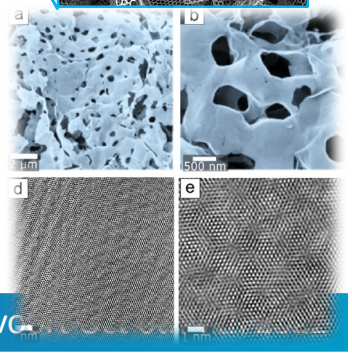
- ✓ Nanoporous with edges and defects

From exfoliated graphite flakes inks upon gelation, dehydration, reduction… very cheap and scalable (V Pellegrini S Bonaccorso and others)



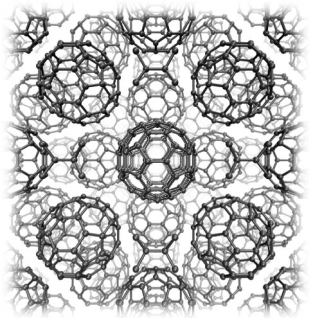
- ✓ Nanoporous interconnected

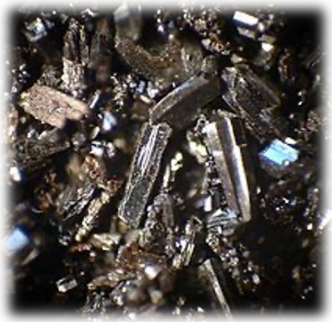
Grown on nanoporous Ni
Vast sp2 surfaces
No defects
(Di Bernardo et alACS Omega 2017)

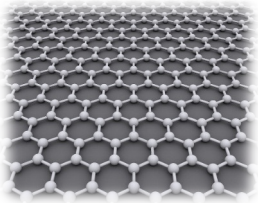


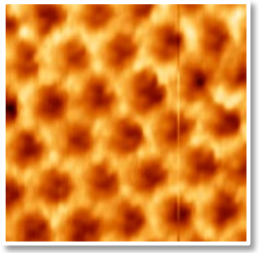
A step backward… which graphene?

- ✓ Fullerenes come in different sizes and can be crystallized in FCC (fullerite), a hard, stable, light (1.95g/cm^3) crystal

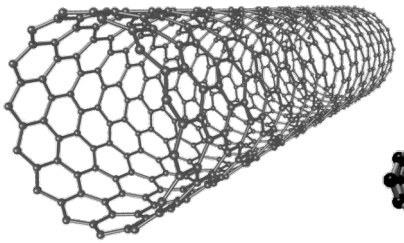


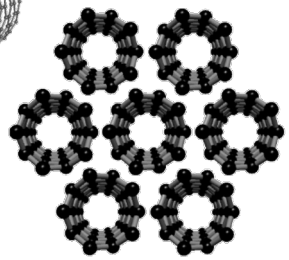


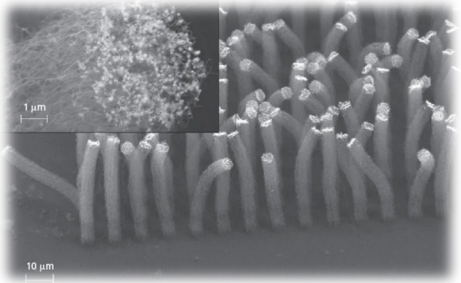


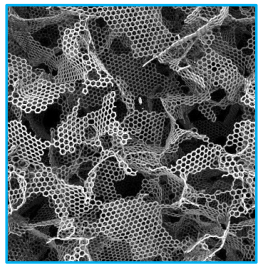


- ✓ Carbon nanotubes come in different diameters (>5Å), can be capped, can be organized in bundles and ropes

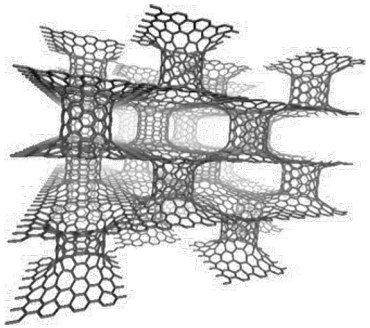


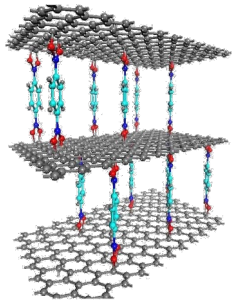






- ✓ Pillared multilayers spaced by nanotubes or organic molecules

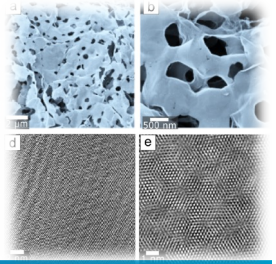




Very difficult synthesis!

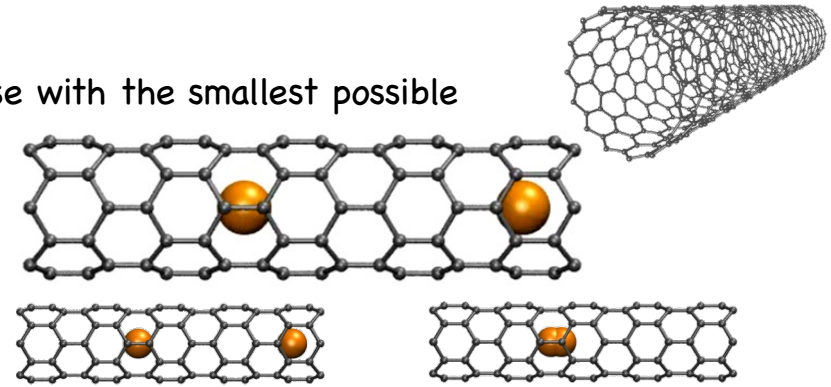
Can any of these materials solve our issues?

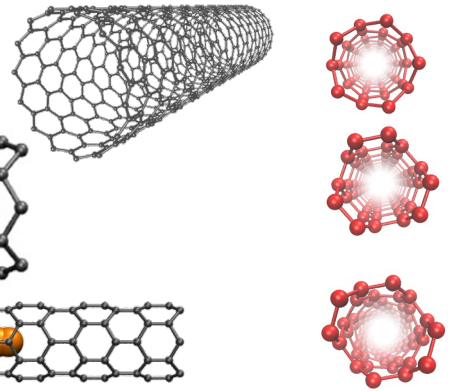
And which one is the best?



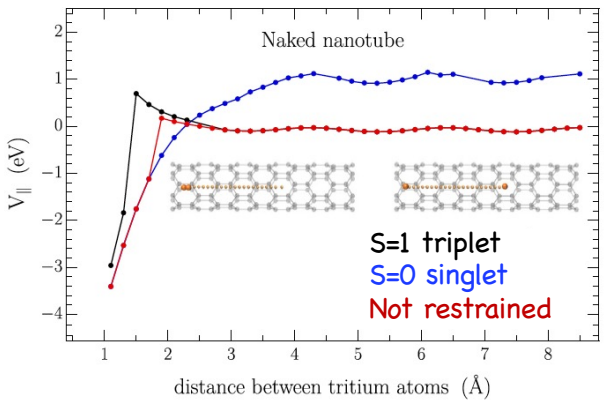
Lert's start from nanotubes

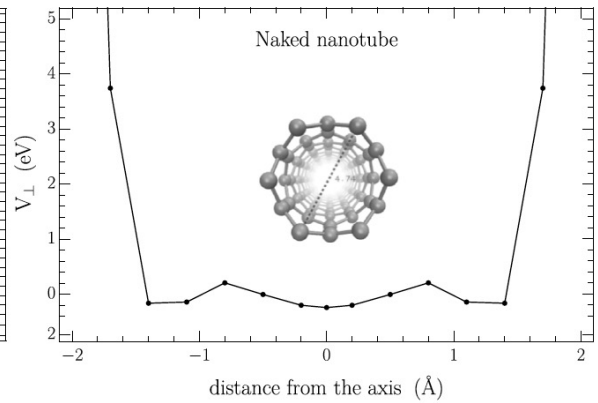
- ✓ In the whole series of nanotubes, we choose those with the smallest possible diameter synthesized
  - ✓ We included two atoms of T in the tube and calculate the energy of the system as they get near (DFT quantum calculation including electronic structure and full relaxation)

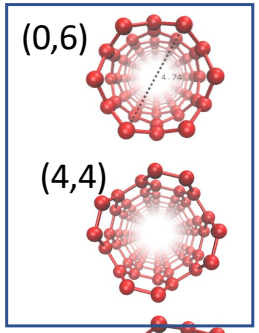


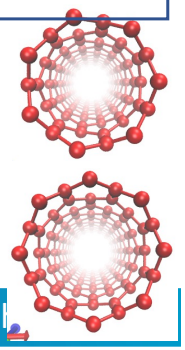


  - ✓ The calculation is performed either letting free the spin state, or in singlet and triplet
    - ➢ The energy profile along the axis is very flat, in either of the spin states although the triplet is stabler
    - ➢ As the atoms get nearer they dimerize in T_2 with no barrier in singlet state, while there is rather a large barrier in the triplet state





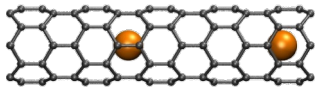


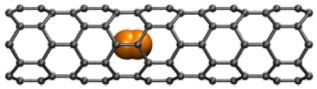


The anti-dimerization effect of an external magnetic field will be enhanced!

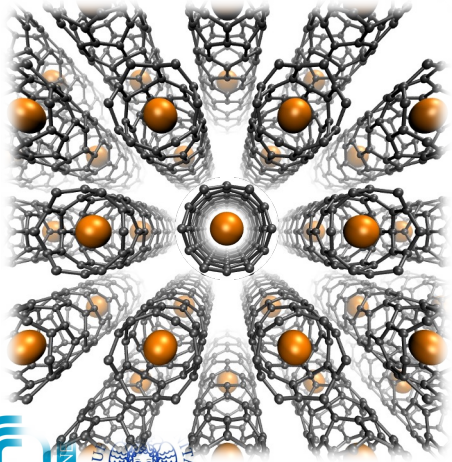
However, there is still a covalently bound state, separated by a ~0.5eV barrier

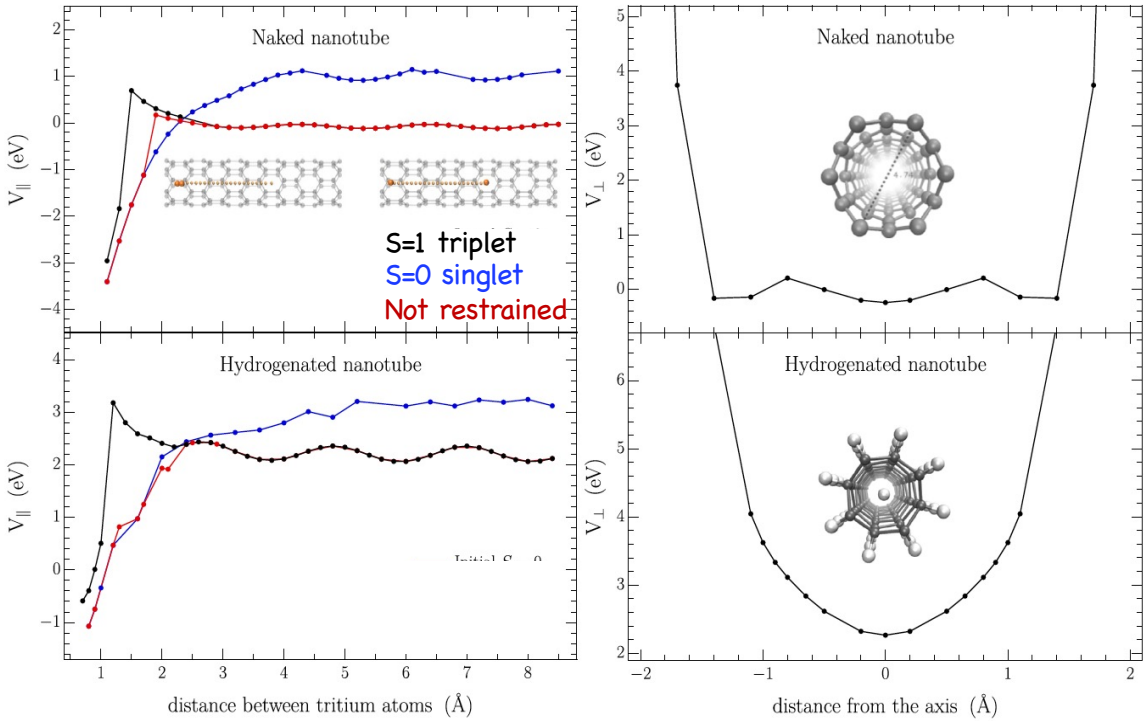
Nanotubes





- ✓ The anti-dimerization effect of an external magnetic field will be enhanced!
- ✓ The passivation of the nanotube (e.g. with externally bound H) prevents the internal T binding
- ✓ A bundle of nanotubes can store T with a density of ~2 μg/cm³ (~1/10 than in graphane)





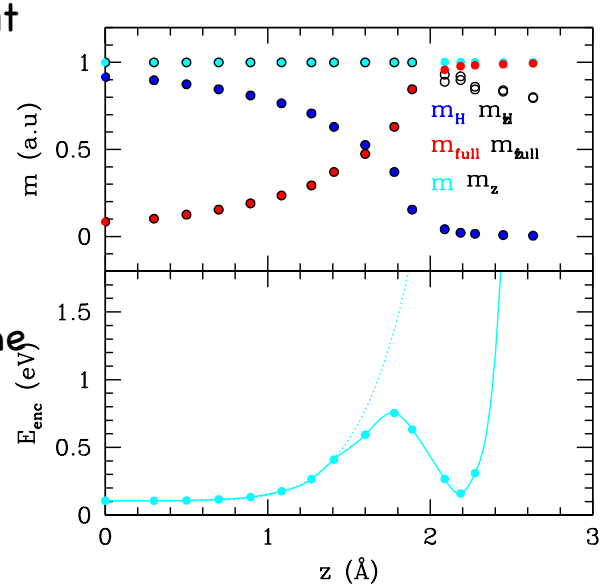
Can we do better?

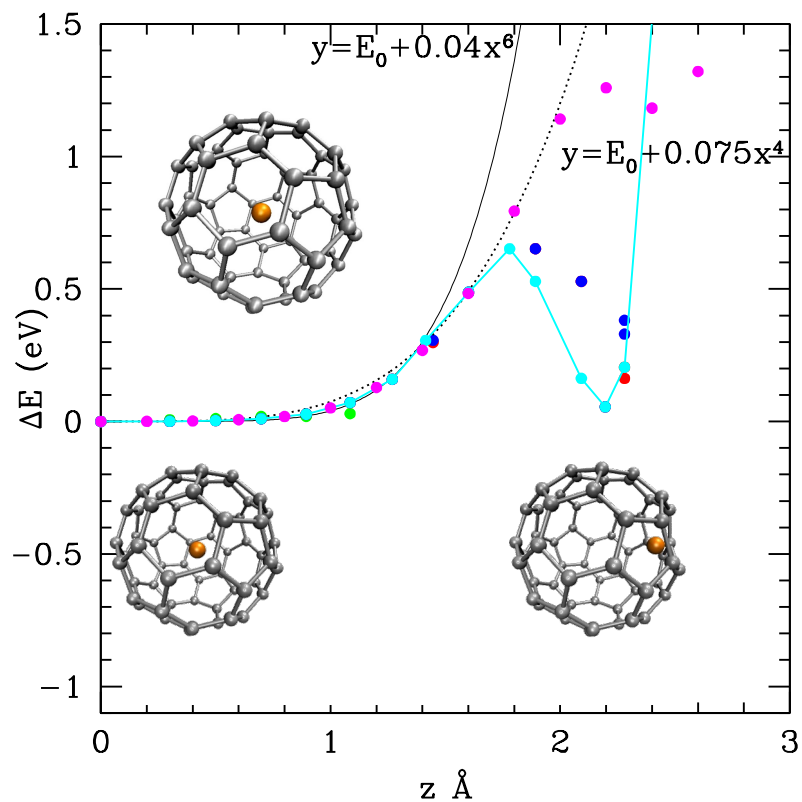
Fullerenes

✓ Homologous calculations were performed on fullerene, moving a caged T towards a C site or towards the center of a pentagon

- The profile to pentagons is purely repulsive
- The profile to C site display a bound state, with deformed fullerene cage
- However, the central well is as large as 3Å
- Fullerene of different sizes are available up to ~1nm

- Upon binding, T transfer its spin to the cage AND the global spin of the system decreases

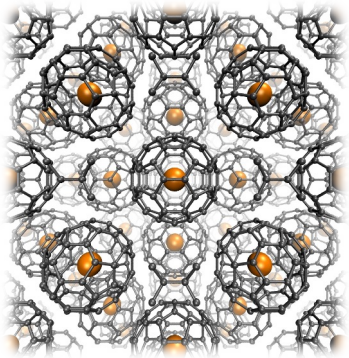


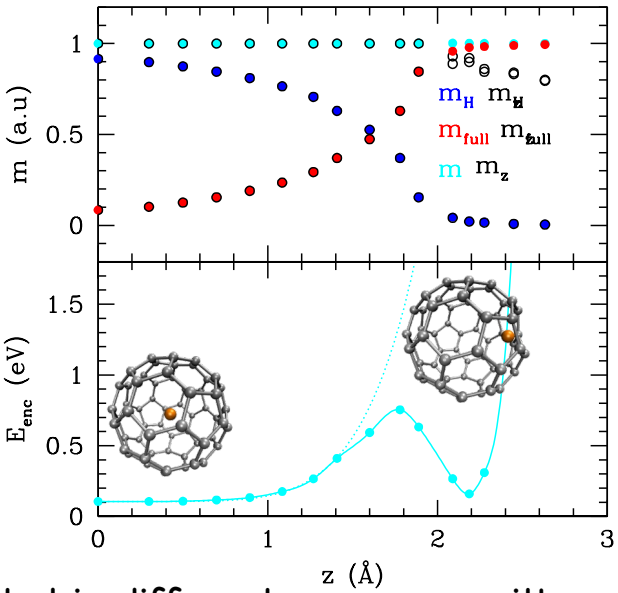


Fullerenes & fullerite

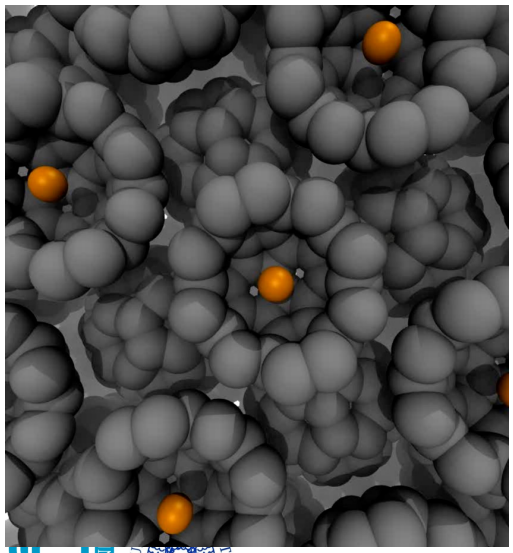
- Within the fullerite crystal the cage deformation might be prevented by crystal restrains, and spin transfer might be prevented by spin cooperation

- The bound state might be destabilized within the crystal

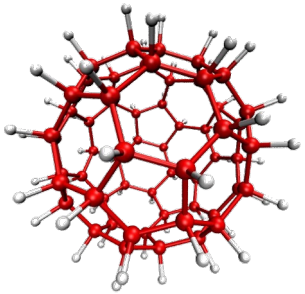


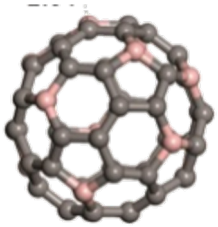


Simulations are in the course!



In addition: Fullerenes can be passivated in different ways, e.g. with hydrogen or by boron doping





- Fullerite does not need external magnetic field to prevent dimerization

- Fullerite can store T with a density of ~0.004 g/cm^3

Summary storage of Tritium

system	Potential (equivalent stiffness)	Env conditions	density
Vacuum, T_2	Very strong ($\kappa \sim 9$ eV/Å^2)	Any	Up to 0.21 g/cm^3 (molecular liquid)
Vacuum, T_2^*	Less strong ($\kappa \sim 2$ eV/Å^2)	Electronic excited state	
Vacuum, T	null ($\kappa \sim 0$ eV/Å^2)	T ~0.3 K, B ~10 T	~0.5 g/m^3=0.5μg/cm^3 (for minutes)
T:graphene	Less strong ($\kappa \sim 1.5$-4 eV/Å^2)	Any	Up to 1.7 μg/cm^2 ~0.17g/cm^3 (graphAne)
T@fullerite	Flat, quartic or sextic with κ dependent on the radius; possible bound state prevented by passivation	Any; B not needed to prevent dimerization, but might help in prevent binding	Up to ~0.0036 g/cm^3 = 3.6 mg/cm^3
T@nanotube	Flat along the axis; parabolic with radius dependent κ in radial dir; possible bound state prevented by passivation	Any; (weak) B to prevent dimerization	Up to ~0.02g/cm^3 = 20 mg/cm^3

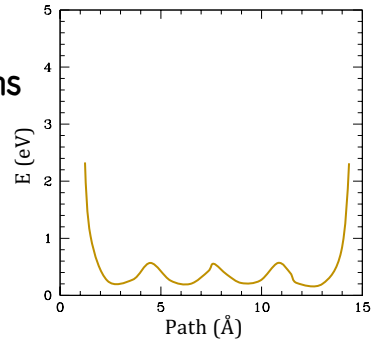
Encapsulated fullerenes and nanotube seems very promising materials

Digression: production of encapsulated fullerenes (notes from a NON expert)

- ✓ Structural electronic and magnetic properties of encapsulated H in fullerenes of various sizes and kinds were theoretically studied for long (e.g. Javan et al Curr Appl Phys 2013)
- ✓ Experimentally, H_2 was encapsulated in fullerenes following a chemical route (Murata et al JACS 2006), but encapsulation of atomic H is elusive (Estreicher et al Chem Phys Lett 1992)
- ✓ A mechanism involving dissociation-adsorption external surface and flipping was proposed by simulations to occur if fullerenes are exposed to beams of atomic H at specific kinetic energy (Beadmore et al JP Cond mat 1994)
- ✓ Conversely, encapsulation of monoatomic metal ions (Li+ Na+ K+) or other elements (N) but also rare-earth, Lantanidies and Actinidies (see e.g. Cai et al Acc Chem Res 2019 and Popov et ale Chem Rev 2013) was achieved. These are mostly synthesized chemically and fully characterized
- ✓ Encapsulation within nanotubes generally follows the physical route (i.e. inclusion and capping, see e.g. Cadena et al Oxford Open Material Sci 2021)

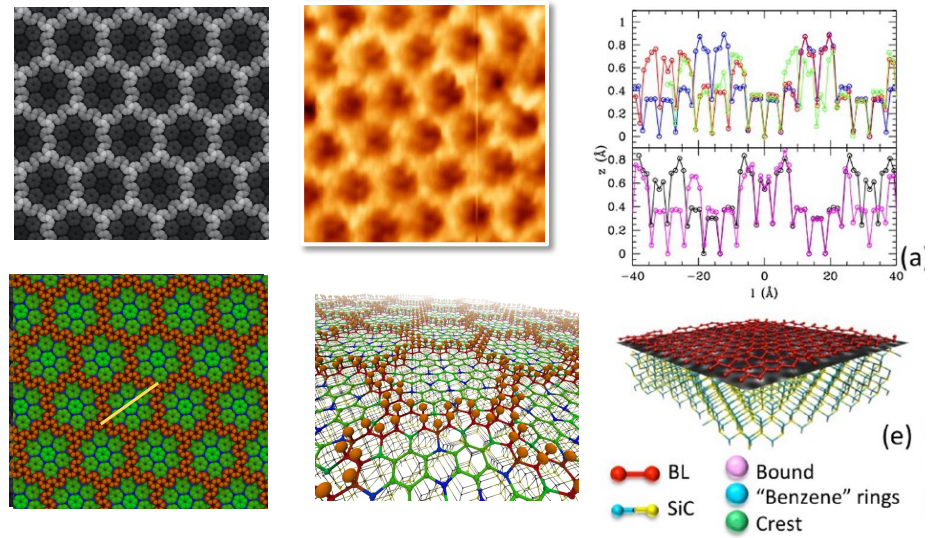
Further ideas

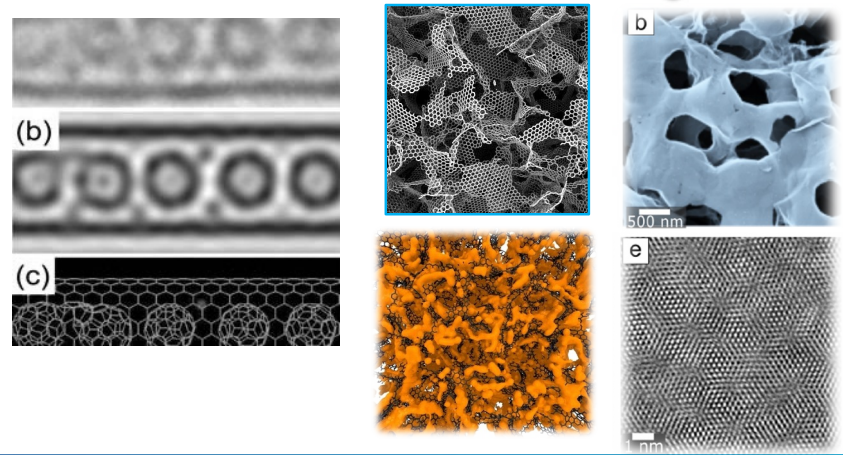
- ✓ The buffer layer on SiC
  - ➢ Has reactive protruding spikes…
  - ➢ Which could be easily passivated wit H
  - ➢ Once this is done, the system is left with rather flat and hydrophobic basins which could host a single T almost free to move



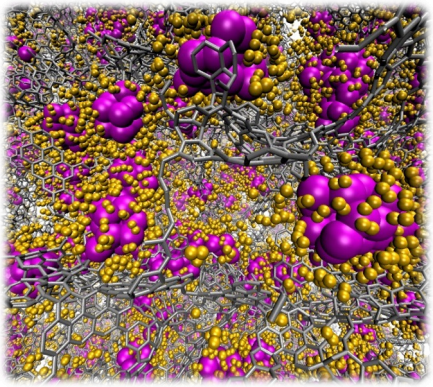
This system could host $\sim 0.2\ \mathrm{ng/cm^2}$ of T

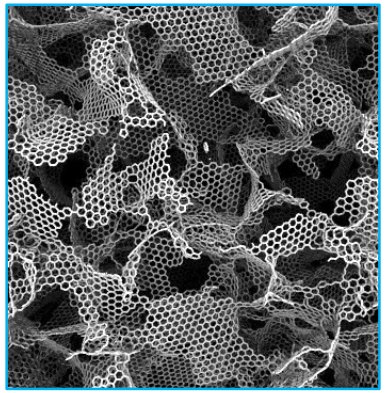
- ✓ Nanoporous graphenes
  - ✓ Can host H_2 (T_2) but atomic H(T) covalently might bind on defects
  - ✓ In defectless nanoporous graphene, atomic H is less prone to chemisorb, but the 10nm cavities are too large to prevent recombination as in fullerenes
  - ✓ However, these cavities are the proper size to host fullerenes cages, possibly encapsulated with T





Further ideas (more challenging)

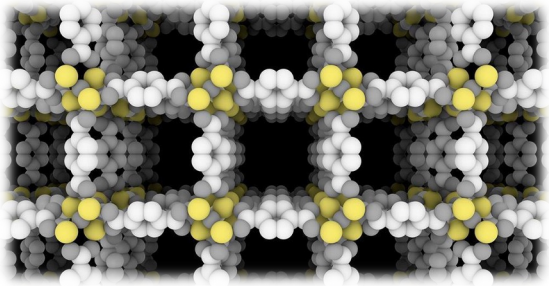




- ✓ Nanoporous graphenes
  - ✓ Can host Metal small clusters
  - ✓ These can split H_2 (e.g. Pt) or bind it with energies intermediate between physi and chemisorption (e.g Ti)

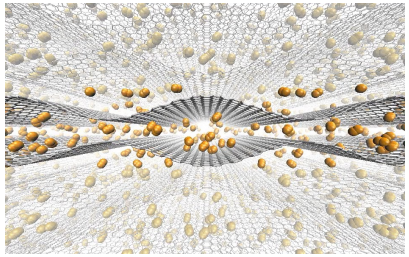
  This may bind loosely H and avoid dimerization

  Takahashi et al JPCC 2016



- ✓ Metal organic frameworks
  - ✓ Can host large quantities of gases
  - ✓ Can be built by chemical routes in a variety of different structures
  - ✓ Can be functionalized in a variety of different ways, and endowed also with magnetic properties

- ✓ pumping gases through multilayers (or nanotubes) Through coherent phonons



phonons can create flux of particles
Can be use to flux tritium through nanotubes
Or multilayers

Camiola et al 2Dmater 2015

Summary and conclusions

- ✓ Binding energies and hopping barriers of H on graphene related materials can be modulated in various ways: structure and dynamics, chemical or electric doping…
- ✓ Concavities as within small nanotubes or fullerene seems optimal conformations to keep the sliding profile very flat
- ✓ Simulations are in the course search for the optimal sizes and structures
- ✓ Further investigation on materials to obtain a similar effect on 2D surfaces are in the course
- ✓ Investigation on 3D graphene-derived different materials (multilayers or nanoporous) are in the course
- ✓ Combination with transition metal clusters and with external magnetic field may enhance the effects

There still much room for design and engineering!

Thank you for your attention

Theo

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