Competitive Adsorption For Clean Air Applications

Paul Rapp

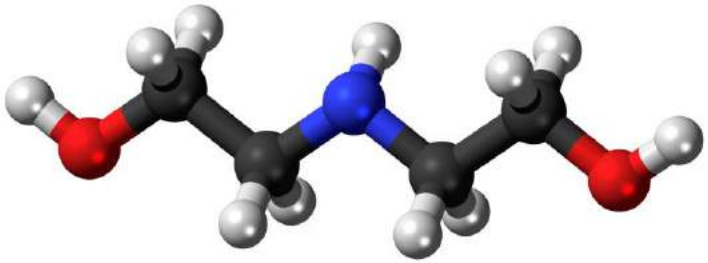
June 2017

Motivation

- Industrial Pollution
- Traffic
- Global Warming
- Acid Rain
- Public Health

Carbon Capture Methods

- Absorbent



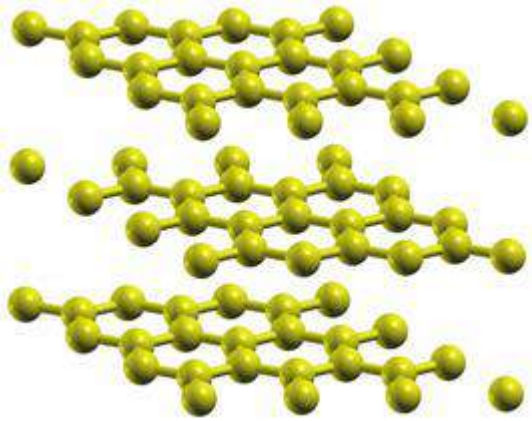
- Amine solutions (absorption):
  - Expensive. ☒
  - Environmental concerns. ☒

- Adsorbent

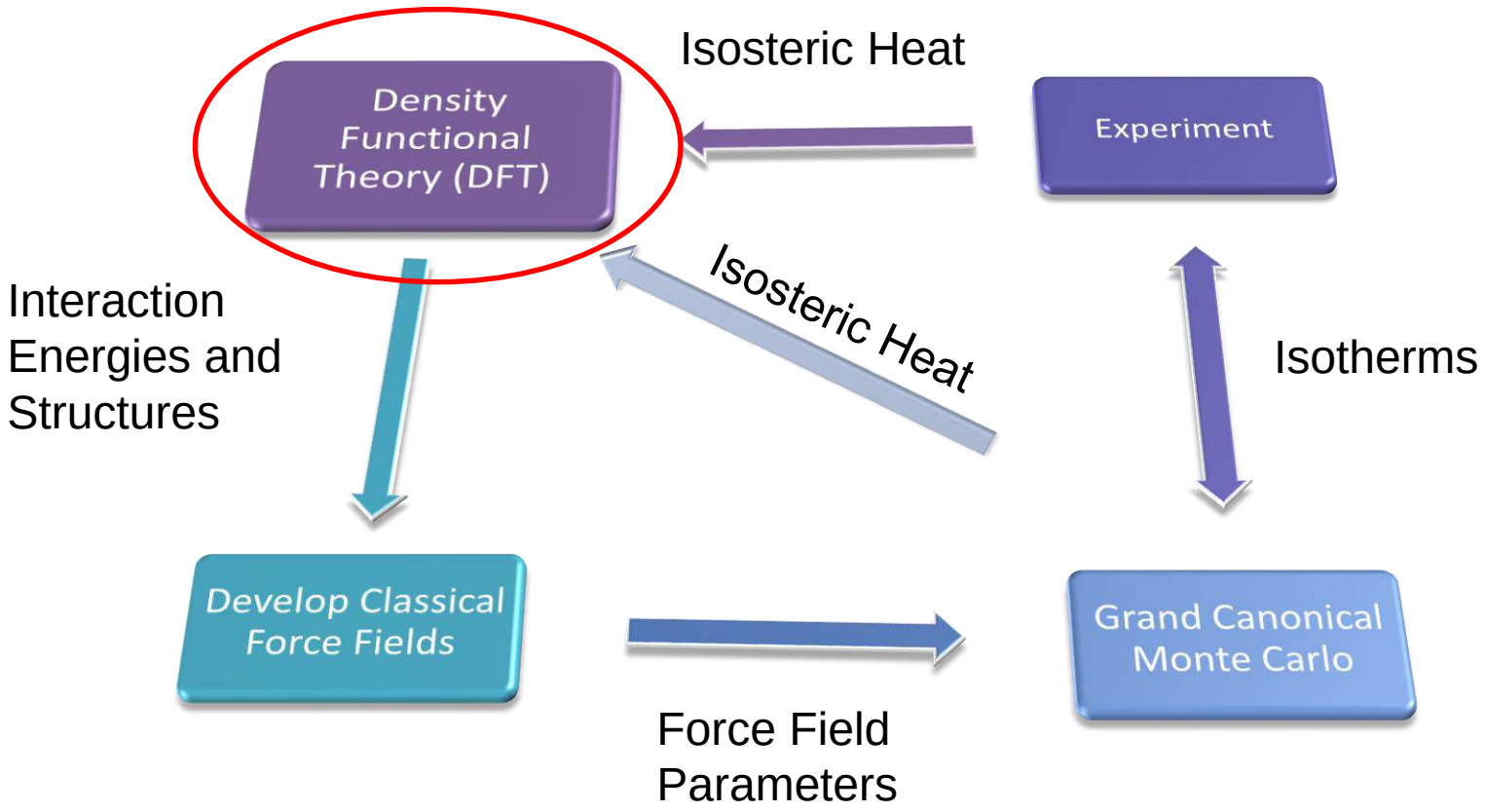
- Activated carbons:
  - Cheap. ☑
  - Environmentally friendly. ☑

Activated Carbons

- Variable structures and chemistry.
- Not well characterised.
- Can we optimise activated carbons for specific pollutant removal?
  - Chemical properties
  - **Textural properties**
- CO2 adsorption on graphite/graphene
  - A simple model system
  - Predictable structure



Research Approach



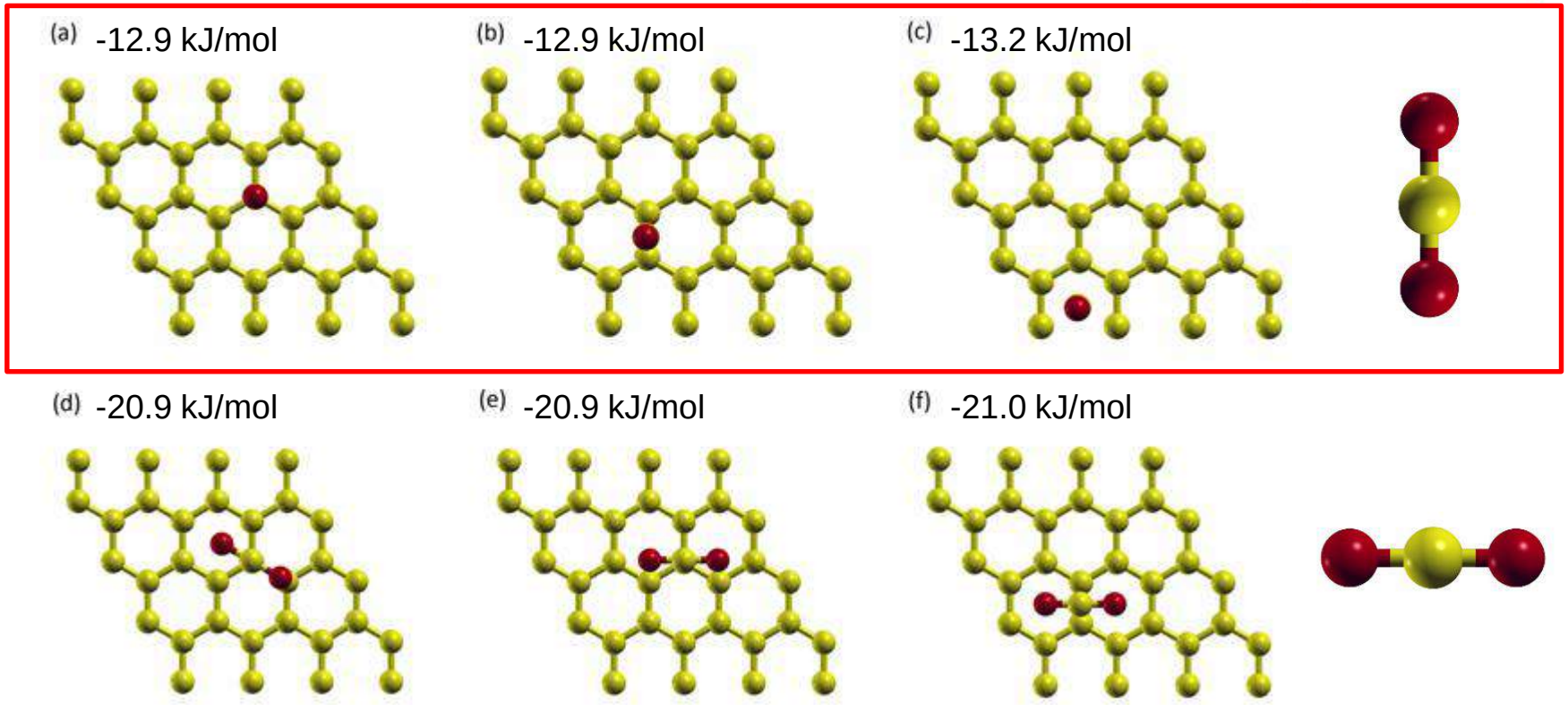
Density Functional Theory (DFT)

- Quantum Espresso [1]
- Functional vdW-DF [2]
- CO_2 on graphene

[1] Paolo Giannozzi et al.,. Quantum espresso: a modular and open-source software project for quantum simulations ofmaterials. Journal of Physics: Condensed Matter, 21(39):395502, 2009.

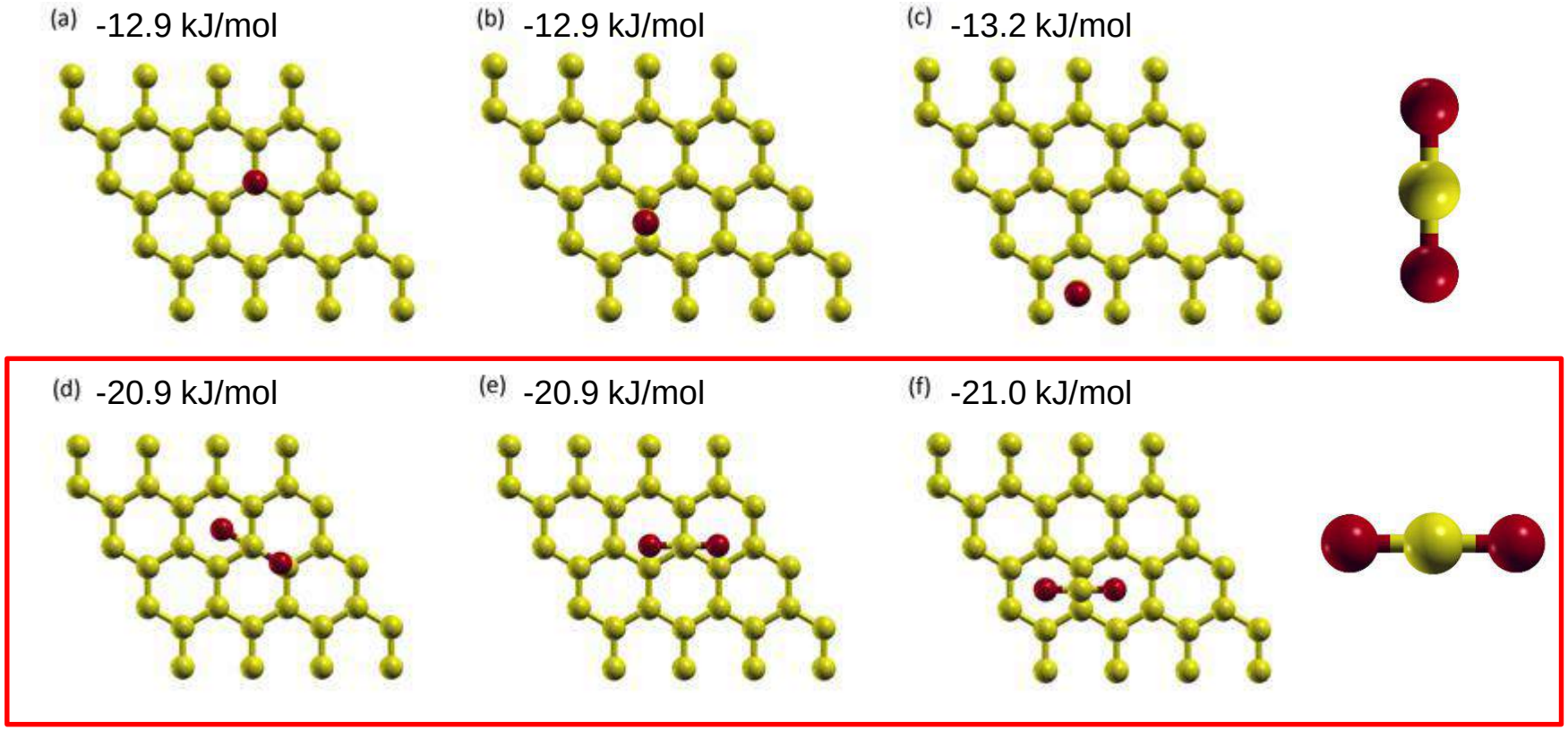
[2] M. Dion, H. Rydberg, D. C. Langreth E. Schroder, and B. I. Llundqvist. Van der waals density functional for general geometries. Physical Review Letters, 92(24):246401, 2004.

Orientation and Site Dependence



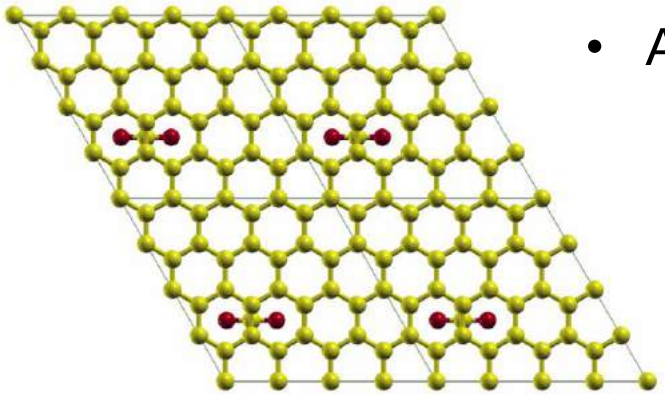
- Negligible surface site preference.
- Flat orientations are energetically favourable

Orientation and Site Dependence

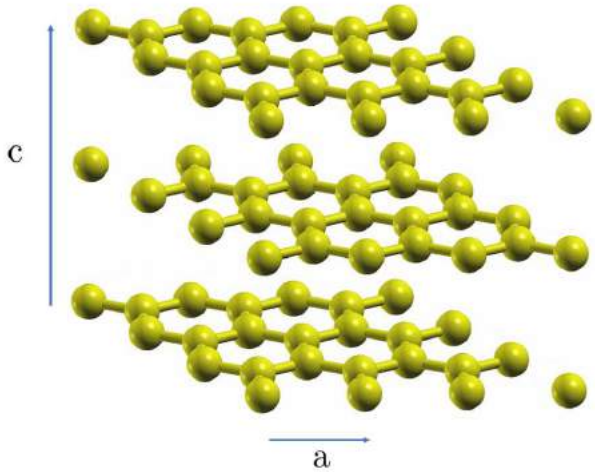


- Negligible surface site preference.
- Flat orientations are energetically favourable

Number of layers



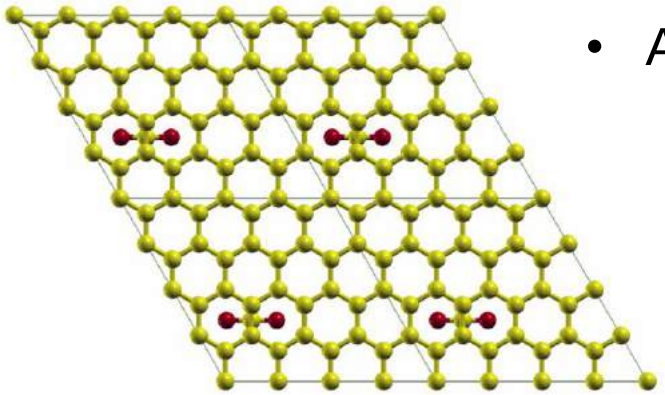
- Adsorption Energy:
  -21.0 kJ/mol
  - Experimental adsorption energy:
    -16.7 to -24.9 kJ/mol [3].
    - Converges at 3 layers



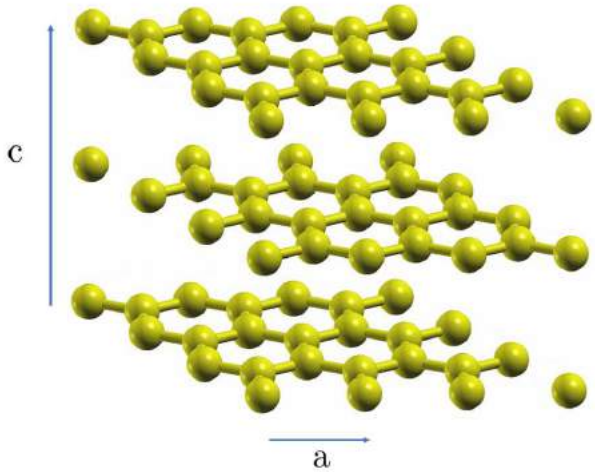
Number of Graphene Layers	Adsorption Energy (kJ/mol)
1	-21.0
2	-22.8
3	-23.2

[3] Philip L. Walker Jr. Chemistry and Physics of Carbon, 6. Marcel Dekker, 1970.

Number of layers



- Adsorption Energy:
  -21.0 kJ/mol
  - Experimental adsorption energy:
    -16.7 to -24.9 kJ/mol [3].
    - Converges at 3 layers

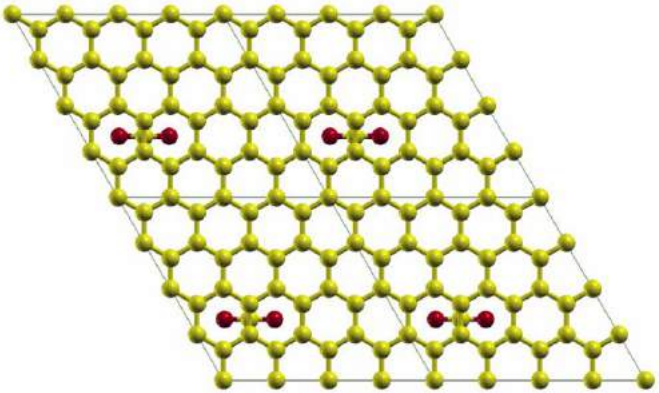


Number of Graphene Layers	Adsorption Energy (kJ/mol)
1	-21.0
2	-22.8
3	-23.2

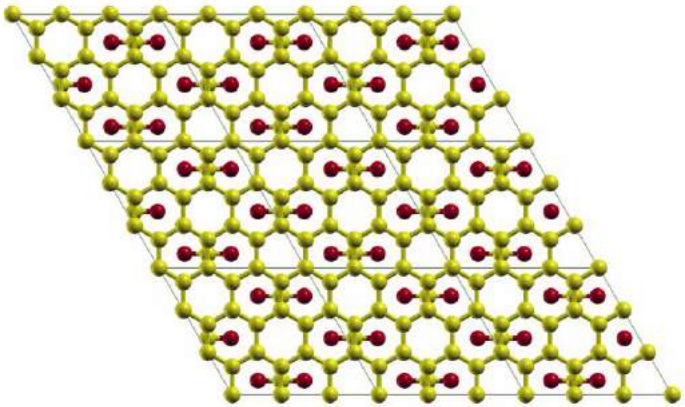
[3] Philip L. Walker Jr. Chemistry and Physics of Carbon, 6. Marcel Dekker, 1970.

Surface Coverage

10.27 wt%

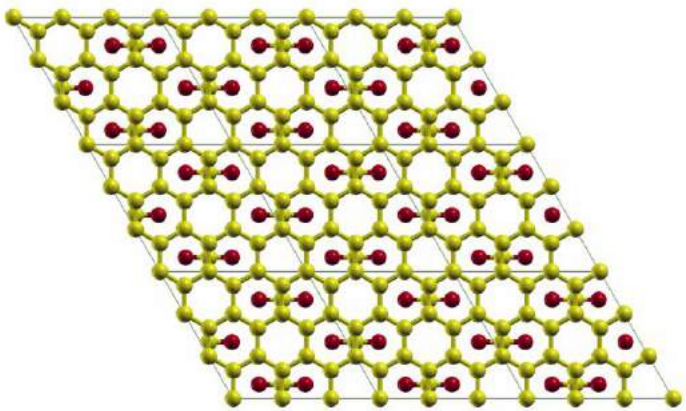


37.92 wt%



Coverage (wt%)	Adsorption Energy (kJ/mol)
10.27	**-21.0**
16.91	-21.6
31.42	-17.8
37.92	**-7.1**
47.81	185.5

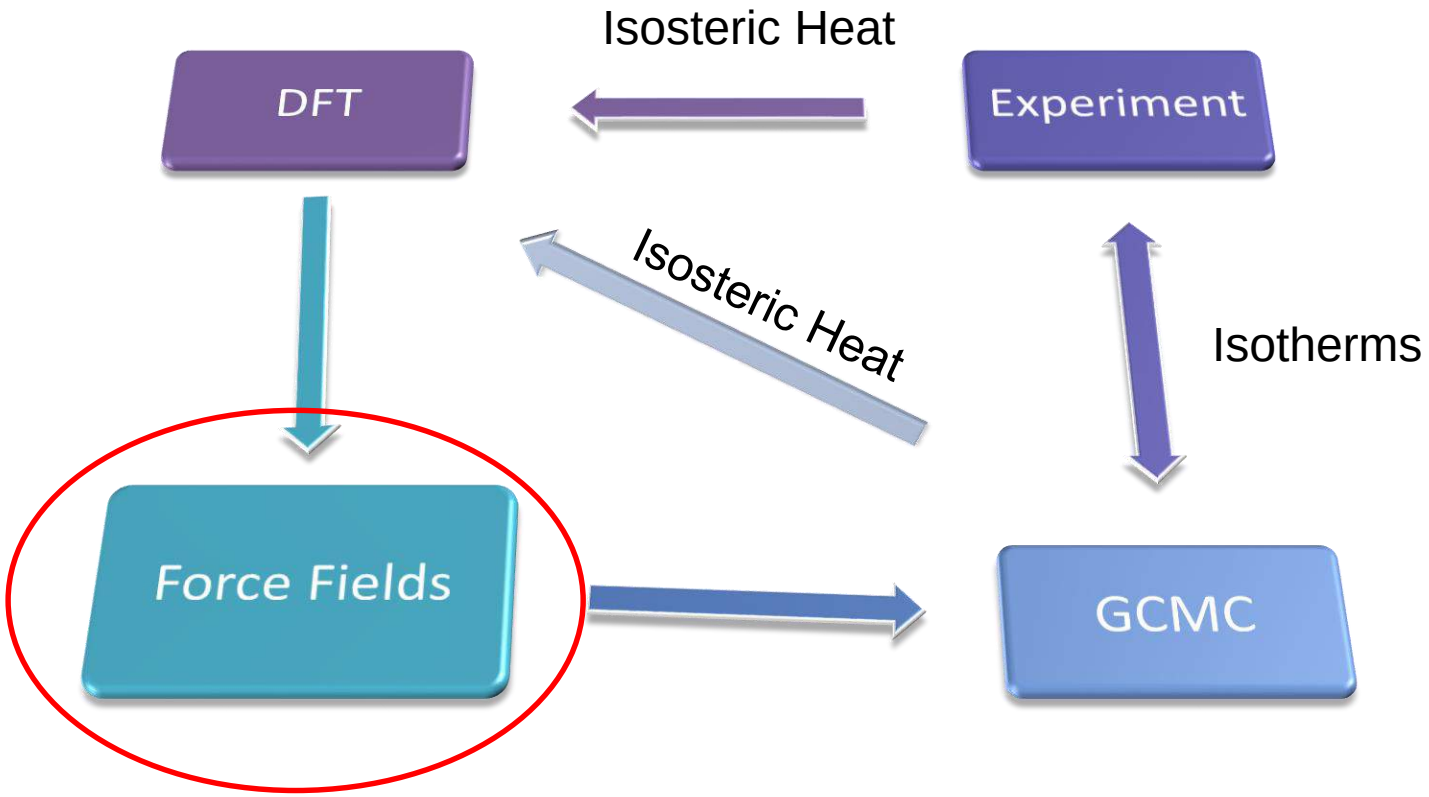
Surface Coverage with Layers



Number of Graphene Layers	Adsorption Energy (kJ/mol)
1	-7.1
2	-11.2
3	-12.5

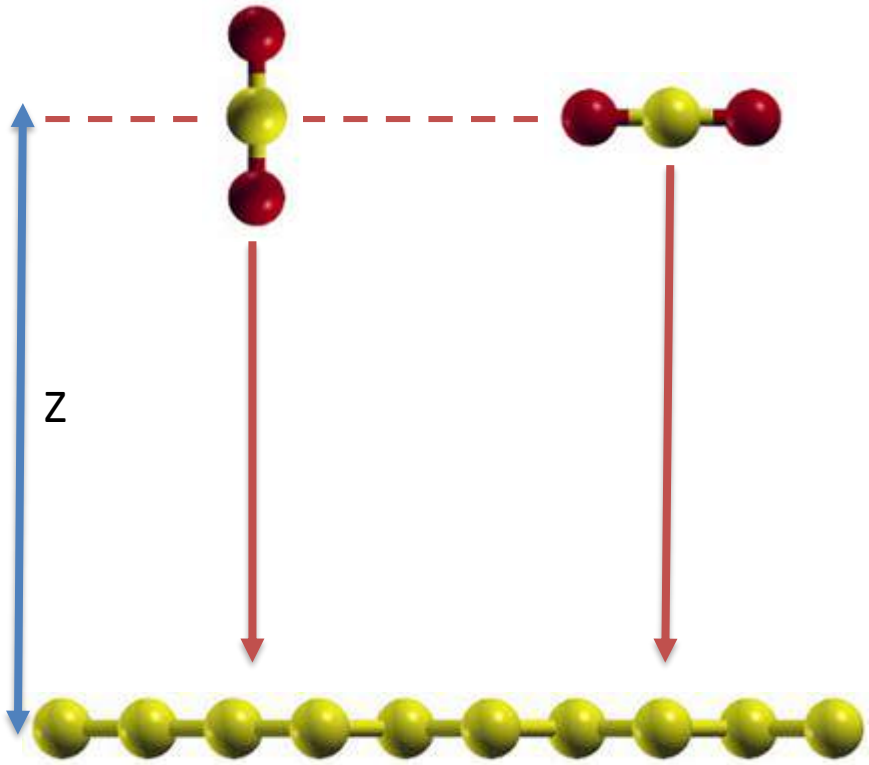
- Converges at 3 layers

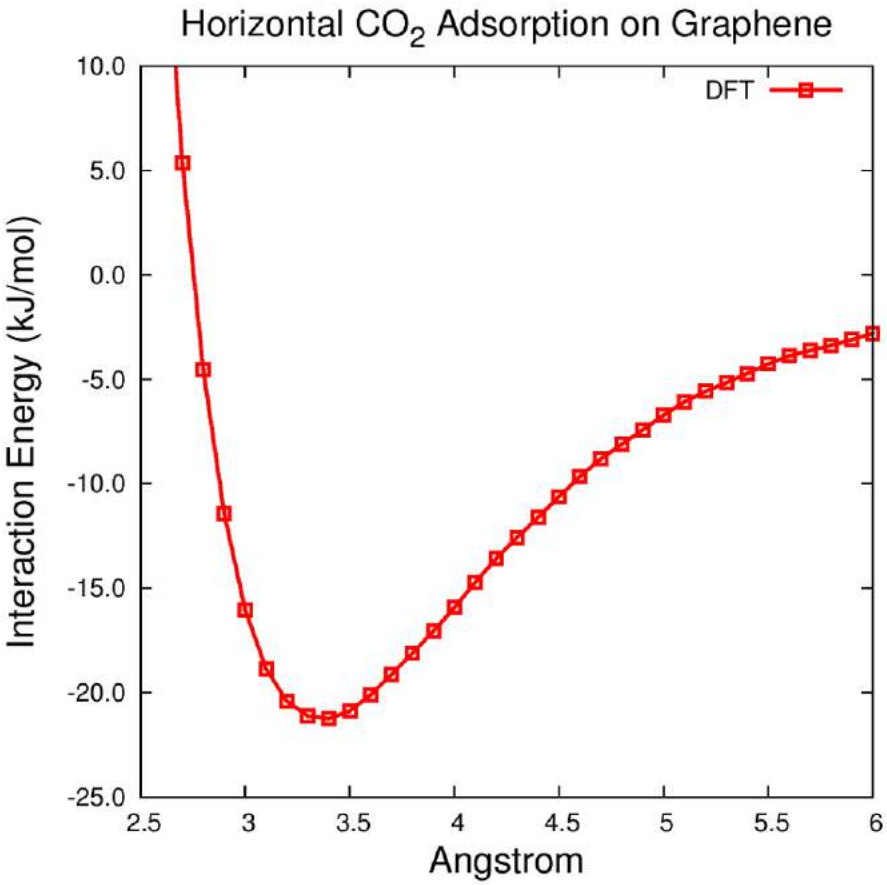
Research Approach



Force Fields

- Aim: Develop a classical force field from DFT data
- Adsorption energy taken for different distances from surface (z)
- Forms DFT adsorption energy profile





Force Fields

Bulk Gas-Gas Interactions:
Fully described by TraPPE

Gas-Surface Interactions:

Use Lennard-Jones potential and parameterise using DFT

$$V_{\mathrm{LJ}} = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$

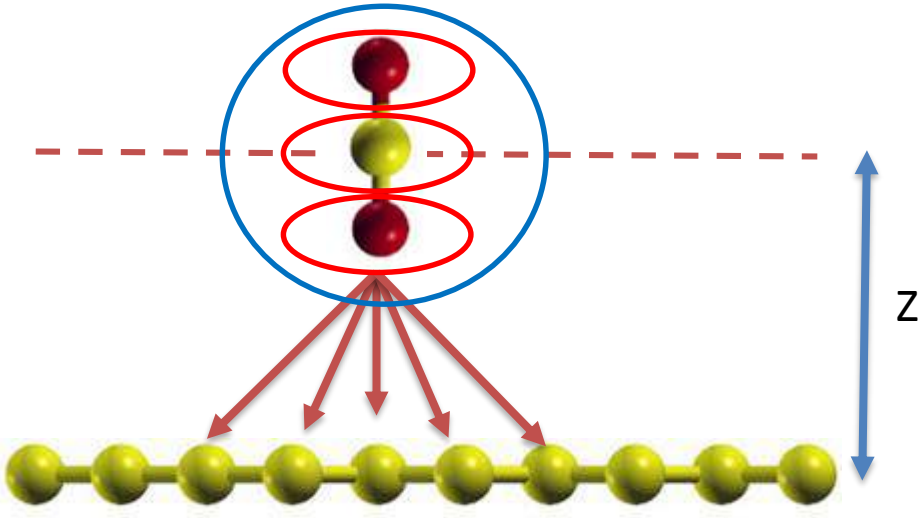
ε is potential well depth
σ is the finite distance at which the inter-particle potential is zero
r is the distance between the particles

Force Fields

- **Steps:**
- Classical adsorption energies are a sum of all molecule-surface pair potentials.

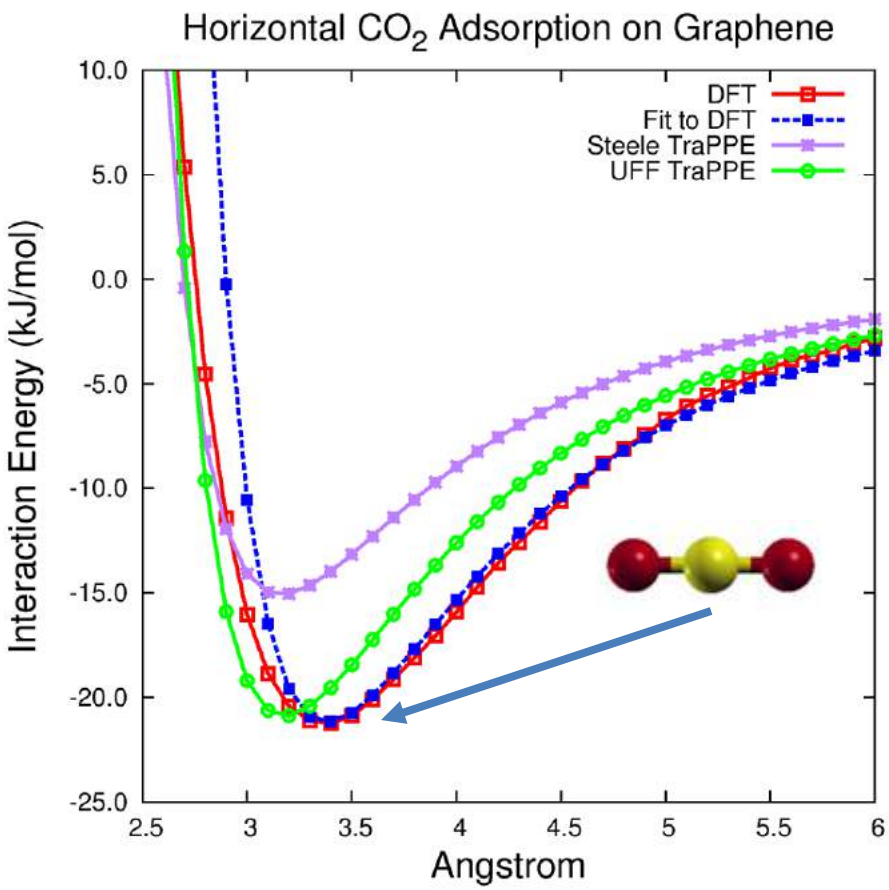
- Optimise Lennard Jones parameters to obtain best fit to DFT data.

- Simultaneously fitting to 2 orientations (flat/vertical) over a range of distances (z).



Force field parameters obtained are *ε and σ* for C_{CO2}-$C_{graphene}$ and O_{CO2}-$C_{graphene}$.

Force Fields (CO_2)



- Forcefield values ε and σ derived from best fit (dashed) lines to DFT curves.

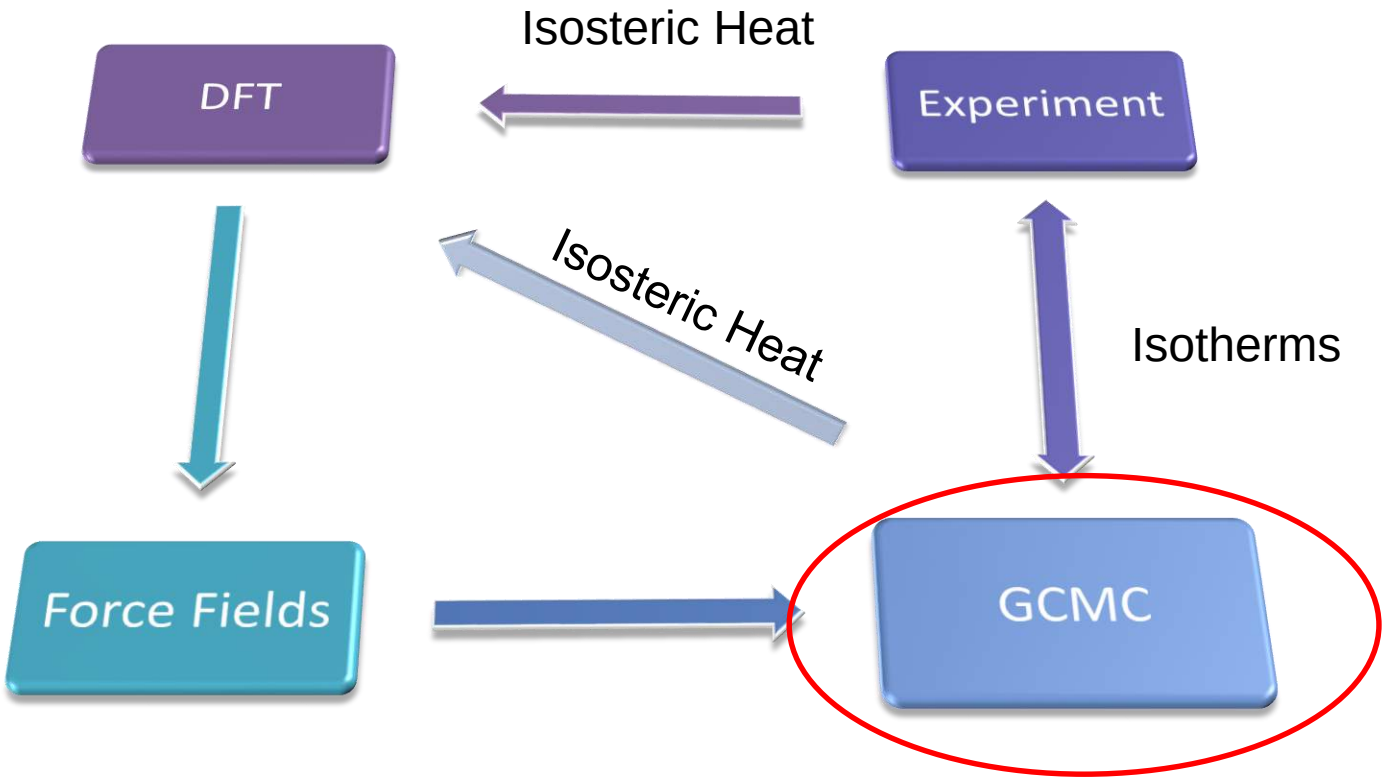
- Comparative forcefields:
- Steele [4]
- TraPPE [5]
- UFF [6]

[4] William A. Steele. The physical interaction of gases with crystalline solids: I. gas-solid energies and properties of isolated adsorbed atoms. Surface Science, 36:317–352, 1973.

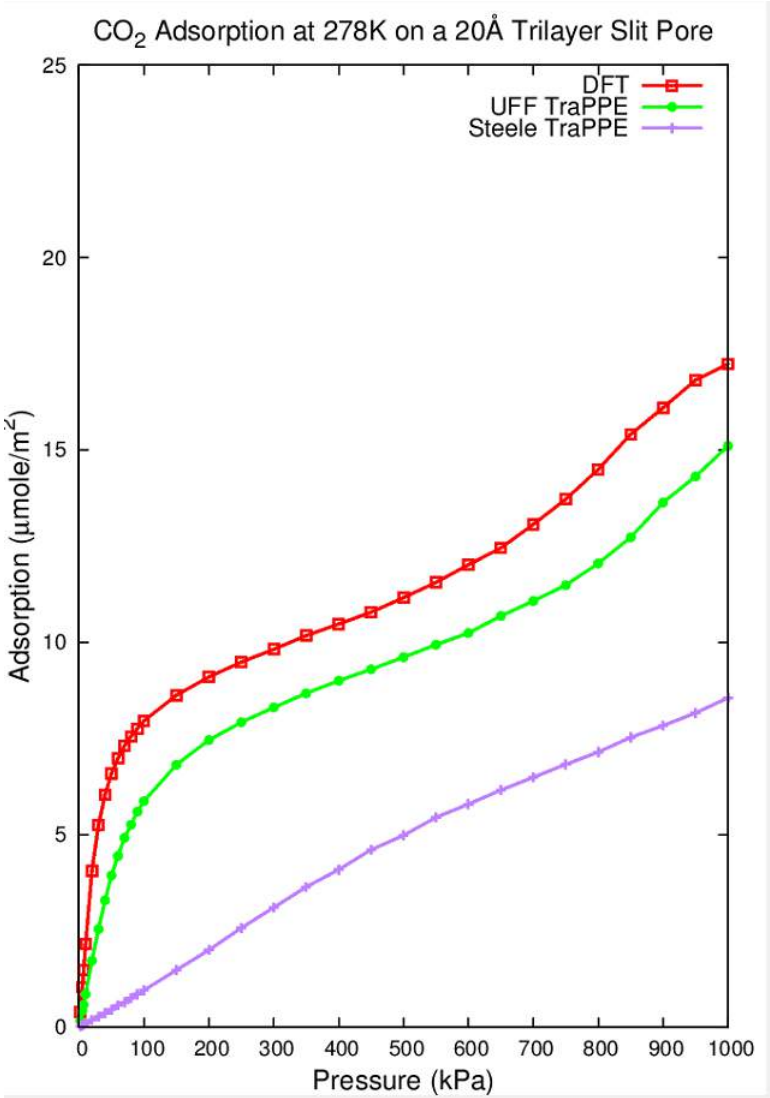
[5] Jeffrey J. Potoff and J. Ilja Siepmann. Vapor-liquid equilibria of mixtures containing alkanes, carbon dioxide, and nitrogen. 47(7):1676–1682, 2001.

[6] A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard III, and W. M. Ski. Uff, a full periodic table force field for molecular mechanics and molecular dynamics simulations. J.Am. Chem. Soc., 114(25):10024–10035, 1992.

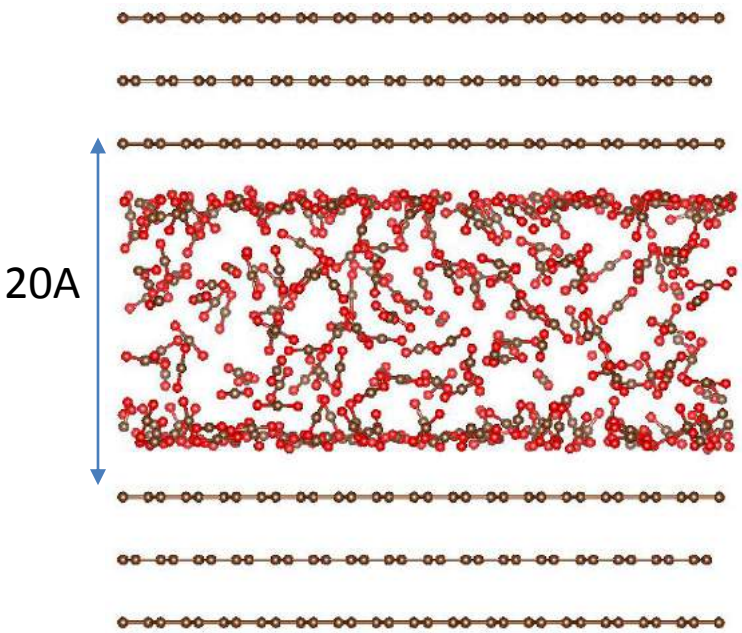
Research Approach



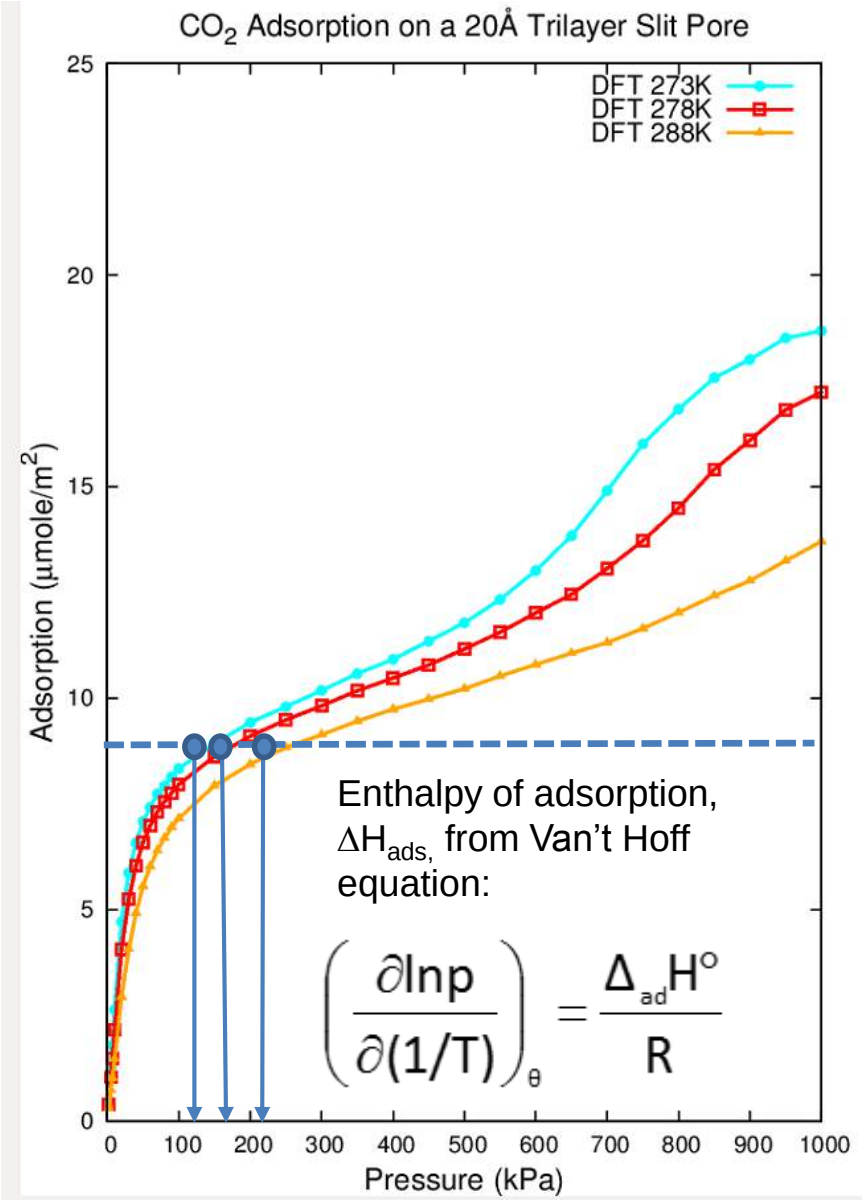
CO_2 Adsorption Isotherm on a 20Å Trilayer Slit Pore



- UFF TraPPE offer similar results to DFT (vdW-DF).
- Disagreement with Steele TraPPE.

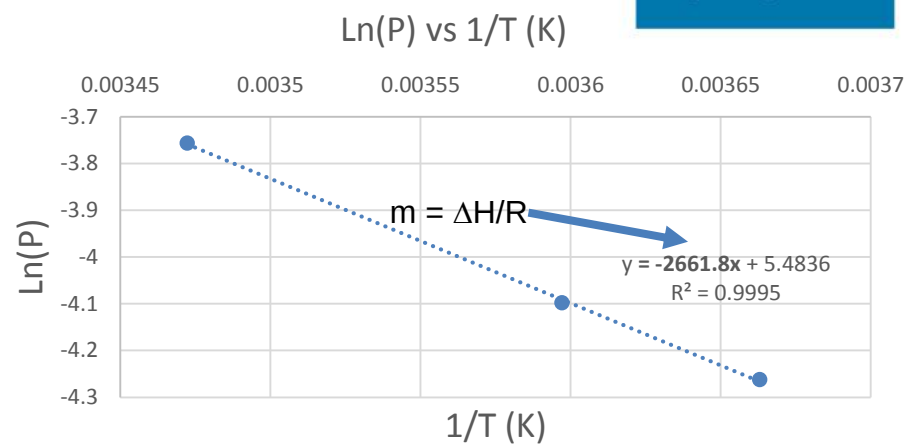


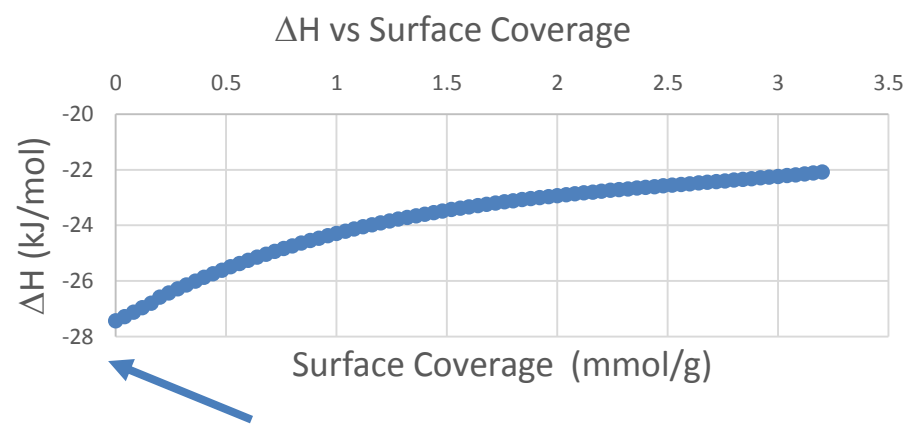
Isosteric Heat for CO_2



Enthalpy of adsorption, $\Delta H_{ads,}$ from Van't Hoff equation:

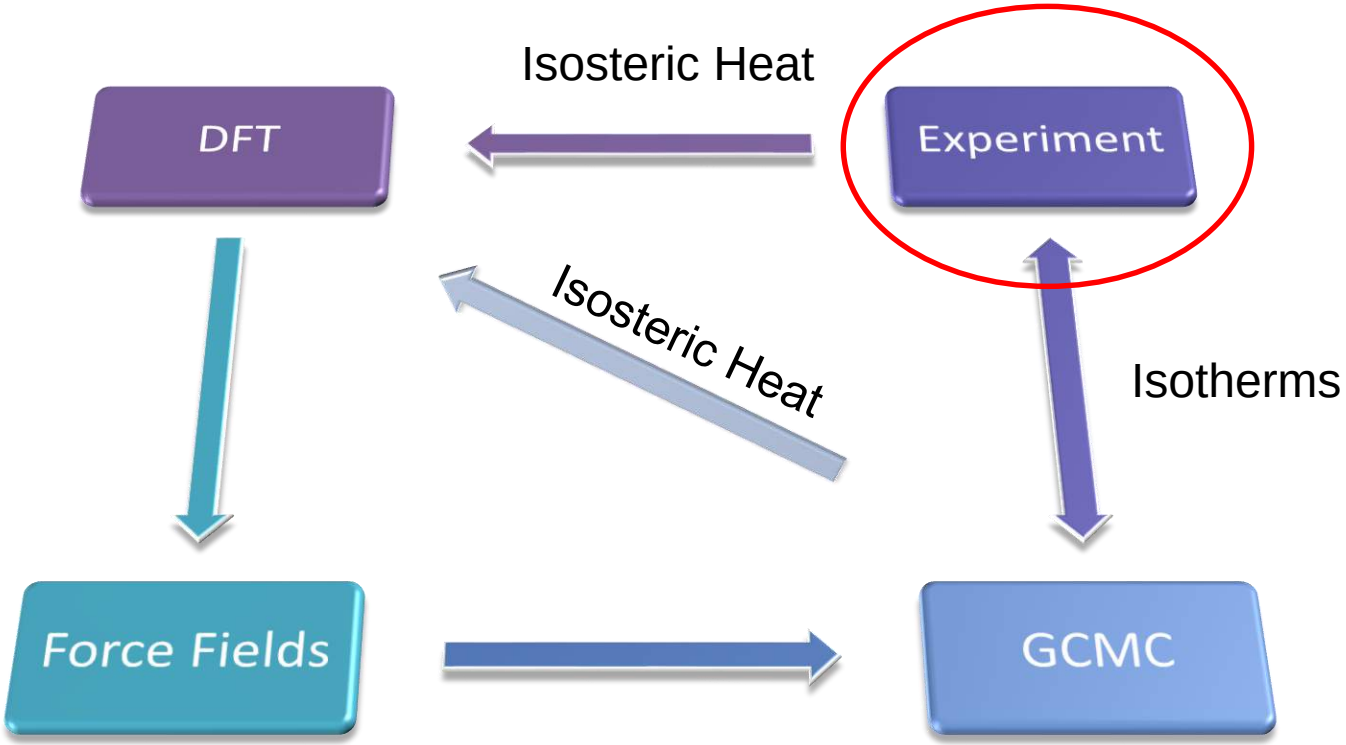
$$\left(\frac{\partial \ln p}{\partial (1/T)}\right)_{\theta} = \frac{\Delta_{ad} H^{o}}{R}$$



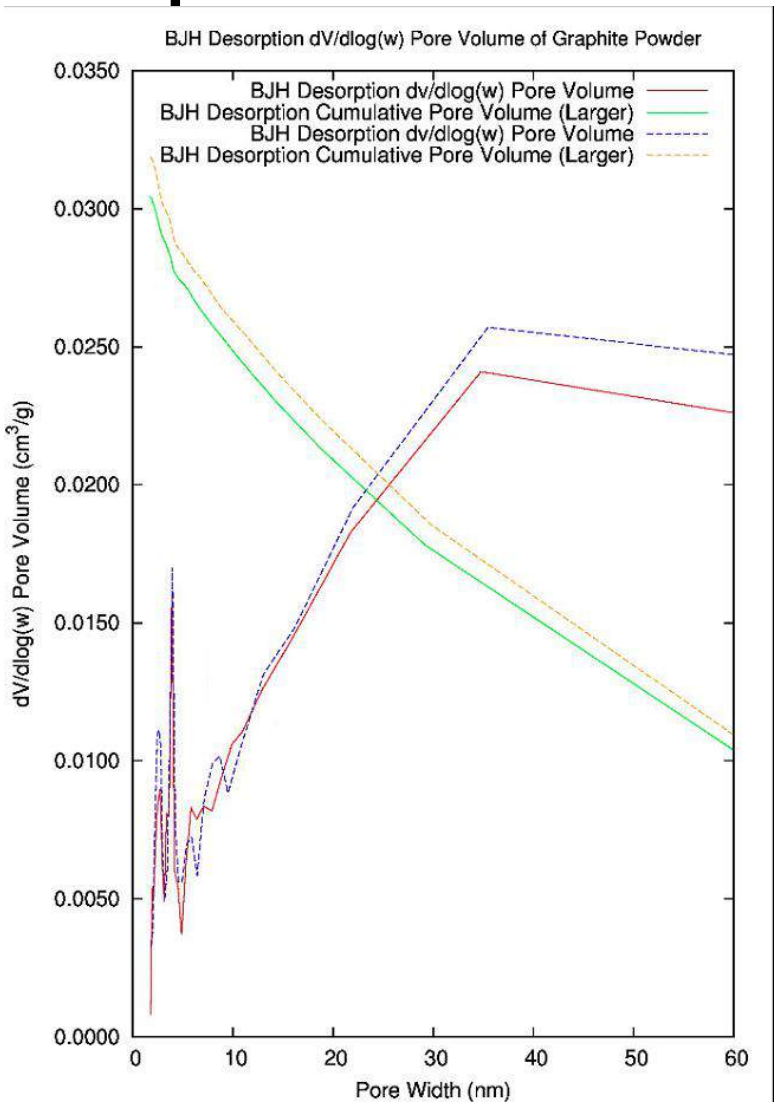


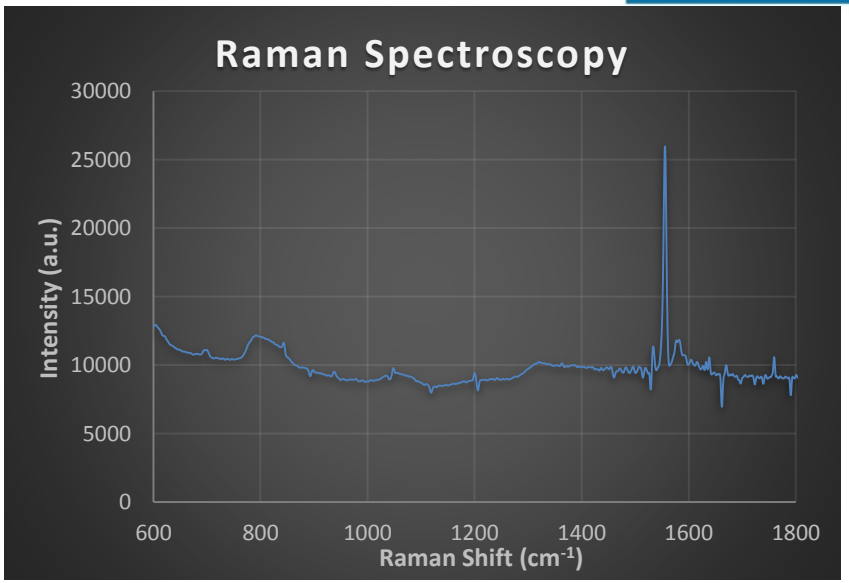
- Isosteric Heat: -27.4 kJ/mol.
- CO_2 DFT: -23.2 kJ/mol.

Research Approach



Experimental Results

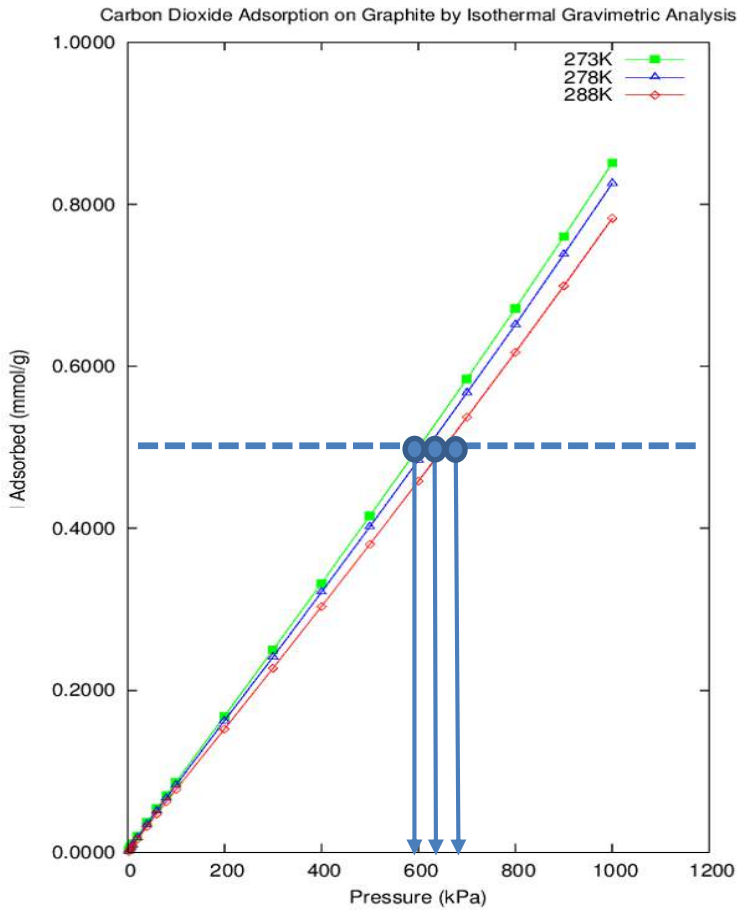


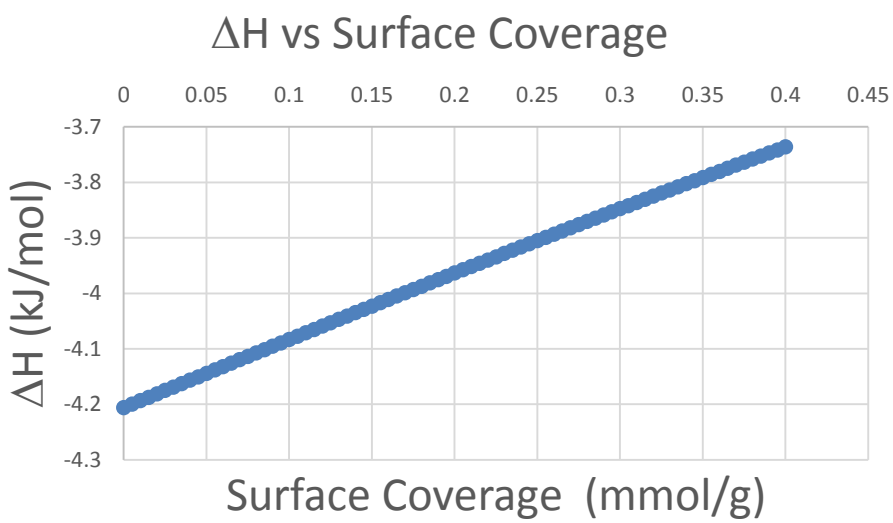


- **<u>BET analysis</u>**
- Mesoporous powder (2-50 nm)
- $8.4 m^2/g$
- **<u>Raman Spectroscopy</u>**
- Peak at $1560 cm^{-1}$ shows sp^2 hybridisation found in graphite [7].

[7] Dudley H Williams and Ian Fleming. Spectroscopic methods in organic chemistry. McGraw-Hill Book Company Europe, 4th ed edition, 1989.

Experimental Results

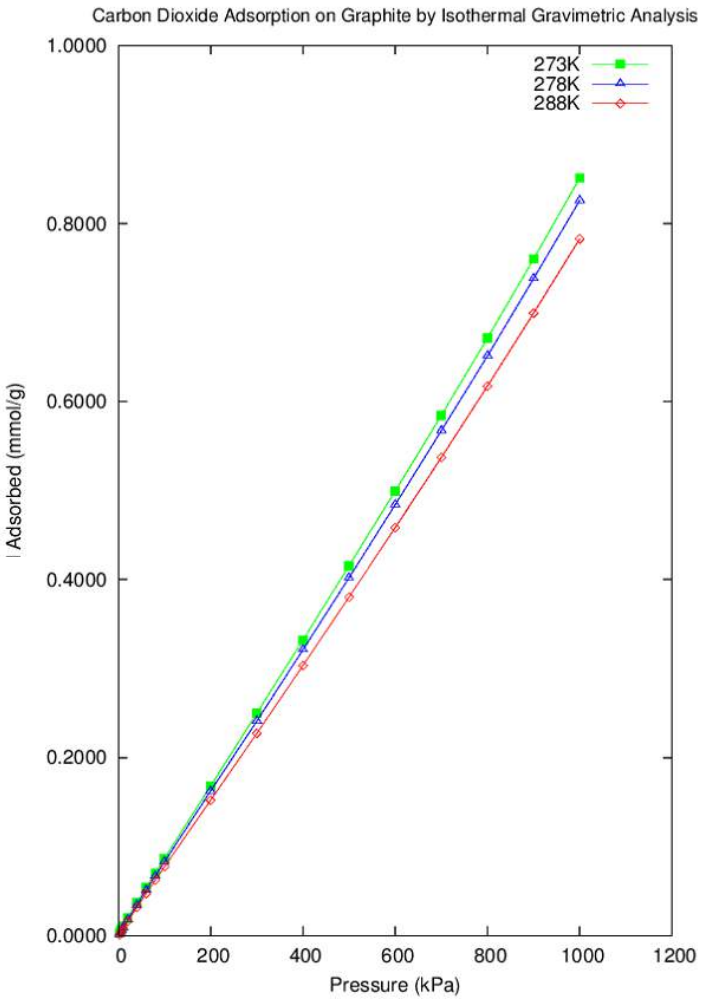




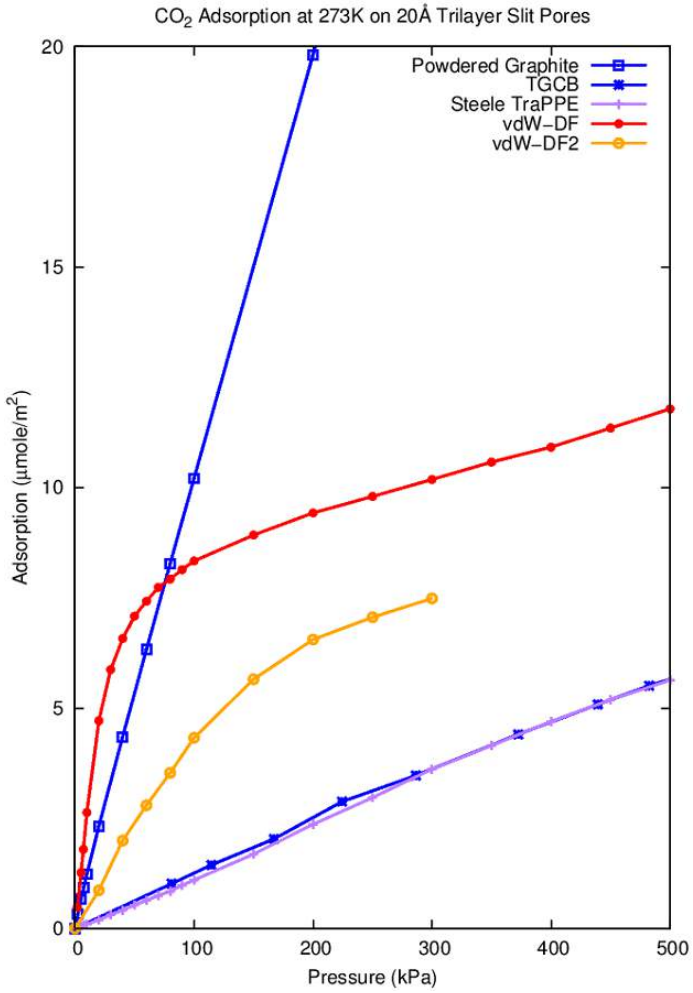
- Isosteric Heat: -4.2 kJ/mol.
- Heterogeneity important.

Experimental Comparison

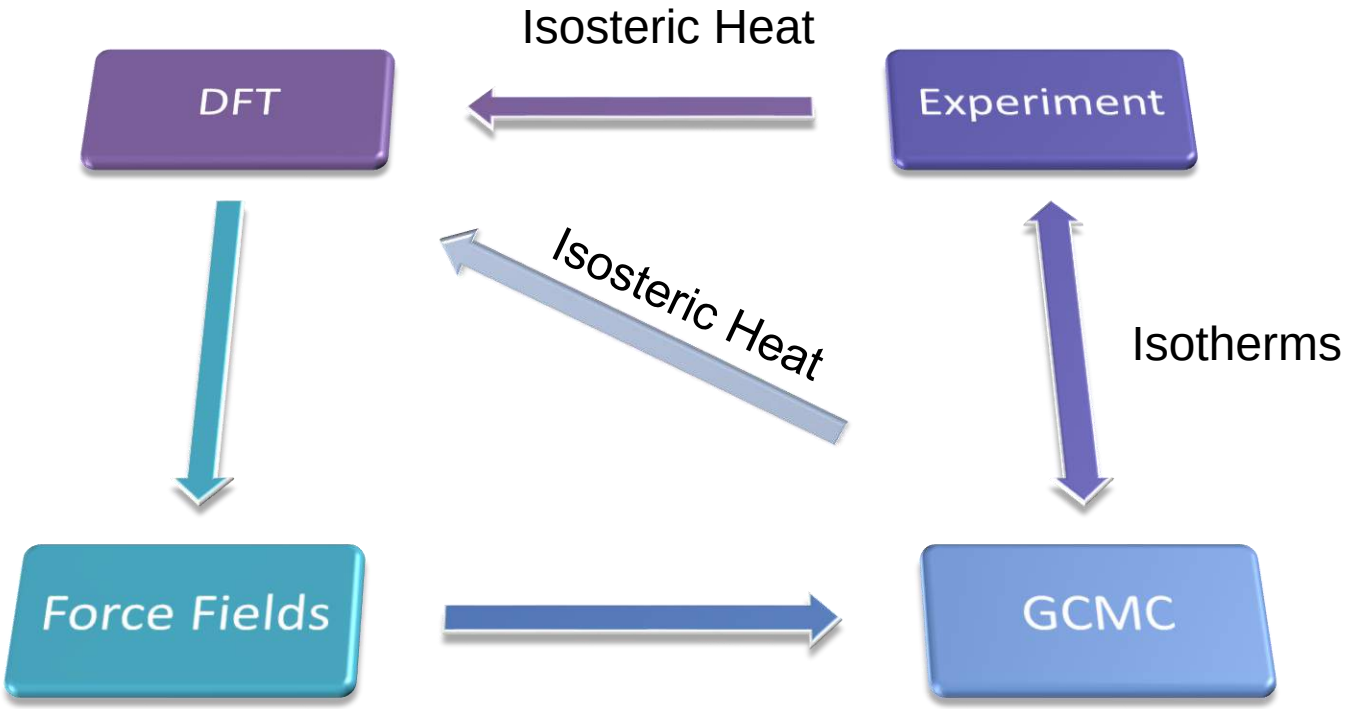
Experimental CO_2 Adsorption



Theory versus Experiment

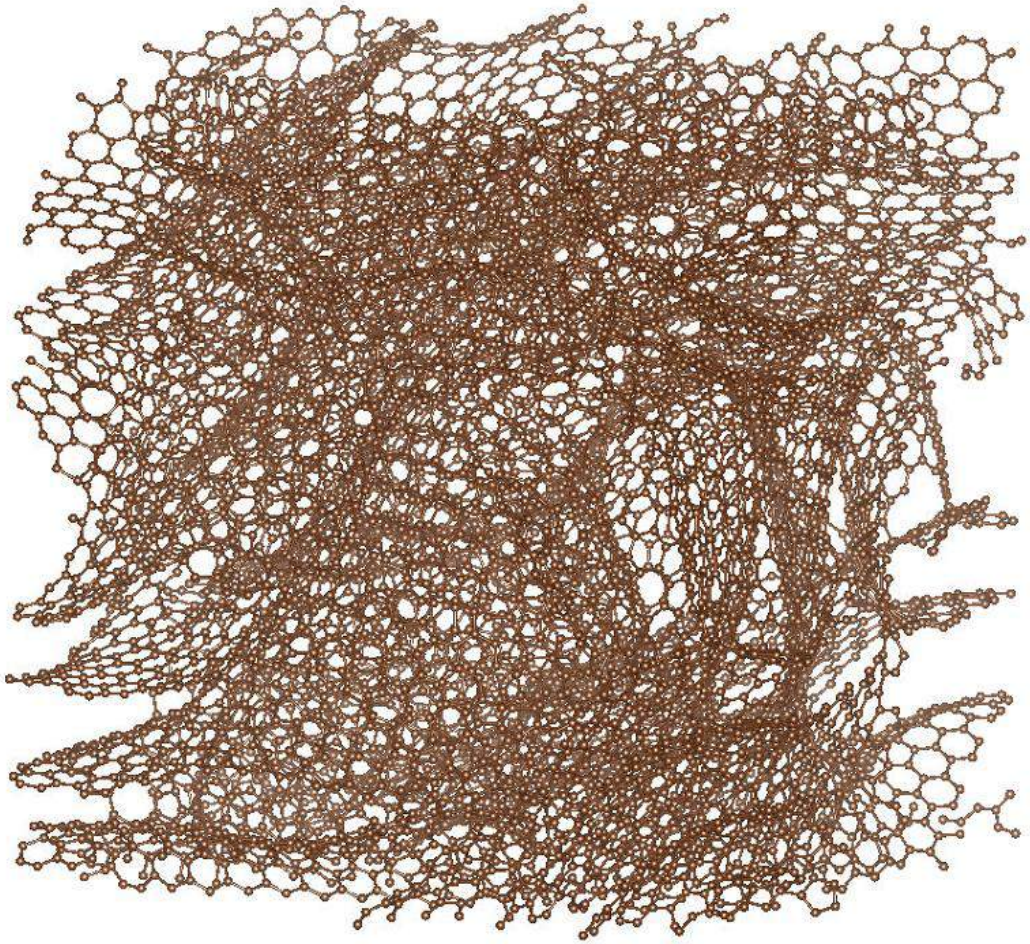


Research Approach Applied to Amorphous Carbon



Amorphous Carbon

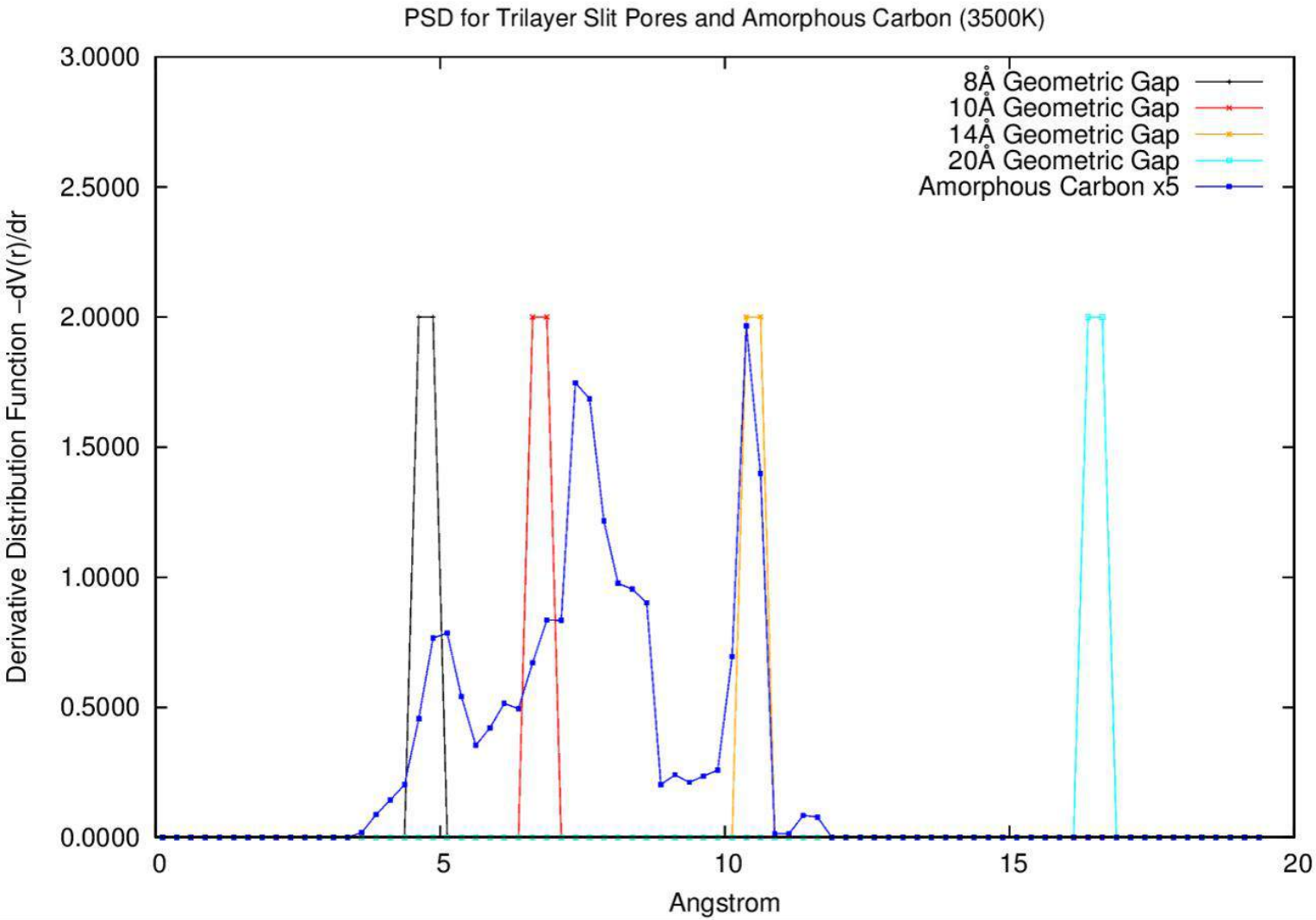
- Structure produced by MD simulations [8].
- Annealed at 3500K.
- 96.38% sp^2 hybridised.



[8] Carla de Tomas, Irene Suarez-Martinez, and Nigel A. Marks. Graphitization of amorphouscarbons: A comparative study of interatomic potentials. Carbon, 109:681–693, 2016.

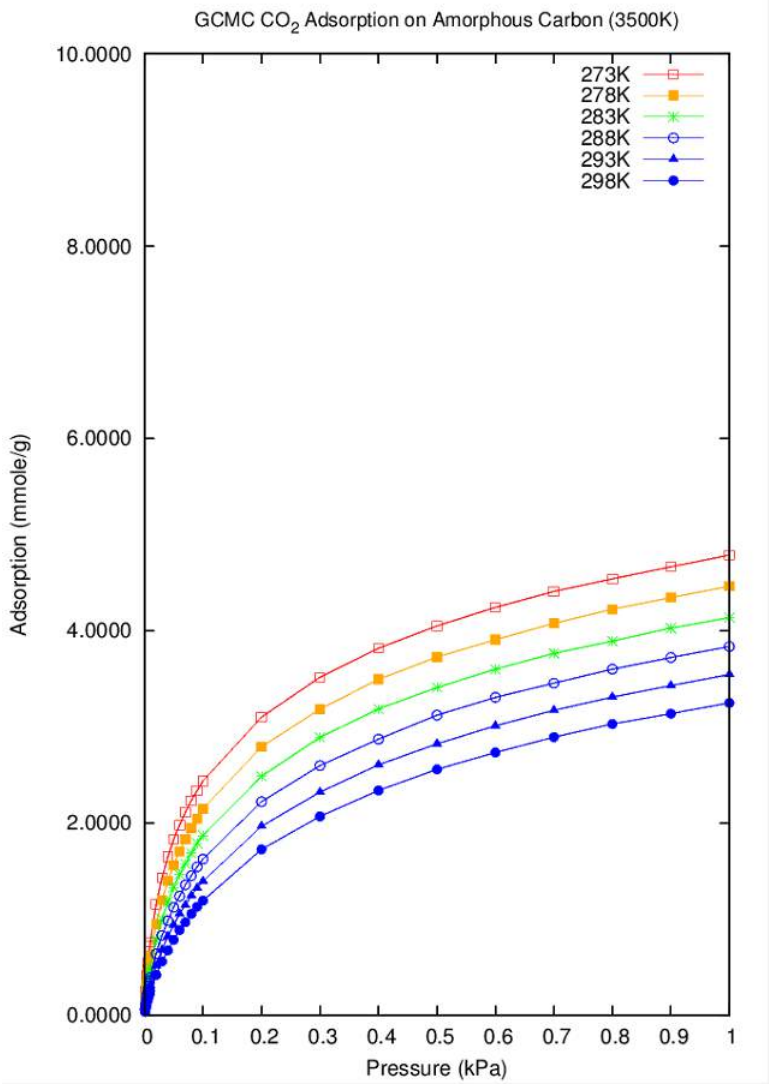
Pore Size Distributions

- A range of Nitrogen accessible microporous pore sizes

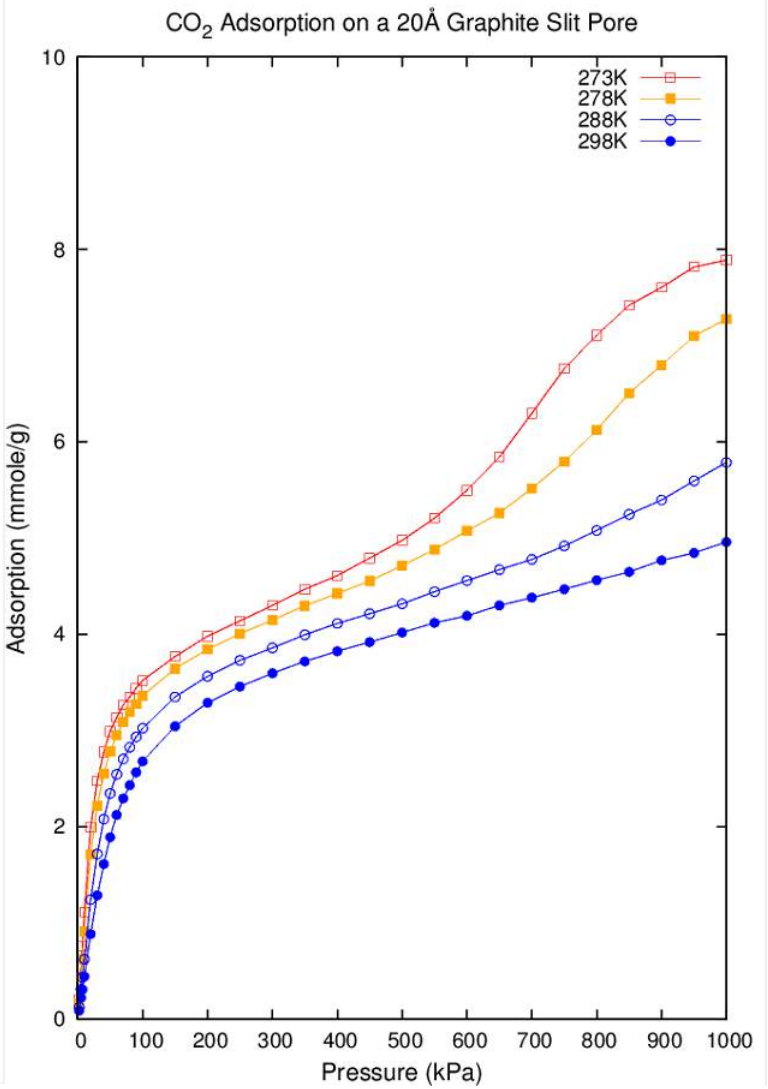


Amorphous versus Slit Pores

- Amorphous



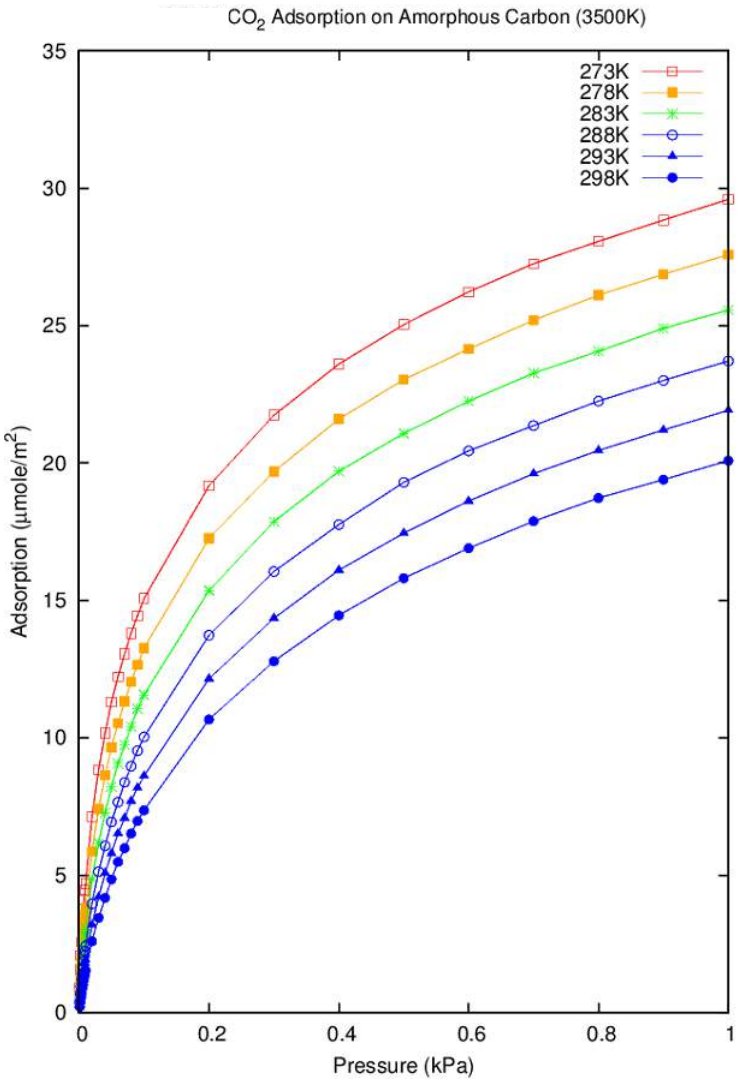
- Slit Pore



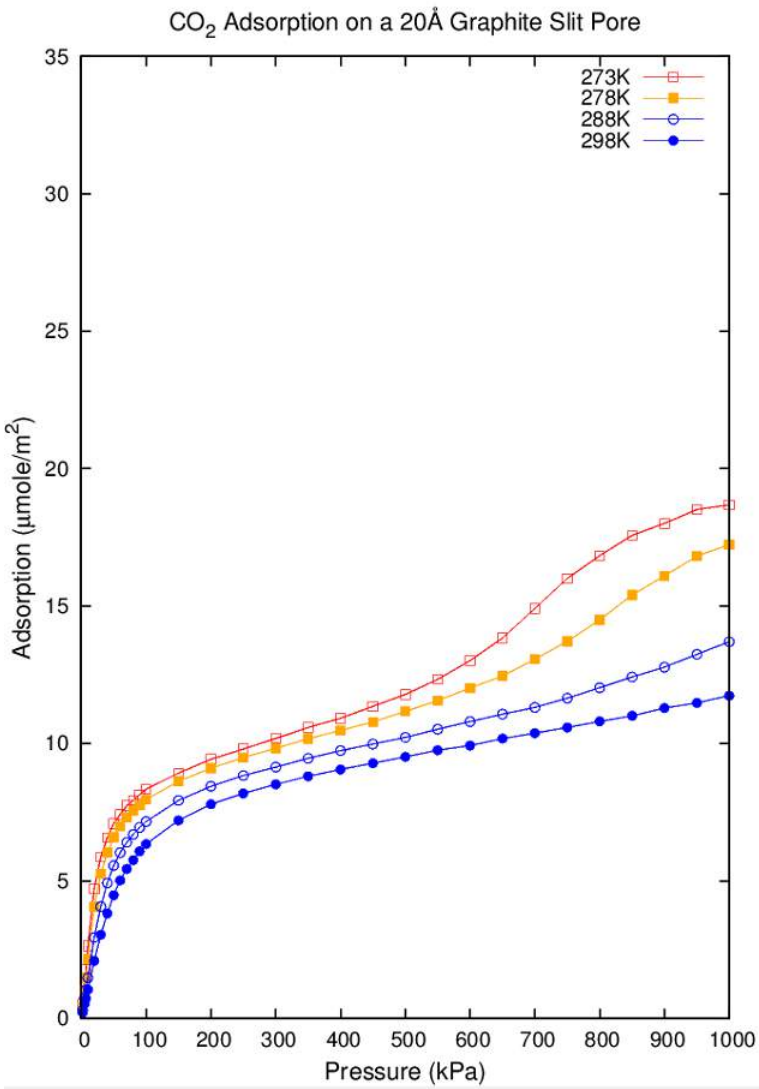
- Enhanced adsorption at low pressure.

Amorphous versus Slit Pores

- Amorphous



- Slit Pore



- Enhanced adsorption based on surface area at low pressure.

Conclusions and Future work

University of Strathclyde Engineering

- DFT data calculated for CO_2 adsorption on graphite/graphene.
- Force fields parameterised from DFT.
- GCMC isotherms generated for slit pores.
- Experimentally we see that structure affects adsorption.
- Amorphous structure shows adsorption enhancement at low pressures, compared to slit pores.

Acknowledgements

Special thanks:

Karen Johnston

Ashleigh Fletcher

Miguel Jorge

Nigel A. Marks

Jon Pena

Colleagues

Thanks For Listening

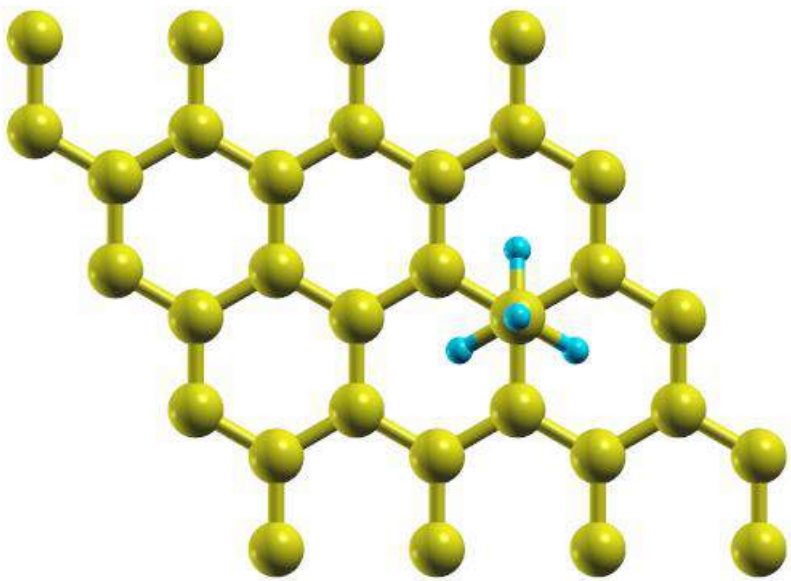
University of Strathclyde Glasgow

Developed Forcefield Values

- **<u>vdW-DF</u>**
- C-C(CO2) Sigma = 3.54 Å
- C-C(CO2) Epsilon = 38.00 K (eff/K_B)
- C-O(CO2) Sigma = 3.07 Å
- C-O(CO2) Epsilon = 79.00 K (eff/K_B)
- High Cutoff 14Å

- **<u>vdW-DF2</u>**
- C-C(CO2) Sigma = 3.37 Å
- C-C(CO2) Epsilon = 21.00 K (eff/K_B)
- C-O(CO2) Sigma = 3.22 Å
- C-O(CO2) Epsilon = 62.00 K (eff/K_B)
- High Cutoff 14Å

DFT Results for Other Species



Other Species on Graphene	Maximum (kJ/mol)
O_2	-32.7
CO_2	-21.0
CH_4	-17.4
N_2	-15.4

- Similar story for Methane and other tested gases
- No site preference
- Orientation important