Computational Evaluation of Flexible Metal-Organic Frameworks for Capture

John Marshall Findley[1,2], Samir Budhathoki[1,2], Jan Steckel[1]
[1]National Energy Technology Laboratory, 626 Cochran Mill Road, Pittsburgh, PA15236, USA
[2]NETL Support Contractor, 626 Cochran Mill Road, Pittsburgh, PA15236, USA

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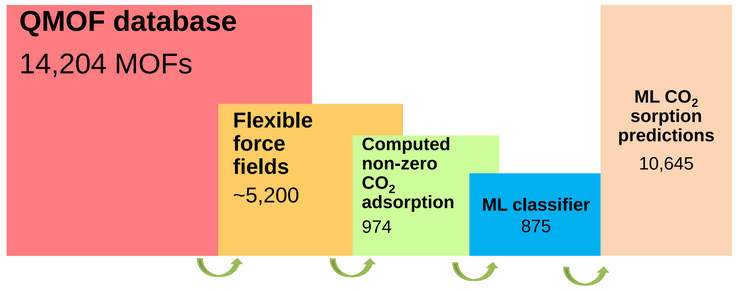
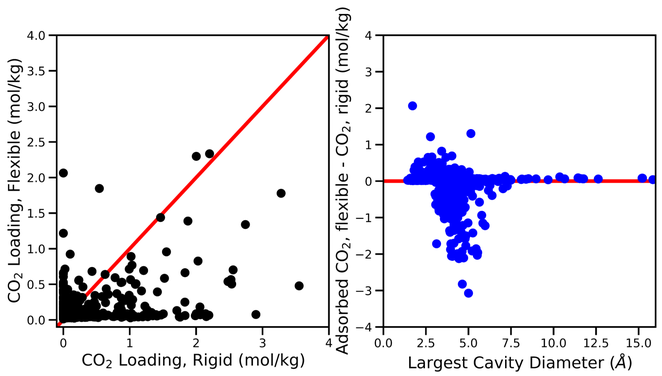
Motivation from Recent Simulation Work



The workflow of screening of flexible metal-organic frameworks (MOFs) for CO_2 sorption for direct air capture (DAC) applications



A comparison of CO_2 uptake for flexible and rigid MOFs in the QMOF database[1] against pore size

- Significant effect of flexibility on CO_2 uptake
- Many small pore MOFs (pore size < 3Å) exhibit increase in uptake with added flexibility

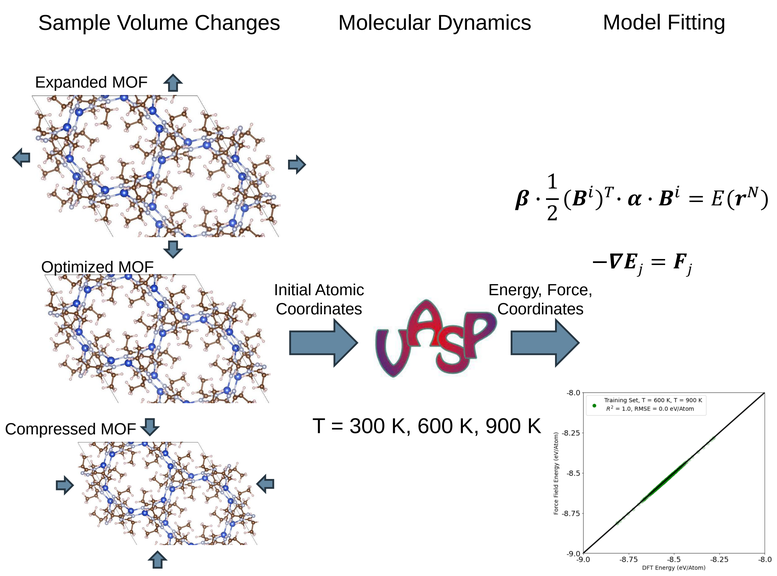
Predicted Top Performing MOFs for DAC

- Using flexible force fields, five MOFs have been identified as having high predicted CO_2 uptake at DAC conditions

MOF Rank	CO_2 Adsorption (mol/kg)	Largest Cavity Diameter (Å)
1	2.29	2.81
2	2.06	1.71
3	1.85	5.13
4	1.77	4.84
5	1.44	3.72

Refining Flexible Models: Machine Learning Force Fields (MLFFs)

- Calculates energies based on machine learning models based on geometric descriptors rather than classical physics-based models
  - Better fits than analytical models
  - Faster than quantum mechanical simulations



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

- Training set "recipe":
  - Ab initio molecular dynamics simulations
  - Changes in system volume (scale lengths by +/- 2%)
  - Perturbation of individual atoms (10 different initializations)
  - Four different temperatures (300 K, 600 K, 900 K, 1200 K)

Best Performing Models

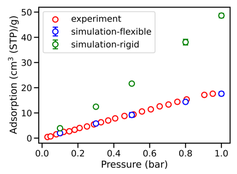
MOF	Fitting Method	Force RMSE (eV/Å)	Force R^2
SNAP	Linear	0.082	0.90
SNAP	Quadratic	0.030	0.99
SOAP	Linear	0.063	0.87

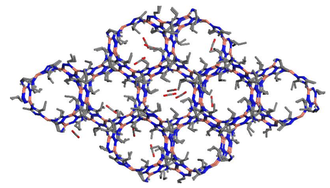
References

[1]Rosen et. al., *Matter* **2021**, 4, 1-20

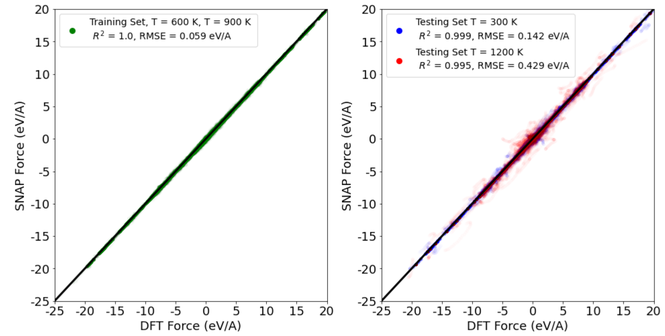
Benchmarking MLFF Predictions

- Benchmarking DFT calculations and MLFF calculations for the MOF, MAF-2
- Ethyl groups can block copper sites during adsorption, resulting in flexibility dependent CO_2 uptakes





The flexibility of MAF-2 has a high impact on adsorption, so it will be an ideal test case for flexible MLFF modeling



A comparison between forces in a flexible MOF, MAF-2 for the training dataset (left) and an independent testing set of configurations (right)

- Good performances for force predictions for SNAP potential
- Next step: benchmark force macroscopic properties using new MLFF
  - Cell volume, bulk modulus, 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:
  - Further validation of MLFF models
  - Development of MLFF models for CO_2 adsorption in the presence of amines

Acknowledgement

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