DFT study of CO_2 adsorption at UiO-66 MOF

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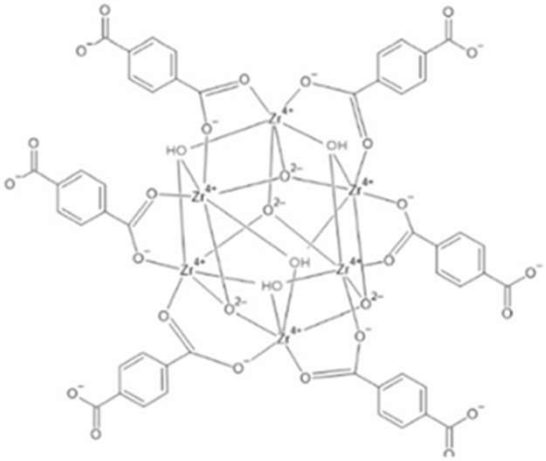
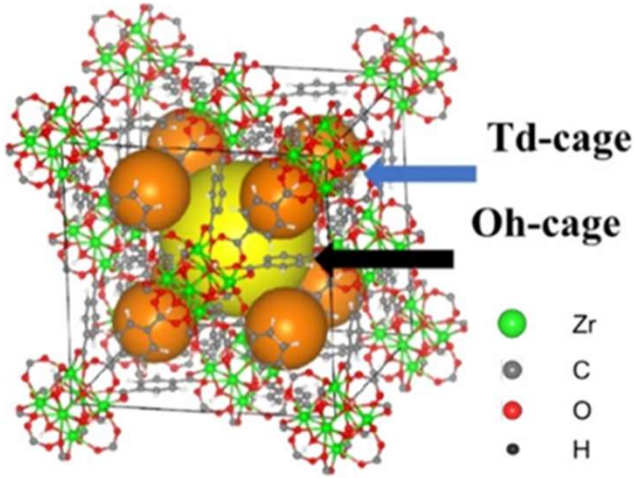
Presentation for CH-253

Motivation



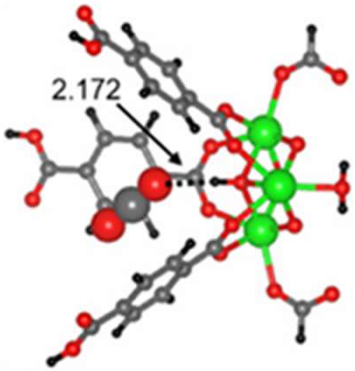


- UiO-66: Highly porous material with exceptional chemical and thermal stability – suitable candidate for CO_2 adsorption.

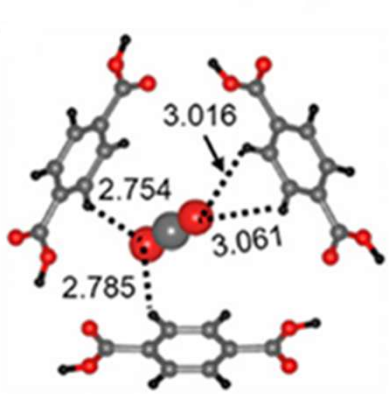
- Multiple sites (named as I, II and III) were identified, which altogether can adsorb 15 CO_2 molecules to one primitive unit cell. *(60 molecules per conventional unit cell – Experimental result).*

Adsorption Sites

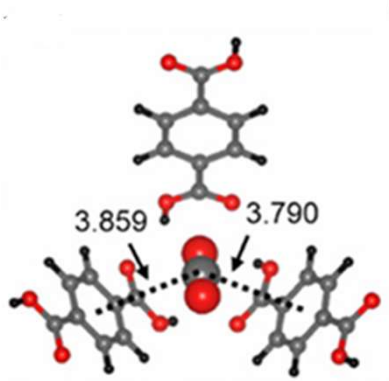
- To obtain the adsorption positions, canonical MC simulations were carried out. *(Atsumi et al., 2023)*
- 16th CO_2 molecule at site 1 – Geometry optimization using DFT



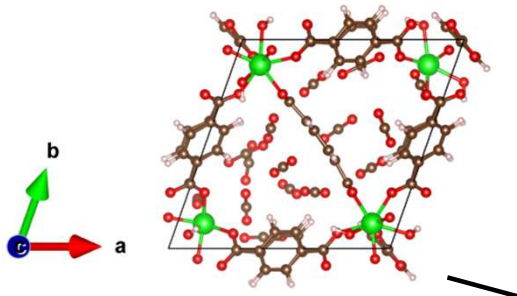
Site - 1



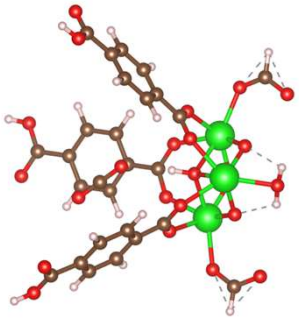
Site - 2



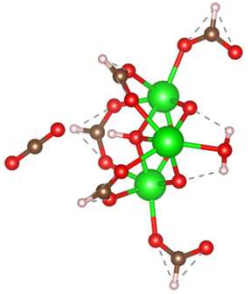
Site - 3



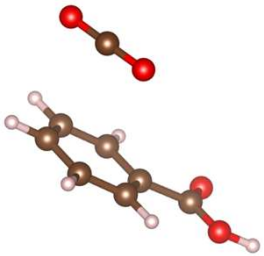
Optimized Structure with 15 CO_2 molecules
(330 atoms)



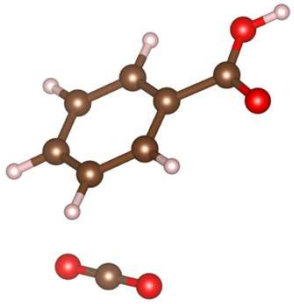
Site C-I
73 atoms
(Cluster Model)



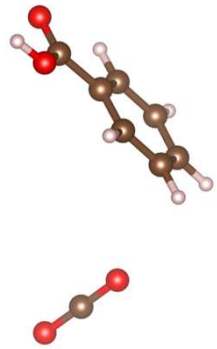
C-Ia
34 atoms (Small Cluster Model –SCM)



C-Ib
18 atoms (SCM)



C-Ic
18 atoms (SCM)



C-Id
18 atoms (SCM)

Computational Methods

- PBE-D3 functional (PBE functional with grimme D3 corrections for van der Waals interactions).
- Pseudopotential: PAW (Projector Augmented Wave Method)
- Optimization: BFGS

- Calculations carried out for site C-Ib (Small Cluster Model)

$$BE = E_{SCM+CO_2} - (E_{SCM} + E_{CO_2})$$

.xyz file ⟶ ASE (Periodic Box) ⟶ Quantum ESPRESSO

- SCM + CO_2 : 20 Å
- SCM : 20 Å
- CO_2 : 15 Å

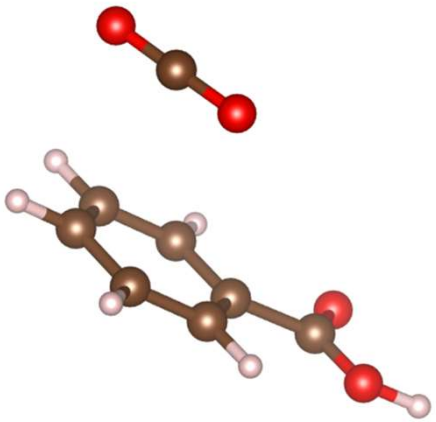


Fig.: Site C-Ib SCM

Convergence: k-point

			C-1b + CO2	
k points	energy (Ry)	natoms	ev/atom	ΔE (mev/atom)
1,1,1	-321.097048	18	-1.311670947	-1.13403E-05
3,3,3	-321.0969839		-1.311670686	3.16358E-06
5,5,5	-321.0969978		-1.311670743	
			C-1b	
1,1,1	-219.362108	15	-1.075304453	-0.000258578
3,3,3	-219.3620469		-1.075304151	4.34314E-05
5,5,5	-219.3620557		-1.075304195	
			CO2	
1,1,1	-101.725734	3	-2.493277802	0.011494794
3,3,3	-101.7262564		-2.493290599	-0.001301775
5,5,5	-101.7262033		-2.493289297	

Convergence: Wave Function Cutoff

		ecutwfc			
		C-1b + CO2			
k points	energy(Ry)	ecut	natoms	ev/atom	ΔE (mev/atom)
1,1,1	-321.0970478	30	18	-1.311670947	0.029664662
	-321.2276712	40		-1.312204539	-1.66667E-07
	-321.2349332	50		-1.312234204	
		C-1b			
1,1,1	-219.3621085	30	15	-1.075304453	0.473984167
	-219.4529788	40		-1.075749896	0.02854152
	-219.4588012	50		-1.075778437	
		CO2			
1,1,1	-101.7257343	30	3	-2.493277802	0.001022734
	-101.7660566	40		-2.494266094	3.44424E-05
	-101.7674619	50		-2.494300536	

Convergence: Charge Density Cutoff

			ecutrho		
			C-Ib + CO2		
k points	energy(Ry)	ecut	natoms	ev/atom	deltaE (mev/ato
1,1,1	-321.097048	120	18	-1.311670947	-0.140023855
	-321.0664056	140		-1.311545775	-0.01485151
	-321.06277	150		-1.311530923	
			C-Ib		
1,1,1	-219.362109	120	15	-1.075304453	-0.147406667
	-219.3353943	140		-1.075173501	-0.016454706
	-219.3320375	150		-1.075157047	

Convergence: Smearing

	degauss				
			C-Ib + CO2		
	energy(Ry)	ecut	natoms	temp(K)	deltaE (mev/atom)
1,1,1	-321.097048	30	18	1597	-3.26797E-07
	-321.0970479			1000	
			C-Ib		
1,1,1	-219.362109	30	15	1597	4.08497E-07
	-219.3621084			1000	

Relaxation and BE calculation

$$BE = E_{SCM+CO_2} - (E_{SCM} + E_{CO_2})$$

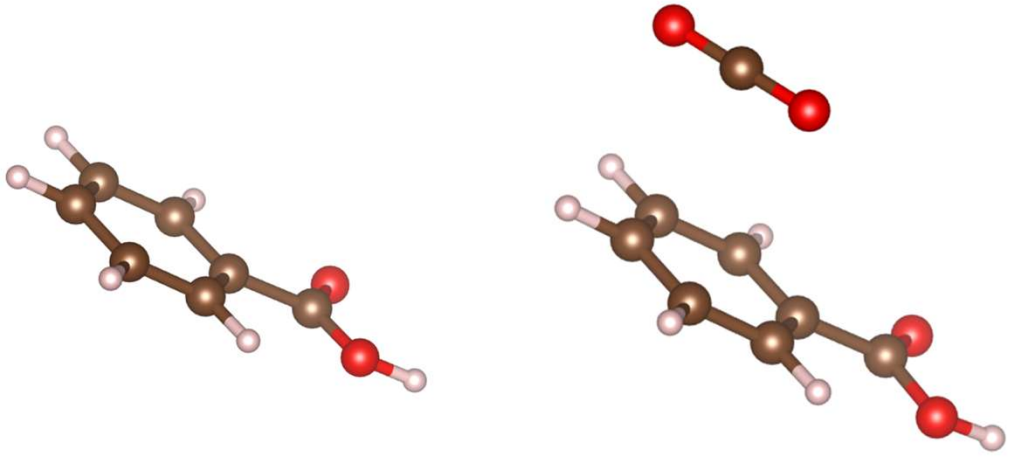
Conversion factor:

1 Ry/molecule = 313.9857 kcal/mol

Calculated: -2.890235229 kcal/mol

Literature: -1.82 kcal/mol

Difference ~ 1.07 kcal/mol



(a) (b)

Fig.: Structures after "relax" calculation on Quantum ESPRESSO

Conclusion and Discussion

	40A Box		
1,1,1	-219.3605225	15	-1.075296679
3,3,3	-219.3604611		-1.075296378

- For the infinite structure, and for Cluster Models: PBE-D3 is used in the literature.
- For Small Cluster Models: Post Hartree – Fock corrections (SCS-MP2) are applied in the literature (Probable cause in the difference in values)

"PBE-D3 overestimates the Adsorption Energy ~ 1.2 kcal/mol *(Atsumi et al., 2023)*"

- Reworked for the isolated SCM in a bigger box (40 Å) to identify if the DFT energy changes.

For 20 Å box: −219.3621085 Ry