Ab Initio Modelling of Tritium Interaction with Graphene

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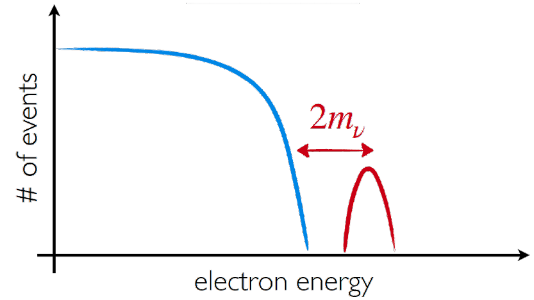
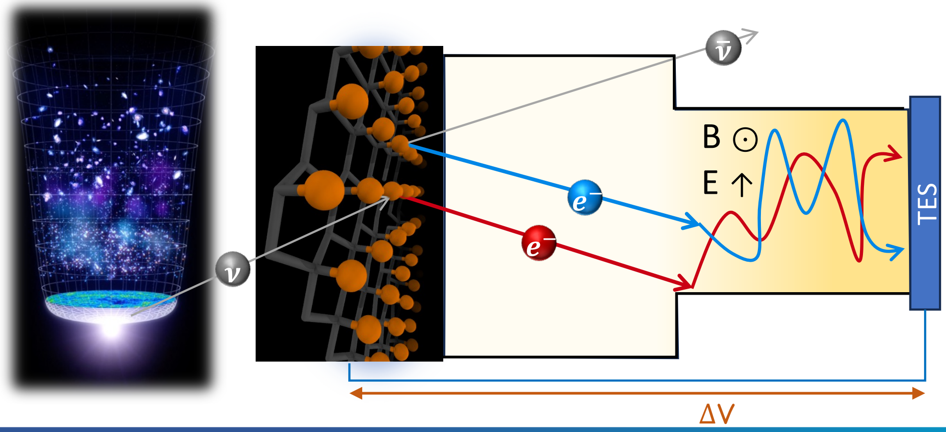
Outline

- **The goal:** design a material for tritium based neutrinos detection for
  - Neutrino mass from β-decay
  - Detection of relic neutrinos



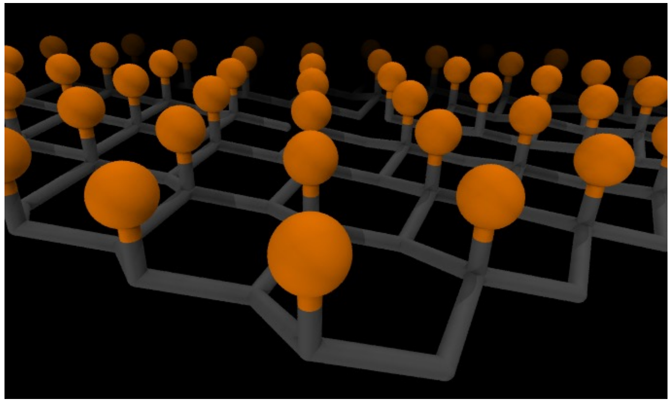
- **The needs:**
  - High events rate ⇒ **large concentration** of tritium
  - e^- efficient collection ⇒ **large exposure** of tritium
  - Filtering and control of ΔV ⇒ **good conductance** of the material
  - High resolution ⇒ **flat tritium potential** (loose binding)

- Why tritium @ **graphene**?
  - **High** tritium loading
  - **Huge** exposed surface
  - **Conductive**
  - **Tunable** interaction potential



Tritium @ graphene

→ **High** tritium loading
→ **Huge** exposed surface
→ **Conductive**
→ **Tunable** interaction potential



Is graphene the ideal material for the tritium based detector?

Not so fast…

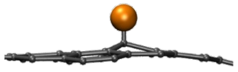
- **Limits of loading**, depending of the "kind" of graphene and conditions of tritiation
- **Limits in conduction**, depending on the amount and distribution of loaded tritium
- **T potential strongly** depending on local/global structure of graphene and magnetization state

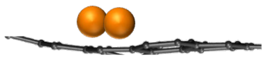
→ **Ab Initio Calculations** to evaluate these issues and optimize the material

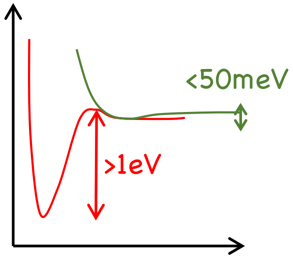
- The day (femtosecond) after…
  → Preliminary calculations of the **ultra-fast dynamics** just after the T→ He transformation

Tritium @ graphene: Loading

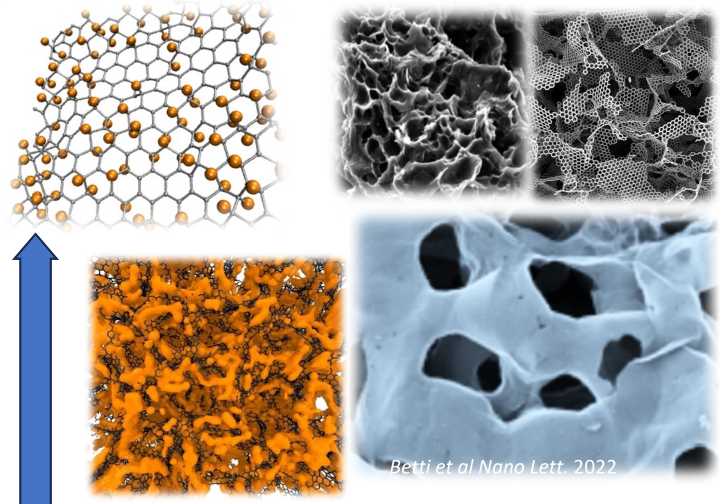
(H)T can be either chemisorbed
or physisorbed on graphene

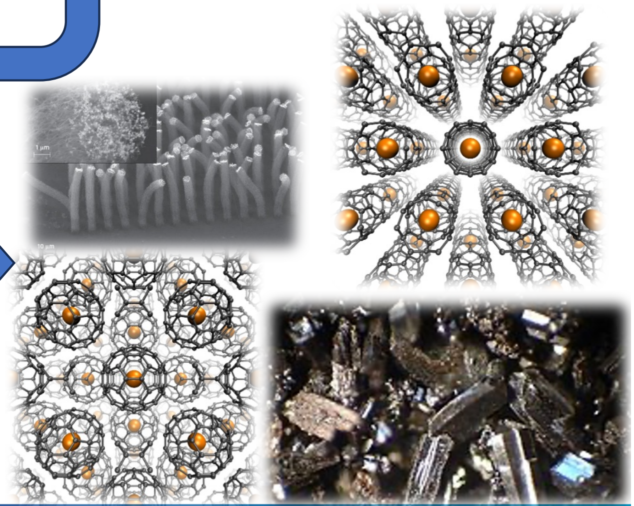






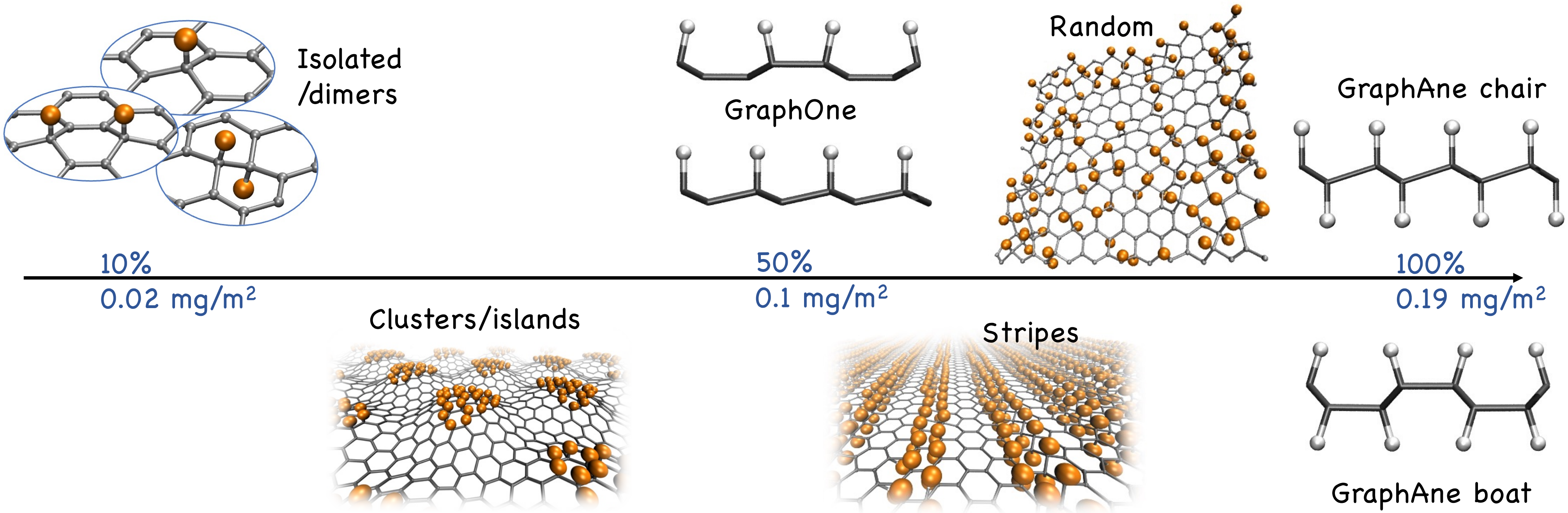
system	state	density
Vacuum, T_2	Molecular liquid	Up to 0.21 g/cm^3 = **200 kg/m^3**
Vacuum, T	Atomic gas/plasma	~0.5μg/cm^3 = **0.5 g/m^3**
T: graphene (rippled, nanoporous)	Chemisorbed (100% loading)	0.019 μg/cm^2 =**0.19mg/m^2** 0.1g/cm^3 = **100 kg/m^3**
T_2@ graphene (nanoporous)	Physisorbed (at 77K, molecular)	Up to 0.03 g/cm^3 = **30kg/m^3**
T@fullerite	encapsulated	Up to ~0.0036 g/cm^3 = 3.6 mg/cm^3 = **3.6 Kg/m^3**
T/T_2@nanotubes	encapsulated	Up to ~0.02g/cm^3 = 20 mg/cm^3= **20 Kg/m^3**





Chemisorbed tritium

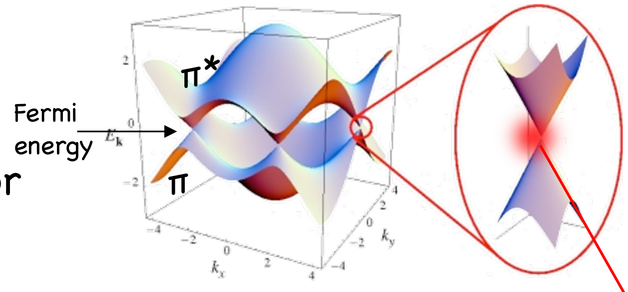
Chemisorption occurs in different configurations and loading levels, depending on the external conditions during tritiation (pressure, temperature, external fields, pristine state of graphene…)

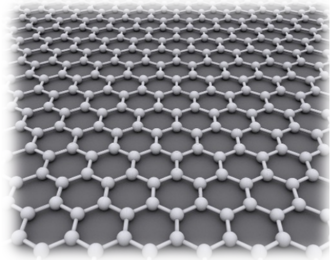


Conductivity, magnetic properties, tritium binding potential:
ALL DEPEND on the level and configuration of loading

Conductivity and band gap

Graphene: hexagonal 2D lattice of C atoms

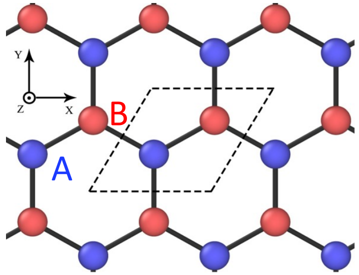


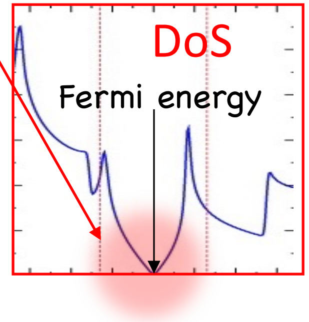


⇒ gap-less semiconductor, with linear dispersion for carriers π (electrons) and π* (holes)

⇒ pseudo-relativistic massless 2D Dirac equation for electrons and holes, at the non relativistic Fermi velocity $v_f = c/300$

$$-iv_f\vec{\sigma}\cdot\nabla\psi(\mathbf{r}) = E\psi(\mathbf{r})$$





(electrons and holes behave as particle/antiparticle)

- ✓ Wide-band flat optical response
- ✓ Exceptional carriers mobility (μ x 1000 of Cu)

But:

- ✗ The carriers density n is null at Fermi Level
- ✗ μ is lowered by scattering with defects
- ✗ The gap opens for any kind of defect

conductance $\sigma = e\mu(n_d)\, n(E_g(n_d))$

⇓

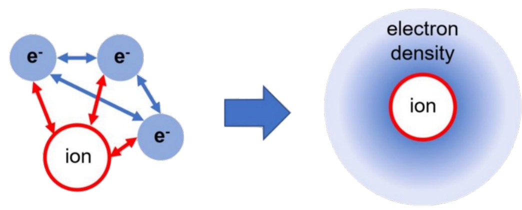
Tritiation reduces the conductance by reducing the mobility and opening the band gap

Density Functional Theory calculations

✓ **Density Functional Theory**: maps the many electron problem onto an independent electron problem within an effective potential dependin on the electron density

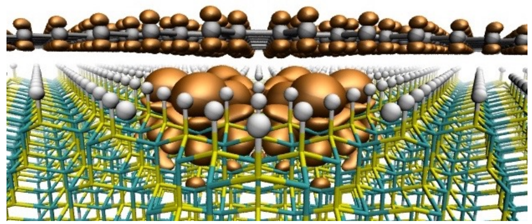
$$H = \left(\frac{-\hbar^2}{2m}\right)\nabla^2 + V_{eff}(r)$$

$$V_{eff} = V(r) + \int \frac{\rho(r')}{|r - r'|}\,dr' + \frac{\delta E_{xc}[\rho(r)]}{\delta\rho(r)}$$



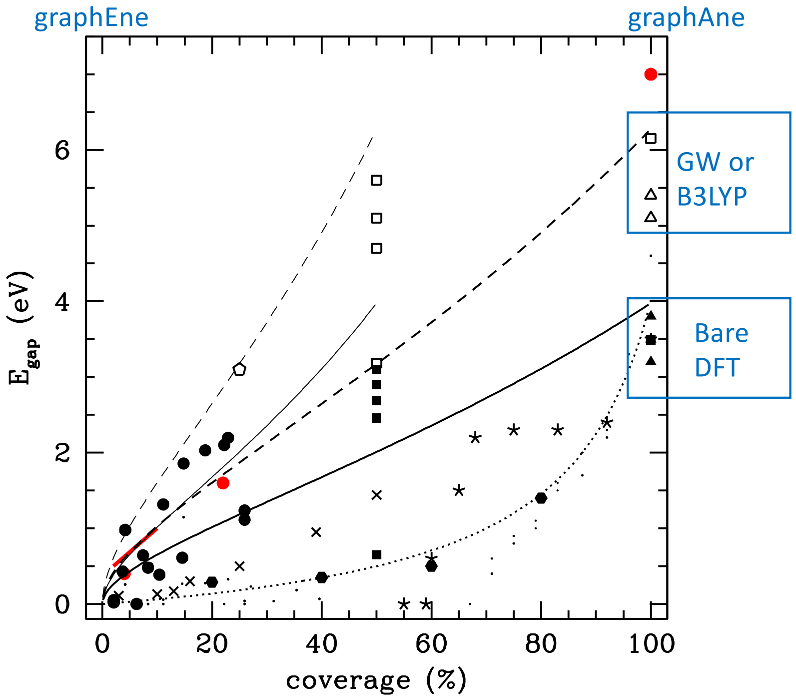
✓ **Outputs**

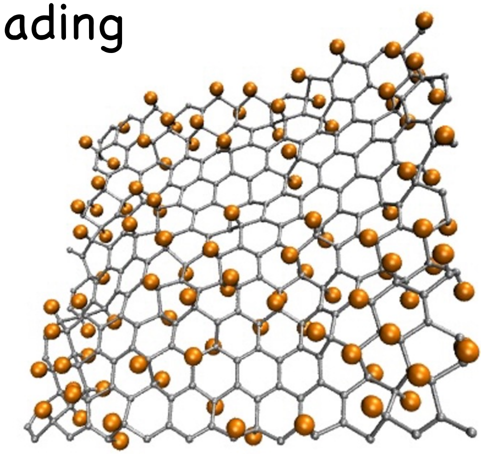
- → Electron density ρ(r) and **full electronic structure** → Bands&gaps, Fermi level, optical properties, transport…
- → Electron spin density ζ(r) → **magnetism**
- → Forces on nuclei → **vibrational properties** and **molecular dynamics**

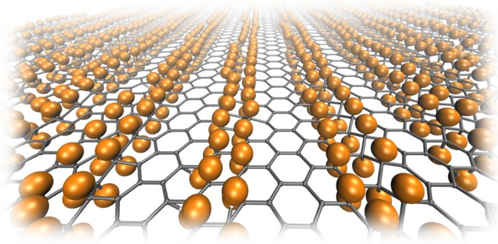


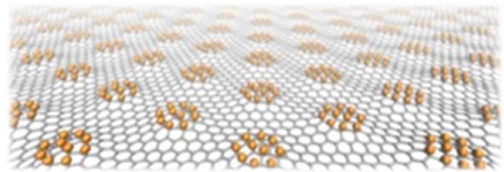
Gap vs coverage

Band gap generally decreases with T loading







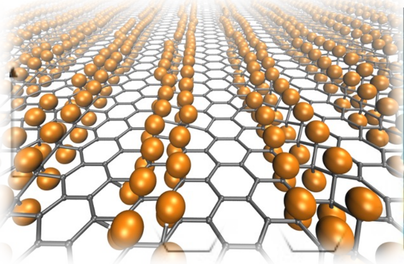


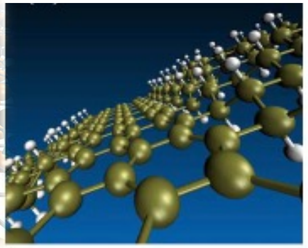
But data from calculations (and exp as well) are very messy mainly because of different hydrogenation modality

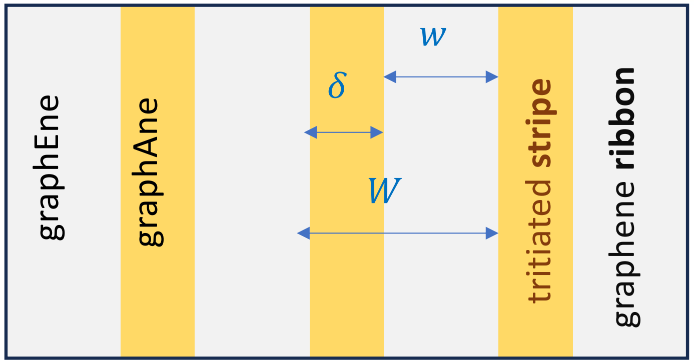
- one or two side
- clusters or random
- geometry of hydrogenation (strips, islands, …)

Gap vs coverage focusing on simple geometries: Tritiation per stripes

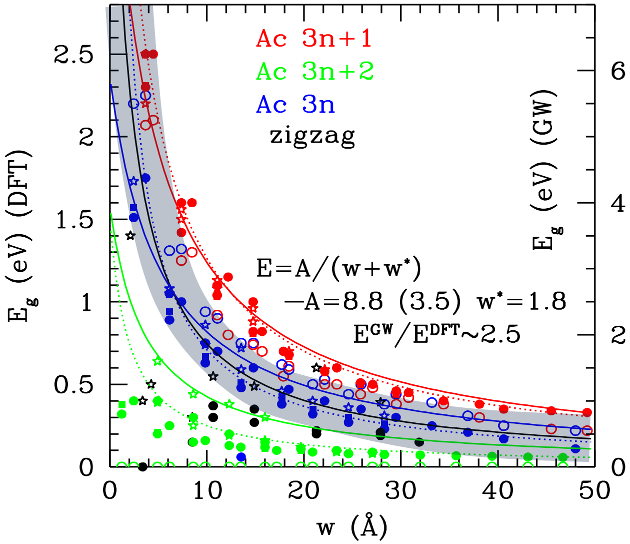
Nanoribbons sculpted in graphane (PRB 2011)



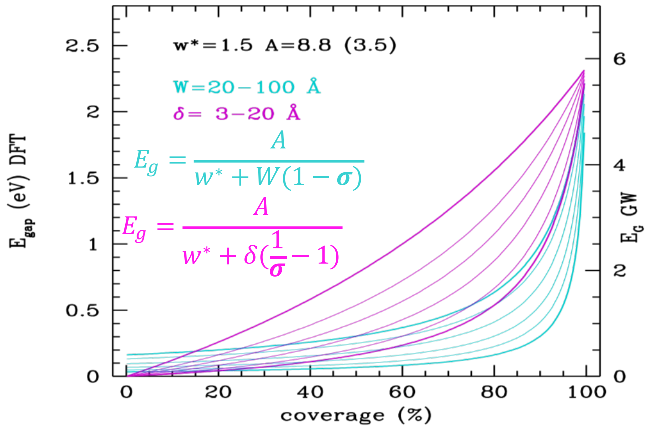


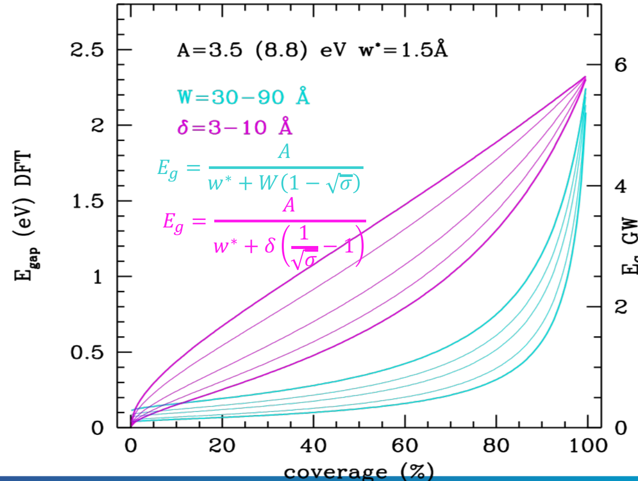


The gap-vs-stripes width dependence is similar to that of graphene nanoribbons…

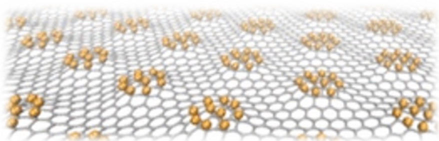


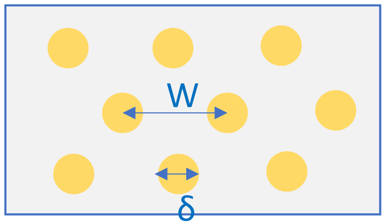
… leading to simple behavior of gap vs coverage





Tritiation per islands





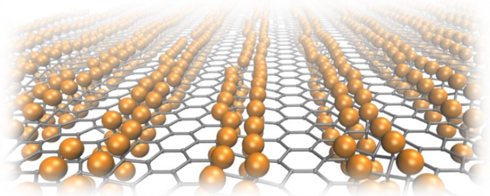
In the per-island tritiation a similar trend can be derived

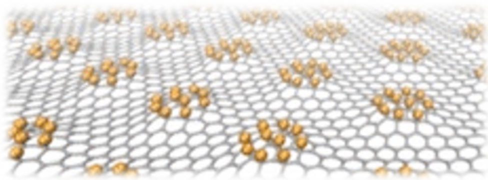
Gap vs coverage

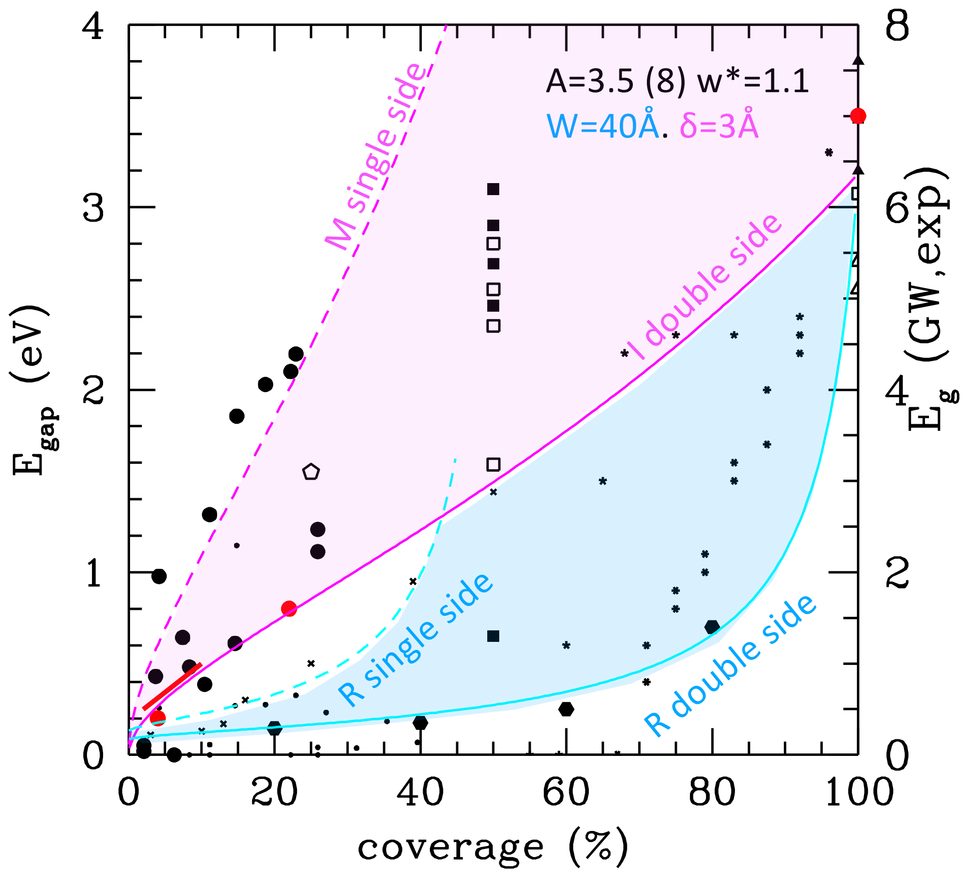
In summary, tritiation by stripes or islands:

✓ Explains the messy data

✓ Suggests ways to combine high coverage with conductivity
  → Double side coverage is better than single side
  → Ordered tritiation leaving connected tritium-free channels is better than disordered



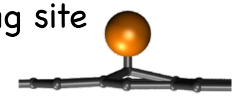


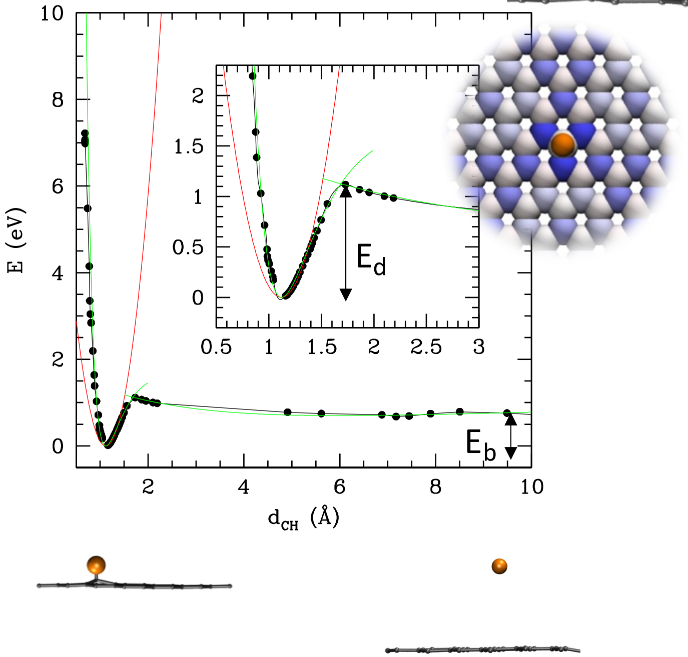


Stability and magnetic properties

Isolated tritium

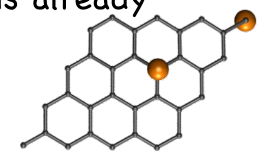
- ✓ $E_b \sim 0.7$, $E_d \sim 1.2$ eV
- ✓ Local lattice deformation (sp2 → sp3)
- ✓ Alternated sub-lattice magnetically polarized around the binding site

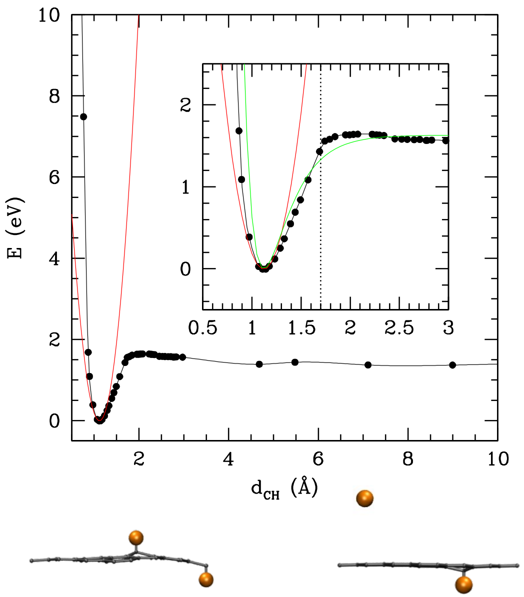




Nearby binding (~ 5Å)

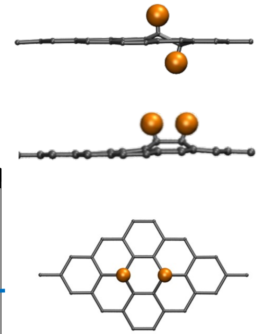
- ✓ $E_b \sim 1.3$, $E_d \sim 1.6$ eV
  larger stability because the lattice is already deformed

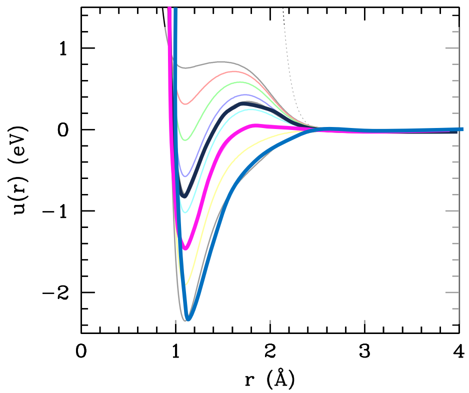




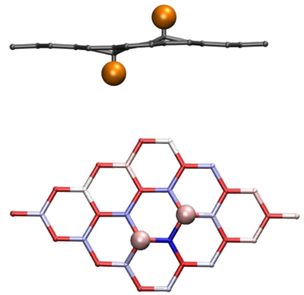
Dimers (~ 1.4-3 Å)

- ✓ The effect is amplified
  E_b , E_d up to 2.5eV





- ✓ Additionally, in the para-dimer the same sub-lattice sites are occupied
  → the magnetization is amplified, but the stability is lowered

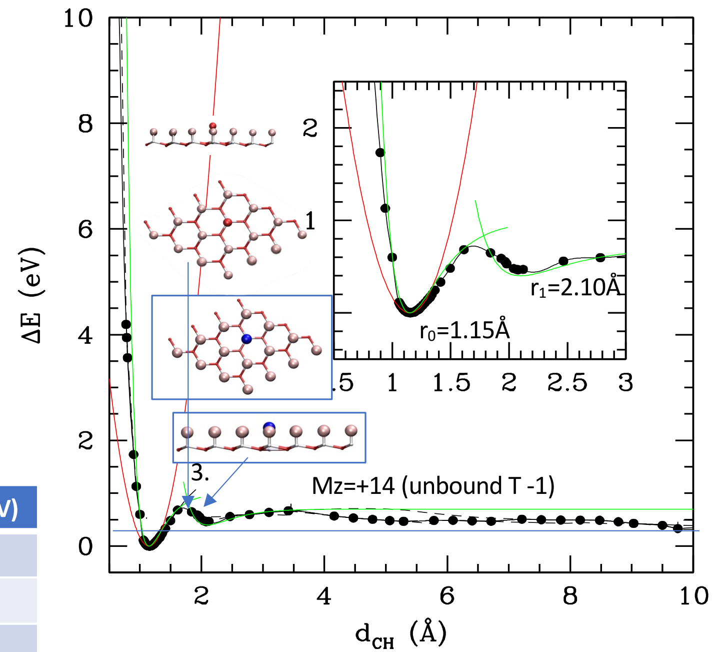


Stability and magnetic properties

- ✓ **GraphOne** chair conformation (50%) is completely magnetically polarized

⇒ Favored ($\sim \mu_B B$ for each unit cell) in magnetic fields

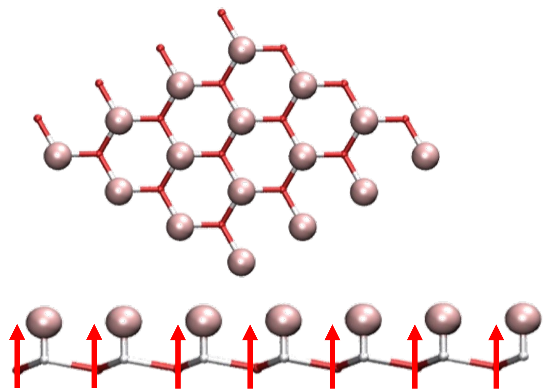
- ✓ The binding is destabilized $E_b \sim 0.4$, $E_d \sim 0.7$ eV
- ✓ Additional barriers spin flip barriers



Summary table

E_b spans 4 eV range

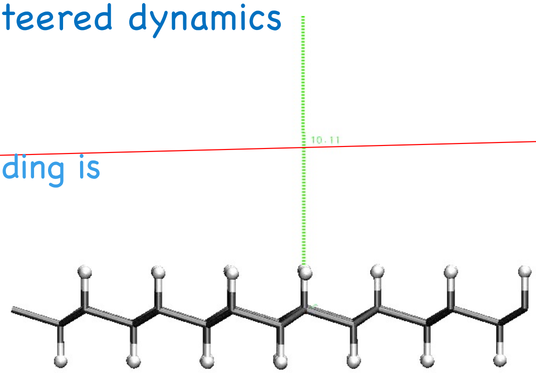
Cov (%)	Conf	Mag	E_d (eV)	E_a (eV)	E_b (eV)
100	Chair	0	4.35-4.38	0-0.3	**4.35**
100	Chair	2	1.5	1.0	0.5
50	chair	16	0.71	0.37	**0.34**
6	2H trans, d=5.7,	0	1.64	0.33	1.31
3	Isolated	2	1.18	0.48	**0.7**
6	Dimer **orto trans**	0	2.55	0.19	**2.36**
6	Dimer **meta trans**	2	0.89	0.29	0.60
6	Dimer **para trans**	0	1.93	0.36	1.57
6	Dimer **orto cis**	0	2.5	0.7	**1.79**
6	Dimer **meta cis**	2	0.92	0.27	0.65
6	Dimer **para cis**	0	2.07	0.32	1.75

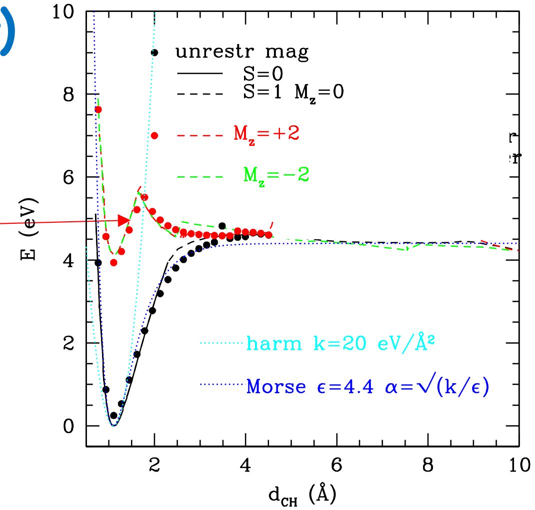


Exploring 3D Binding potential of T in 100% graphene (chair)

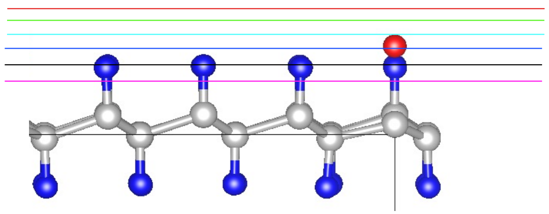
- ✓ $E_b \sim E_d \sim 4.4$ eV
- ✓ The bound state is non magnetic
- ✓ spin singlet-triplet transition occurs during detachment
- ✓ If the system is forced in the magnetized state, the binding is destabilized, but a barrier of ~1.5eV appears

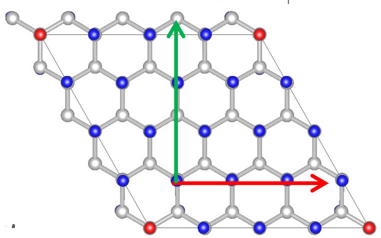
Steered dynamics





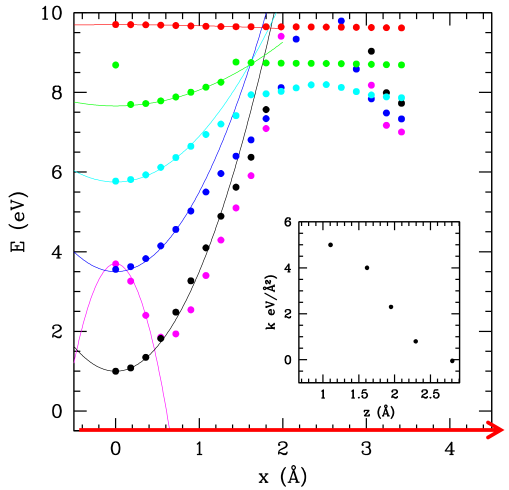
- ✓ The lateral potential of T was explored steering it on x y planes at increasing z

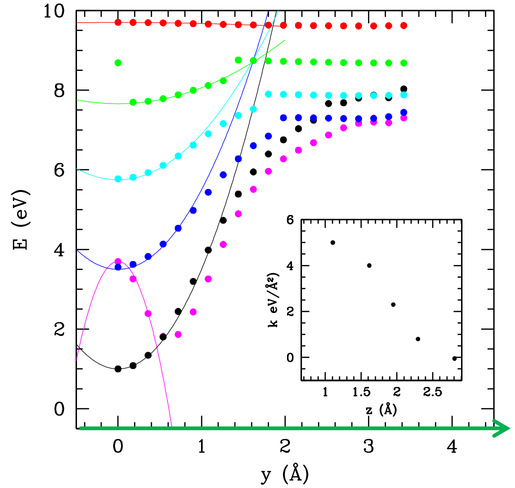




→ Complete mapping of the potential for evaluating solid state effects on the resolution (→A Esposito et al)

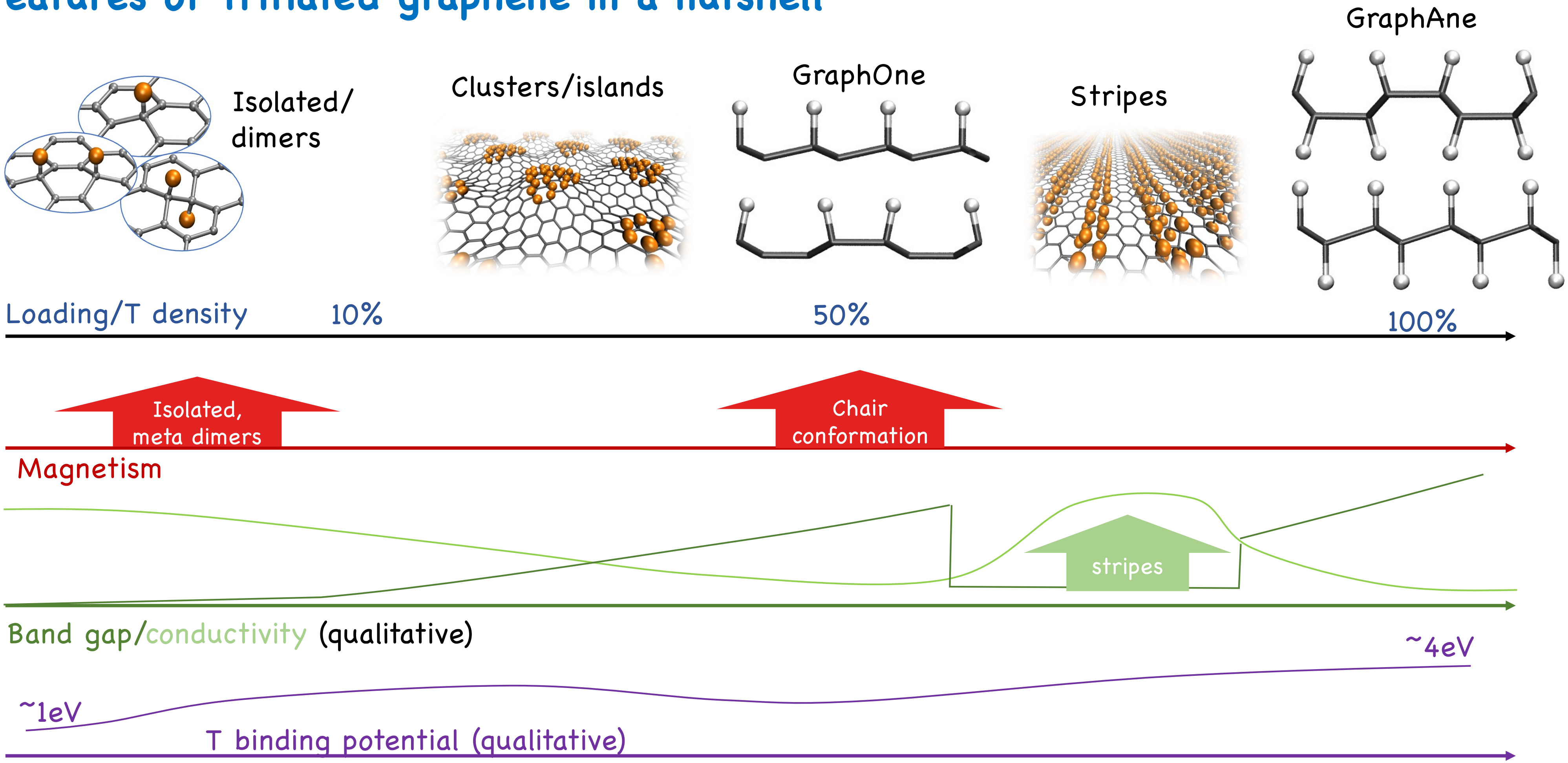
→ The lateral potential stiffness decreases as the bond is elongated





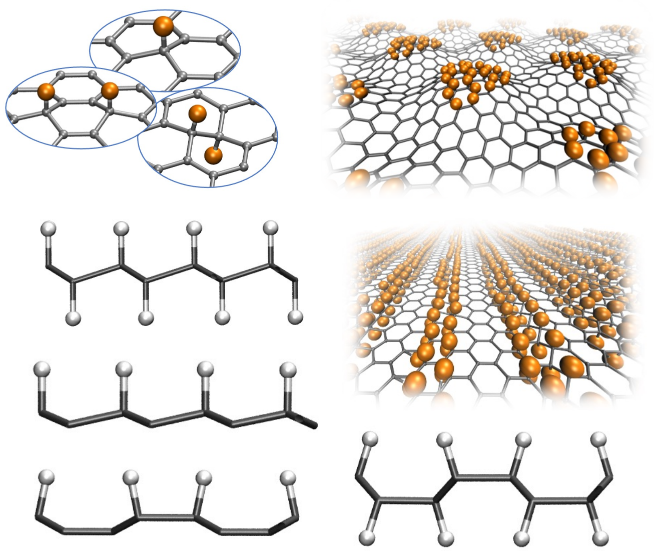
El fields could modulate the potential and control the "solid state" effects on resolution

Features of tritiated graphene in a nutshell

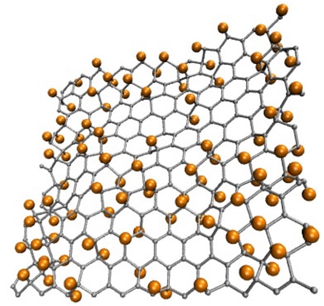


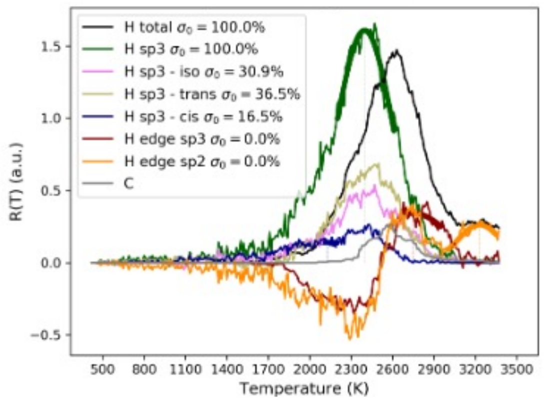
Features of tritiated graphene: the realistic case

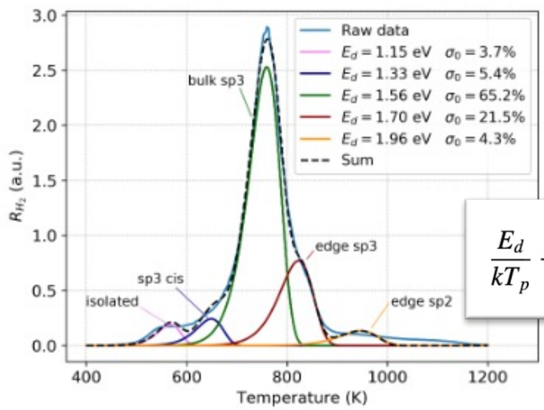
"Regular" structures…



… but the real one are more like this







Multi-methodological analysis of hydrogen desorption from graphene

Francesco Delfino[a], Carles Ros[b], Sidney M. Palardonio[b], Nina M. Carretero[c], Sebastián Murcia-López[c], Juan Ramón Morante[c], Jordi Martorell[b,d], Zacharias Fthenakis[a], Mauro Francesco Sgroi[e], Valentina Tozzini[a,f], Luca Bellucci[a,*]

- ✓ The real structures properties will be an average of the regular ones, weighted by their occurrence
- ✓ Desorption energies were evaluated by Programmed thermal desorption expt and Classical Molecular dynamics simulations
- ✓ In particular, on a ~65% double side loaded sheet: E_d= 1-2eV, compatible with a combination of dimers and small clusters

$$\frac{E_d}{kT_p} + \ln\left(\frac{E_d}{kT_p}\right) = \ln\left(\frac{\nu T_p}{\beta}\right)$$

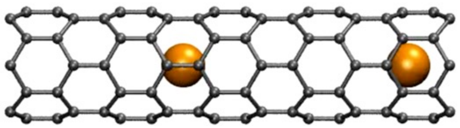
(Simulations on different configurations are in the course)

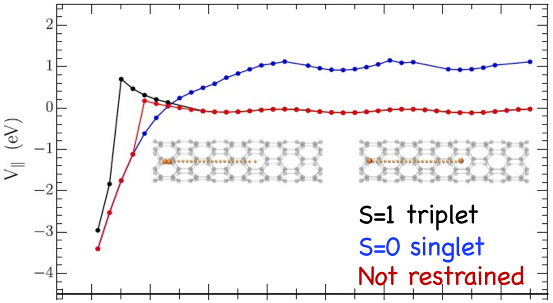
LESGO

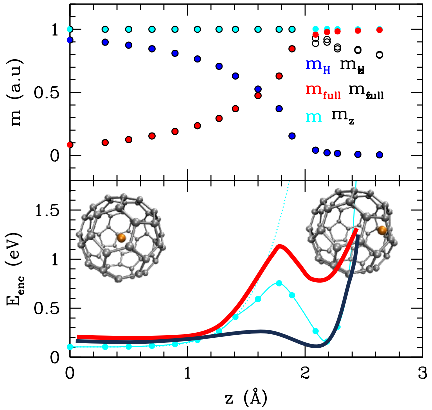
Luca Bellucci et al

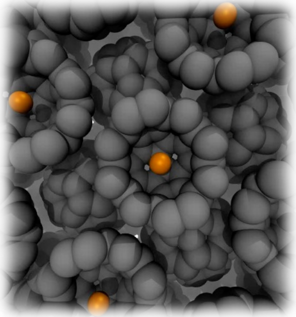
Loosely bound T for neutrino capture

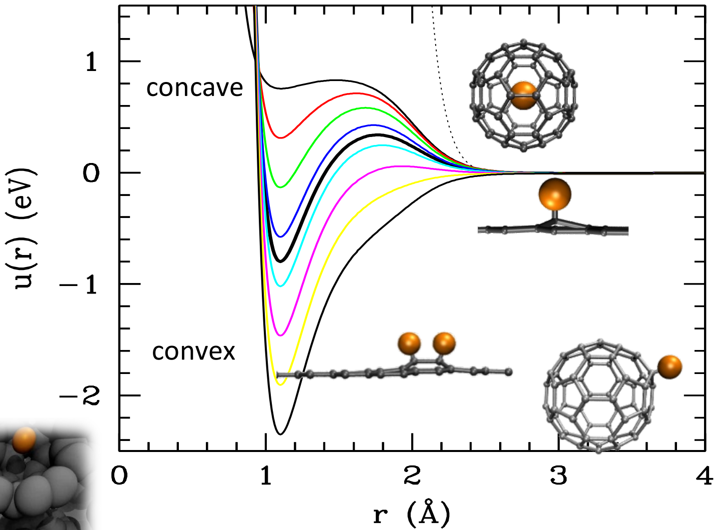
- ✓ The dependence of the T binding potential on the local curvature of the sheet is very strong
- ✓ encapsulated T within nanotubes and fullerenes is very loosely bound
- ✓ Flat potential along the nano tube axis



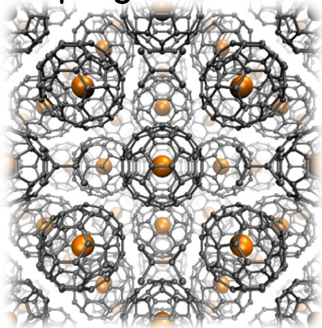


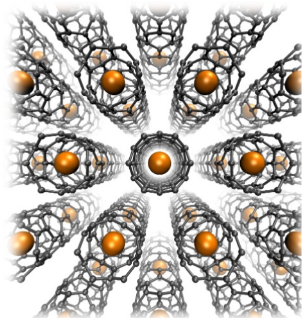






- ✓ The potential in the center of fullerene is also flat and magnetization dependent (work in progress)





- ✓ Relatively high densities in compact forms (fullerite and nantubes bundles)

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PRB 2022 PTOLEMY colaboration

Heisenberg's uncertainty principle in the PTOLEMY project: A theory update

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Possible material for relic neutrinos detection?

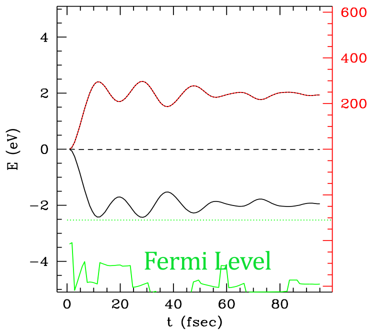
Dynamics after the T decay or ν capture

(Very preliminar)

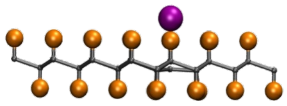
system	charge	Mag μ_B/cell M, M_z	$\Delta E = E_0 - E_{fin}$ (eV)
1. isolated	+1	0	-2.72
2. grounded	neutral	1	-5.18

What happens next? Just after the T→ He transformation

1. Isolated system: after the β release the system is iso-electronic with graphane and magnetically neutral but charged due to the He^+



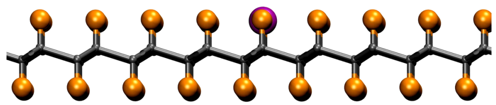
He is released as neutral atom, leaving the system charged with 1 missing electron



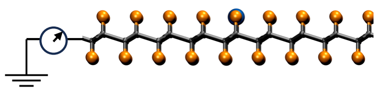
Charge 1+

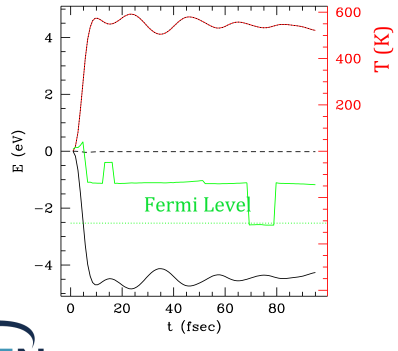
2.7 eV energy gain upon release

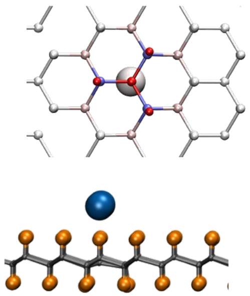
There is however a weakly vdW bound state



2. Grounded system: after the β release the system draws one electron and becomes neutral, but magnetized. The system releases He with double energy than in the isolated case, though a very weakly vdW bound state still exist





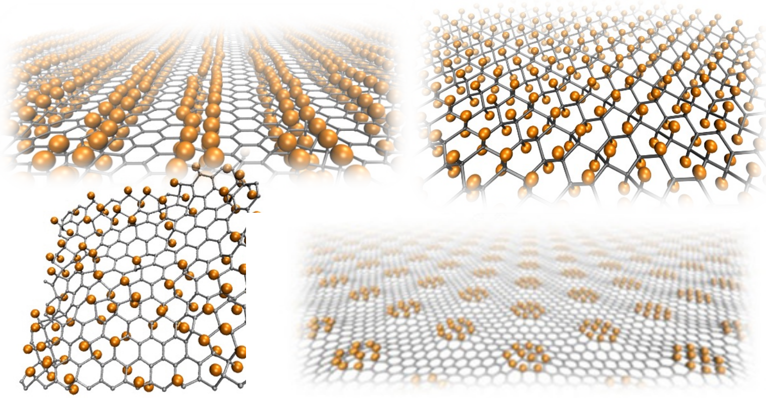


In both cases, very specific vibrational modes and electric signals are activated upon He release

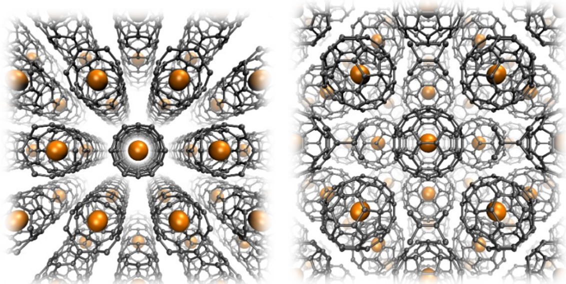
Could these vibrations and currents be used for detection?

Conclusions

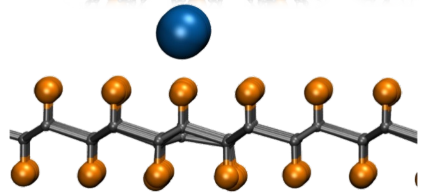
- ✓ We explored by ab initio calculations and simulations different conformations of T chemisorbed on graphene
  - ✓ Increasing loading generally opens the gap but there are favorable conformation for conduction with high loading
  - ✓ The system is magnetic in very specific conformations (alternate occupation)
  - ✓ The T binding potential depends very much on the configuration and loading
  - ✓ Random conformations are easier to obtain, but less favorable for detection purposes



- ✓ Encapsulated graphene results in a flat potential for T



- ✓ After the T->He transition
  - ✓ He tends to be released
  - ✓ Specific electric and vibrational signals are generated



Thank you for your attention

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