Molecular Dynamics of Li–C–H Surfaces

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ABSTRACT

Ø Chemistry and sputtering/reflection dynamics in lithiated carbon material, bombarded by slow deuterium atoms is studied.

Ø 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 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.

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.
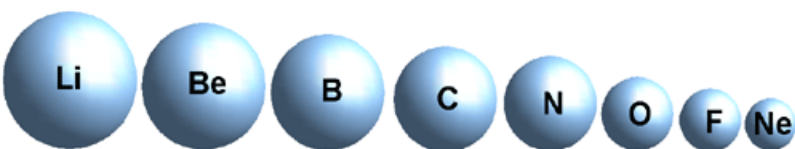

Electronegativity

Electronegativity Values

	< 1.0
	1.0 — 1.4
	1.5 — 1.9
	2.0 — 2.4
	2.5 — 2.9
	3.0 — 4.0
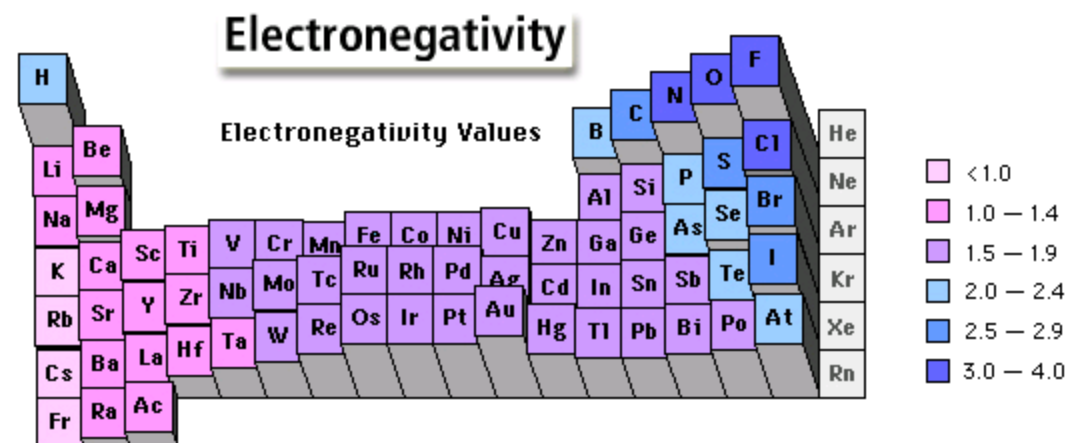
Consequence: Bonding between Li and other atoms covalent and polar;
Long-range nonbonding:
Coulomb : $1/R$
Lennard-Jones : $1/R^6$, $1/R^{12}$

Electronegativity and size of atoms related!

Charging changes at each simulation step: Quantum-Classical Molecular dynamics 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)
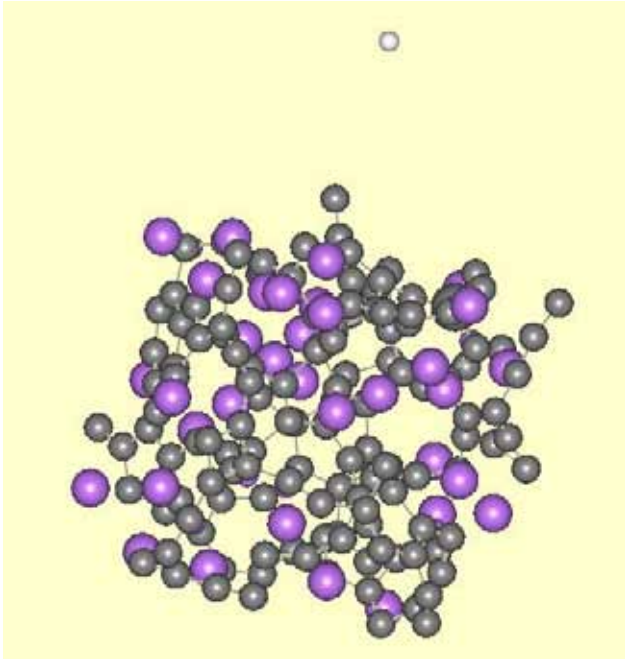
Parameterization for Li-C-H provided by K. Morokuma group (Kyoto-Taiwan-ORNL)

Method:
[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).

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Simulation of deuterium impact to lithiated carbon surface

- Cell of **200 atoms** of lithiated amorphous carbon (32% of Li), at **300K** by random seed of Li in **amorphous carbon** and **energy minimization**, followed by thermalization
- bombarded by **5 eV D** atoms,
- **Perpendicularly** to the shell interface
- 4800 **random trajectories**

4800 processors of Cray XT5 (Jaguar),
Time step 1fs, 6 hours: 200-400 ps.

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Findings by counting indicates preferable bonding of D to Li-C a than to C

• Of 4800 trajectories, 2967 led to D retention

   -Number of D bound to Li-C is 896
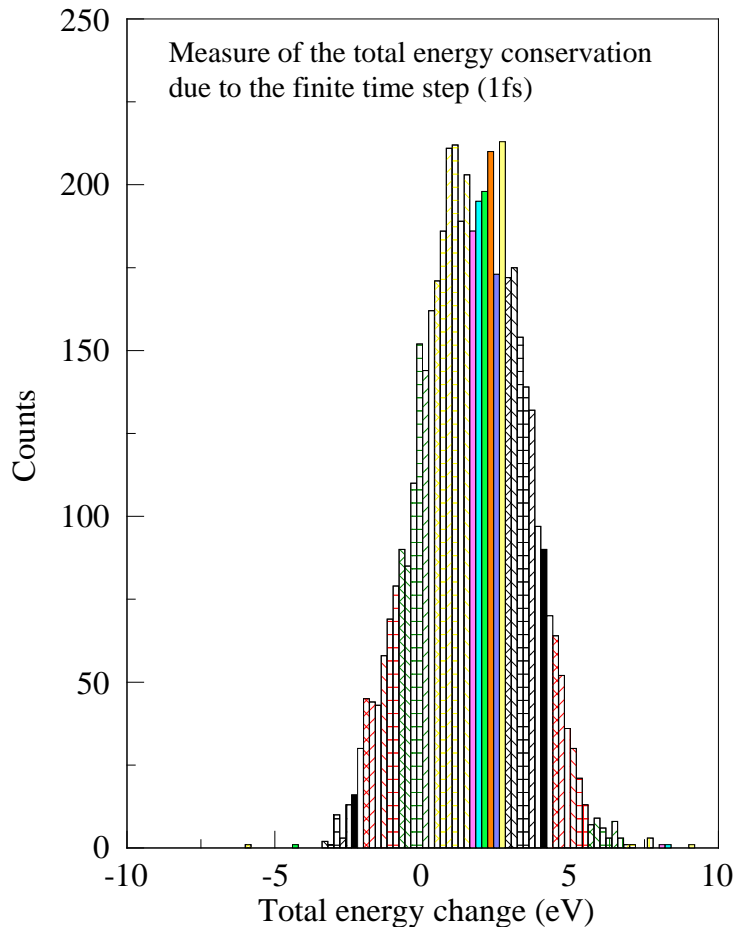   -Number of D bound to C only is 824
   -Number of D bound to Li only is 351

Possible interpretation of the results:
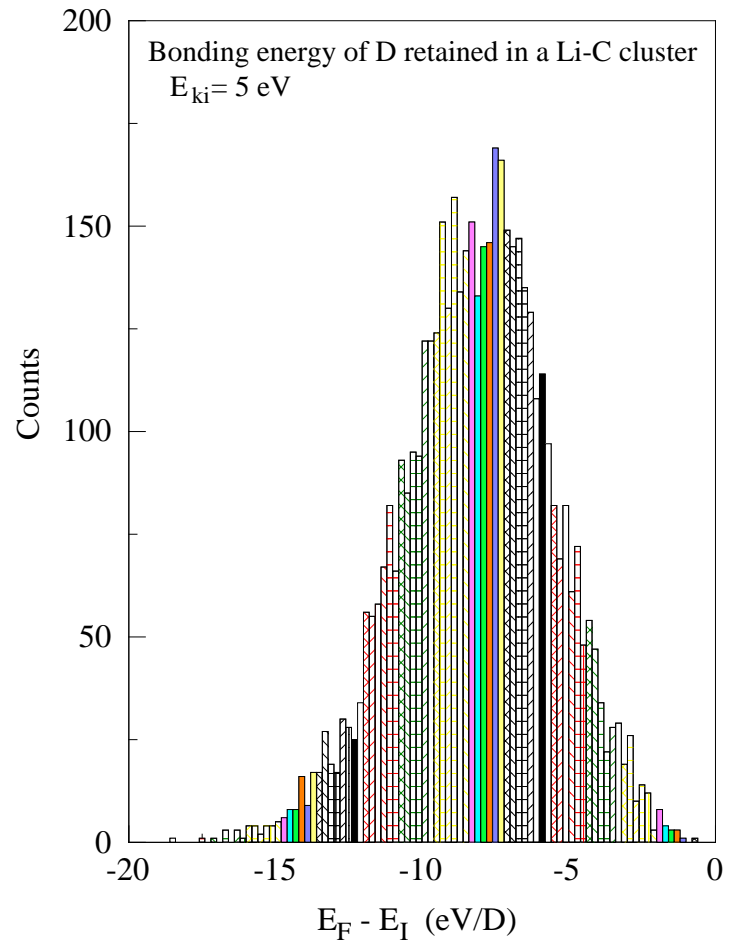
There is 3 times more C than Li ,
Probability to bond to Li-C is 3 times larger (3/4) than the one to C (1/4)
Findings in qualitative agreement with Purdue experiments. (Li-C-D).

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Measure of the total energy conservation due to the finite time step (1fs)

Counts

Total energy change (eV)

Bonding energy of D retained in a Li-C cluster
$E_{ki} = 5$ eV

Counts

$E_F - E_I$ (eV/D)
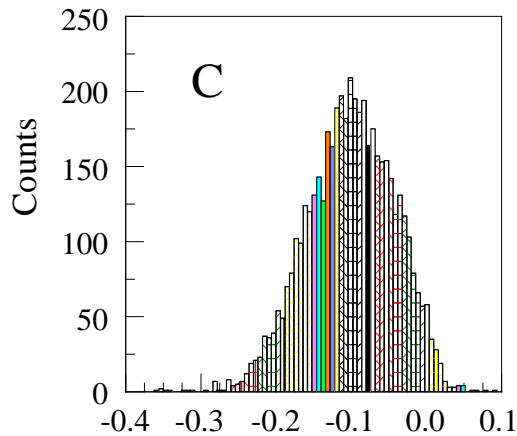
Ideally this is zero with infinitesimal time step

This is expected ~5 eV rather than ~7 eV
But there is a shift and width of energy due to large time step (1 fs)
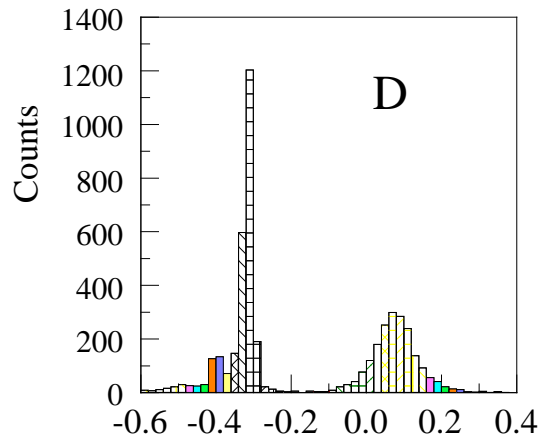
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Charging of bound D and randomly chosen atoms of C and Li

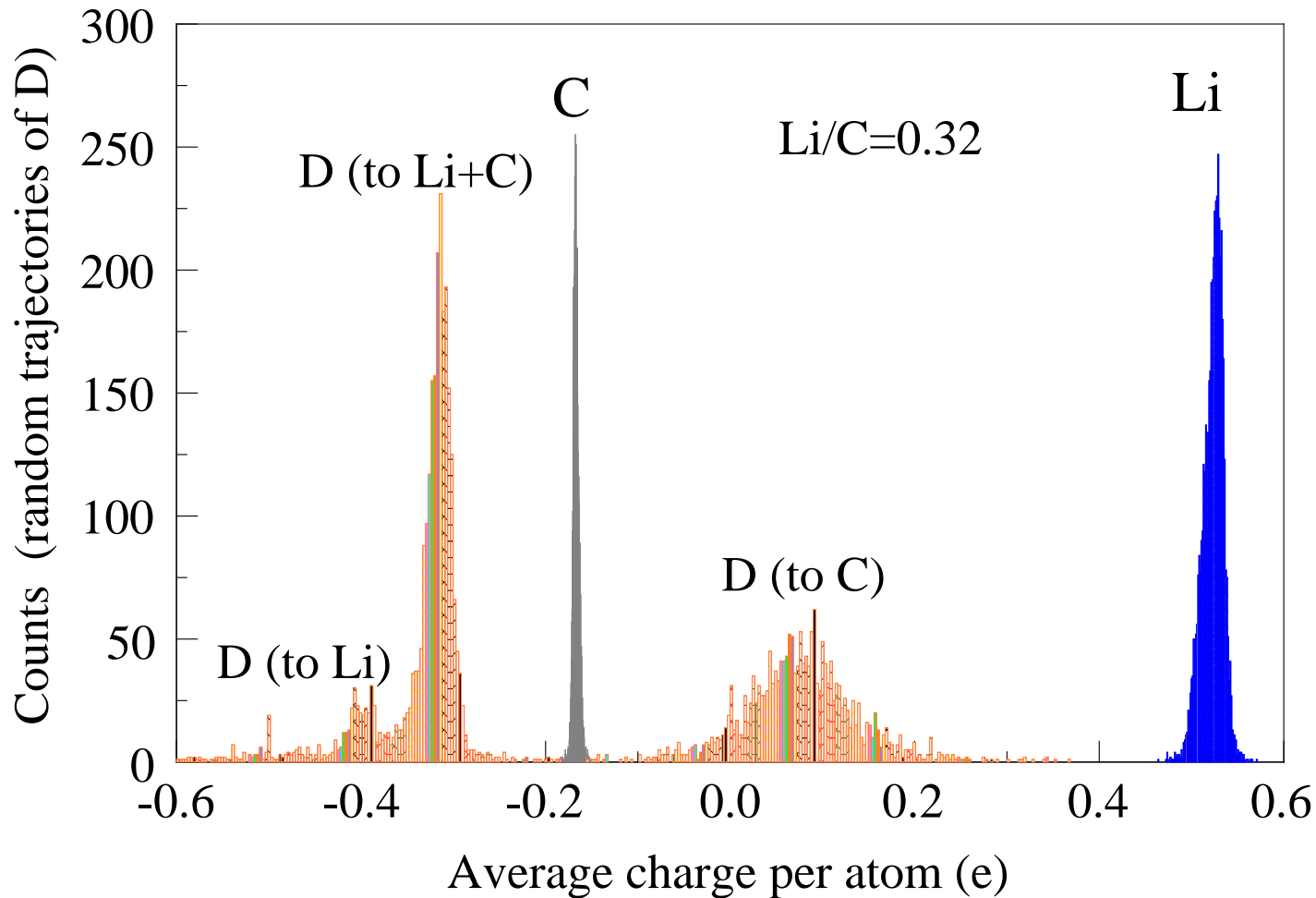Charge of a Carbon atom after D impact (e)
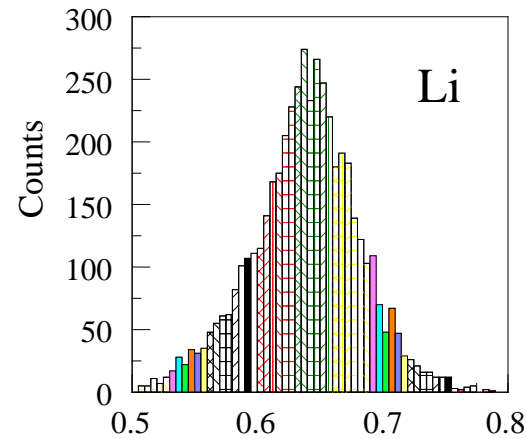
Charge of a Li atom in cluster after D impact (e)

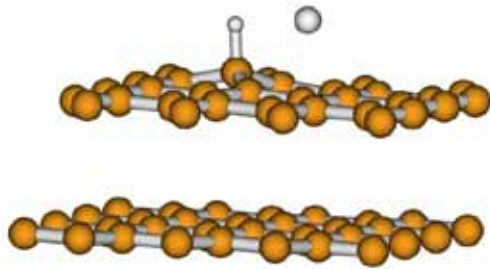Charge of Deuterium at the end of impact (in e)

Many possibilities:
Single trajectory is misleading

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Recent quantum-mechanical, PWDFT "static" calculations of Alain Allouche of CNRS (Marseille) finger -point in the same direction:

- **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)

- **graphene 4-layers, Li inside the slab, H on surface**
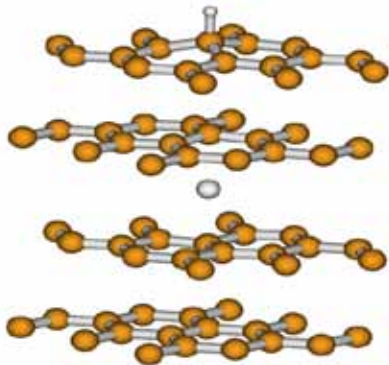
The bonding E enhancement is also observed when Li is sandwiched 1 layer below the surface layer, but disappears when Li is 2 layers below the surface.

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Conclusions

•A possibility to get a negatively charged hydrogen in vicinity of Li and of C only leads to two peaks in D: negative and positive.

•Negative D charging dominant which supports the conclusions above on dominance of Li-C-D complexes over Li-C. The dominance of two peaks corresponding to D bonding is also consistent with Purdue TDS (thermal desorption spectroscopy) experiments both in-situ at Purdue and with the PMI probe in NSTX

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

NEXT:
•   Li-C-H-O :short-term

•   Quantal methods also establishes ability to conduct lithium-refractory metal interactions (e.g. Li-Mo or Li-W PFC work). : long-term

Acknowledgements

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