Material Surfaces, Grain Boundaries and Interfaces: Structure-Property Relationship Predictions

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Understanding Many-Particle Systems with Machine Learning Tutorials
IPAM, UCLA

Ti-C Parameterization

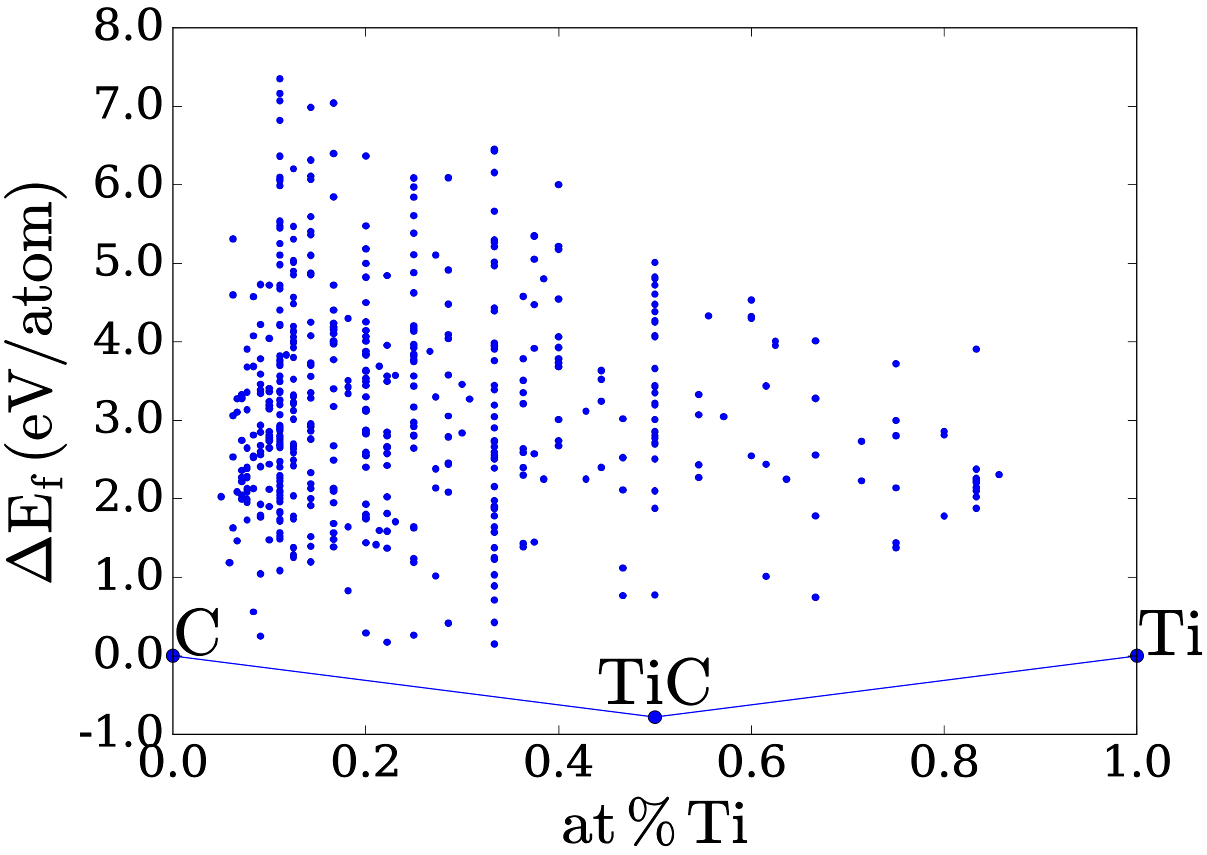
- Parameterize a COMB3 potential for TiC
- Exhibits satisfactory bulk, surface and point defect properties for the ground state structure of bulk TiC
- Also optimize for molecular Ti-C-O-H interactions such as occur in molecular systems such as Ti-(OC_3H_7)$_4$ or TTIP

	TARGET	COMB3
a (Å)	4.33[a]	4.34
ΔH_f (eV)	-1.56[b]	-1.52
B (GPa)	241[c]	262
C_{11} (GPa)	500[c]	504
C_{12} (GPa)	113[c]	144
C_{44} (GPa)	175[c]	204

	TARGET	COMB3
V_{Ti} (eV)	14.38[d]	5.39
V_C (eV)	5.91[d]	18.45
Ti_i (eV)	12.47[d]	22.35
C_i (eV)	8.89[d]	16.16
$\gamma_{(001)}$ (J/m^2)	2.3[e]	3.6

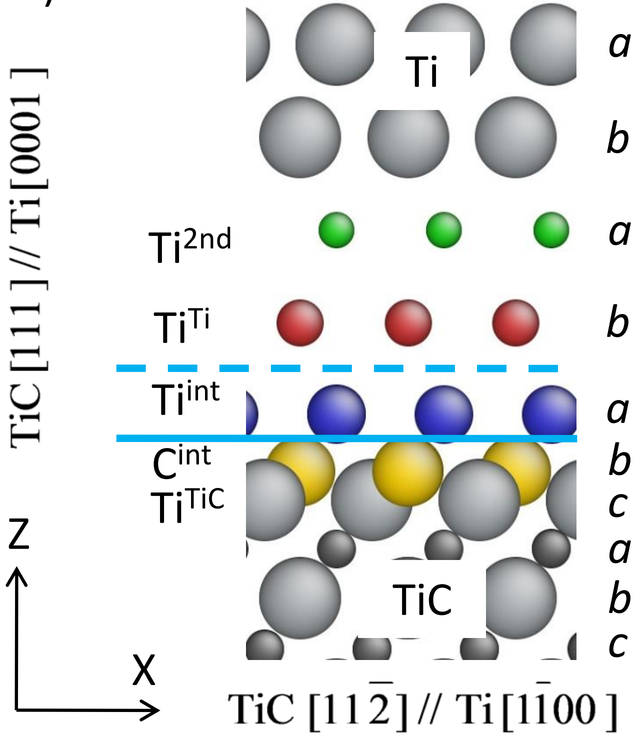
a. J.L. Murray, *OH: ASM International* (1987)
b. L.F.S. Dumitrescu LFS, *Z. Metallkd* (1999)
c. G. Simmons, *Cambridge: MIT Press* (1971)
d. T. Liang et al. (under revision)
e. A. Arya, *J. Chem. Phys.* (2003)

Genetic algorithm to investigate predicted phases

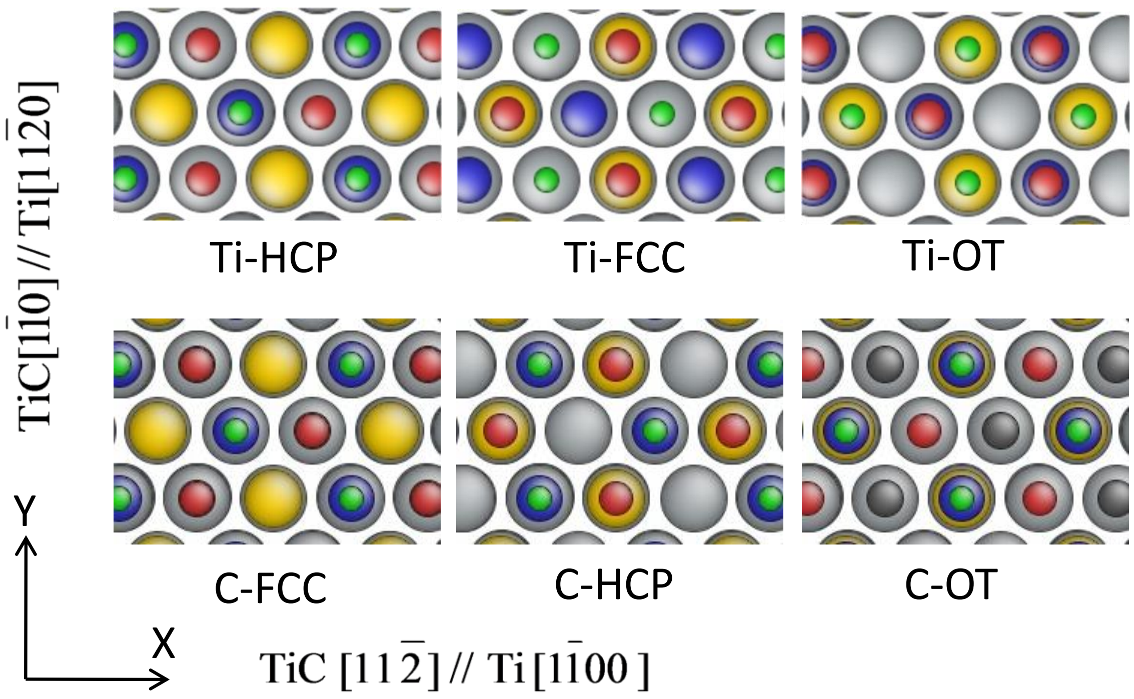


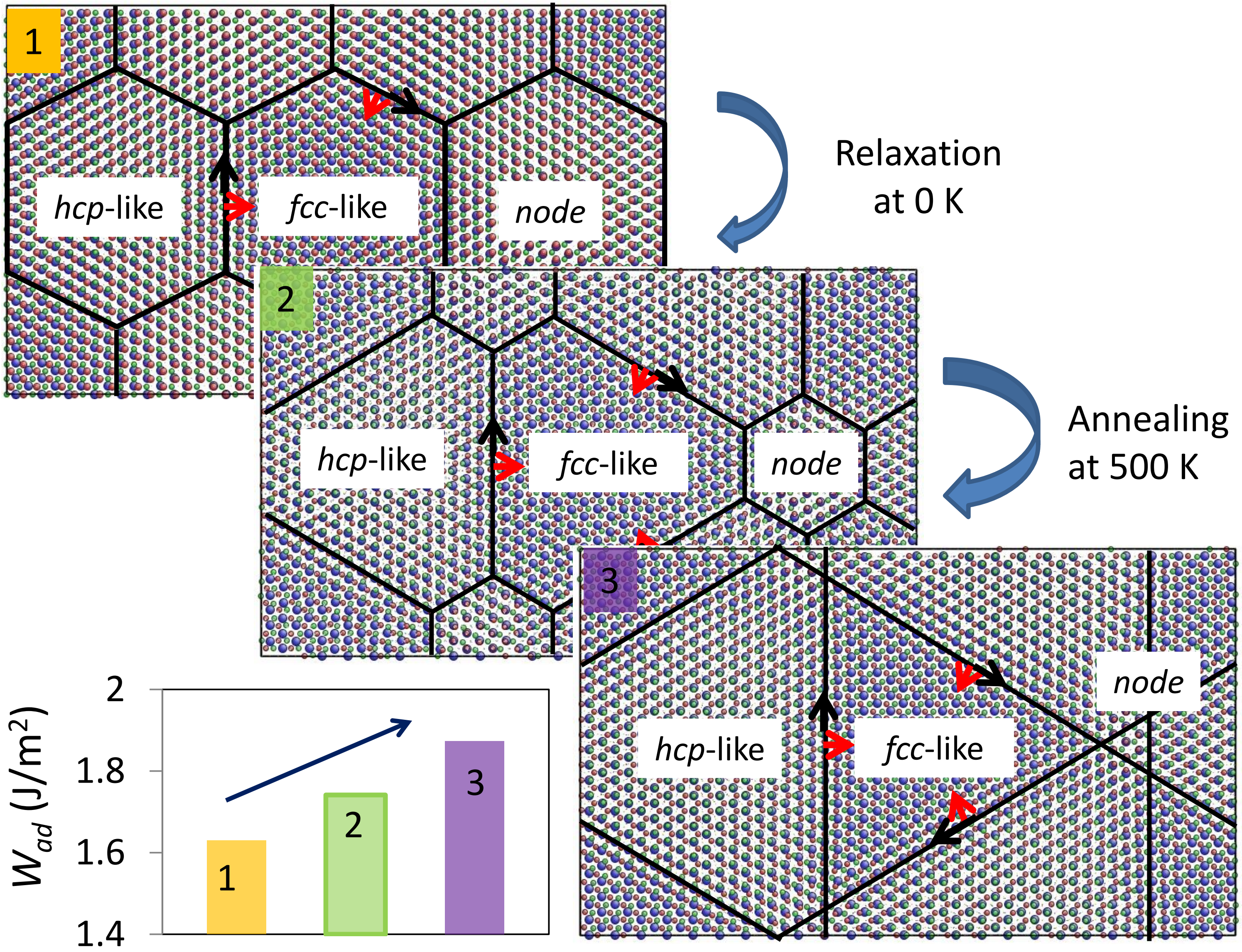
Ti/TiC Interfaces

a) Side view



b) Top view

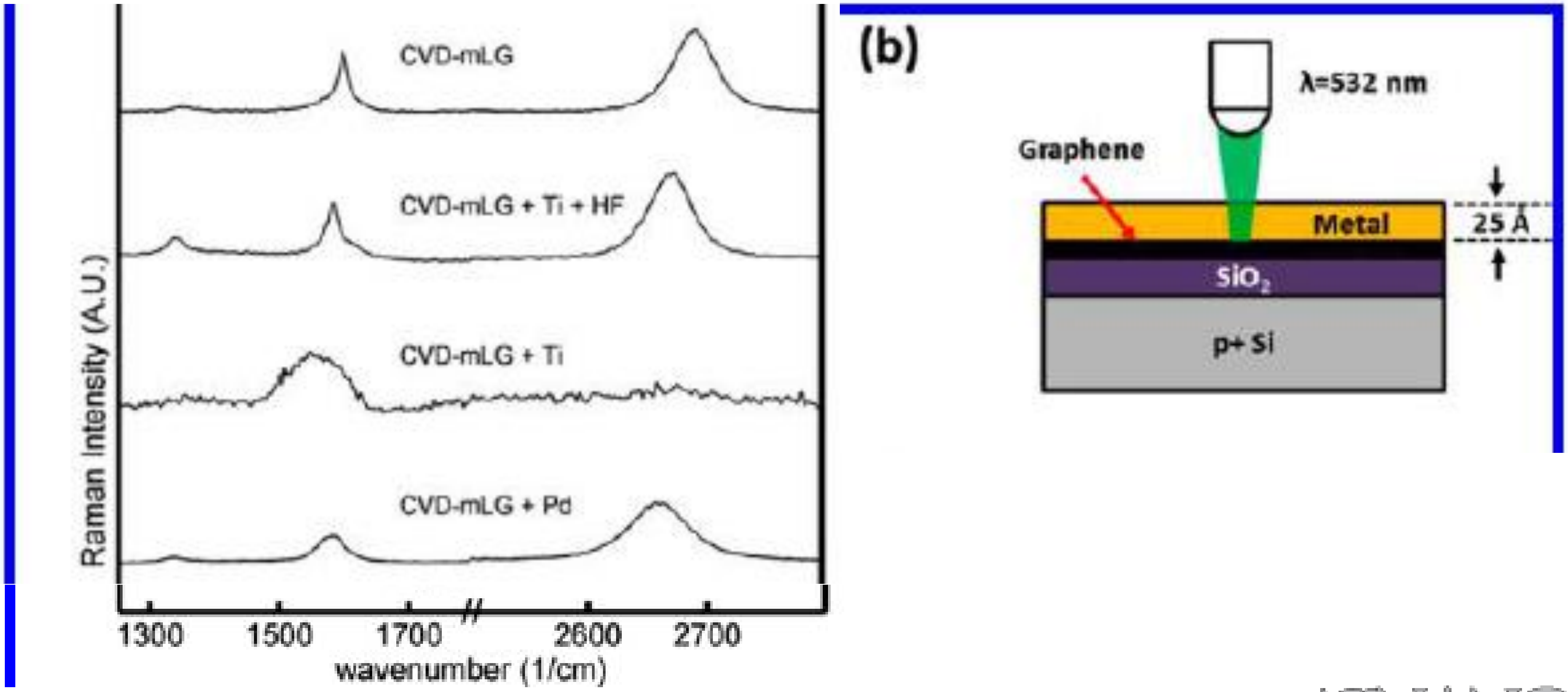




Relaxation
at 0 K

Annealing
at 500 K

Experimental Results of Ti on Graphene



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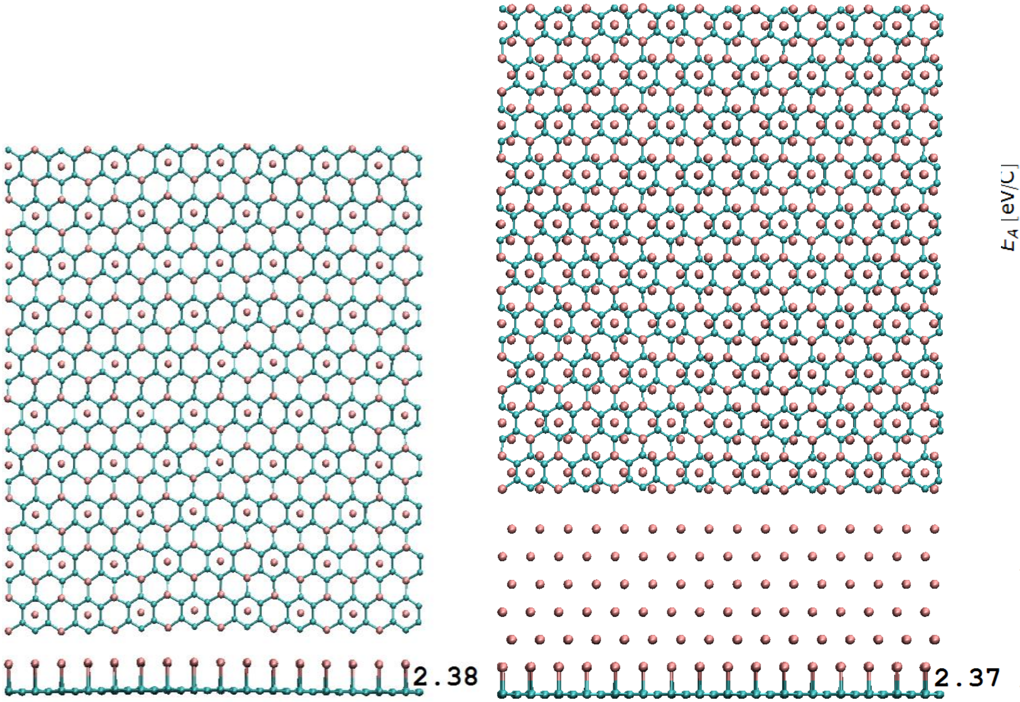
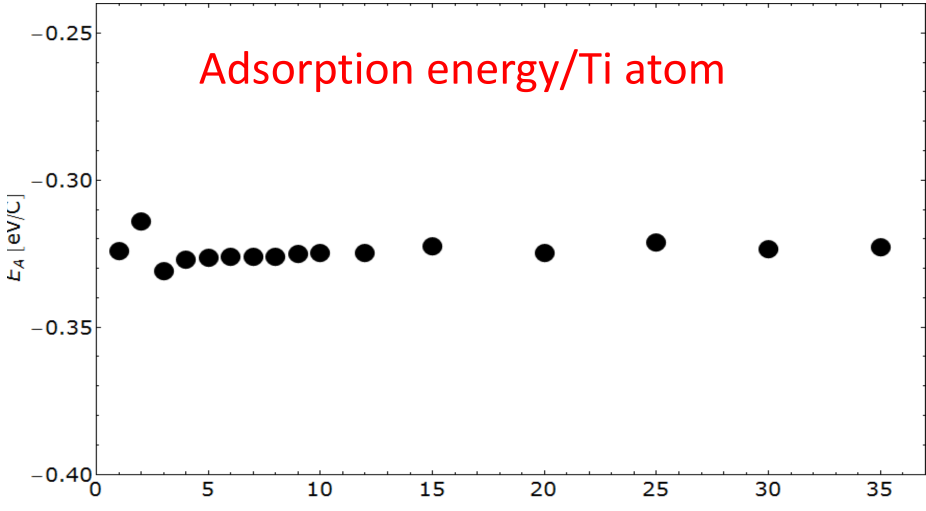
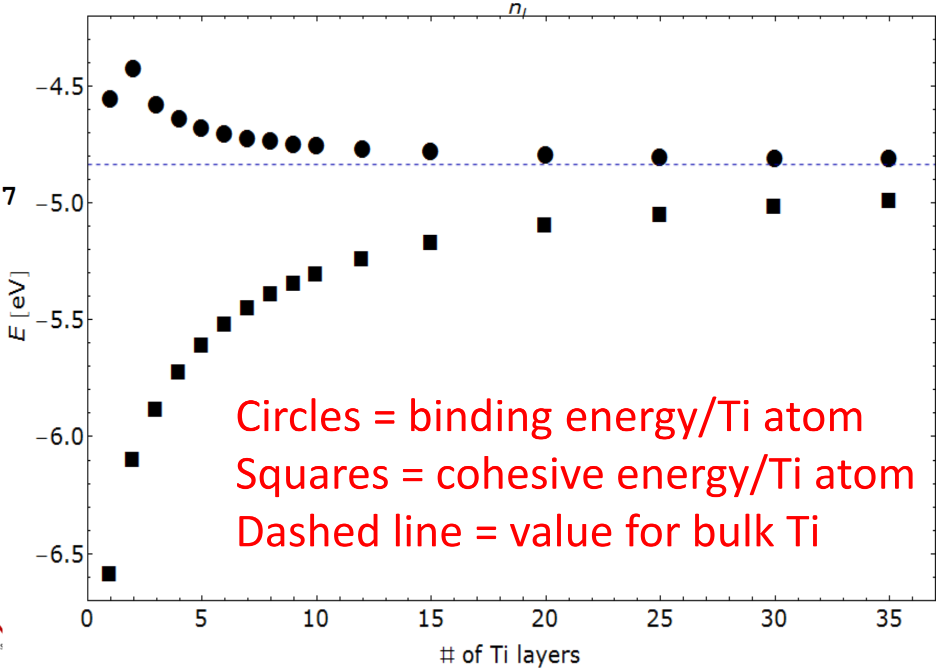
Raman spectra of pure graphene, **graphene after removing Ti film**, Ti film on graphene and Pd film on graphene for comparison. Raman shows that graphene structure remains after removing Ti thin film.

Predicted Interactions of Ti with Graphene




Adsorption energy/Ti atom

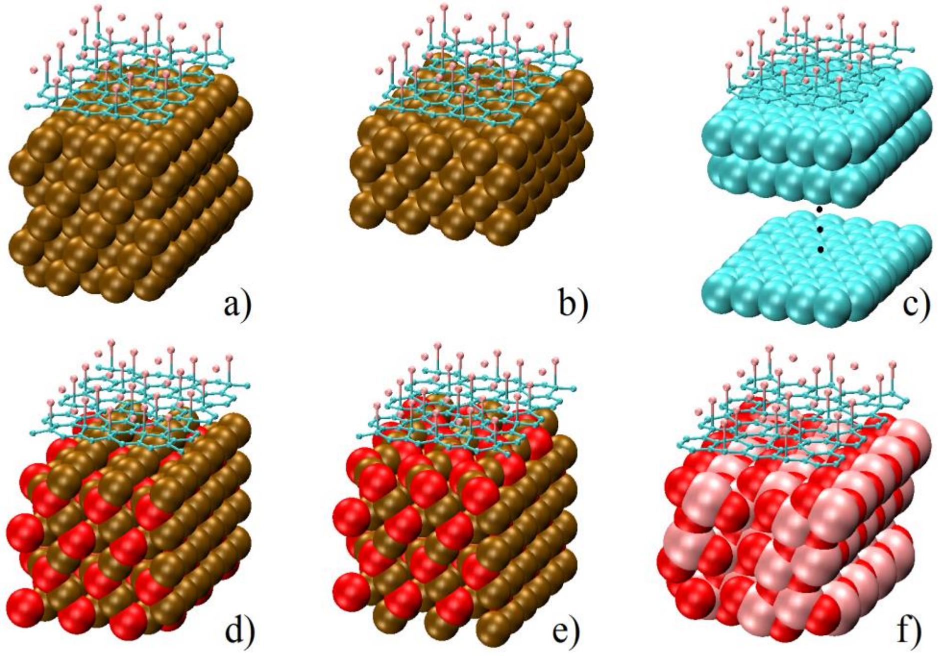

Circles = binding energy/Ti atom
Squares = cohesive energy/Ti atom
Dashed line = value for bulk Ti

Energies of different Ti thin films on graphene

A. F. Fonseca et al. (in preparation)

Influence of Substrate on Ti/Graphene Adsorption

substrate	none	Graphene	Cu (111)	Cu (100)	Cu_2O:Cu (110)	Cu_2O:CuO (110)	Anatase Ti_2O (101)
E_A [eV/C]	-0.318	-0.3269	-0.4579	-0.4573	-0.5194	-0.4543	-0.0433
ΔE_A [eV/C]	0	-0.0089	-0.1399	-0.1393	-0.2014	-0.1363	+0.2747



(a) Cu(111)
(b) Cu(100)
(c) Graphene
(d) Cu_2O:Cu(110)
(e) Cu_2O: CuO(110)
(f) Anatase TiO_2 (101)

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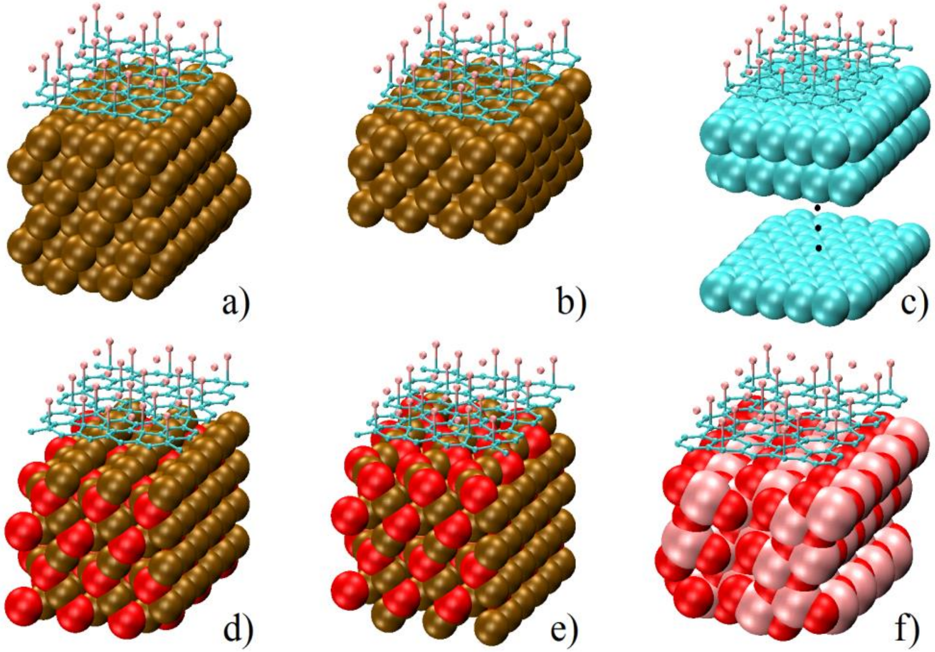
Influence of Substrate on Ti/Graphene Adsorption

Induced charges on the surface (first row) of atoms of the substrate

1 layer of graphene	Cu (111)	Cu (100)	Cu_2O:Cu (110)	Cu_2O:CuO (110)	Anatase TiO_2 (101)
+ (C)	+ (Cu)	+ (Cu)	+ (Cu)	+ (Cu)	- (O)



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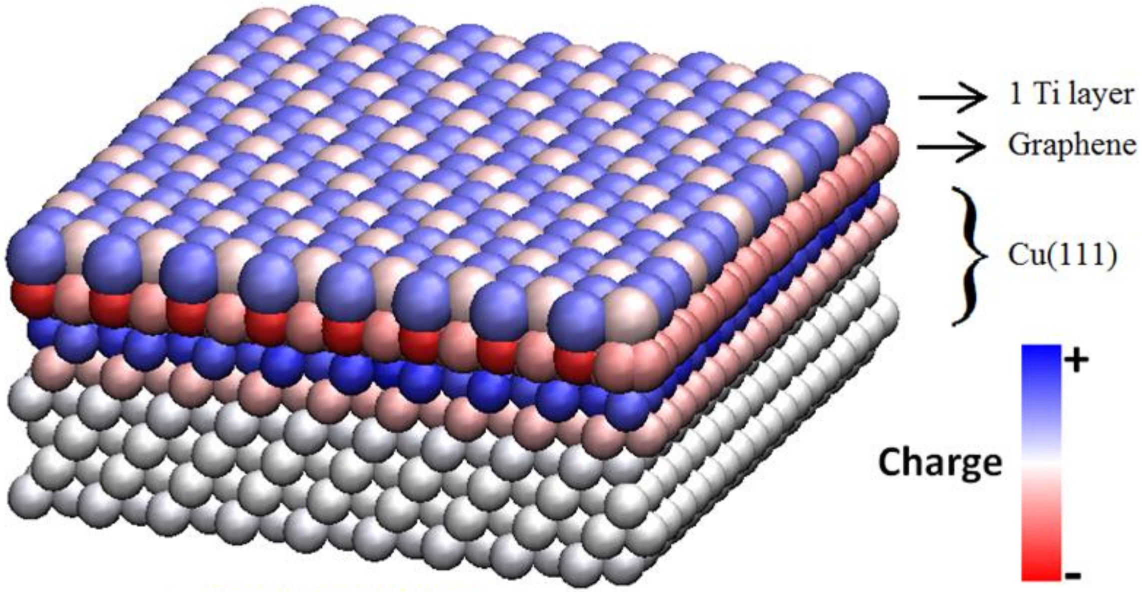

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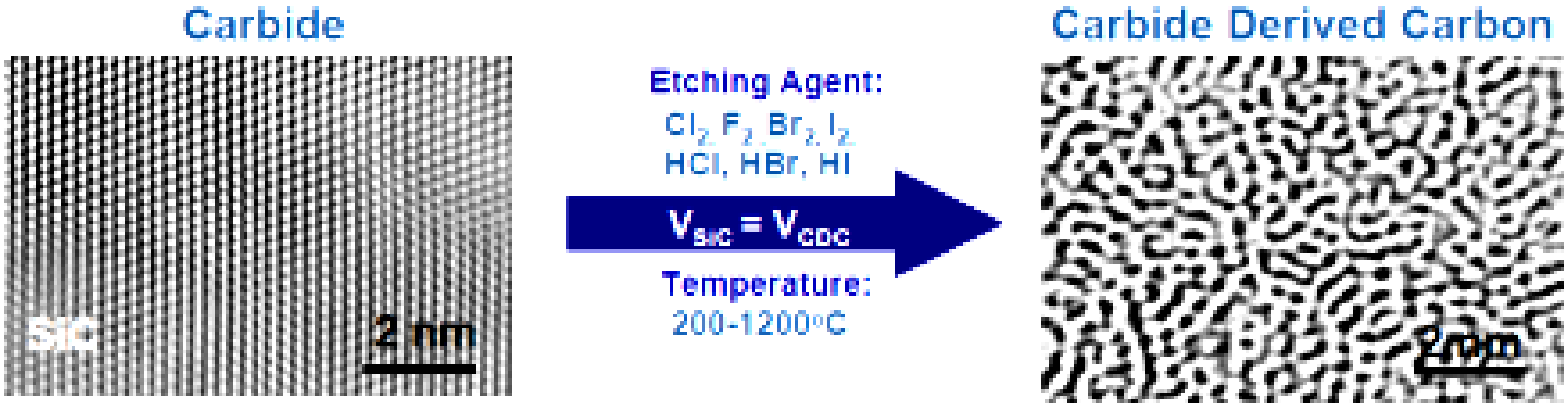
Large the POSITIVE CHARGE of substrate,
large the ADHESION of Ti-graphene on the substrate

A. F. Fonseca et al. (in preparation)

Carbide-Derived Carbon (CDC)



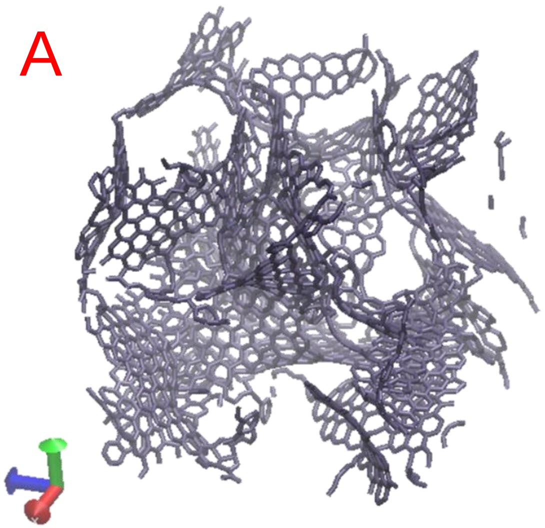
- Carbide precursors:
  SiC, TiC, Al_4C_3, ZrC
- Etching Agent:

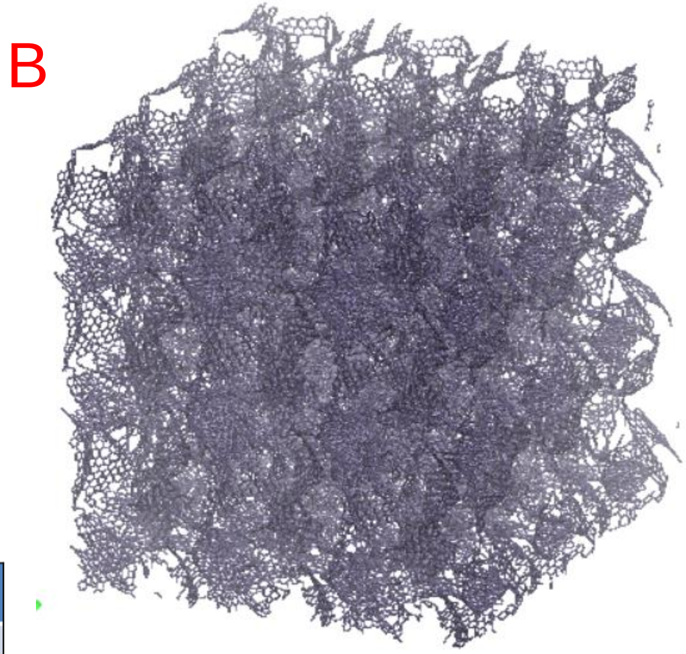
  Cl_2, F_2, Br_2, I_2, HCl, HBr, HI
- Characteristics:
  Mixture of sp-, sp^2-, sp^3-bonded carbons
  Porous
  High surface area

CDC Structure Optimization

- Generated using Hybrid Reverse Monte Carlo simulations (Prof. Suresh Bhatia, University of Queensland)
- Stable after relaxation in MD simulations with the COMB3 potential

CDC model of
different sizes
(A) 4 nm
(B) 12 nm



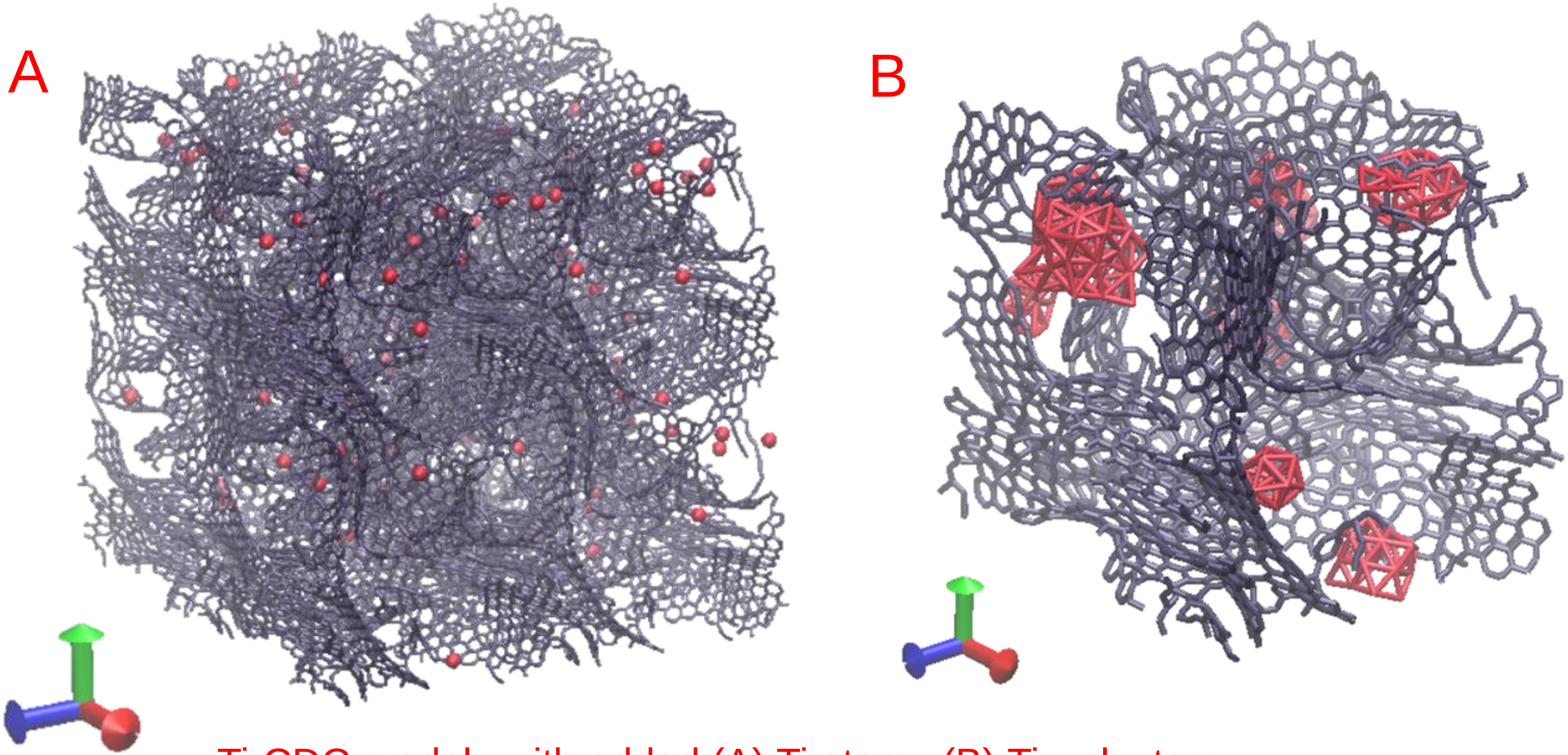


Change of carbon's coordination number (CN) distribution (%)						
CN	0	1	2	3	4	5
Initial	0.33	1.32	23.53	74.25	0.59	0
Final	0	0.03	19.99	78.74	1.24	0

A.H. Farmahini, *J. Phys. Chem. C* (2013)

CDC+Ti Structures

- Ti atoms or clusters added throughout the structure
- Systems are evolved at 300-900K using MD simulations

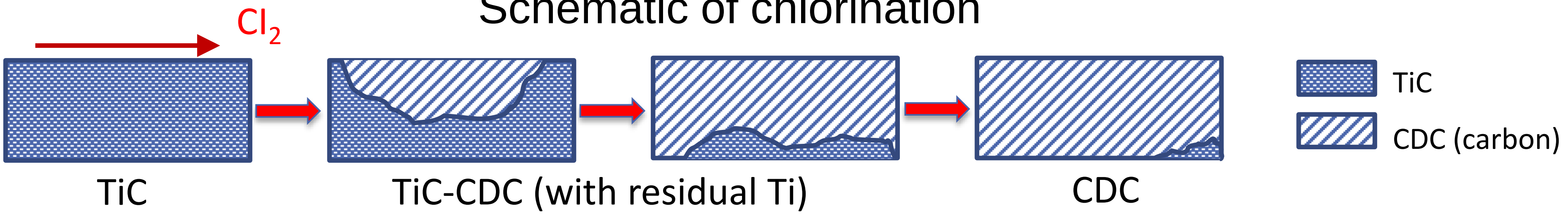


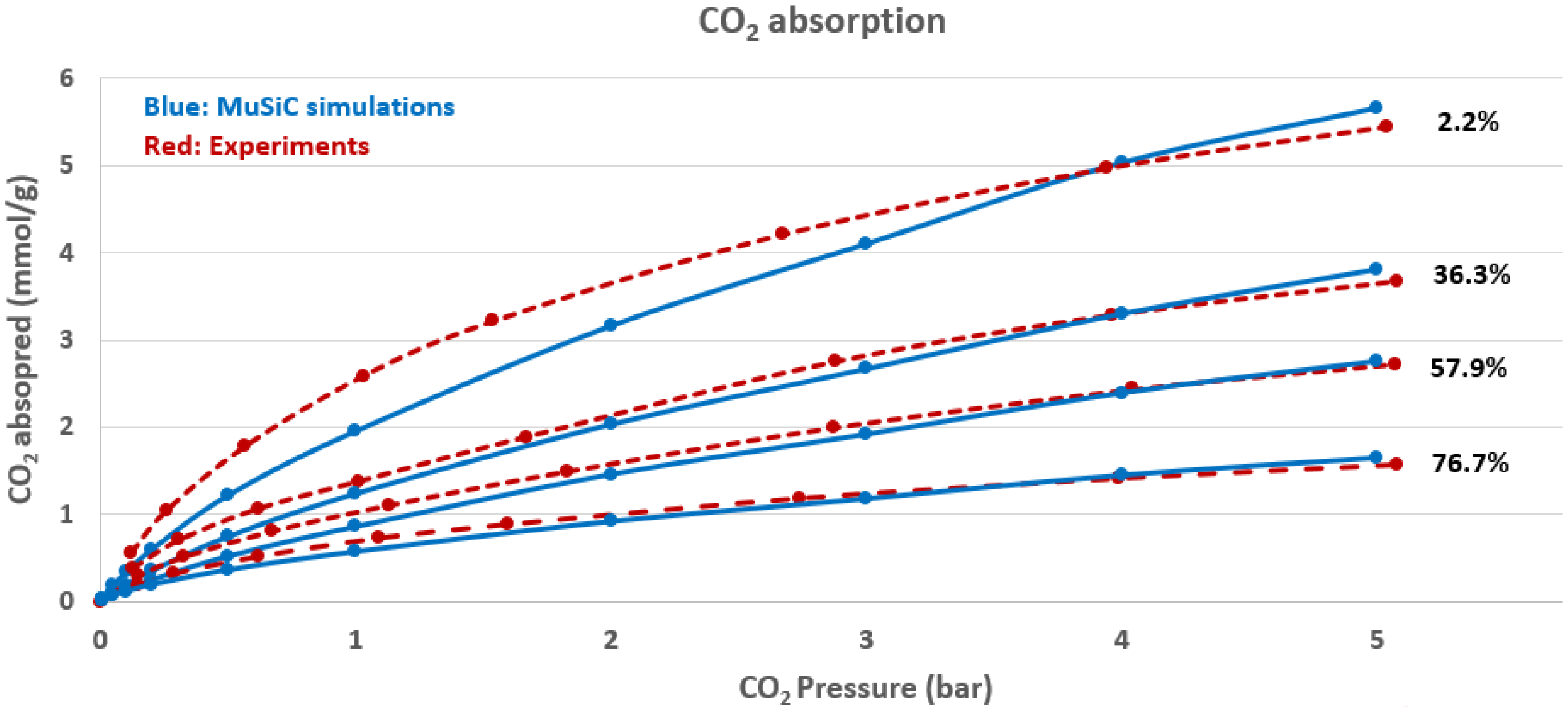
Ti-CDC models with added (A) Ti atoms (B) Ti_{13} clusters

D. Zhang et al. (in preparation)

Weighted Combination of Models

Schematic of chlorination





Absorption of weighted combination

D. Zhang et al. (in review)

Summary

- Thin films of Ti do not disrupt graphene structure
- Graphene vacancies have mixed effect on Ti-graphene interaction
- Substrates have significant effects on Ti-graphene interactions (mainly due to electrostatic interactions between charges that were induced in both graphene and the surface of substrate)
- Predictions of COMB3 potentials are consistent with DFT results
- These potentials may be used to investigate Ti-CDC systems

Functional Form of the COMB3 Potential

$$E_T = \sum_i \left\{ \begin{aligned} & E_i^{Self}(q_i) + \frac{1}{2}\sum_{j\neq i}\left[V_{ij}^{short}\left(r_{ij},q_i,q_j\right) + V_{ij}^{Coul}\left(r_{ij},q_i,q_j\right)\right] \\ & + B_i(q_i) + C_i\left(r_{ij},\theta_{ijk}\right) + E^{polar}\left(q_i,r_{ij}\right) + E^{vdW}\left(r_{ij}\right) \end{aligned} \right\}$$

- **Self energy**: ionization energies and electron affinities; includes penalty function to capture change in self-energy due to the field from the ionic lattice
- **Short-range interactions**: reactive bond-order potential
- **Coulomb interactions**: Coulomb integral over the charge densities
- **Charge and angular correction terms**
- **Polarization**: Atomic polarizabililty for organic systems
- **van der Waals energy**

S.R. Phillpot and S.B. Sinnott, Science (2009)
T. Liang et al., Materials Science and Engineering R (2013)

COMB and ReaxFF

COMB3:

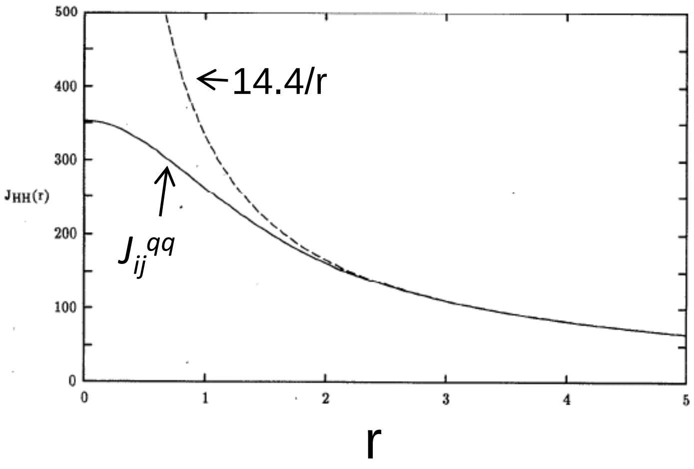
- Charge density function, ρ
- Core charge, Z
- Coulomb integrator, J^{qq}, J^{qz}
- DirectSum

$$f(|\mathbf{r}-\mathbf{r}_i|) = \xi_i^3 \pi^{-1} \exp(-2\xi_i|\mathbf{r}-\mathbf{r}_i|)$$

$$\rho_i(\mathbf{r};q_i) = Z_i\delta(|\mathbf{r}-\mathbf{r_i}|) + (q_i - Z_i) f_i(|\mathbf{r}-\mathbf{r_i}|)$$

$$J_{ij}^{qq} = \left[\rho_i|\rho_j\right] = \int d^3r_1 \int d^3r_2 \frac{\rho_i(\mathbf{r}_1)\rho_j(\mathbf{r}_2)}{r_{12}}$$

$$E^{qZ}[\{q\},\{r\}] = \sum_i \sum_{j>i} \left(q_i J_{ij}^{qz} q_j + q_j J_{ji}^{qz} q_i\right)$$



ReaxFF:

- Point charge
- No core charge
- Shielded Coulomb
- Tap function

$$-\ \mathrm{Tap} \cdot C \sum_{j \neq i}^{N} \frac{q_j}{\left[r_{ij}^3 + (1/\gamma_{ij})^3\right]^{1/3}}$$

~1/r -> Coulomb catastrophe when r is infinitely small

- Both 1/r at long distance
- To avoid Coulomb catastrophe at short distance
  - ➢ Coulomb integrator over charge density in COMB3
  - ➢ Shielding parameter γ in ReaxFF

COMB and ReaxFF

~ 1/r -> does not converge at infinitely long distances; the Ewald Summation method is costly

COMB3 uses Direct Sum

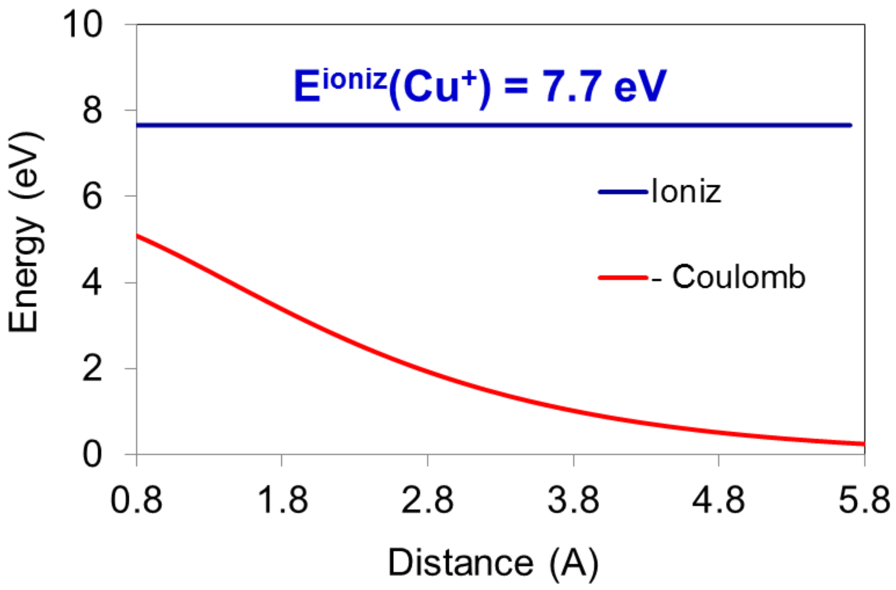
- Coulomb cutoff
- Design for crystals
- Underestimate the Coulomb in molecules

ReaxFF uses the Taper Function

$$- \mathrm{Tap} \cdot C \sum_{j \neq i}^{N} \frac{q_j}{\left[r_{ij}^3 + (1/\gamma_{ij})^3\right]^{1/3}}$$

- Coulomb cutoff
- The Taper function can adjust the strength of Coulomb interactions

Coulomb + Ionization



- Energy minima at infinitely short distances
- No charge transfer

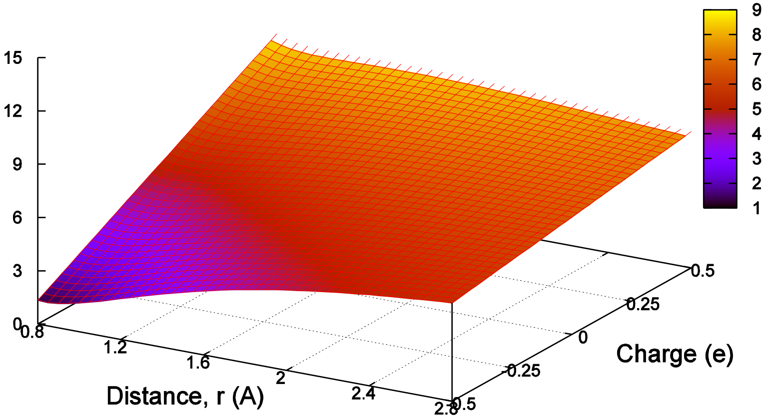
COMB and ReaxFF

Coulomb + Ionization -> underestimates charge transfer

COMB3 adds field effects

$$F_i^{Field}(r_{ij},q_j)=\frac{1}{4\pi\varepsilon_o}\sum_{j\neq i}^{NN}\left(\frac{P^X q_j}{r_{ij}^3}+\frac{P^J q_j^2}{r_{ij}^5}\right)$$

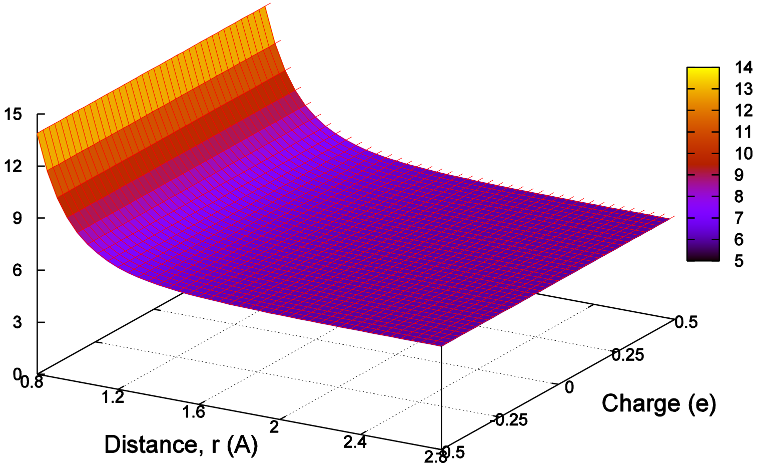
Electonegavitity



ReaxFF modifies the ionization energy curve

$$\chi_i^0 q_i + \frac{1}{2}J_i^0 q_i^2$$

Self-Coulomb



- COMB3 still underestimates charge transfer
- Original version of ReaxFF may have large residual charge in the case of bond dissociation; being resolved via integration with ACKS2 method

PennState

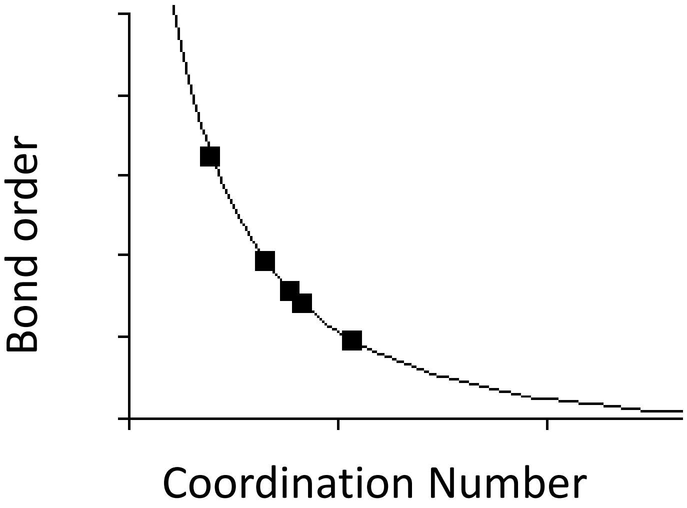
Short Range Bond Order Differences

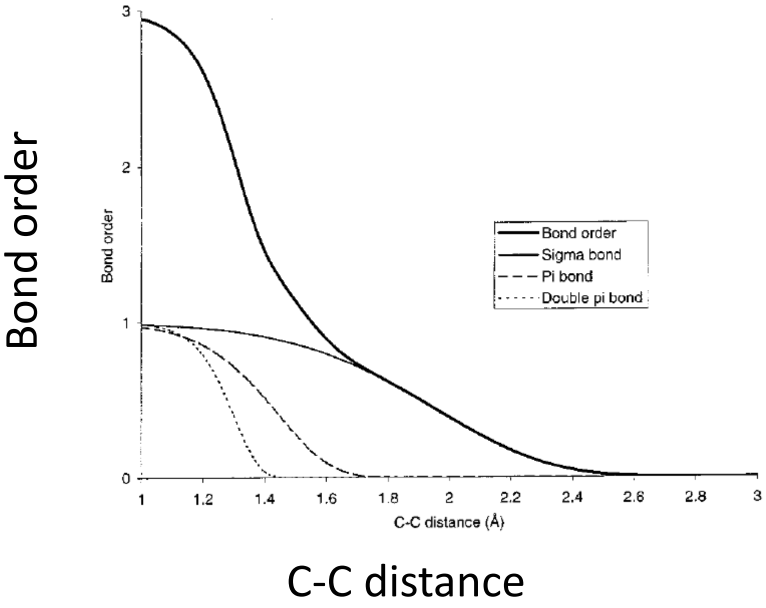
COMB3:

- Abell-Tersoff-Brenner
- Bond order evaluated based on CN, bond angle, torsion …
- Bond order scales the pairwise attraction
- Uses Tersoff cutoff function

ReaxFF:

- The bond order is first evaluated from bond length
- All other energy terms can be scaled by a bond order
- No cutoff function is used



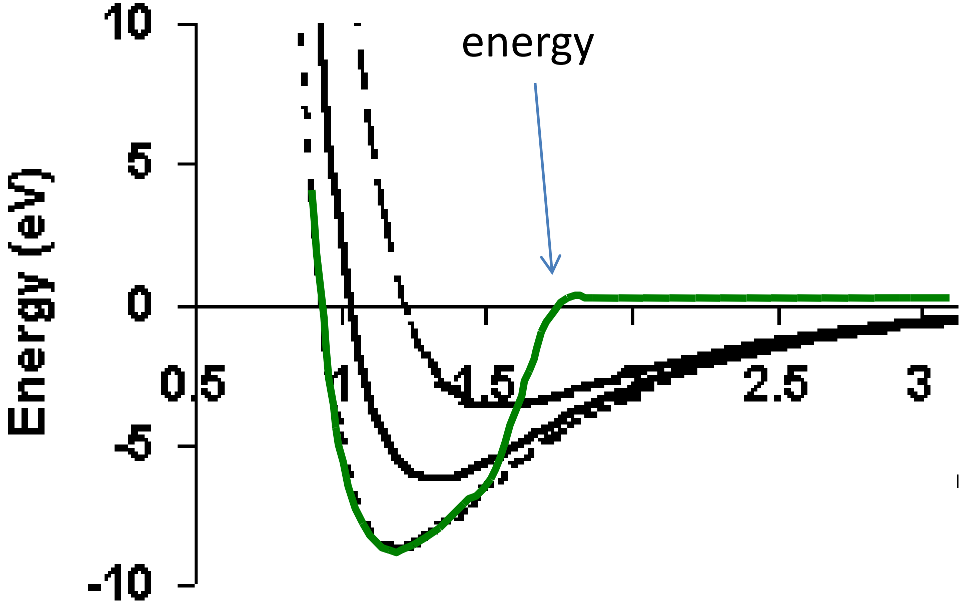


- Bond order in COMB3 is not directly related to distance
- CN increase -> increased electron-electron repulsion -> increased bond length

COMB3 and ReaxFF

Cutoff Function

Unrealistic energy and forces inside cutoff region for COMB3



Unrealistic modification on energy

Parameterization

- COMB3 is more focused on crystals than molecules since DirectSum works better.
- ReaxFF can do a better job for transition states since there is no cutoff on short-range interaction.

T. Liang et al., Annual Rev. Mater. Res. **43** (2013)
Y. K. Shin et al., MRS Bulletin **37** (2012)