Feasibility study of carbon dioxide capture on functionalized graphane sheets

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- Computational methodology
- CO_2 adsorption over

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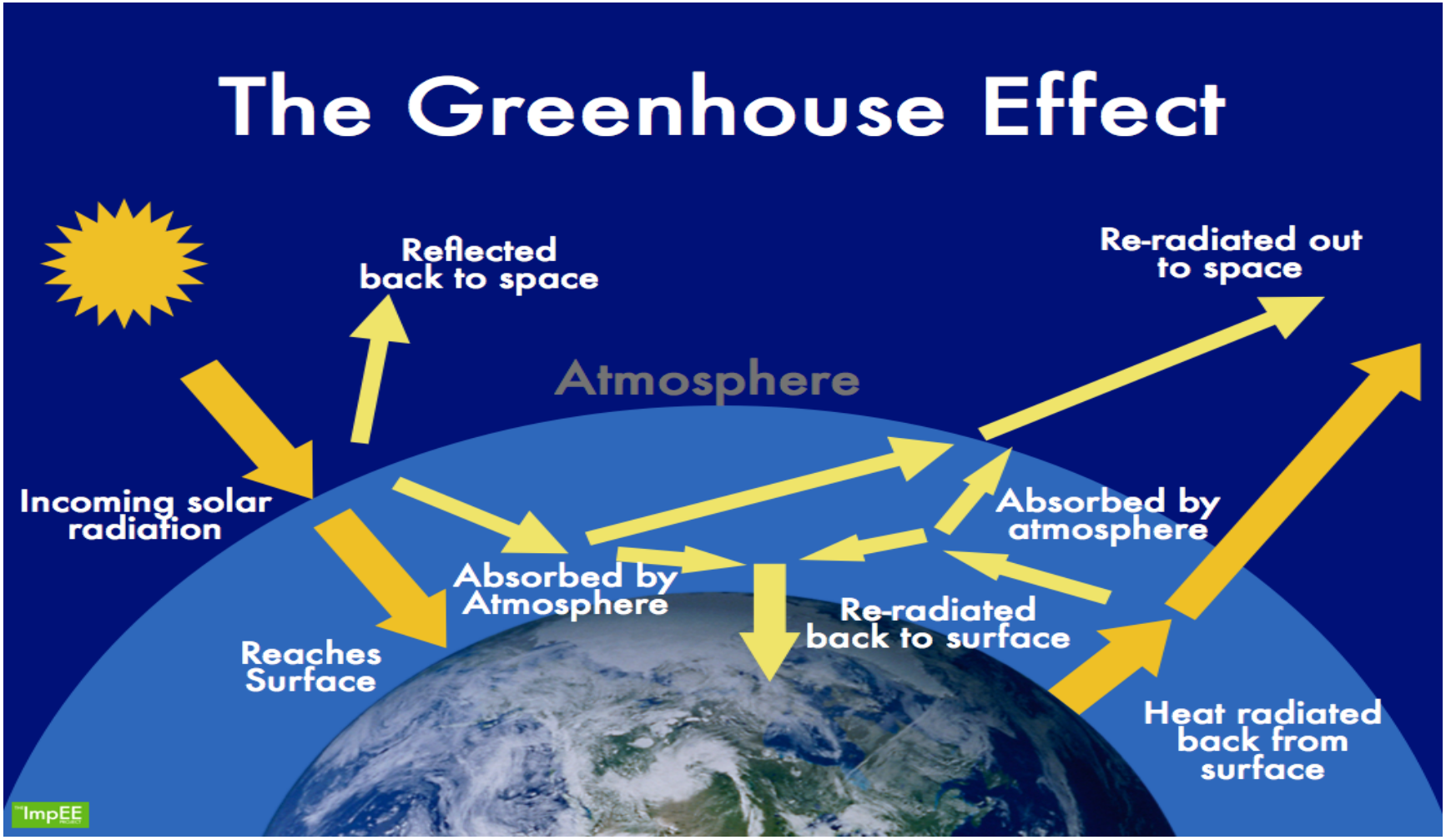
  Grafted $-NH_2$, $-OH$ and $-COOH$ Graphanes

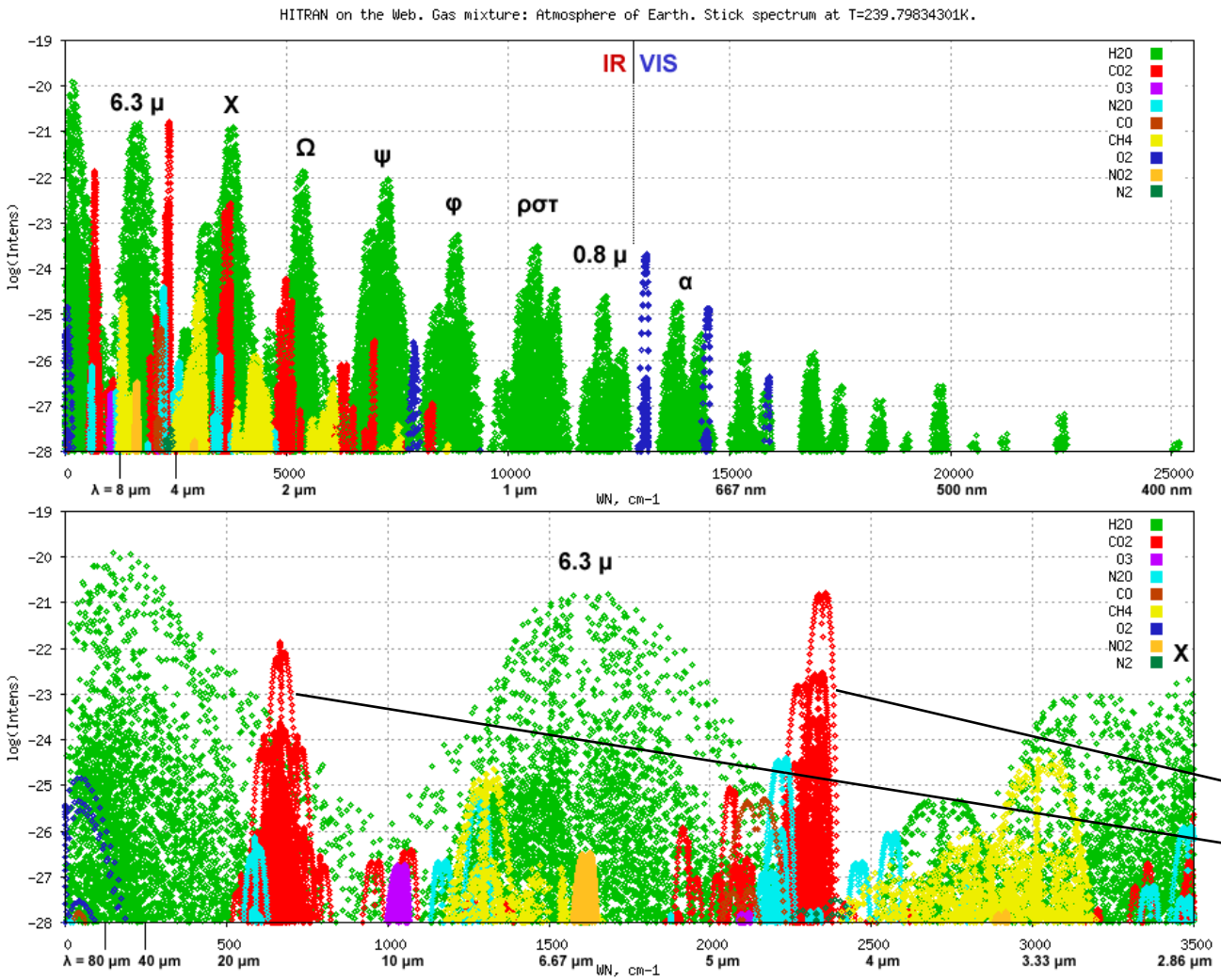
- Conclusions

Introduction- The Greenhouse Effect



http://1.bp.blogspot.com/-GRAGL2k4L8o/Ti6-C2J6SQI/AAAAAAAAAPU/JTOjRqHrzG8/s1600/Greenhouse_Effect.png

Introduction- The Greenhouse Effect



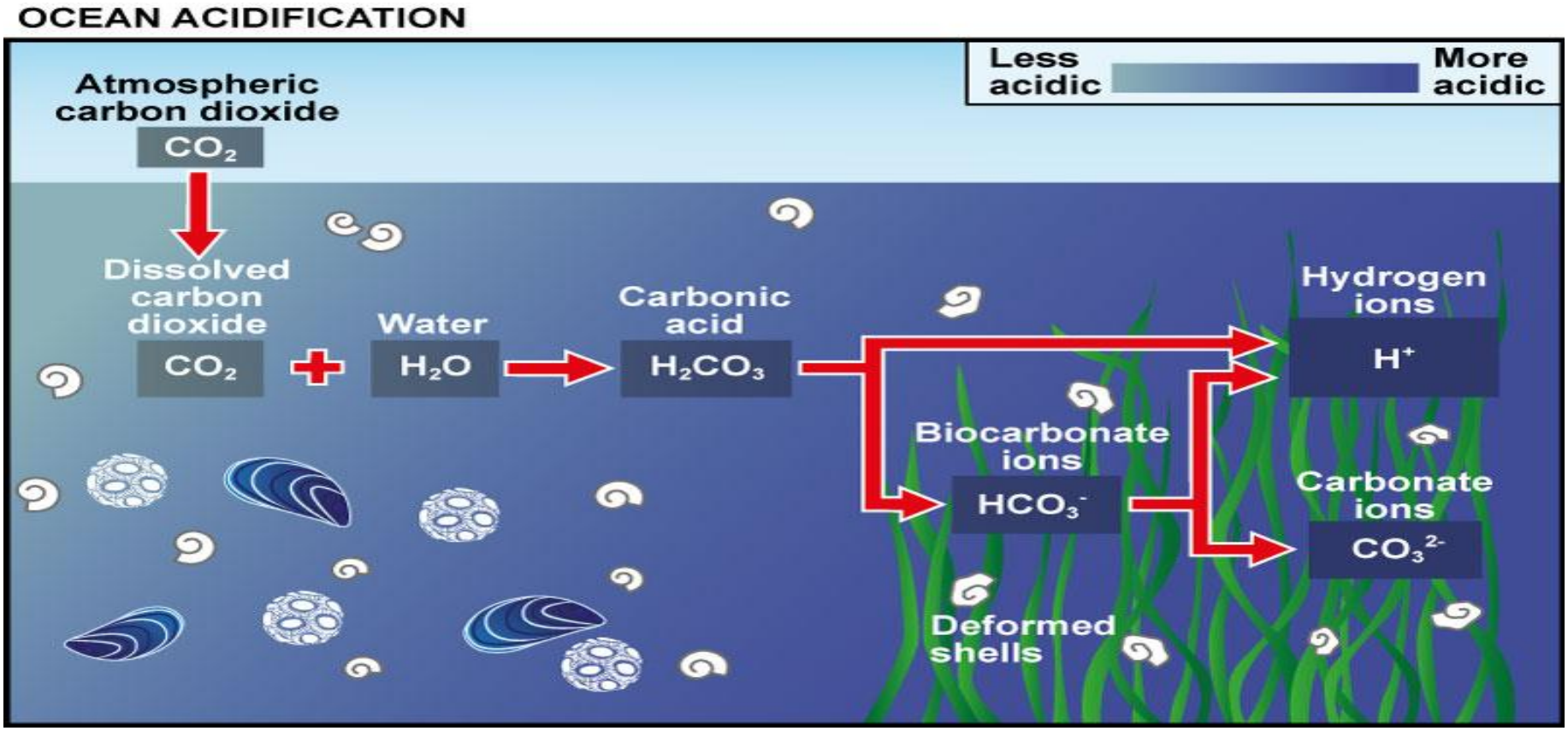
The concentration of CO_2 :

310 to 390 ppm

CO_2

http://upload.wikimedia.org/wikipedia/commons/a/ad/Synthetic_atmosphere_absorption_spectrum_2.gif

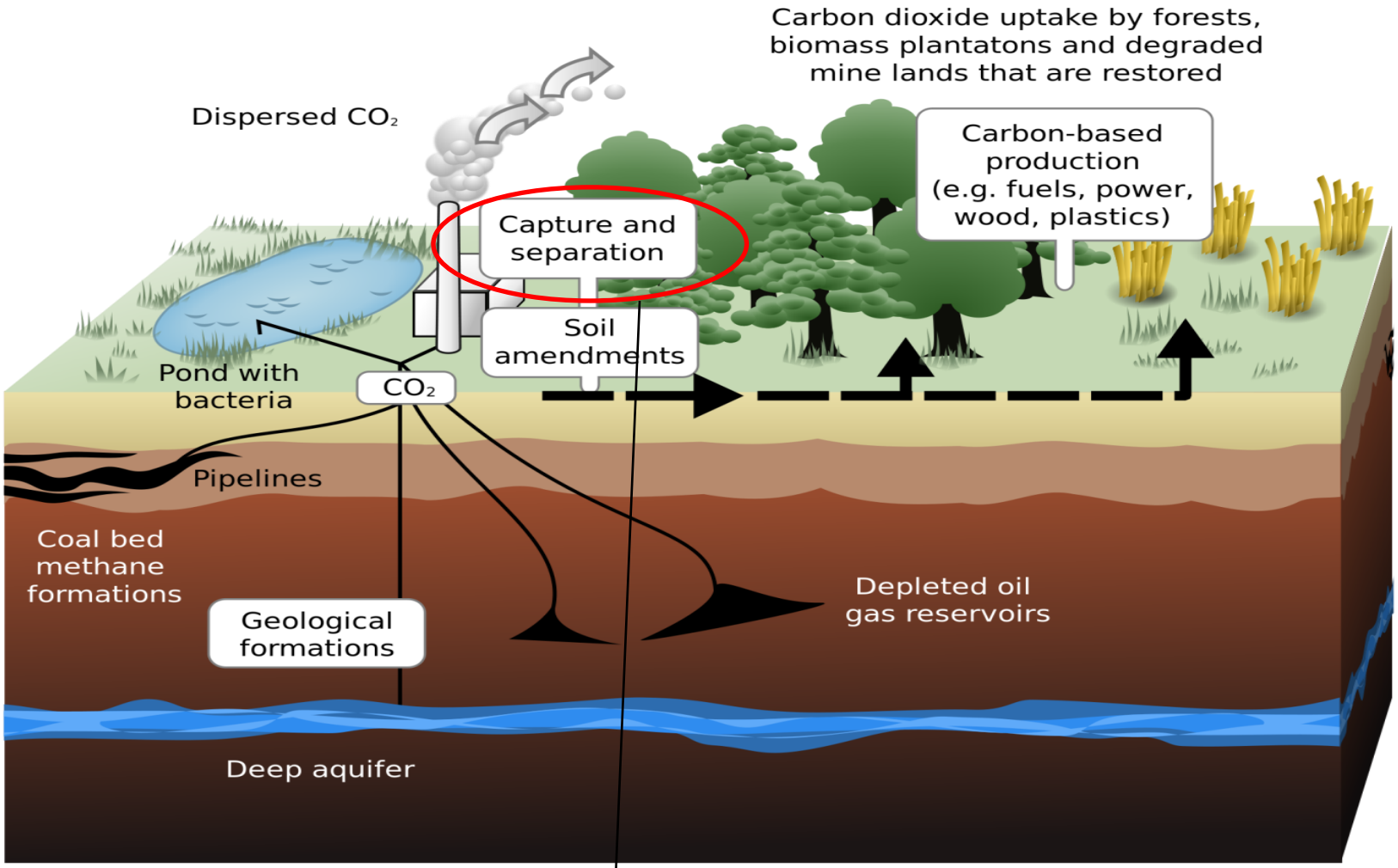
Introduction- The Ocean Acidification



http://www.oceanacidification.org.uk/Oarp/media/images/oa_800.jpg

pH: 8.2 to 7.8

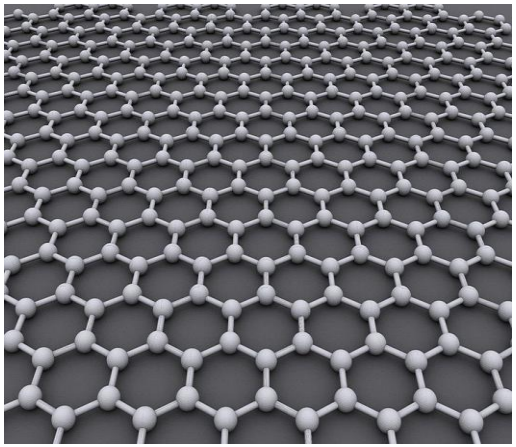
Introduction- Carbon capture and storage (CCS)



http://upload.wikimedia.org/wikipedia/commons/thumb/b/b5/Carbon_sequestration-2009-10-07.svg/2000px-Carbon_sequestration-2009-10-07.svg.png

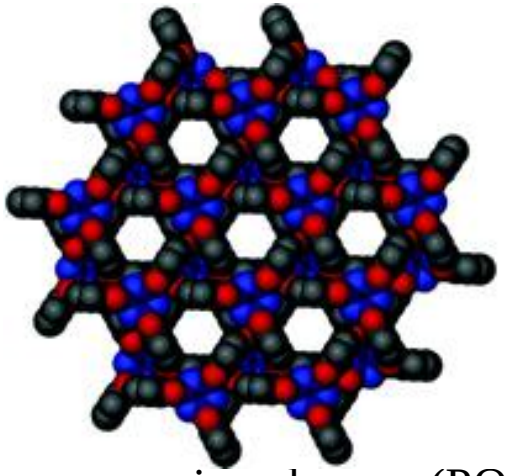
At stationary point source

Introduction- adsorbent materials for CO_2



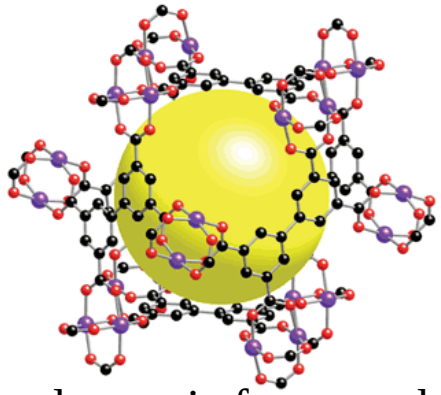
Graphene/graphite

http://upload.wikimedia.org/wikipedia/commons/9/9e/Graphen.jpg



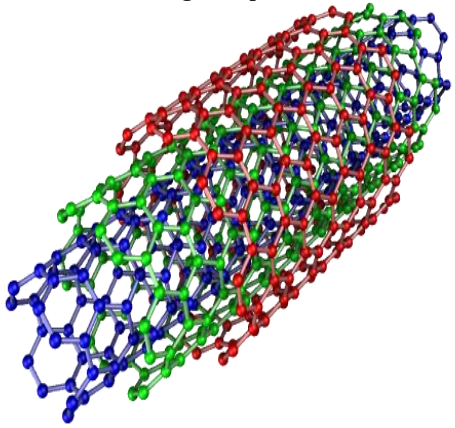
Porous organic polymers (POPs)

http://blogs.rsc.org/ce/files/2012/01/GACA0BKYKI-JPEG1.jpg



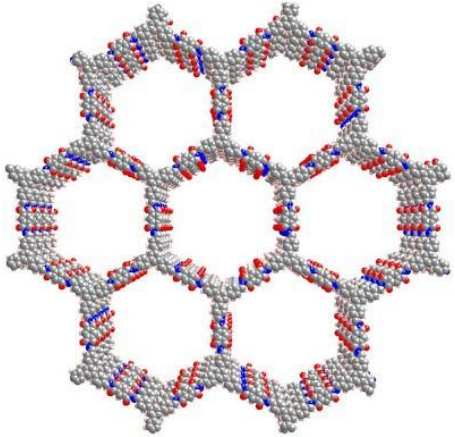
Metal organic frameworks (MOFs)

http://www.chem-station.com/en/wp-content/uploads/2014/04/8334cov1aamolecule.gif



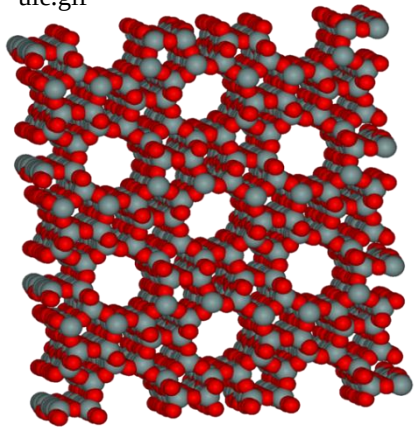
Carbon nanotubes (CNTs)

http://www.foodengineeringmag.com/ext/resources/TECH_FLASH/TF-8-10-Carbon-Nanotube.gif



Covalent organic frameworks (COFs)

http://www.pmatlab.com/_/rsrc/1378661496871/Research-interest/wp3.jpg?height=384&width=400



Zeolites

http://upload.wikimedia.org/wikipedia/commons/5/58/Zeolite-ZSM-5-3D-vdW.png

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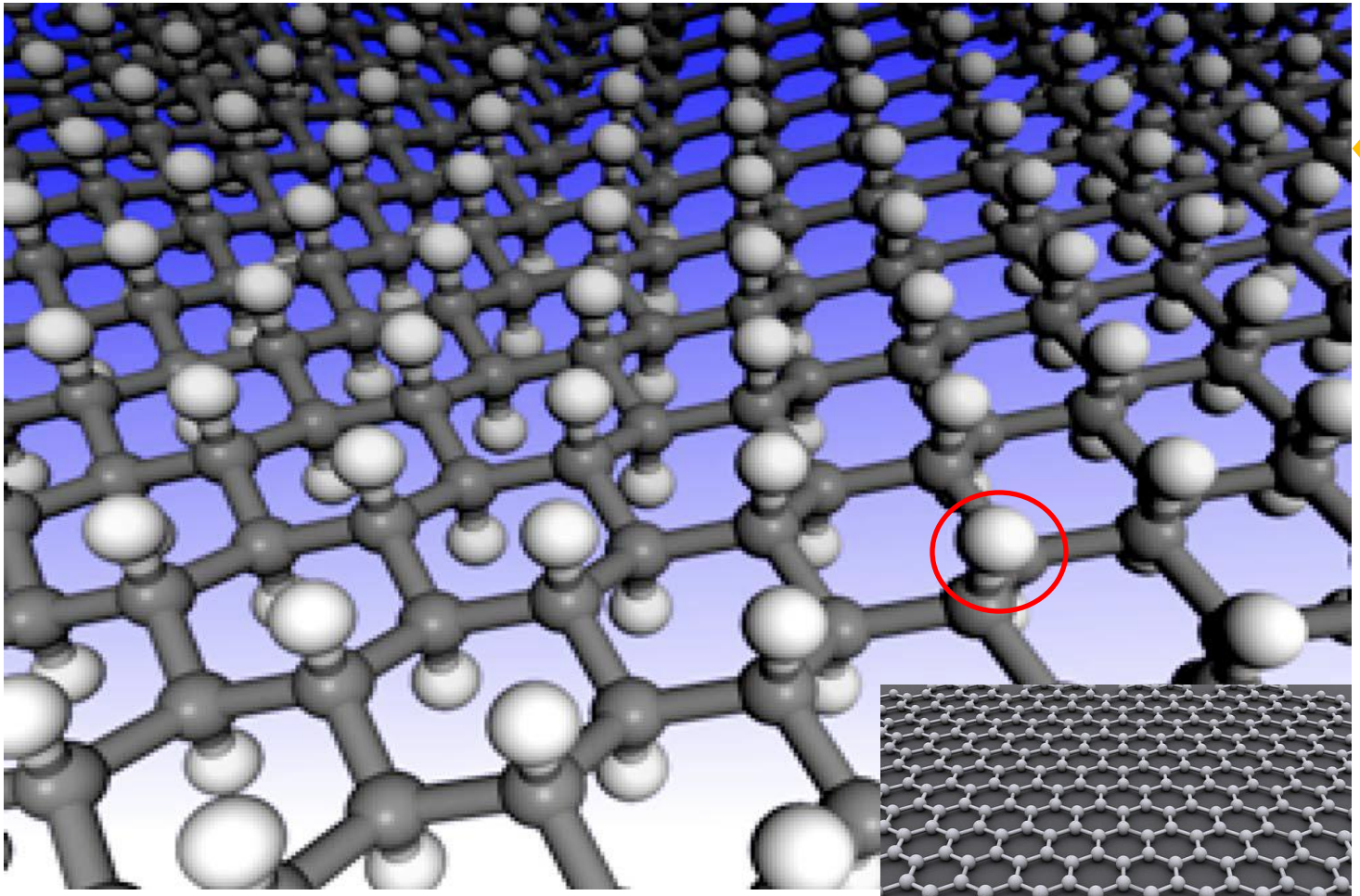
Introduction- Graphane



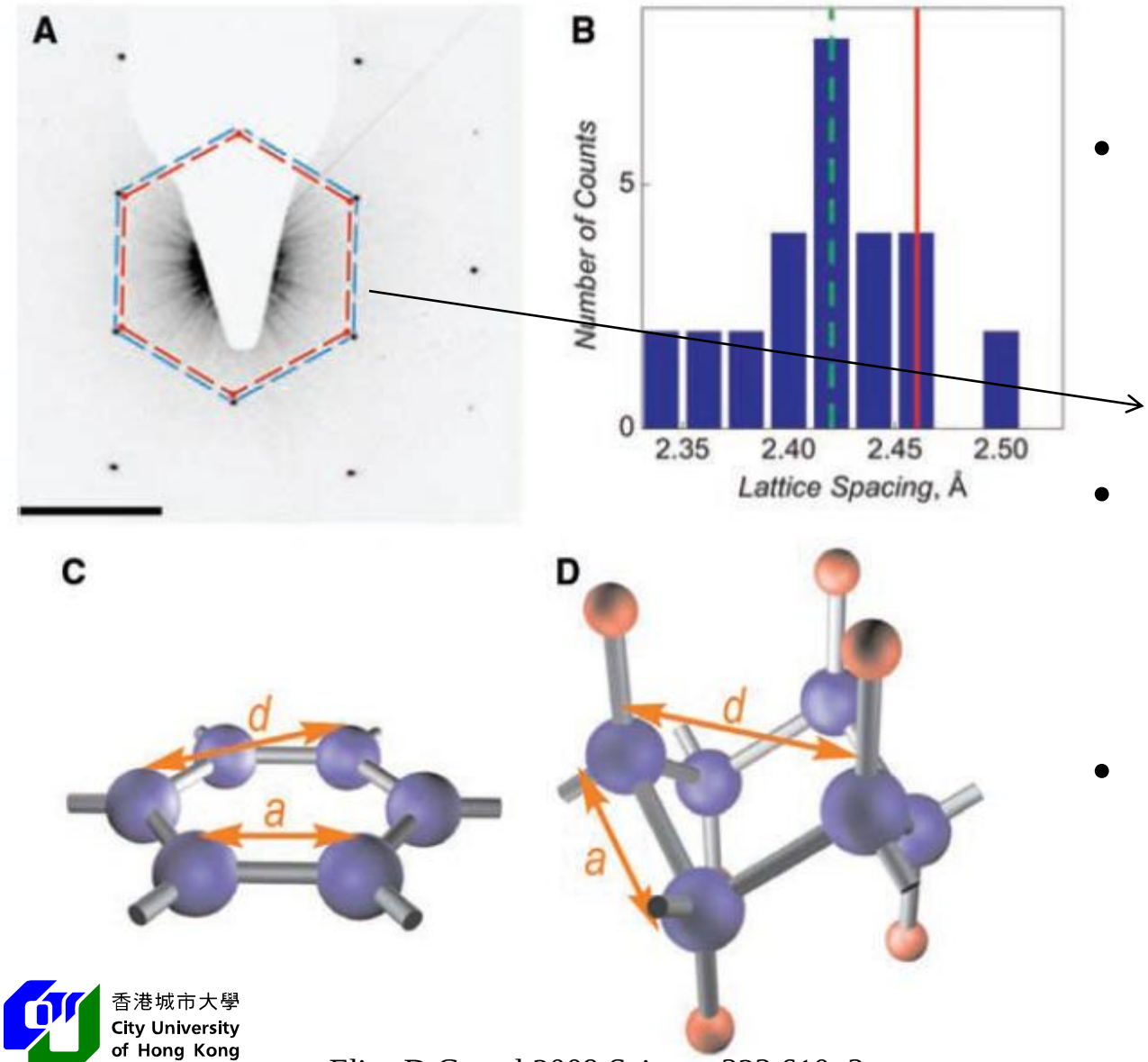
Graphane

- 2-D polymer of C and H with unit formula $(CH)_n$
- That is, hydrogenated graphene

https://michaelgr.files.wordpress.com/2009/01/graphane-01.jpg

Graphene

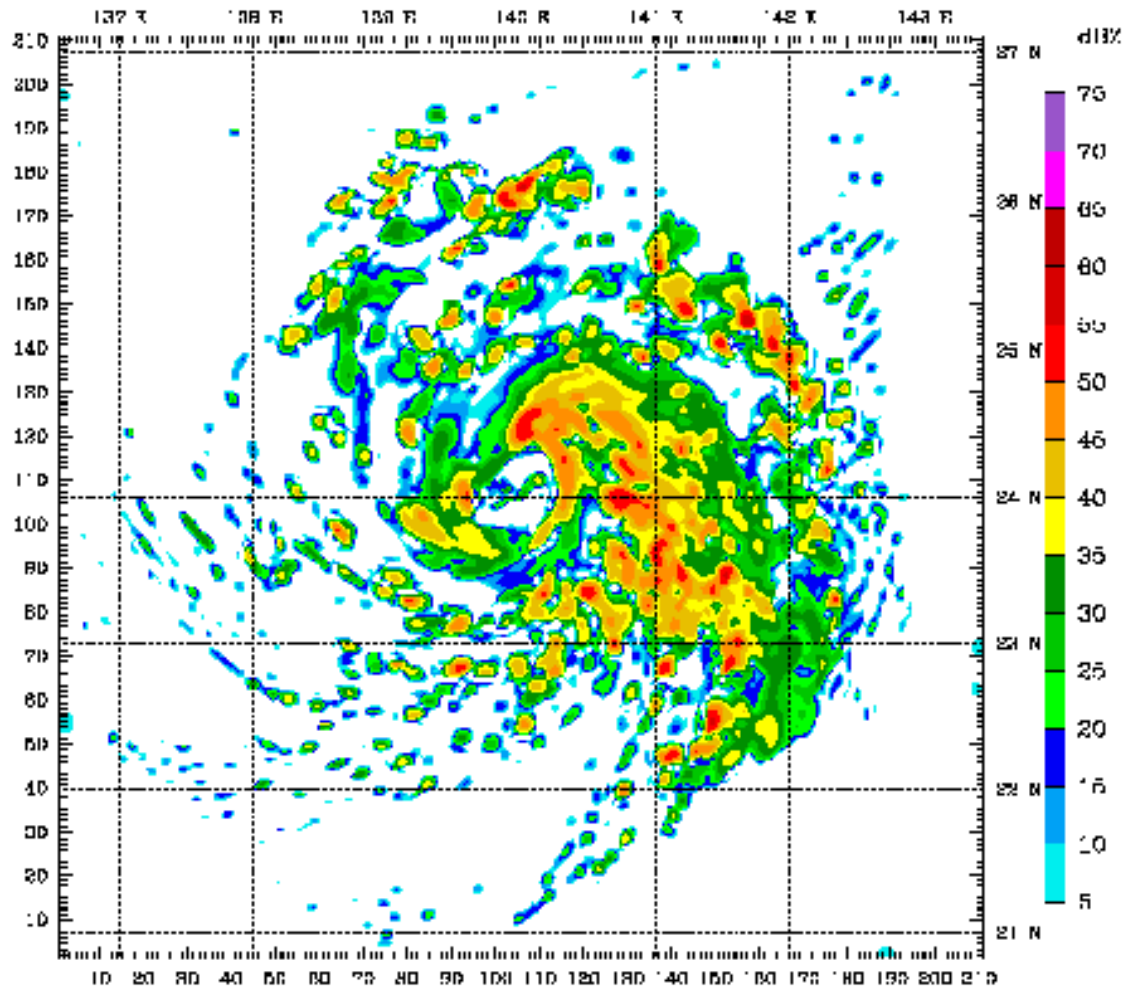
Introduction- Graphane



- Graphene + plasma(atomic) ⟶ hydrogen graphane.
- TEM of graphane: crystalline, hexagonal
- The period is shorter than graphene.

Elias D C et al 2009 Science 323 610–3

Introduction- Modeling and Simulation (M&S)

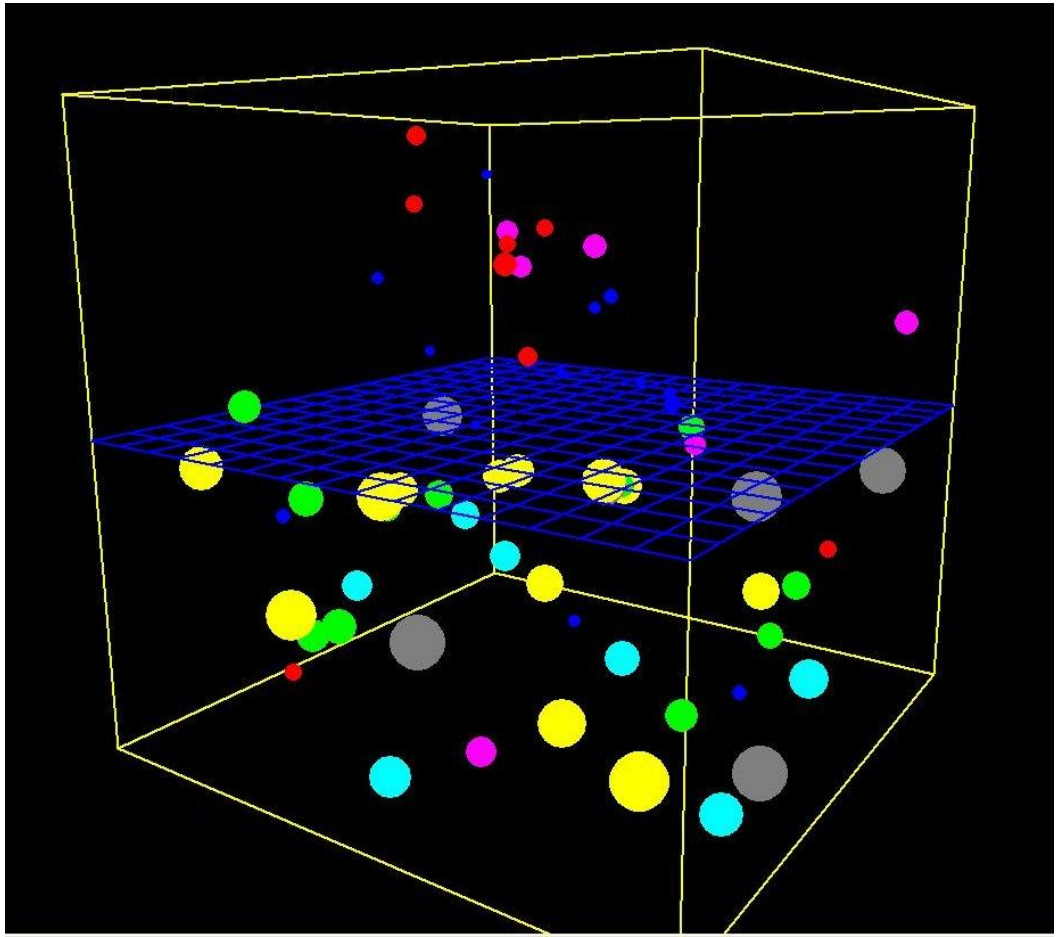


https://upload.wikimedia.org/wikipedia/commons/8/8b/Typhoon_Mawar_2005_computer_simulation_thumbnail.gif

- **M&S** is getting information without actually testing it in real life.
- **M&S** is using abstract models to simulate the system.

Introduction- Modeling and Simulation (M&S)

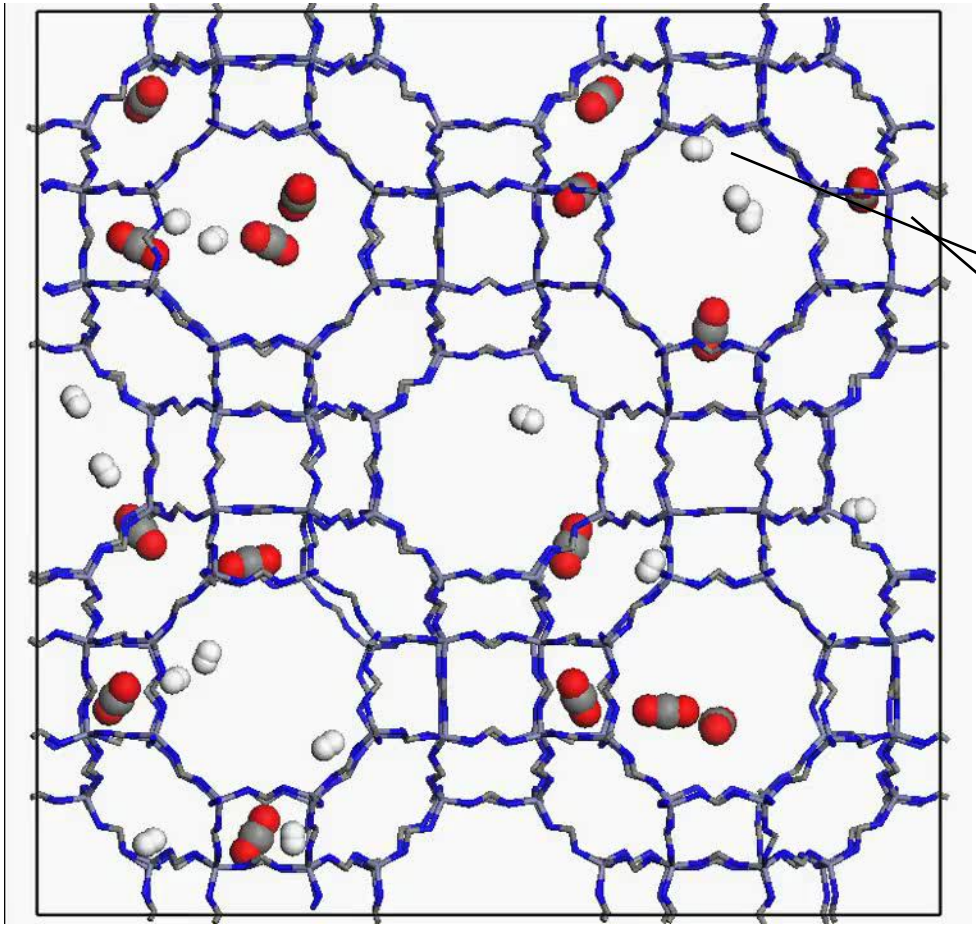
- Cheaper and safer;
- More convenient;
- Faster;
- A coherent synthetic environment.



Computer simulation of the process of osmosis

https://upload.wikimedia.org/wikipedia/commons/4/45/Osmosis_computer_simulation.jpg

Introduction- Adsorption

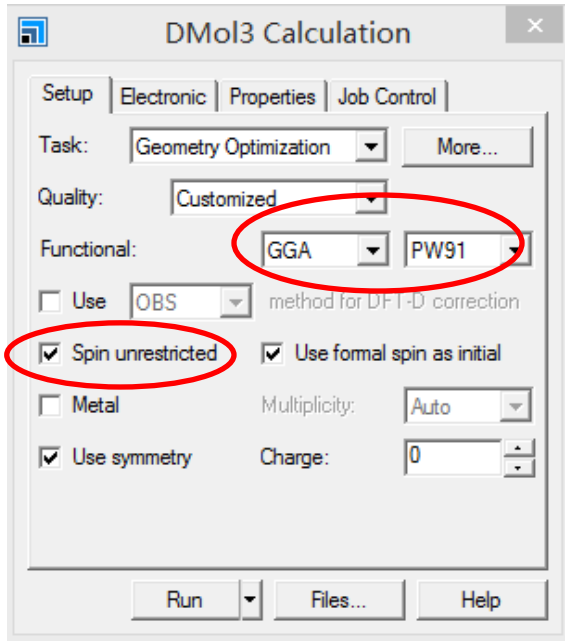


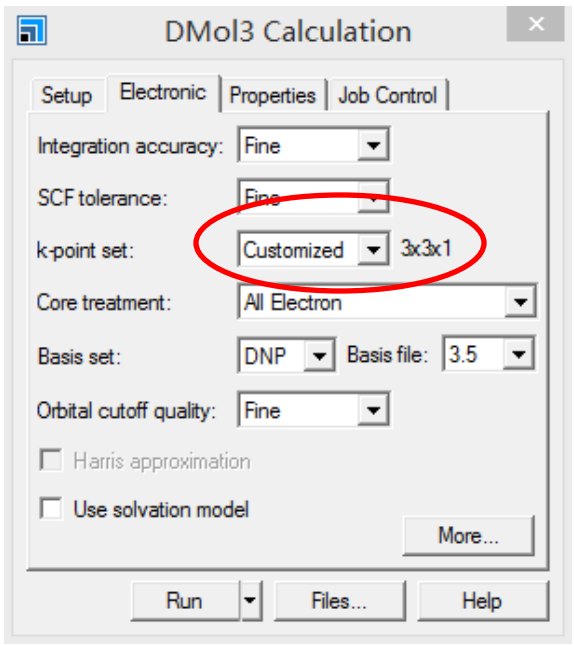
https://www.youtube.com/watch?v=RCgE2KQ-cqs

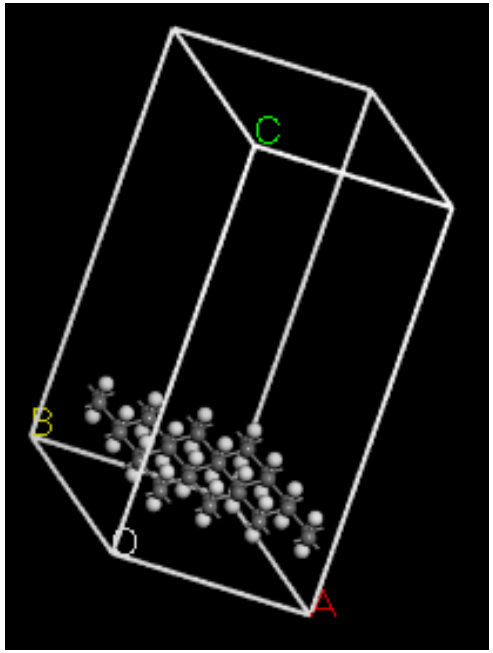
ZIF-11(Zeolitic Imidazolate) adsorption with hydrogen (**H_2**) and carbon dioxide (**CO_2**)

Computational details

- Material Studio , DMol^3 program package (based on DFT);
- Generalized gradient approximation (GGA), Perdew−Wang (PW91);
- A 3 × 3 × 1 Monkhorst−Pack (MP) k-point mesh was used for all of the surfaces;
- A vacuum layer of 15 Å was added perpendicular to the single layer surface.
- All calculations were spin-polarized.



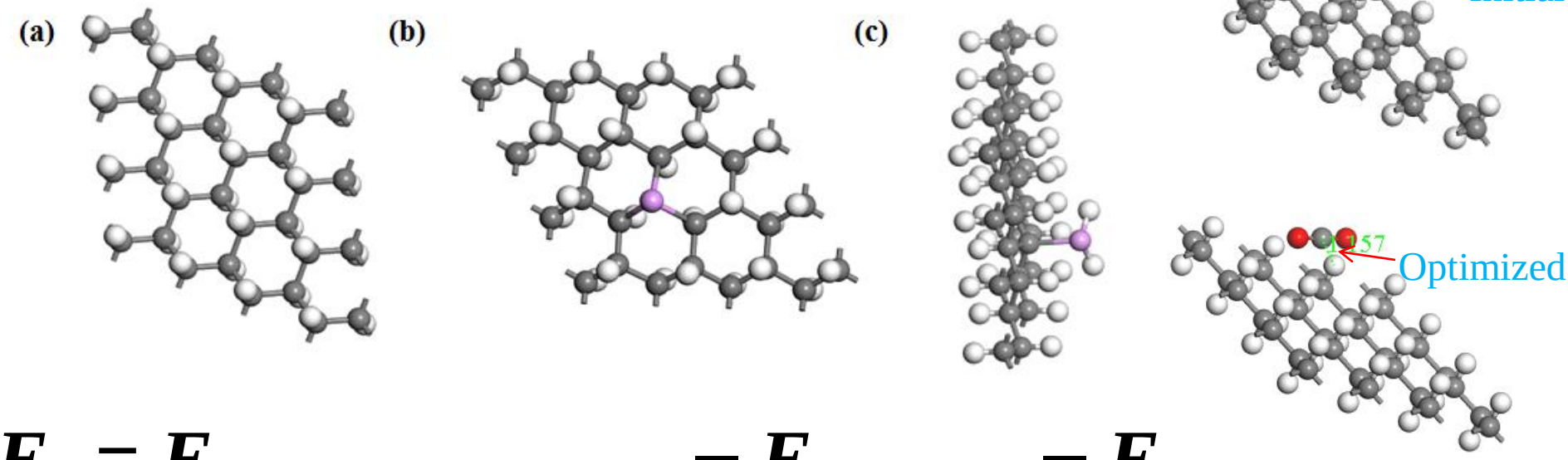




Computational details

- The unit cell of graphane was optimized as a = b = 2.46 Å, modeled as a 4 × 4 supercell of graphane (32 C atoms plus 32 H atoms).

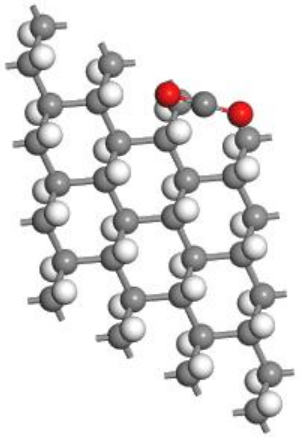
Bare graphane | P-doped graphane | PH_2-grafted graphane



$$E_a = E_{adsorbent-adsorbate} - E_{adsorbent} - E_{gas}$$

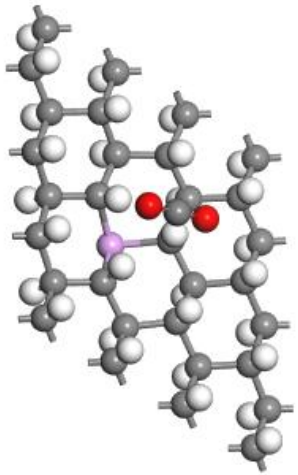
CO_2 Adsorption over P-Substituted Graphanes

Graphane+CO_2



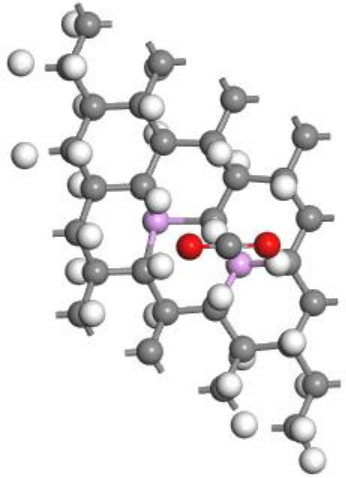
E_a = -3.313kJ/mol

GAP+CO_2



E_a = -4.895kJ/mol

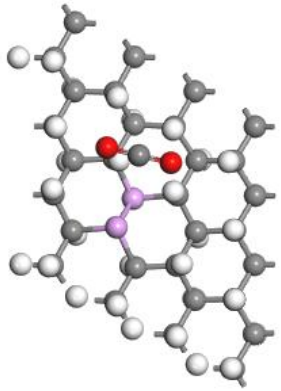
GA2P-meta+CO_2



E_a = -4.763kJ/mol

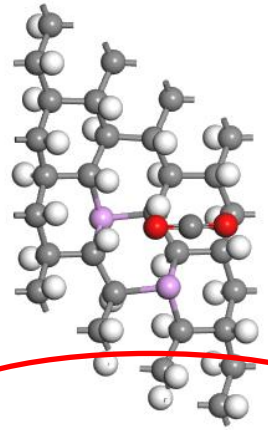
- The adsorption energy results suggest that higher P concentration gives more exothermic CO_2 adsorption.
- All CO_2 adsorption over P-substituted graphane is weak independent of P-doping concentration.

GA2P-para+CO_2



E_a = -8.573kJ/mol

GA2P-ortho+CO_2



E_a = -9.861kJ/mol

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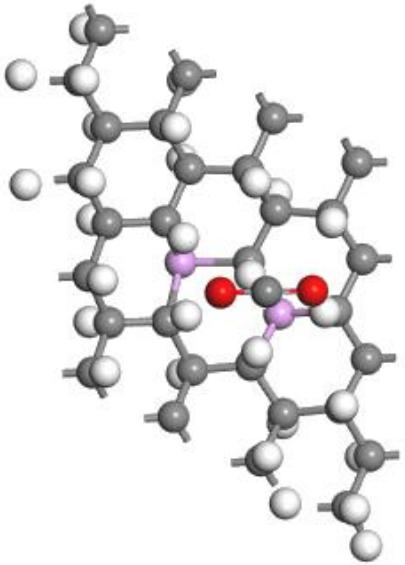
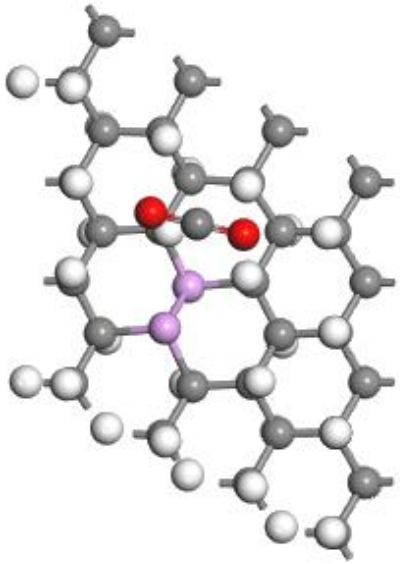
CO_2 Adsorption over P-Substituted Graphanes

GA2P-meta+CO_2



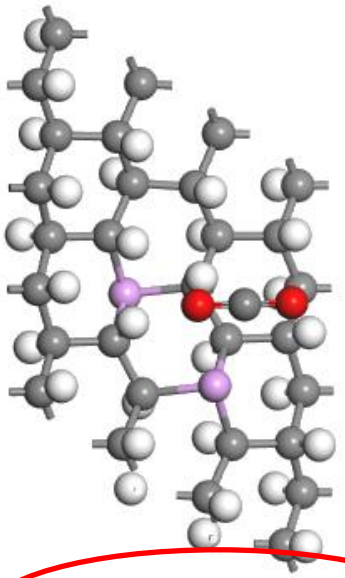
E_a = -4.763kJ/mol

GA2P-para+CO_2



E_a = -8.573kJ/mol

GA2P-ortho+CO_2

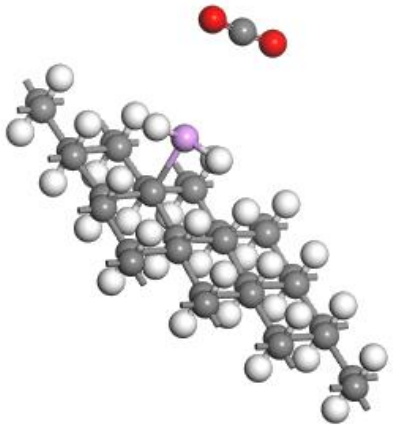


E_a = -9.861kJ/mol

- E_a: ortho > para > meta.
- Higher P doping, more van der Waals (vdW)

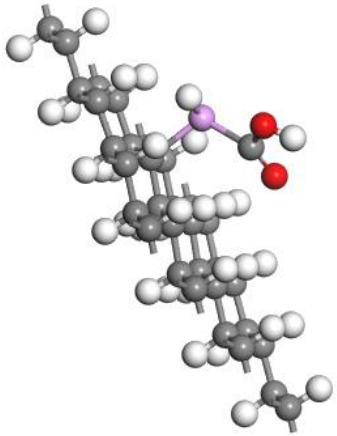
CO_2 Adsorption over Directly Grafted PH_2-Graphanes

GAPH_2 + CO_2 (Physical)



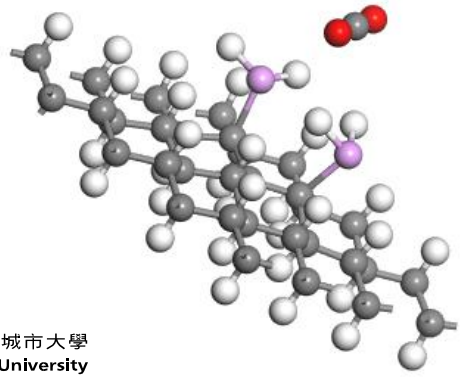
E_a = -6.762kJ/mol

GAPH_2 + CO_2 (Chemical)



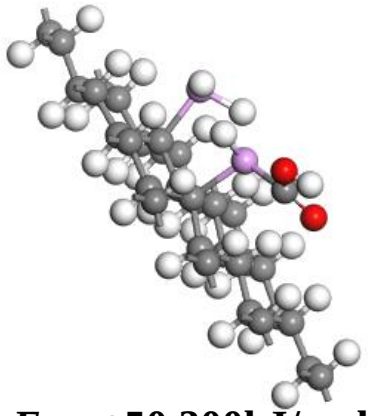
E_a = +42.997kJ/mol

GA2PH_2 + CO_2 (Physical)



E_a = -6.504kJ/mol

GA2PH_2 + CO_2 (Chemical)

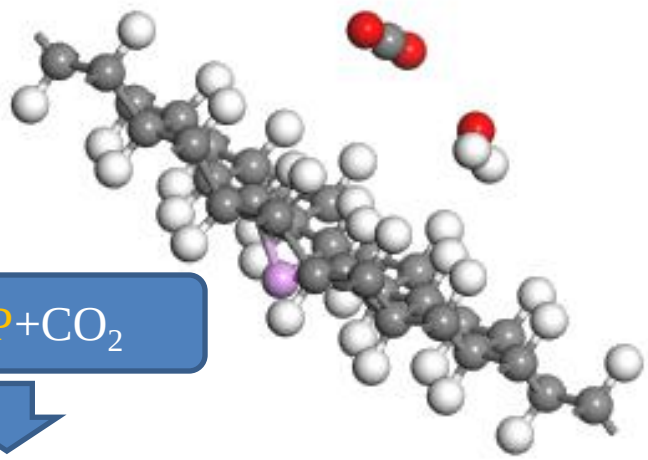


E_a = +50.300kJ/mol

- Adsorption of CO_2 over PH_2-grafted graphane is relatively weak.
- PH_2- reaction with CO_2 is not favorable.
- Higher density of PH_2- sites does not enhance the CO_2 adsorption energy.

CO_2 Adsorption over P-Substituted/Directly Grafted PH_2-Graphanes in the presence of water

GAP+CO_2+H_2O (physical)

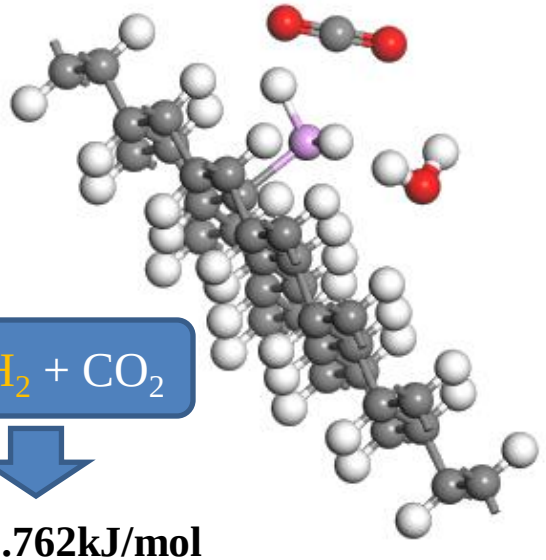


GAP+CO_2

E_a = -4.895kJ/mol

E_a = -31.787kJ/mol

GAPH_2+CO_2+H_2O (physical)



GAPH_2 + CO_2

E_a = -6.762kJ/mol

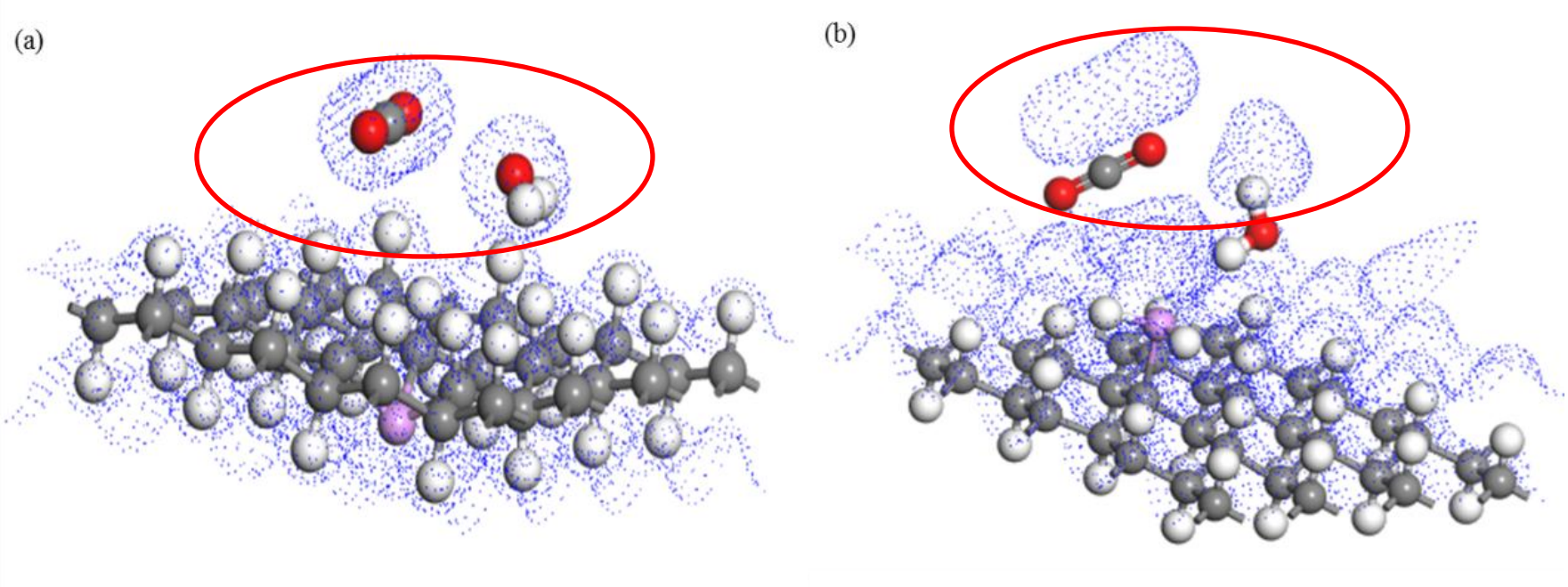
E_a = -41.794kJ/mol

The presence of H_2O strongly enhances CO_2 adsorption over both P-substituted and PH_2-grafted graphanes.

Analysis-electron density

The electron density for GAP+CO_2+H_2O

The electron density for GAPH_2+CO_2+H_2O



No electron cloud was found overlapping among the CO_2, H_2O molecules and the GAP or GAPH_2 sheet in both adsorption system, indicating that the two adsorption systems were physical.

Analysis-Partial density of state (PDOS)

PDOS of P in GAP+CO_2+H_2O

PDOS of CO_2 in GAP+CO_2+H_2O

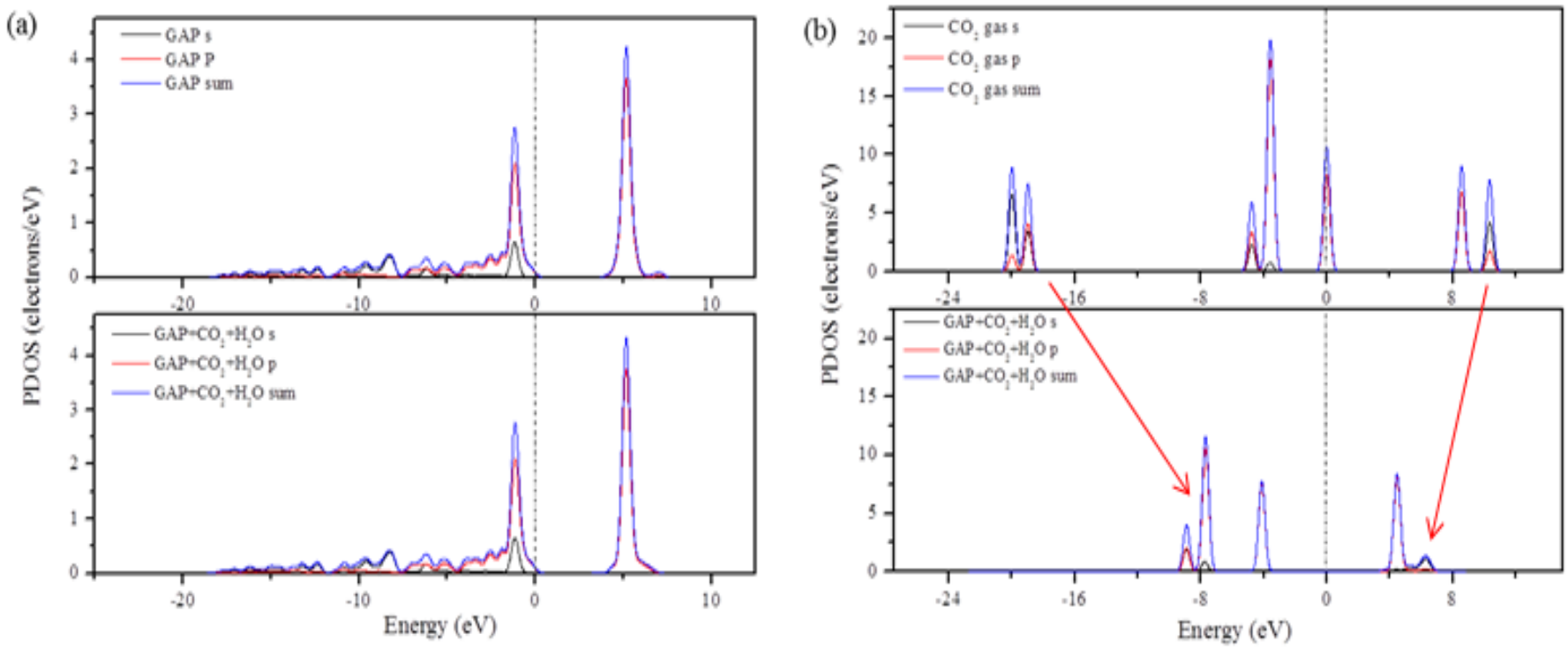


Fig. a: no obvious change around the Fermi level; the p orbital has slight change .

Fig. b: significant PDOS difference for CO_2; caused by electron transferring.

Analysis-Partial density of state (PDOS)

PDOS of PH_2 in $GAPH_2+CO_2+H_2O$

PDOS of CO_2 in $GAPH_2+CO_2+H_2O$

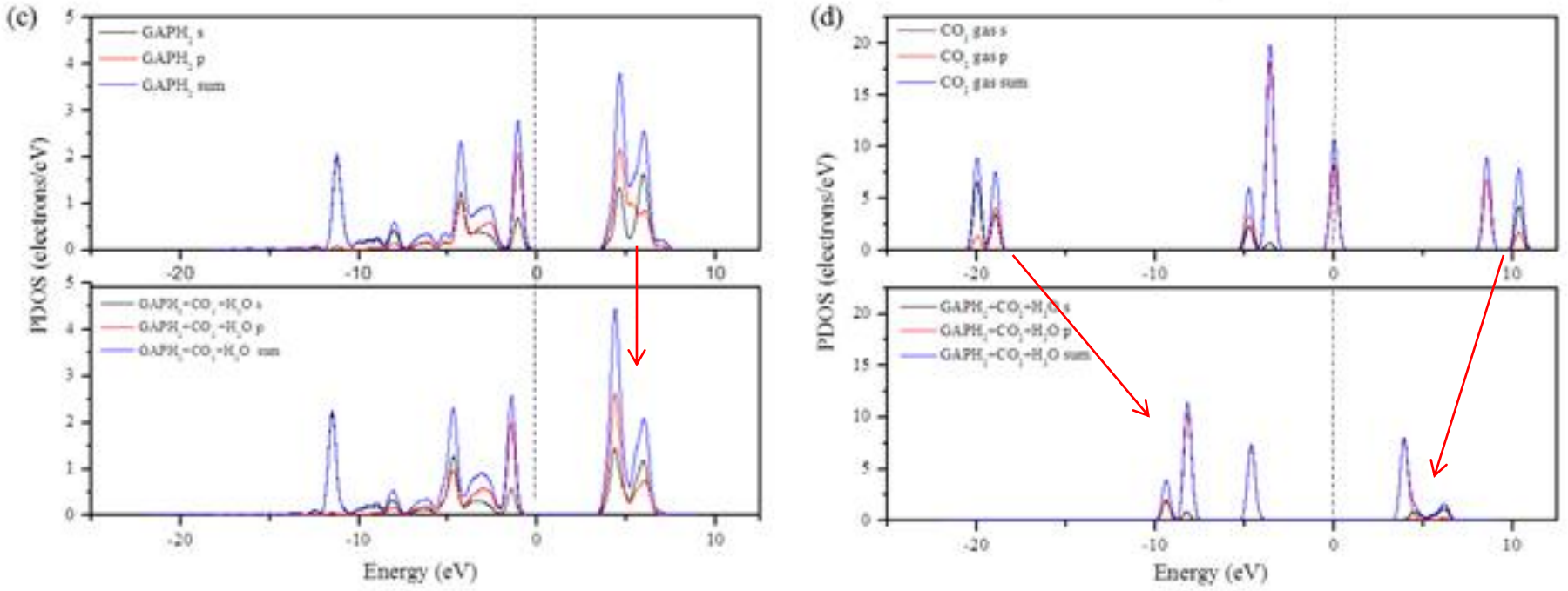


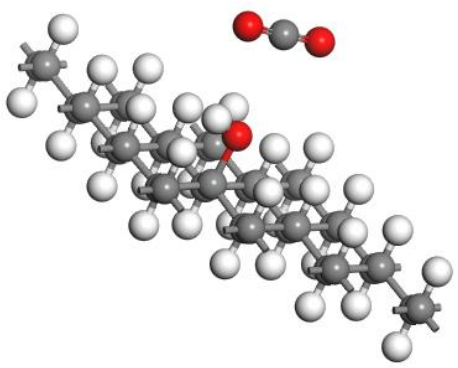
Fig. c: mild shift of both s and p orbitals.

Fig. d: great PDOS difference of CO_2; also caused by electron transferring.

CO_2 Adsorption over $-NH_2$, $-OH$ and $-COOH$ Grafted Graphanes

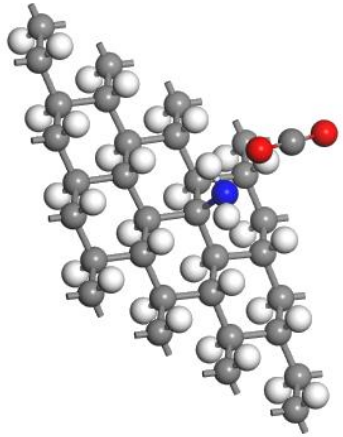
When a second $-OH$ group was introduced in the proximity of a $-OH$ site on graphane, CO_2 adsorption can be greatly enhanced.

GAOH + CO_2



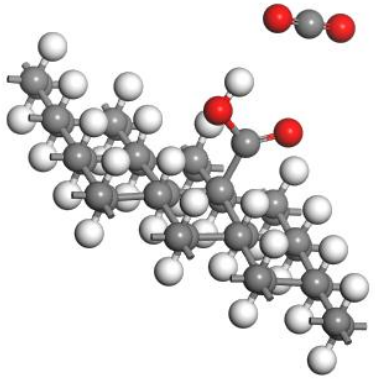
E_a = -9.678kJ/mol

$GANH_2$ + CO_2



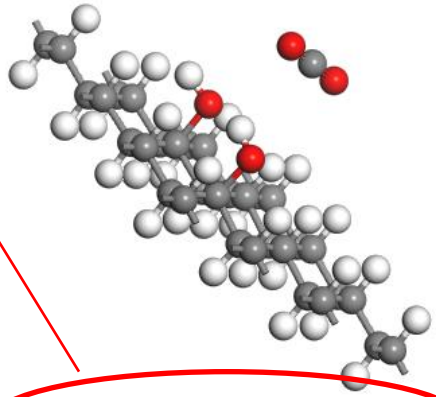
E_a = -10.743kJ/mol

GACOOH + CO_2



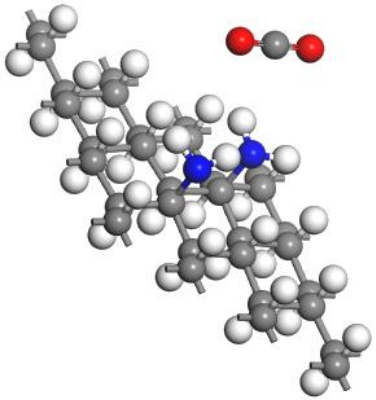
E_a = -12.667kJ/mol

$GA(OH)_2$ + CO_2



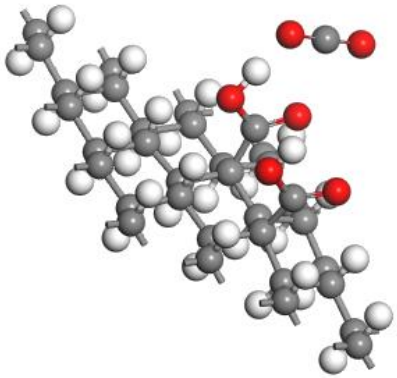
E_a = -44.889kJ/mol

$GA(NH_2)_2$ + CO_2



E_a = -4.594kJ/mol

$GA(COOH)_2$ + CO_2

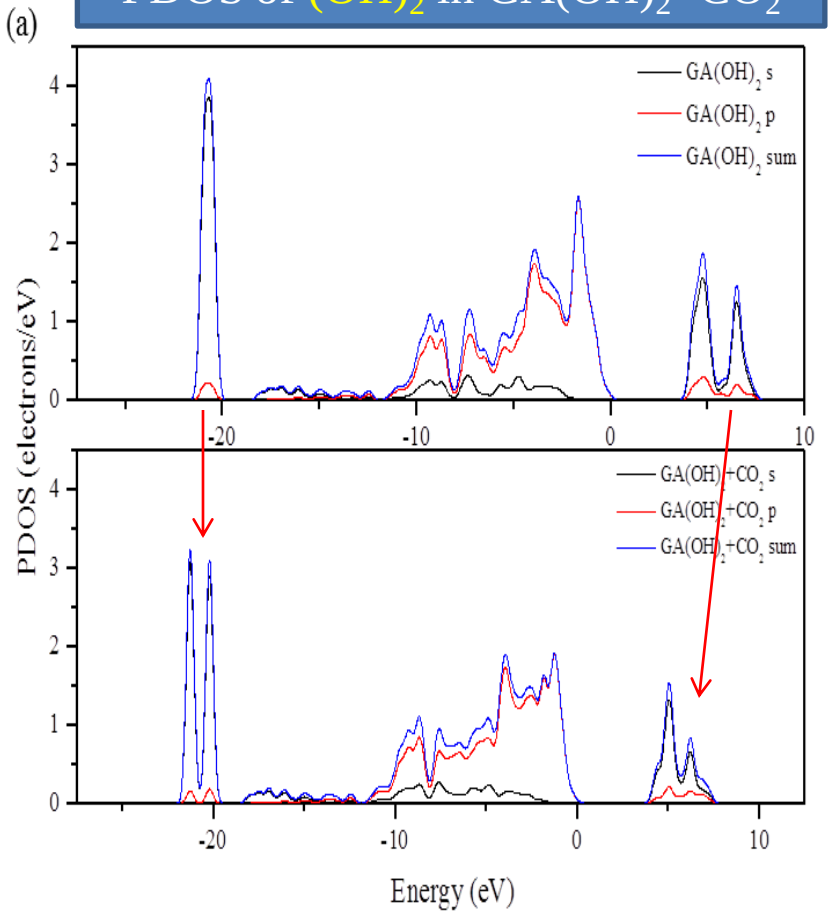


E_a = -20.028kJ/mol

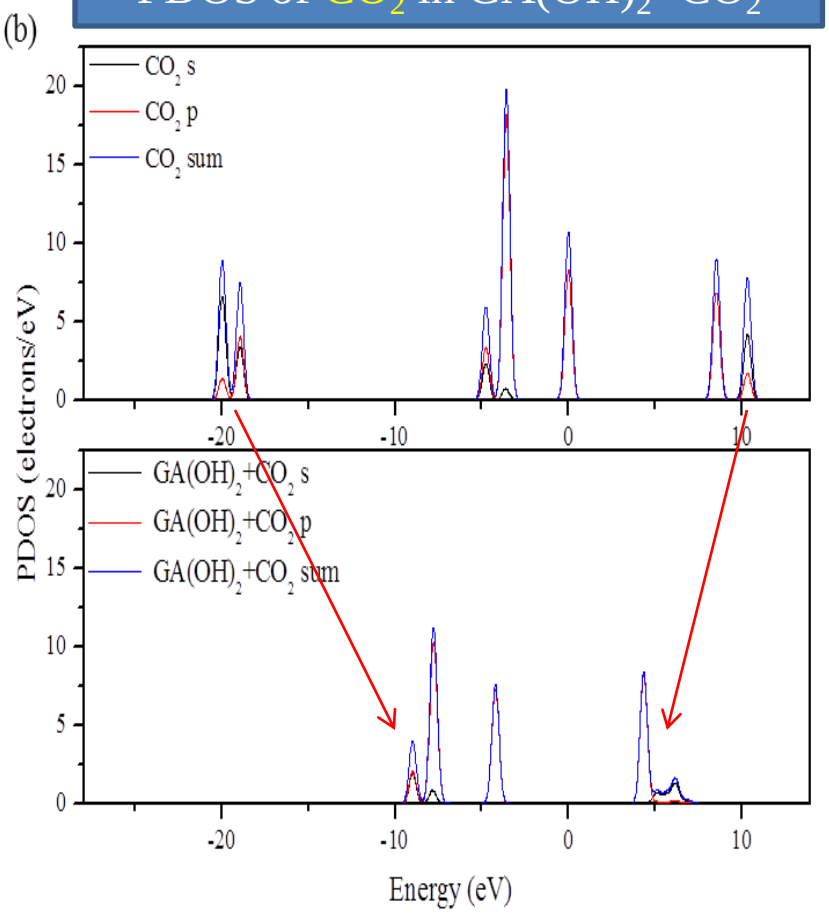
香港城市大學
City University of Hong Kong

Analysis-Partial density of state (PDOS)

PDOS of $(OH)_2$ in $GA(OH)_2+CO_2$



PDOS of CO_2 in $GA(OH)_2+CO_2$



The PDOS of both –$(OH)_2$ and CO_2 have significant changes. The large amount of electron transferring is suspected to cause the sizable change.

Overview

	E_a(kJ/mol)	h_{C-H} (Å)	h_{C-P} (Å)	h_{O-P} (Å)	h_{O-H} (Å)	$h_{C-O/N/C}$ (Å)
GA+CO_2	-3.313	2.981	--	--	--	--
GAP+CO_2	-4.895	3.873	5.328	--	--	--
GA2P-meta+CO_2	-4.763	3.122	5.110	--	--	--
GA2P-para+CO_2	-8.573	3.271	4.247	--	--	--
GA2P-ortho+CO_2	-9.861	3.109	3.518	--	--	--
GAPH_2+CO_2(physi)	-6.762	3.786	3.464	--	--	--
GAPH_2+CO_2(chemi)	+42.997	--	--	--	--	--
GA(PH_2)$_2$+CO_2(physi)	-6.504	3.551	3.579	--	--	--
GA(PH_2)$_2$+CO_2(chemi)	+50.300	--	--	--	--	--
GAP+CO_2+H_2O	-31.787	3.618[a], 2.882[b]	5.557	5.459	3.315	--
GAPH_2+CO_2+H_2O	-41.794	3.581[a], 3.953[b]	3.838	3.473	2.886	--
GAOH+CO_2	-9.678	2.869	--	--	--	2.906
GA(OH)$_2$+CO_2	-44.889	2.817	--	--	--	3.141
GANH_2+CO_2	-10.743	2.971	--	--	--	3.161
GA(NH_2)$_2$+CO_2	-4.594	3.010	--	--	--	3.484
GACOOH+CO_2	-12.667	2.828	--	--	--	3.725
GA(COOH)$_2$+CO_2	-20.028	3.153	--	--	--	3.784

Conclusions

- CO_2 adsorption over various functionalized graphane was studied using DFT.

- CO_2 adsorbs weakly on a P-functionalized graphane. The adsorption can be strengthened with the presence of co-adsorbed H_2O (about -42 kJ/mol with PH_2-grafted on graphane).

- Under dry conditions, CO_2 adsorption can be greatly enhanced with the presence of two −OH groups grafted on graphane (about -45 kJ/mol).

- This work provides an atomic-level strategy in the design of functionalized graphane for carbon dioxide capture and storage.

Thank you for your attention

Material Studio

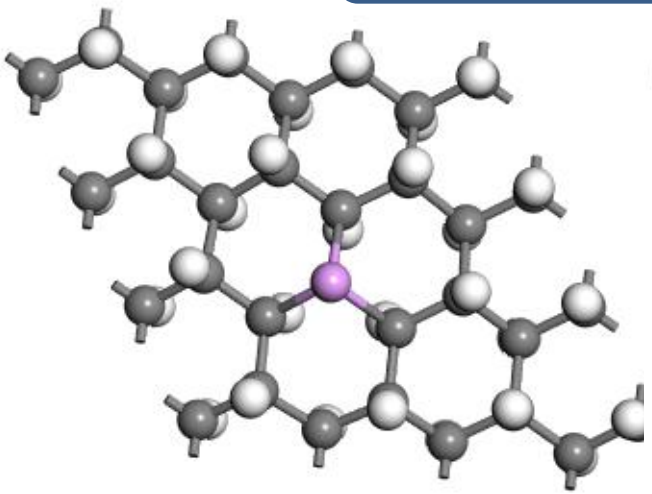
- **Materials Studio** is a software for simulating and modeling materials.
- It is developed and distributed by Accelrys.
- Materials Studio is a complete modeling and simulation environment designed to allow researchers in materials science and chemistry to predict and understand the relationships of a material's atomic and molecular structure with its properties and behavior.

Density Functional Theory (DFT)

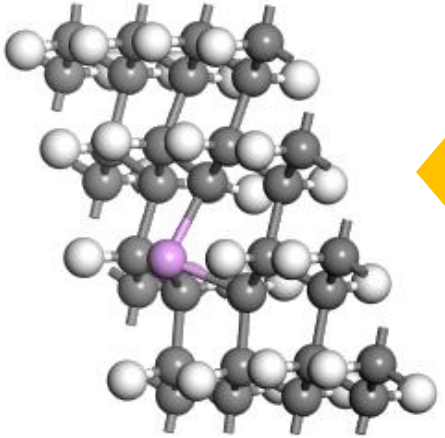
- **Density functional theory (DFT)** is a computational quantum mechanical modeling method.
- To study the electronic structure of many-body systems.
- The most popular simulation approach in condensed-matter physics, computational chemistry and materials science.
- Its basic theory is using functionals of spatially dependent electron density to determine the properties of a many-electron systems.

Doped & Grafted

P-doped graphane



Top view

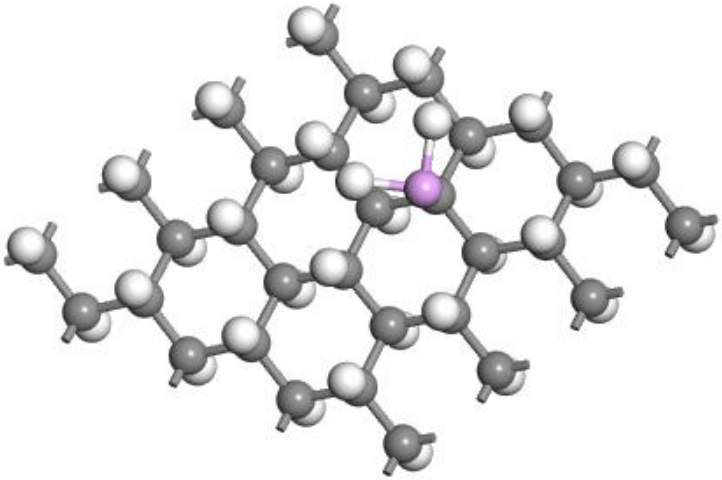


Side view

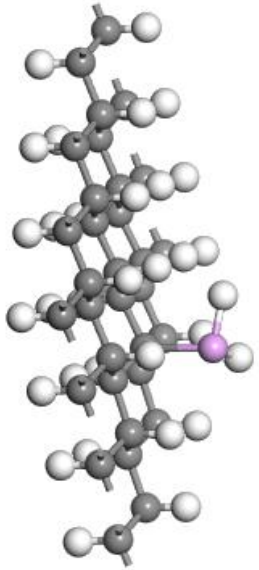
P-Doped Graphane - C atom was replaced by P atom

PH_2-grafted graphane

PH_2-Grafted Graphane - H atom was replaced by PH_2 groups



Top view



Side view

CO_2 Adsorption over $-NH_2$, $-OH$ and $-COOH$ Grafted Graphanes

- The CO_2 adsorption energy can be tuned in a substantial range with varied types and locations of functionalities on graphane.[22]

- Generally, for the types of functionalities on adsorbent surfaces govern the adsorption thermodynamics on CO_2 capture,[26] four functional groups (hydrogen H-, hydroxyl OH-, amine NH_2- and carboxyl COOH-) are usually considered to improve the gas adsorption capacity and selectivity performance.[27]

- It should be mentioned that the CO_2 adsorption efficiency or capacity depends on not only the interaction strength between CO_2 and adsorbents but also the availability of adsorption sites, which could be affected by textural properties of adsorbents.

- minimize the interaction between the periodic images of the mentioned sheets.

Electron Density and Density of States

- Electron density is the measure of the probability of an electron being present at a specific location.

- The density of states (DOS) of a system describes the number of states per interval of energy at each energy level that are available to be occupied.

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