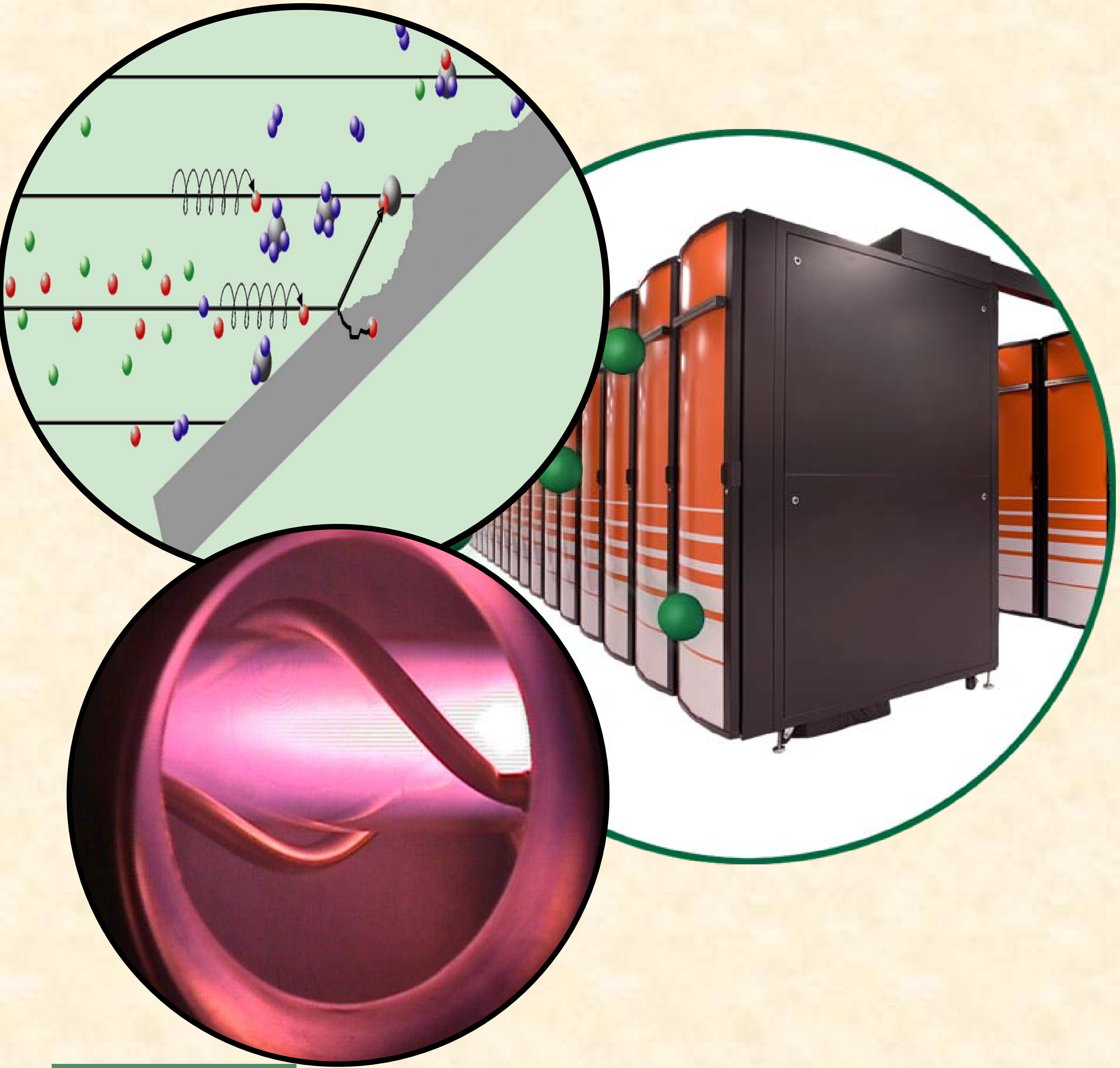
Computer Simulations of Plasma-Carbon and Lithiated Carbon Interface



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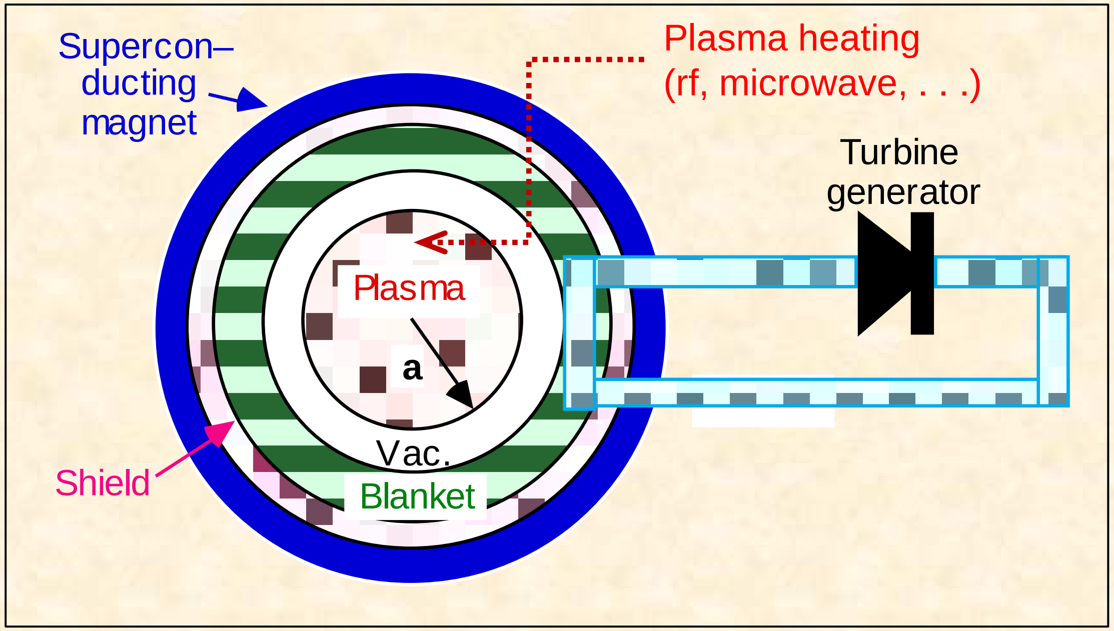
ORNL LDRD program

Poster at PFMC-13/FEMaS-1, May 2011, Rosenheim

All energy from D-T fusion reactions passes through first wall

- Flux of (particles + heat + 14 MeV neutrons) ~10 MW/m^2

Schematic magnetic fusion reactor



Why PMI important?

Why lithium in the diveror?
First wall?

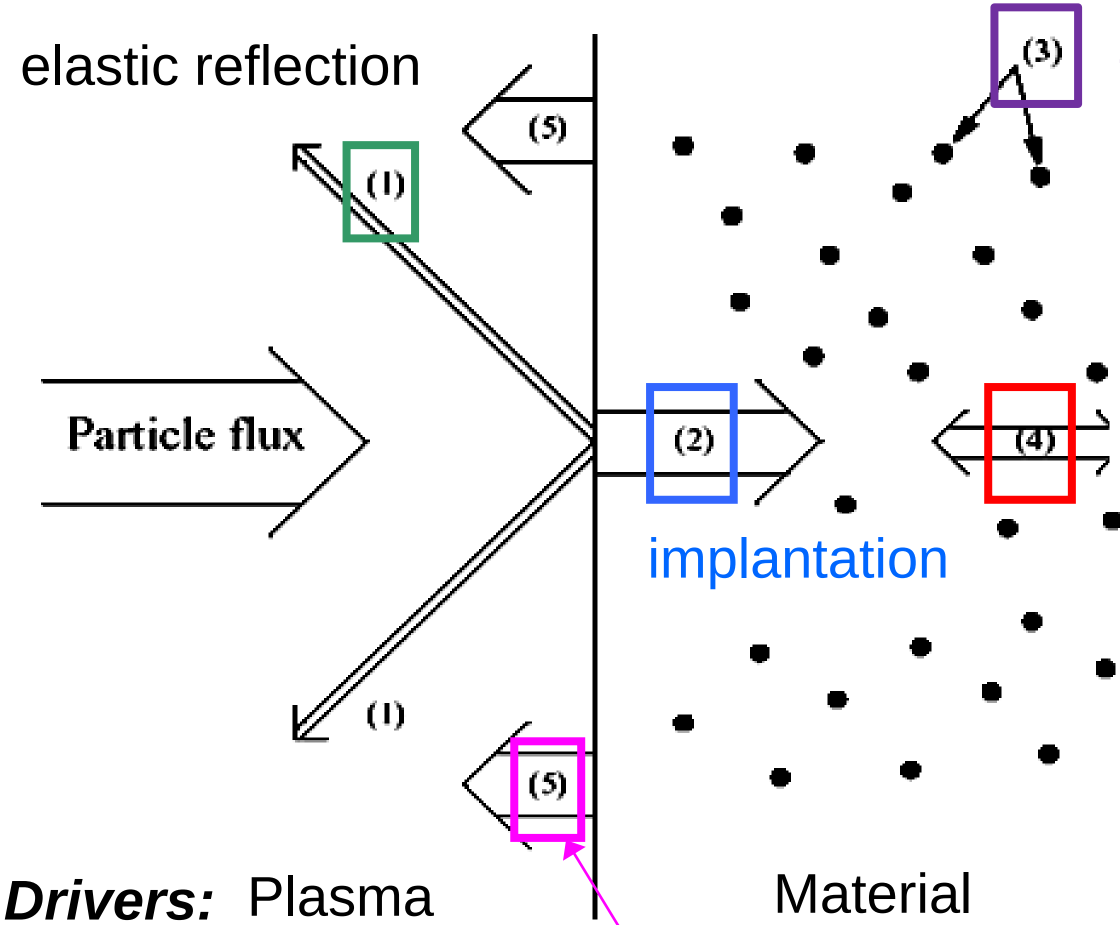
Unlike nuclear fission where energy is volume-distributed

A FUSION REACTOR IMPLIES MANY INTERFACES
BETWEEN THE PLASMA AND MATERIALS

Key role of PMI in fusion research well recognized in US:
FESAC 2007, RENEw Workshops, OFES priorities,….

PMI has many fundamental processes & synergies

When an ion or neutral arrives at a surface it undergoes a series of elastic and inelastic collisions with the atoms of the solid.



elastic reflection

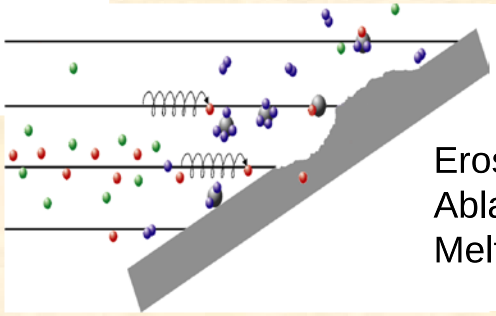
trapping/detrapping
retention

diffusion, permeation

implantation

Material

Damage Effects:
Vacancies, bubbles, blisters, dislocations, voids, neutrons?



Re-deposition
Co-deposition

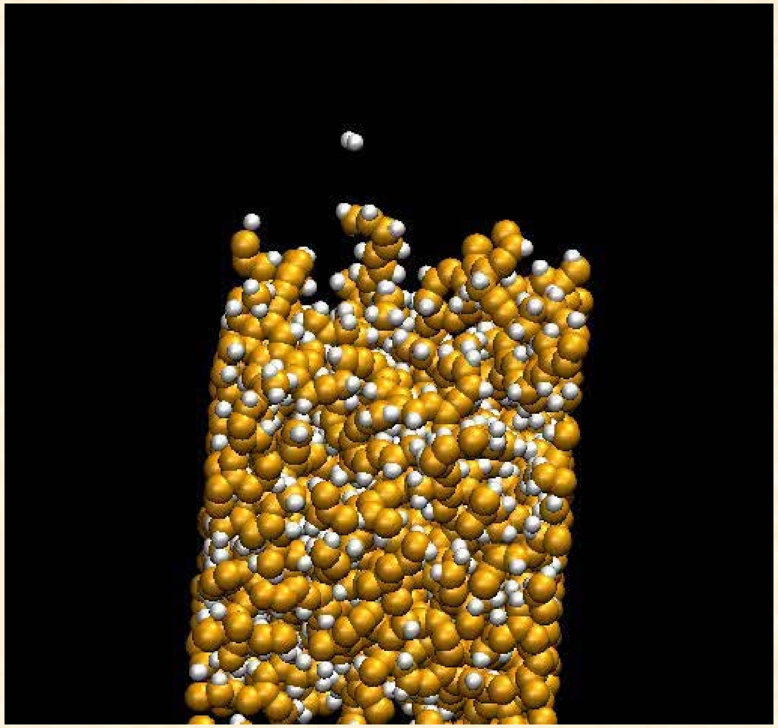
Erosion
Ablation
Melting (metals)

Drivers: Plasma
Multi -T, -n, -species,
plasma irradiation,
neutrons
sheath acceleration

re-emission &
sputtering &
chemistry

Give rise to synergistic effects

What does flux of 10^{25} particles/m^2s mean (ITER) for a typical atomistic (MD) simulation?



At a box of surface of 3 nm lateral dim?
a few thousands atoms (carbon)

The flux is 0.01 particle/nm^2ns
1) 1 particle at the interface surface of the cell each 100 ps.

But for deuterium with impact energy less then 100 eV: Penetration is less than 2 nm, typical sputtering process takes up to 50 ps
Each impact independent, uncorrelated!

In effect interaction of an impact particle with nanosize macromolecule Functionalizes it!
News is that each particle will change the surface for the subsequent impact!

Much was learned from carbon surfaces:

- PMI extremely difficult interfacial problem (Material mixing create SURFACE entity; its scale depends on impact energy: for sub-100eV => nm-ns scales

- PMI science can be built from bottom-up recognizing its multiscale character and building form shortest time/spatial scales (fs/Angstrom) up

- Theory&modeling of PMI has to be validated by experiment (and v.v.)

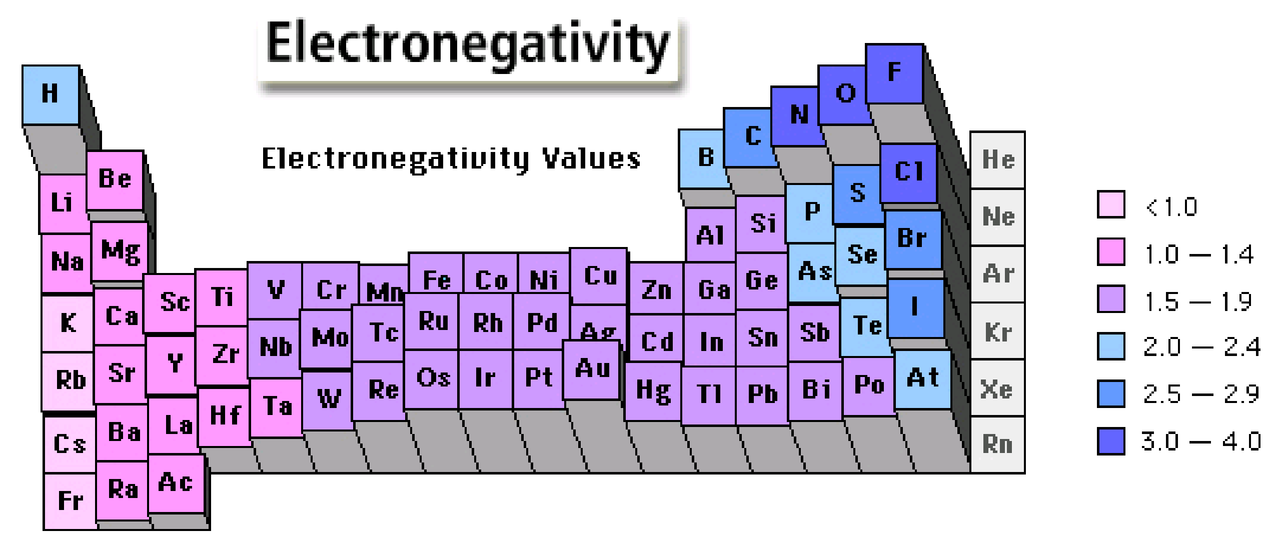
- Irradiation create dynamical surface, changing interface, cumulative bombardment is the key for remarkable agreement with experiment

- Surface responds to synergy in plasma irradiation (angles, energies, particles), NOT following linear superposition principle; NEED plasma irradiation modeling and experiments; dedicated plasma devices a must

- Possible inclusion polarization effects in potentials (Li-C-H, Be-C-H,…) and extension to qunatum0classical approaches an essential step forward ???? : ooops – here is the problem!!!!

Lithium dynamics: Problem to study theoretically because Li polarizing features when interacting with other elements

Electronegativity is chemical property of an element defining its tendency to attract electrons: Li has it exceptionally low in comparison to H , C, O, Mo, W.

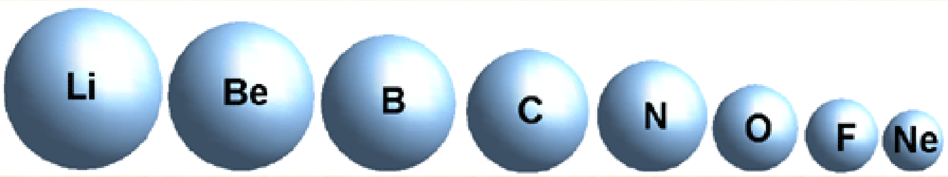


Consequence: Bonding between Li and other atoms covalent and polar;

Long-range nonbonding:

Coulomb :1/R

Lennard-Jones :$1/R^6$, $1/R^{12}$



Electronegativity and size of atoms related!

Goals: Validate experiment, understand

- Chemistry and sputtering/reflection dynamics in lithiated carbon material, bombarded by slow deuterium atoms is studied.
- The objectives of this research are two-fold:

1) To develop the realistic methods for computational simulation of the Li-C-H, validated by experiments.
2) To explain the specifics of the chemistry of deuterium bonding in lithiated carbon. Experiments from Purdue indicate that bonded C-Li-O? sites are preferable for H bonding: **Lithium will always bind with oxygen (when present) and carbon, and incoming deuterium will then interact preferably with existing Li-O and Li-C structures.**

Quaternary system Li-C-O-H

Li-C , Li-H, Li-O are of very different electronegativities: **long range interactions**

$$E_{tot} = E_{bound} + E_{nobound}$$

$$E_{nobound} = E_{coul} + E_{vdW}$$

$$E_{coul} = \sum_{i} \sum_{j>i} \frac{q_i q_j}{r_{ij}}$$

$$E_{vdW} = \sum_{i} \sum_{j>i} D_{ij} [(\frac{\sigma_{ij}}{r_{ij}})^{12} - 2(\frac{\sigma_{ij}}{r_{ij}})^{6}]$$

Charging changes at each simulation step: Quantum-Classical Molecular dynamics a must

Electrons: Quantum mechanically at each step, resulting in charges and forces
Nuclei: Classical motion

Employed the **Self-Consistent-Charge Density-Functional Tight-Binding (SCC-DFTB)** method (developed, by Bremen Center for Computational Materials Science, Germany)
It is **an approximation to the DFT method** in which only valence orbitals are considered, and difficult Integrals parameterized in advance.
In comparison to other TB methods: Improved self-consistent interaction of electronic charges

This enables computational efficiency about 1,000 time faster than ab initio quantum methods (and about 1,000 time slower than Classical Molecular Dynamics)

Parameterization for Li-C-H-O provided by K. Morokuma group (Kyoto-ORNL-Emory)

[1] M. Elstner, D. Porezag, G. Jungnickel, et al, Phys. Rev. B 58, 7260 (1998)
[2] G. Zheng, M. Lundberg, J. Jakowski, at al, Int. J. Quantum Chem. 109, 1841 (2007).

Quantum-mechanical simulation of deuterium impact to lithiated and oxidated carbon surface

Employed the **Self-Consistent-Charge Density-Functional Tight-Binding (SCC-DFTB)** method (developed, by Bremen Center for Computational Materials Science, Germany)

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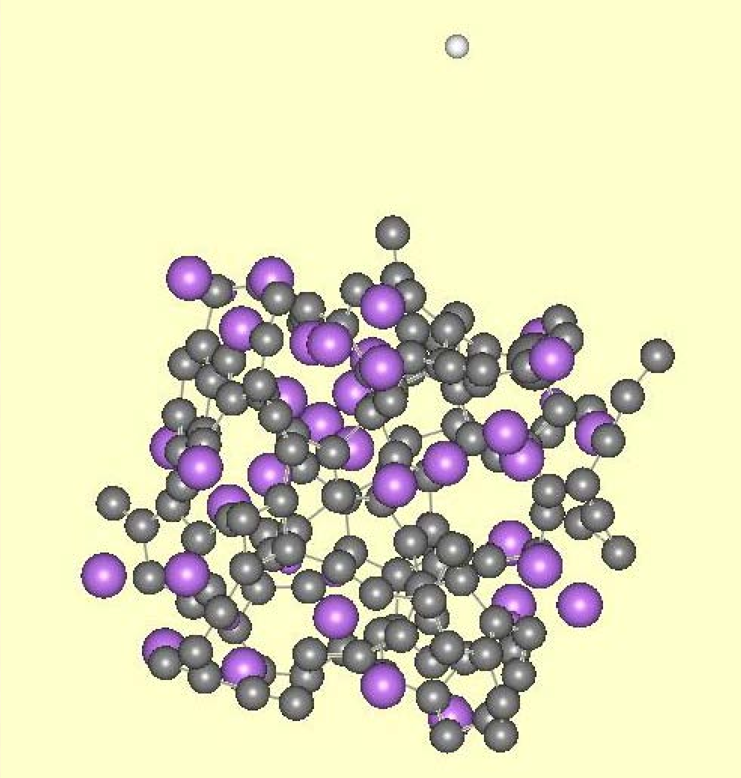
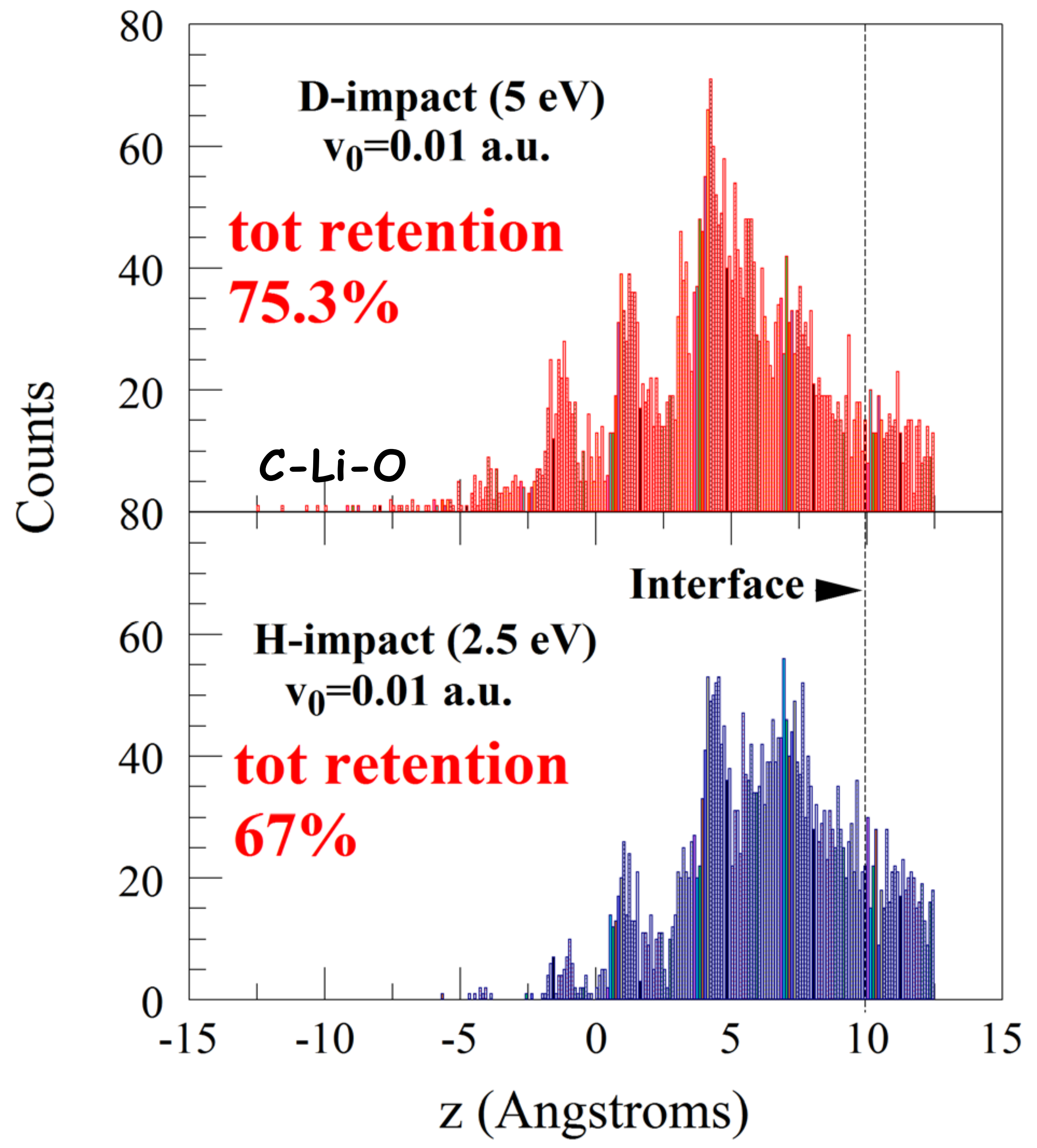


- Cell of **a few hunreds of atoms** of lithiated and oxidated amorphous carbon (~30% of Li, < 10% of O), at **300K**
- By random seed of Li and O in **amorphous carbon** and **energy minimization**, followed by thermalization
- bombarded by **5 eV D** atoms and **2.5 eV H**,
- **Perpendicularly** to the shell interface
- 5004 **random trajectories**

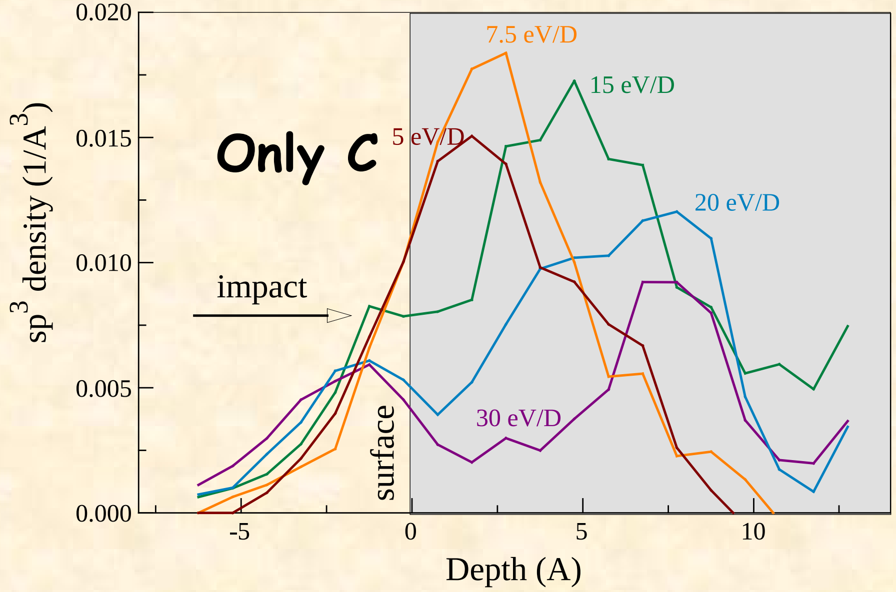
The cell swelled during the structure optimization

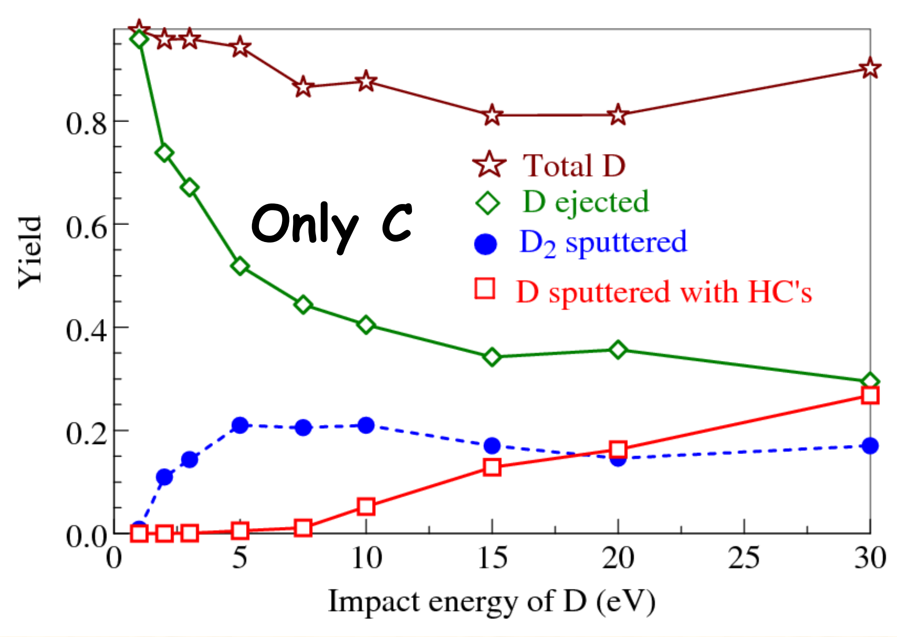
5004 processors of Cray XT5 (Jaguar, Kraken),
Time step 0.2-1fs, 24 hours: 200-400 fs.
One run over 120,000 CPU hours (TeraGrid project)

Penetration of D and H into C-Li-O easier than into C

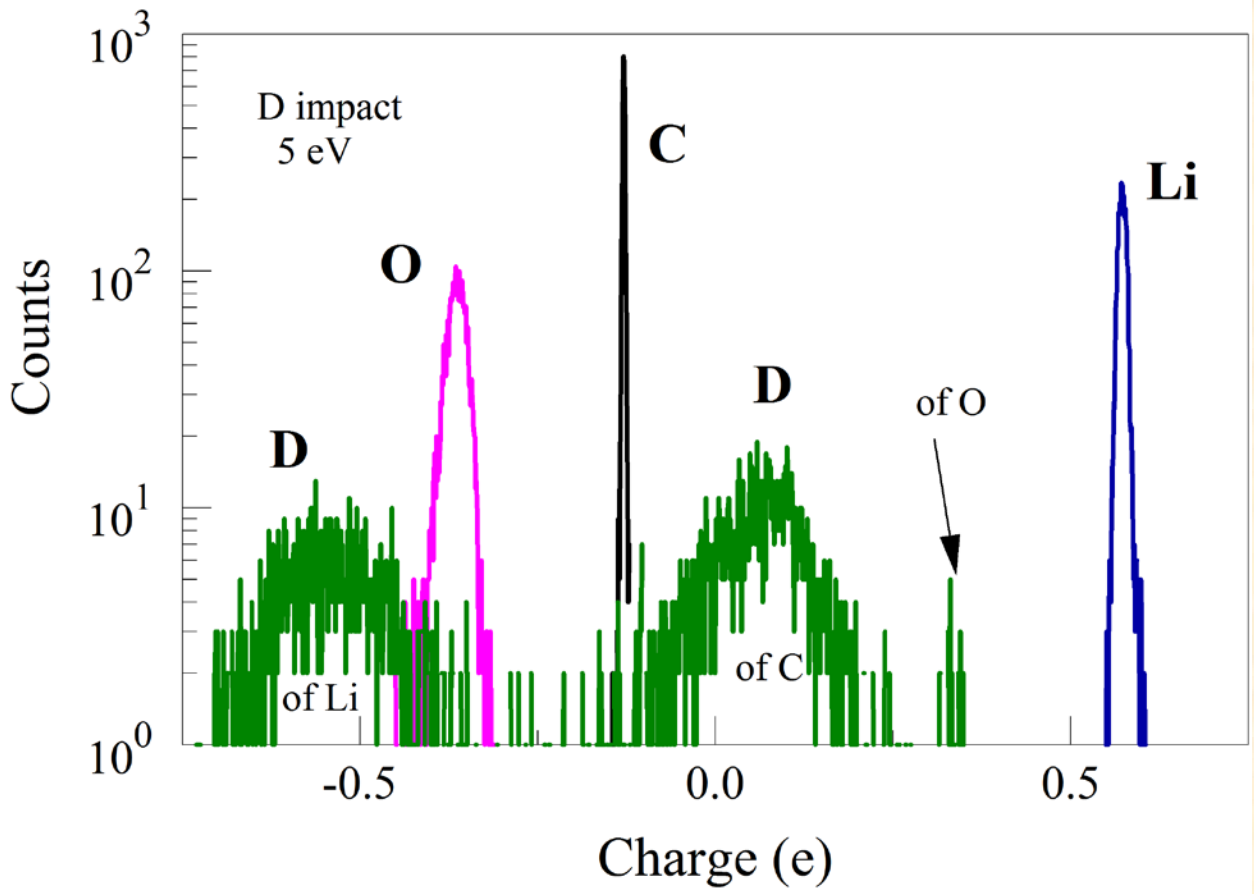

tot retention 75.3%

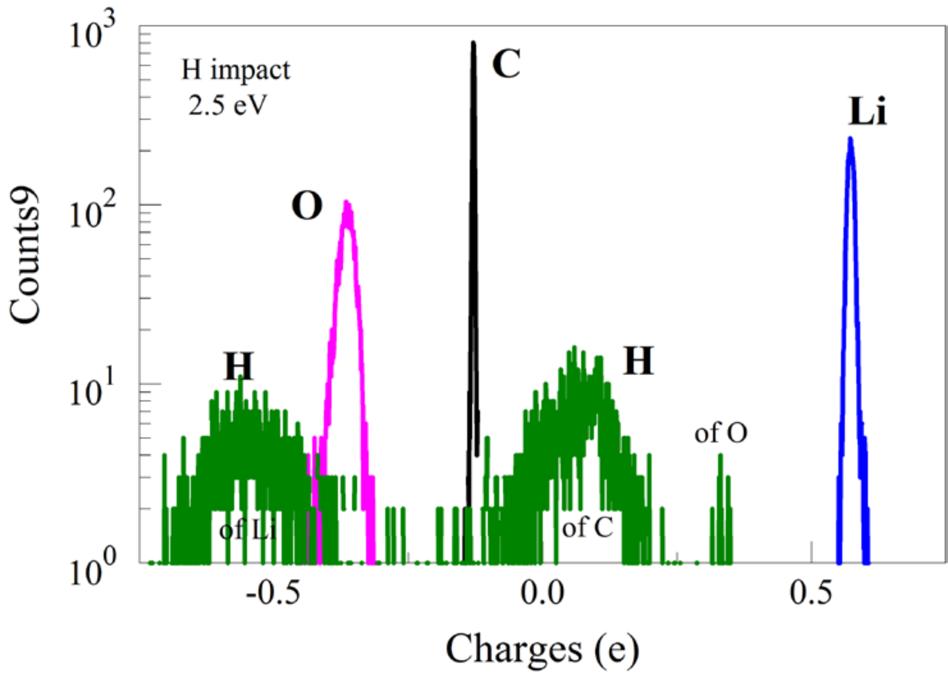
tot retention 67%


Only C


Only C

Final distribution of charges for retained D (H) atoms reveals the dominant chemistry

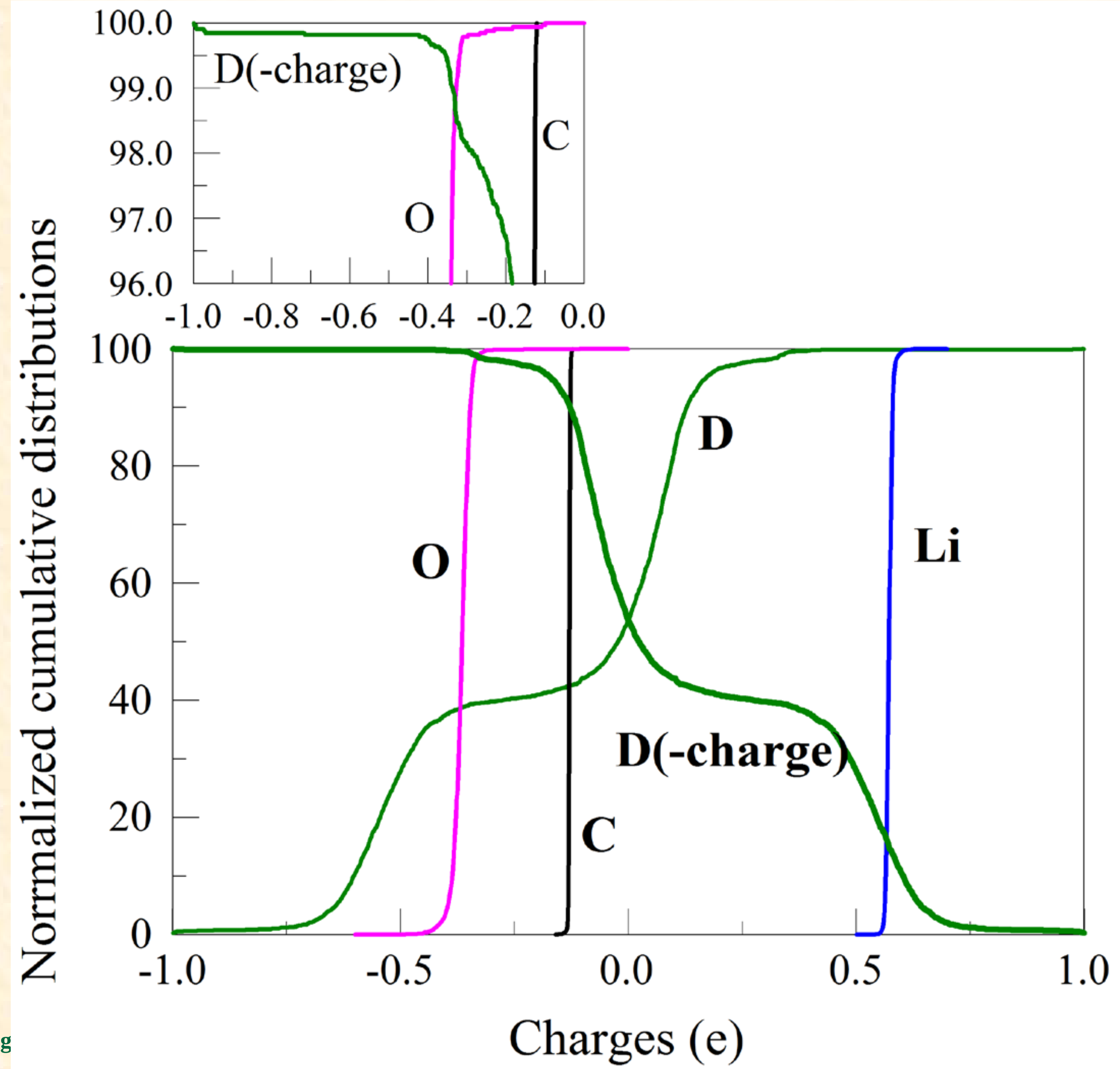




No isotope effect for chemistry
(also found in D on C-H)

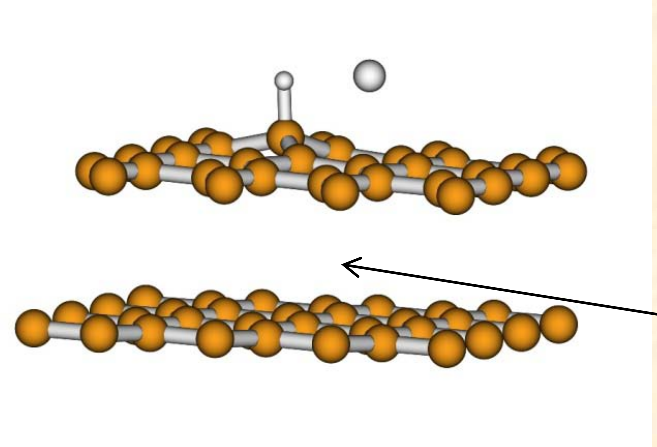
Large percentage of impact D (40%) prefer closeness of Li to settle down

Not much attention to O (already bonded to Li)



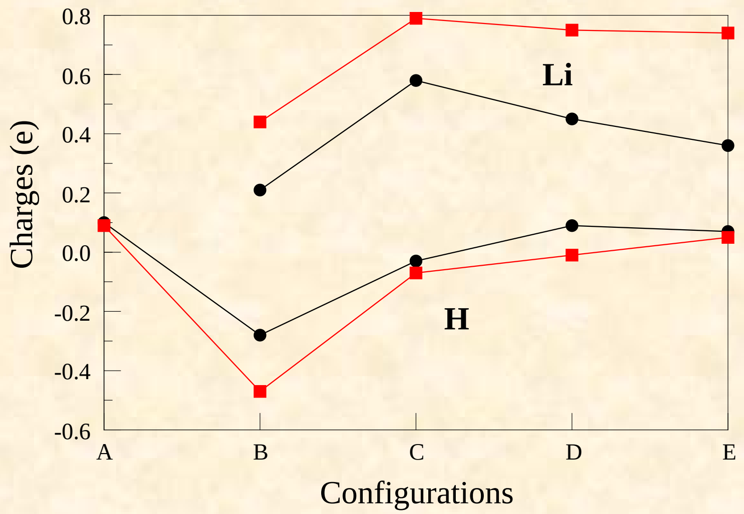
Quantum-mechanical, PWDFT “static” calculations finger -point in the same direction, Qualitatively benchmark the DFTB findings:

- **graphene bilayer with Li and H on the surface**



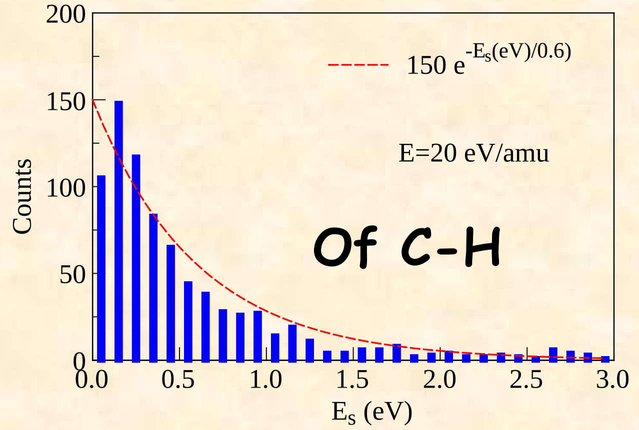
When a lithium atom is co-adsorbed on surface bonding energy of H grows up to values ranging from -2.2 to -2.5 eV, with decreasing the Li-H distance. (compared with -1.9 eV for pure graphite)

The bonding E enhancement is also observed when Li is sandwiched 1 layer below the surface layer (**conf. E)**

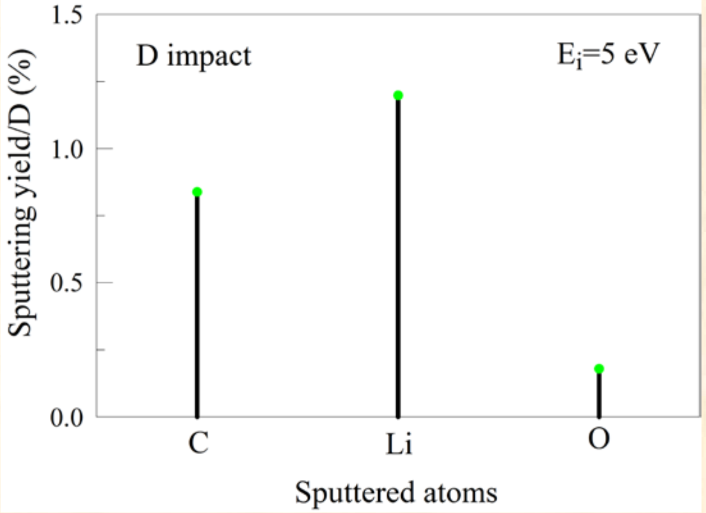


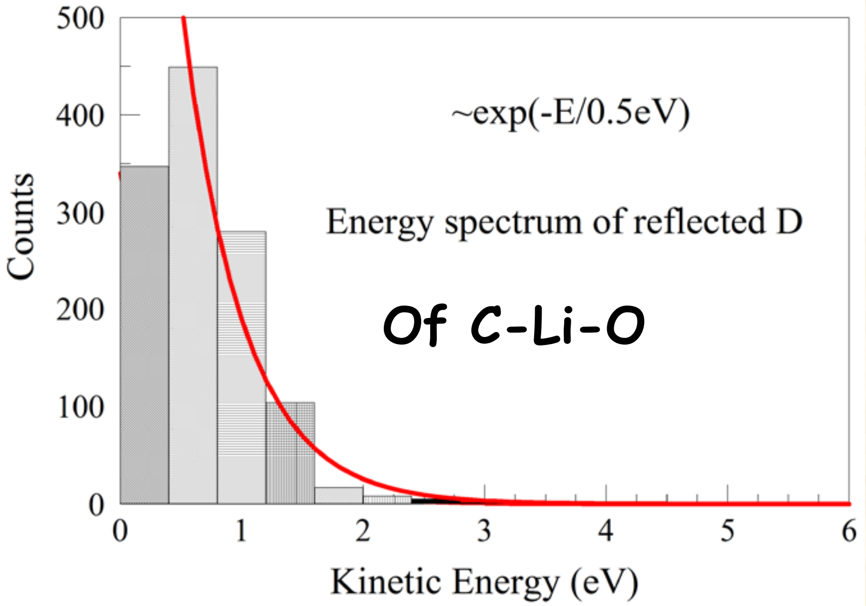
PFMC-13, Poster, May 2011, Rosenheim

Ejected (reflected) D (H) well thermalized to few
(5) thousands K like in sputtering of CH's of C ?????
Sputtering enhanced!!!



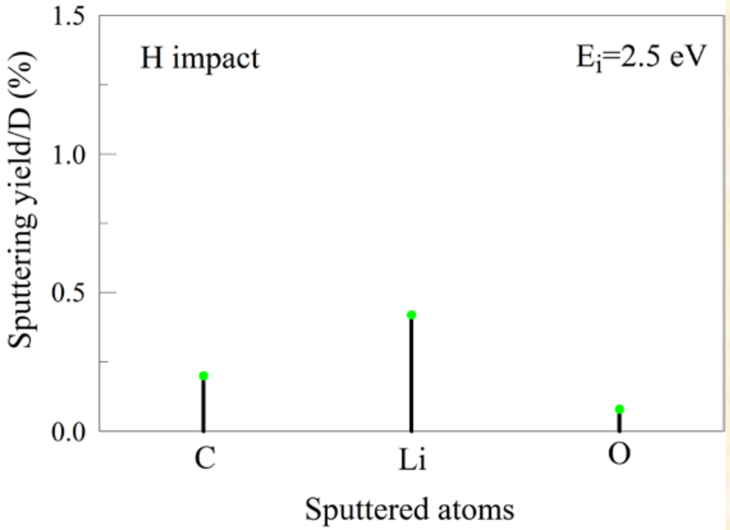
Of C-H





Energy spectrum of reflected D

Of C-Li-O



Isotopic effect significant

Conclusions: In what direction to expand the quantal approach?

- A possibility to get a negatively charged hydrogen in vicinity of Li and of C and O only leads to two (3) peaks in D charge : negative and positive. Consistent with the Purdue experiments. **Polarity of Li is a key for enhanced D retention.**

- **Quantal method** seems to be a more efficient and possible only correct choice for self-consistent treatment of polarized materials

- Enhanced chemical sputtering, isotope dependent

- **Chemistry independent on the impact energy and mass since it happens when the projectile thermalizes!!!**
- Purdue experiment confirms!
- C. Taylor, JP Allain

NEXT (2011):
- Li-C-H-O –Mo-He
- H-Cumulative interactions

- W-Be-C-H-He