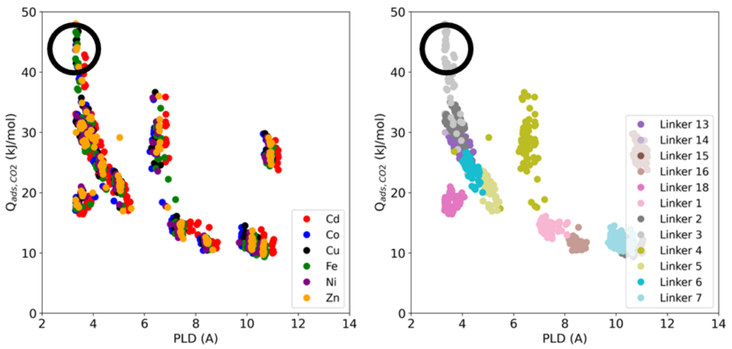
Machine Learned Force Field Modeling of Metal Organic Frameworks for CO_2 Direct Air Capture

John Marshall Findley[1,2]; Jan Steckel[1]
[1]National Energy Technology Laboratory, 626 Cochran Mill Road, Pittsburgh, PA 15236, USA; [2]NETL Support Contractor, 626 Cochran Mill Road, Pittsburgh, PA 15236, USA

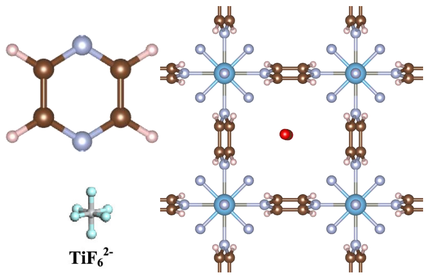
Research & Innovation Center

NATIONAL ENERGY TECHNOLOGY LABORATORY

Motivation from Recent Simulation Work



An initial screening of a database of anion pillared metal organic frameworks (MOFs)[1] for CO_2 heat of adsorption as a function of pore limiting diameter (PLD).



The optimal linker (pyrazine) and the CO_2 adsorption site in one of the best performing MOFs, TIFSIX-3-Zn.

- Linker type influenced heat of adsorption more than metal
- Best performing MOFs had CO_2 adsorption sites at the center of 4 fluorine groups

Predicted High Performing MOFs for Direct Air Capture (DAC)

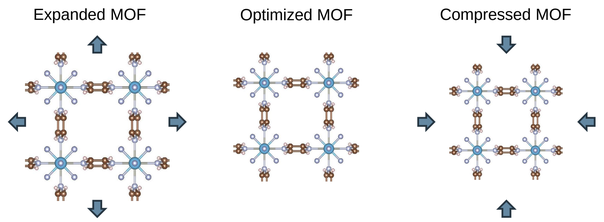
- Using **classical** force fields, four MOFs have been identified for further study using MLFF methods

MOF Rank	CO_2 Heat of Adsorption (kJ/mol)	Linker	Fluorine Group	Metal Center
1	57.5	Pyrazine	TiF_6	Cu
2	56.5	Pyrazine	SiF_6	Cu
3	52.4	Pyrazine	TiF_6	Ni
4	50.5	Pyrazine	TiF_6	Zn

Flexible Models: Machine Learning Force Fields (MLFFs)

- Calculates energies and forces using machine learning models fit to reproduce the results of density functional theory (DFT) calculations
  - Better fits than analytical models
  - Faster than quantum mechanical simulations

Sample Volume Changes



Sample CO_2 Adsorption

A description of the workflow for training MLFFs based on the results of ab initio calculations.

- Training set “ingredients”:
  - Energy, Forces from DFT
  - Ab initio molecular dynamics simulations (300 K, 450 K)
  - Changes in system volume
  - Adsorption of CO_2
  - SNAP Potential + Lennard-Jones (LJ) + Coulomb
    - Charges assigned by density derived electrostatic and chemical method (DDEC)
    - Lennard-Jones from universal force field (UFF)

Model Fitting Results

Configurations	Energy R^2	Force R^2
Empty MOF	0.99	0.98
CO_2 – Loaded MOF	0.99	0.97

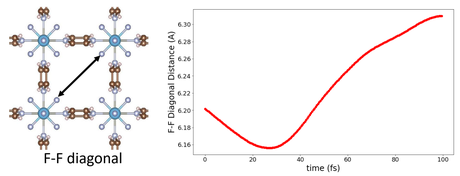
Performance metrics for energies and forces predicted for the MOF, TIFSIX_3_Zn compared to DFT data for **testing data.**

References

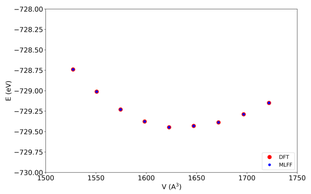
[1]Gu et. al., *ACS Appl. Mater. Interfaces* **2021**
[2]Forrest et al., *Crystal Growth and Design* **2019**
[3]Ullah et al., *Angewandte Chemie* **2022**

Benchmarking MLFF Predictions

- CO_2 adsorption depends on the fluorine-fluorine distances in the pore
- Rigid force fields overpredict adsorption in SIFSIX[2] and TIFSIX[3] MOFs
- Ab initio molecular dynamics (AIMD): flexible Si-F bonds affect the fluorine-fluorine distances
  - This makes TIFSIX and SIFSIX ideal test cases for flexible MLFFs



The fluorine-fluorine diagonal distance in the pores of TIFSIX_3_Zn as a function of time in an AIMD run.



A comparison of energies vs. optimized cell volumes for an empty TIFSIX_3_Zn MOF.

Property TIFSIX_3_Ni	Experimental Value (If Available)	DFT Prediction*	MLFF Prediction
Unit Cell Volume (Å^3)	1,526	1,552	1,552
Density (g/cm^3)	1.65	1.62	1.62
$\Delta E_{ads,CO2}$ (kJ/mol)	N/A	-60.1	-59.8

*Unit cell optimization data was included in training data.

- Good performances for force predictions for MLFF potential
- Next step: benchmark force macroscopic properties using new MLFF
  - CO_2 adsorption isotherms

Conclusions

- Five MOFs were selected for further study due to high CO_2 uptake
- MLFFs are being benchmarked for predictions of MOF structure
- Future work will mainly focus on:
  - CO_2 uptake in all MOFs in this set
  - The effect of humidity (co-adsorption with H_2O)

Acknowledgement

This work was performed in support of the U.S. Department of Energy’s (DOE) Office of Fossil Energy and Carbon Management’s Carbon Dioxide Removal Program and executed through the National Energy Technology Laboratory (NETL) Research & Innovation Center’s Carbon Dioxide Removal Field Work Proposal.

Disclaimer