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

John Findley
NETL Support Contractor

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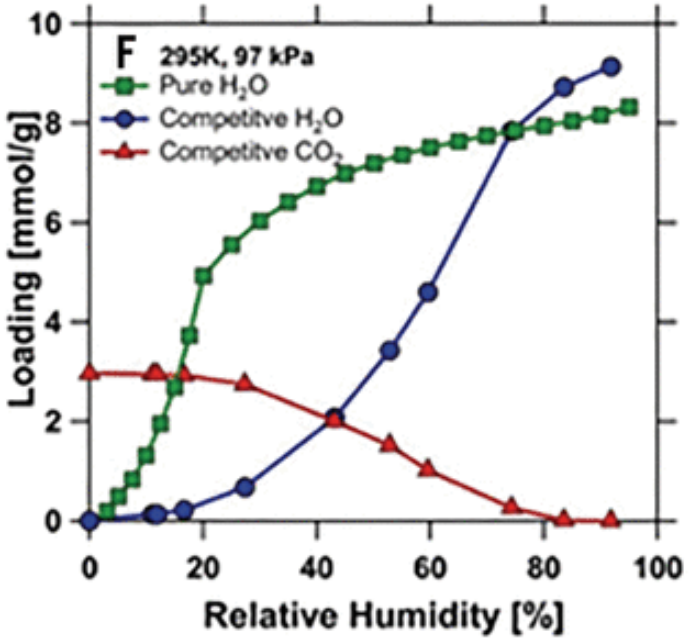
Physisorbent MOFs for CO_2 Capture

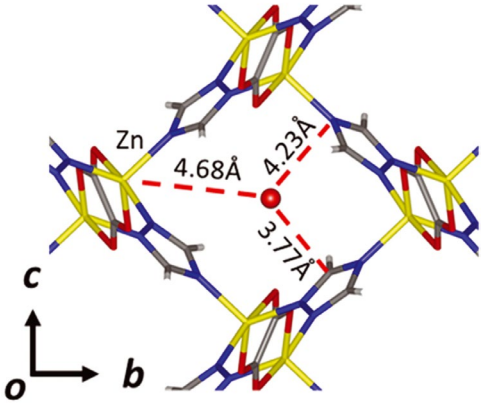
Characteristics of a Good Physisorbent

- Characteristics of a good direct air capture (DAC) sorbent
  - Strong CO_2 adsorption
  - Regenerable
  - Not hindered by humidity

- Example: CALF-20
  - Successfully used for point source
  - Little effect of humidity up to 30% RH
  - Strong **dispersion** interactions (CO_2 > H_2O)

- Finding a MOF for DAC
  1. Strong CO_2-MOF interactions ($\Delta E_{ads, CO2}$ < -50 kJ/mol)
  2. Weak H_2O adsorption



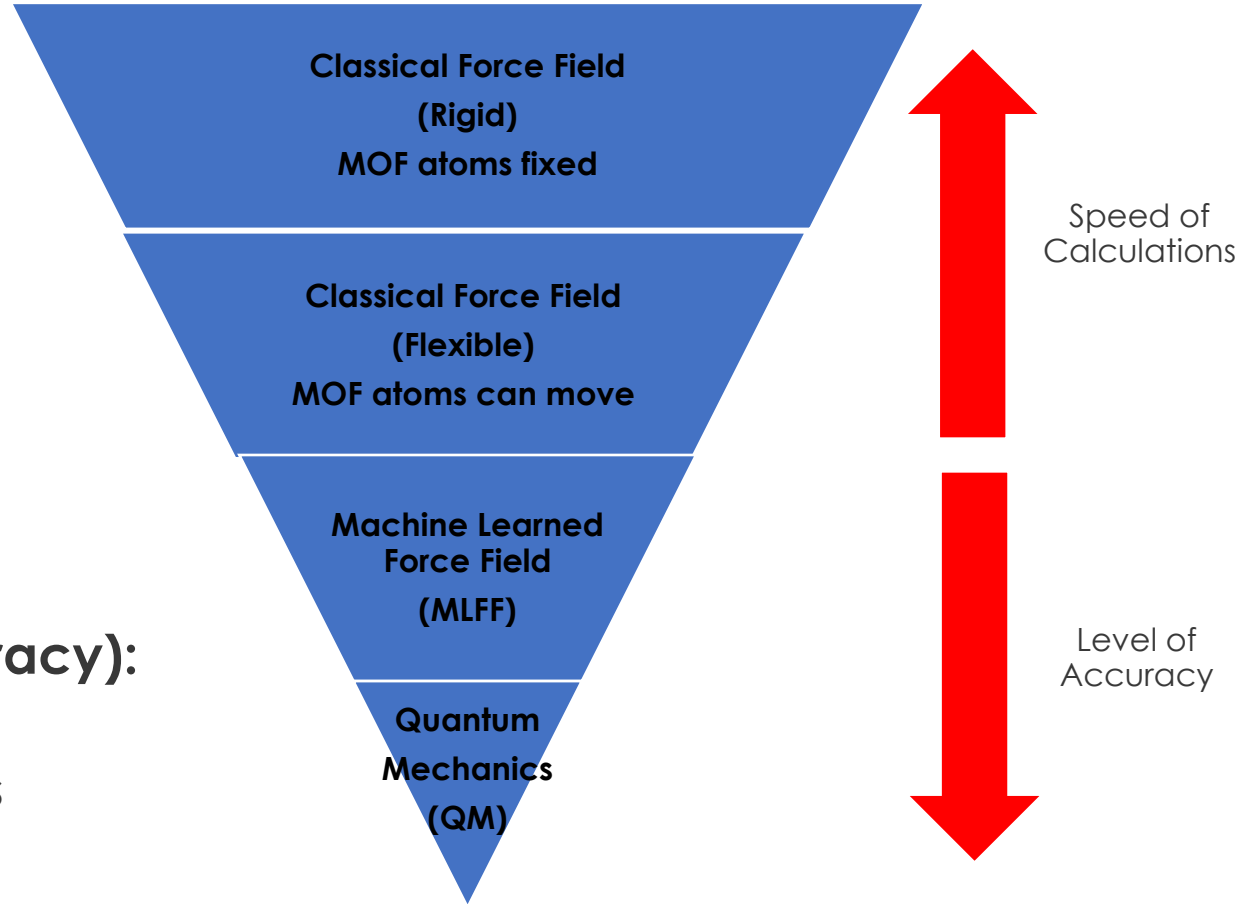


[1]Lin et al., *Science* (2021)

Levels of Calculations

Machine Learned Force Fields Connect Classical and Quantum Simulations

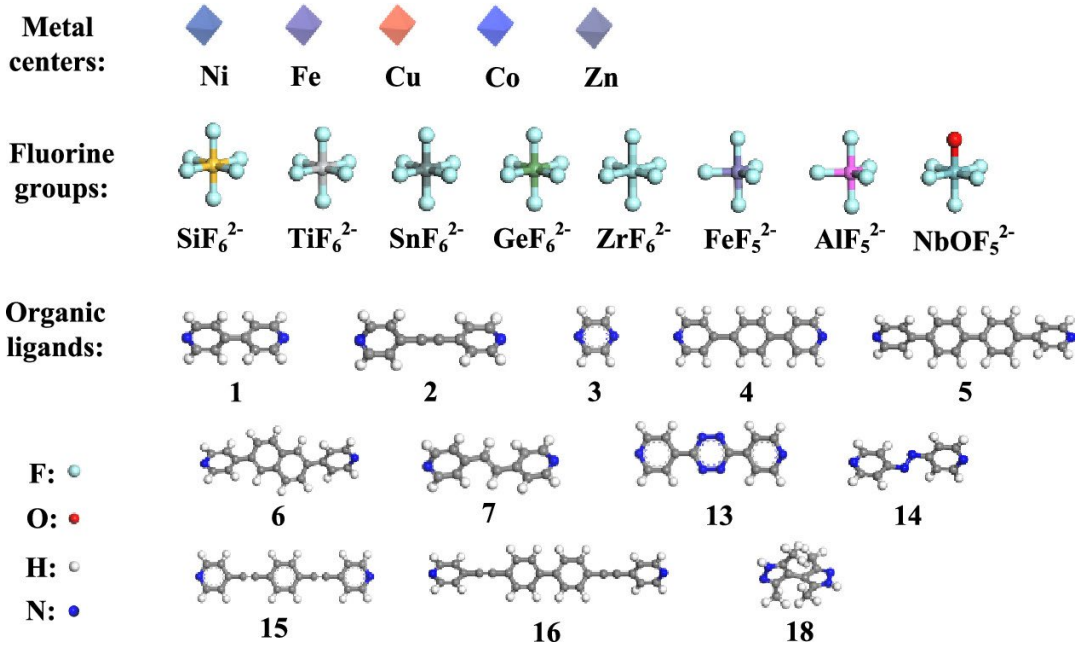
- **Classical Force Field (speed):**
  - **Rigid:** MOF atoms fixed during simulation
  - **Flexible:** MOF atoms can move
  - Energy, force from analytical function
    - Adsorption isotherm, diffusivity
- **Machine Learned Force Field (MLFF):**
  - Energy, Force from ML model
    - Better fitting to QM calculations
- **Quantum Mechanical (QM) methods (accuracy):**
  - Accurate, slow
  - Compute energy, forces, determine structures

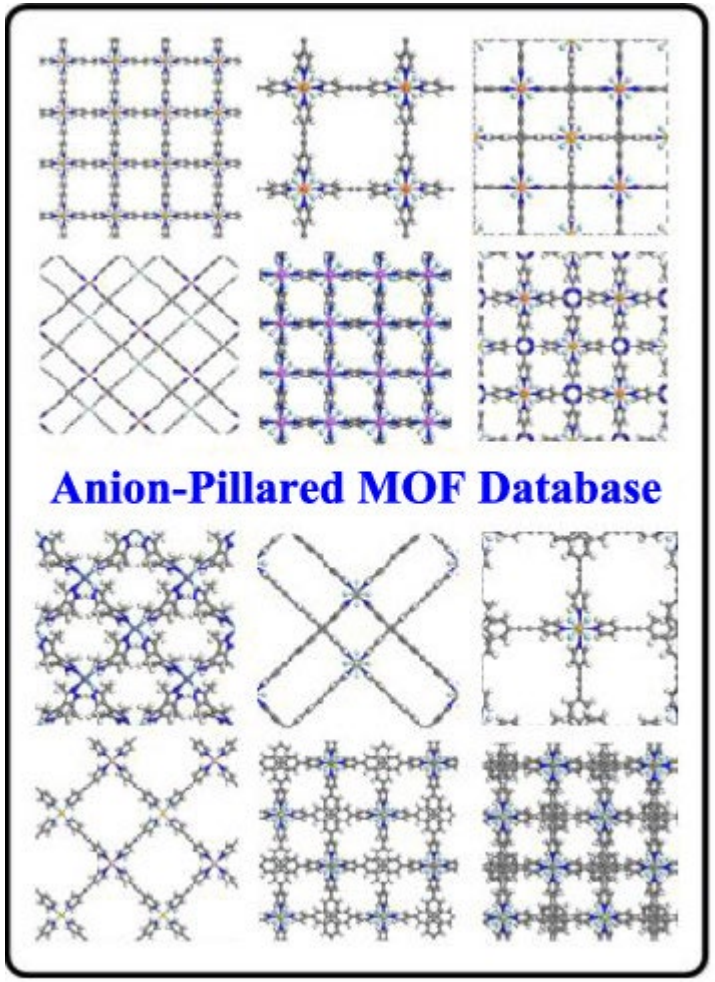


Screening for Strong Physisorbing MOFs

Anion-Pillared MOFs for Capture

- **Goal:** Identifying MOFs with strong CO_2 adsorption
  - Database from Gu and Sholl (2021)[2]
    - Metals not exposed
    - Tunable metal center, fluorine groups, linkers





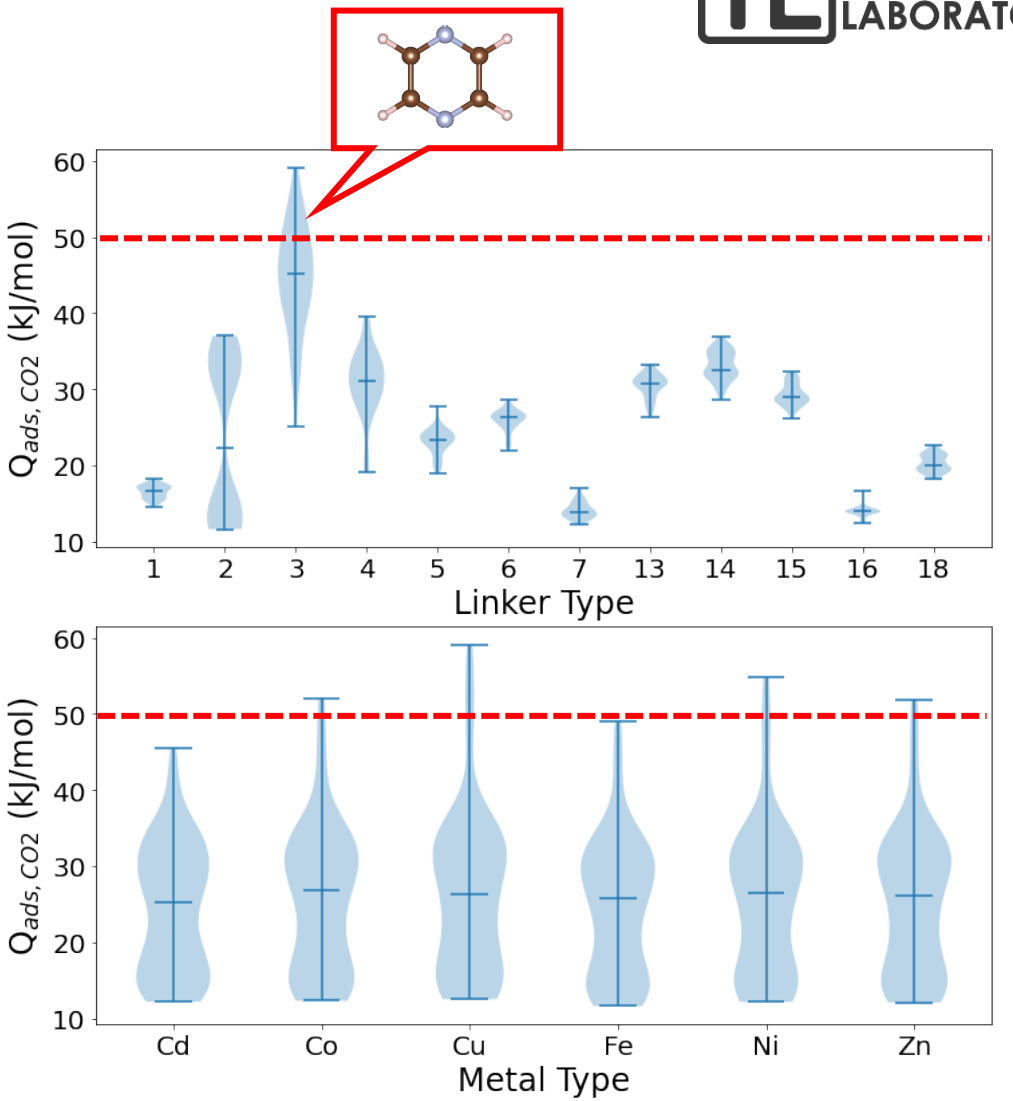
[2]Gu et al., *ACS Appl. Mater. Interfaces* (2021)

Screening for Physisorbent MOFs

MOFs with Pyrazine Linkers Perform Best

- Computed heats of adsorption
  - ~8000 total MOFs
  - > 10 MOFs with Q_{ads} > 50 kJ/mol
  - Strong association with linker type
  - Weak association with metal

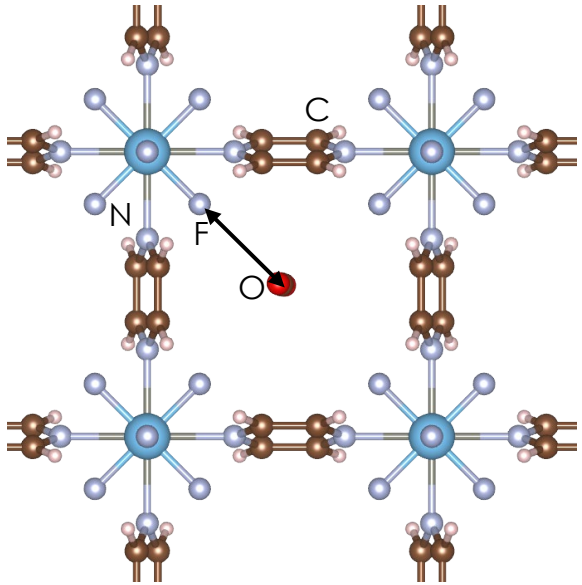
- MOFs with pyrazine linkers outperform others
  - Why pyrazine?
    - Why is the effect of metal so small?



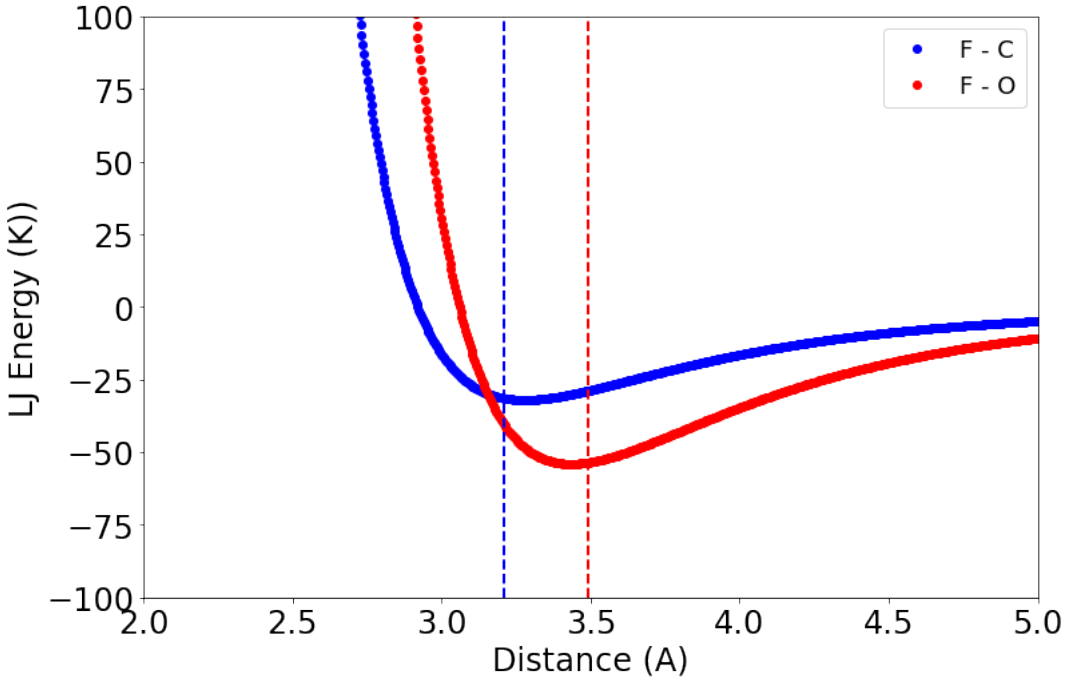
Studying the Adsorption Site

CO_2 Adsorbs at Fluorine Ring Centers

- CO_2 adsorbs at the center of 4 fluorines
  - "tug of war"
  - Near optimum distance for CO_2 – F dispersion interactions
  - $E_{dispersion} \approx E_{Electrostatic}$



TIFSIX_3 Zn	ΔE_{ads} (kJ/mol)
Classical FF	-53.0
DFT	-52.1

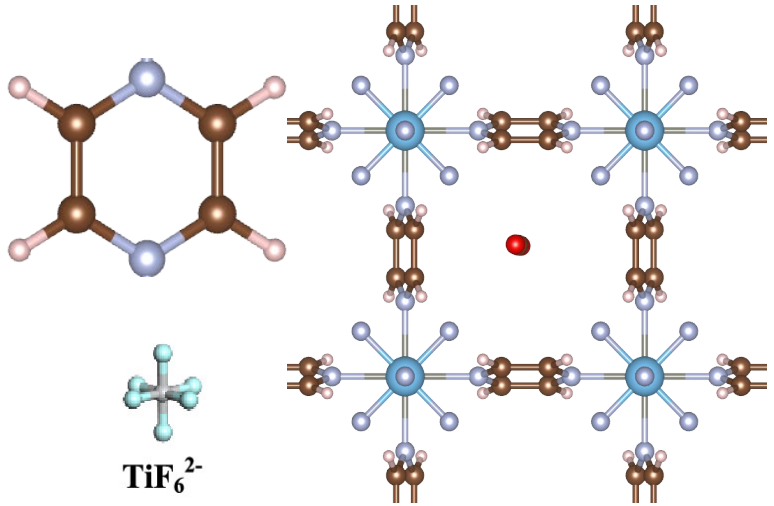


Screening for Physisorbent MOFs

MOFs with Pyrazine Linkers Perform Best

- Two MOFs from screening have been tested for DAC:
  - **TIFSIX_3_Ni[3,4]:** 1.2 mmol/g CO_2
  - **SiFSIX_3_Cu[5]:** 1.24 mmol/g CO_2
- Performance warrants more advanced simulation methods
  - Predict uptake in dry, humid conditions

MOF	$\Delta H_{ads, CO_2}^0$ (kJ/mol)
TIFSIX_3_Cu	-57.5
SIFSIX_3_Cu	-56.5
TIFSIX_3_Ni	-52.4
TIFSIX_3_Zn	-50.5

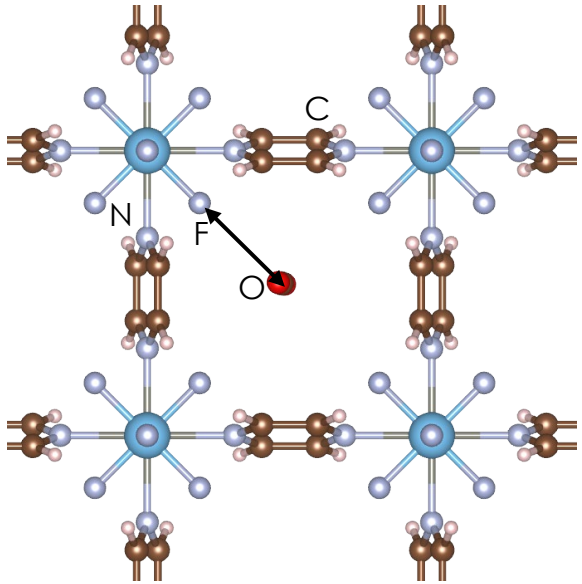


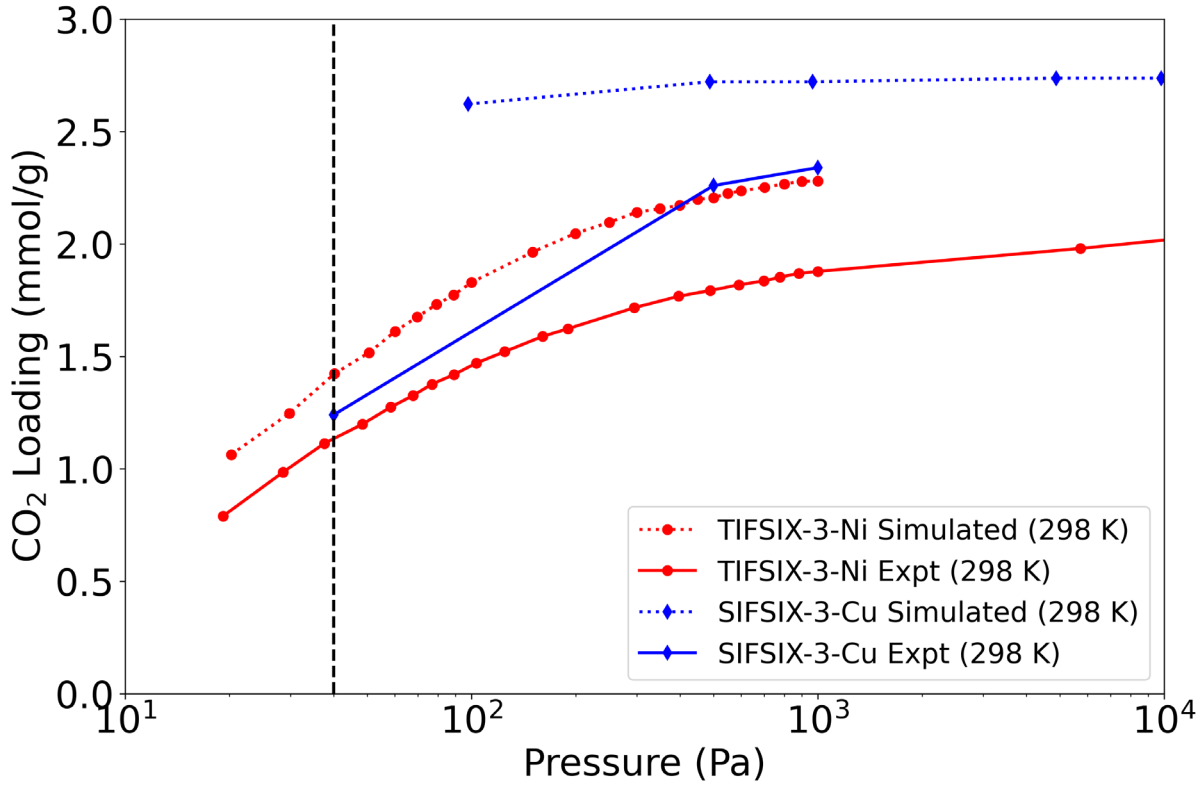
[3]Ullah et al., *Angewandte Chemie* (2022)
[4]Low et al. *Energy& Fuels* (2024)
[5]Shekhah et al., *Nature Communications* (2014)

Performance of Rigid Force Fields

Worse Performance at Low Pressure

- CO_2 adsorption overpredicted using rigid force fields
- Does flexibility play a role?



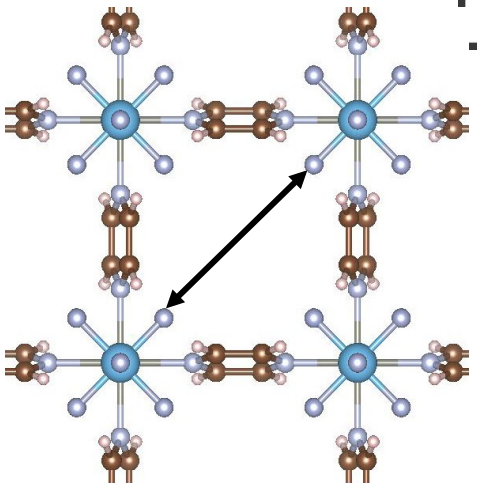


[3]Ullah et al., *Angewandte Chemie* (2022)
[4]Low et al. *Energy& Fuels* (2024)
[5]Shekhah et al., *Nature Communications* (2014)
[6]Mulcair, *Dissertation* (2017)
[7]Forrest et al., *Crystal Growth and Design* (2019)

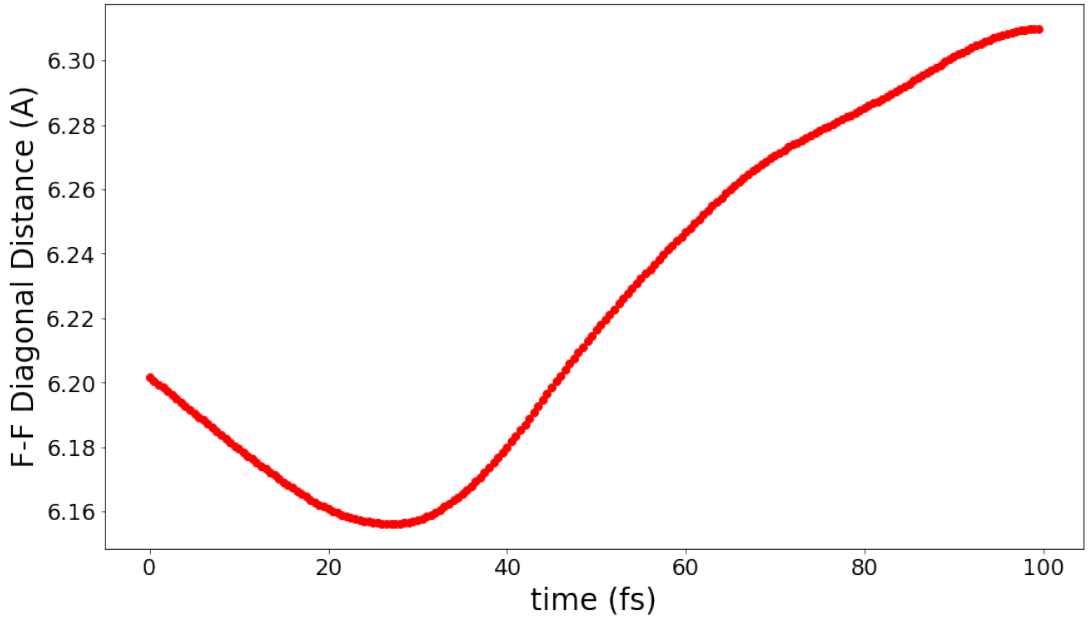
Why Do We Need MLFFs?

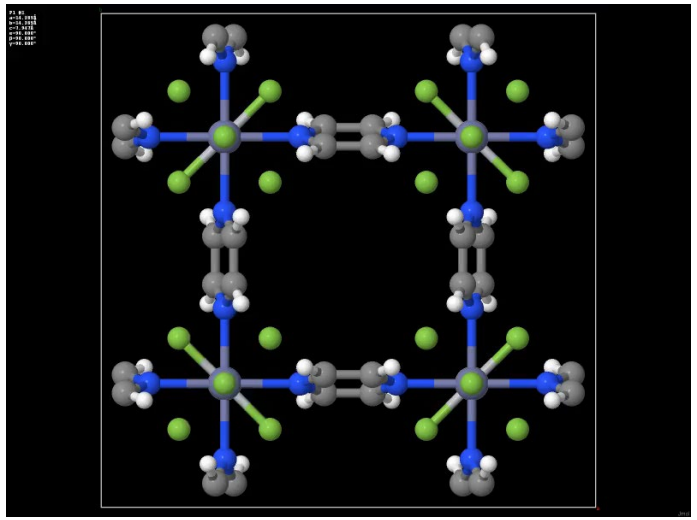
Flexible SiF_6 and TiF_6 can Cause Changes in Window Size

- Poor performance of rigid force fields
  - Overprediction at low P_{CO2}
- DFT molecular dynamics:
  - Significant motion of fluorine atoms
  - Fluorine location affects adsorption strength



F-F diagonal



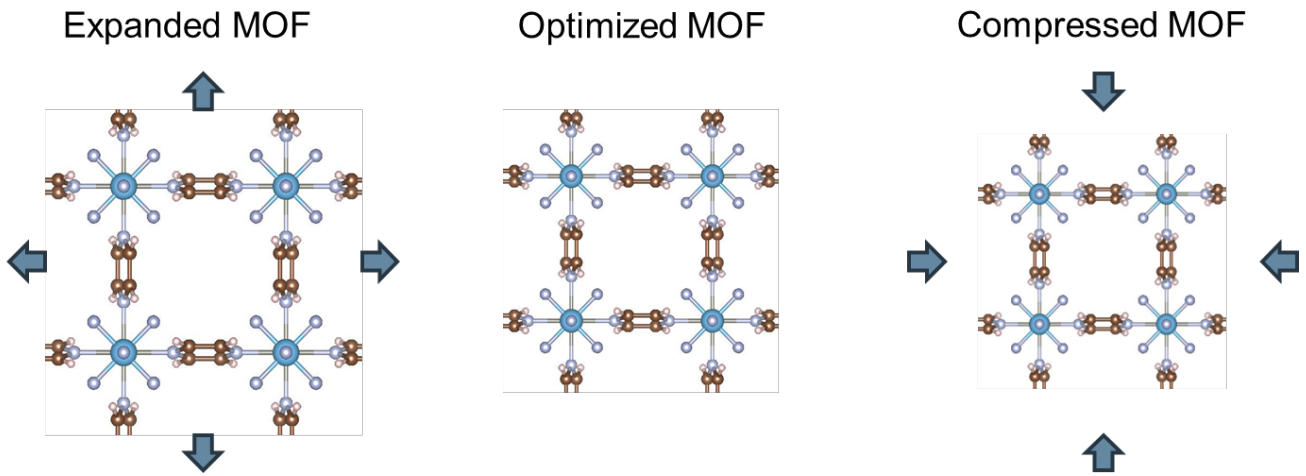


MLFF Training Recipe

MLFFs Trained on Accurate DFT Data

- **Training Configurations**
  - Favorable (low energy) and unfavorable (high energy)
  - MOF with and without CO_2
- **MLFF Method**
  - Hybrid SNAP/classical potential
  - MLFF handles short range
  - Classical handles long range

Sample Volume Changes



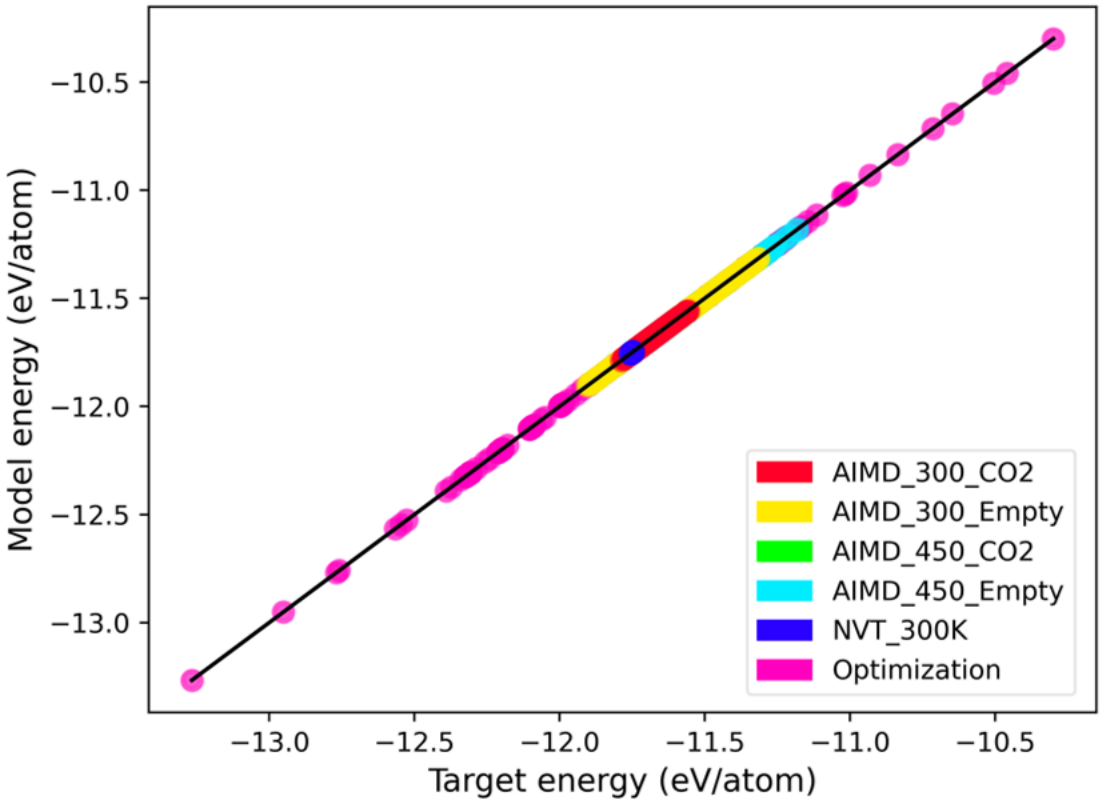
Sample CO_2 Adsorption

Performance of MLFF Model (Empty)

MLFF Describes MOF Structure and Flexibility (TIFSIX_3_Zn)

- Prediction of energy vs. volume curve is almost perfect (bottom)
  - Related to bulk modulus
- Compared energies/forces in QM-based dynamics calculations, performance is good
  - 7000 training configurations
  - 1800 testing configurations

Data (Testing set)	R^2 Energies	R^2 Forces
Structure Optimization	0.998	0.990
AIMD – 300 K	0.991	0.981
AIMD – 450 K	0.990	0.975



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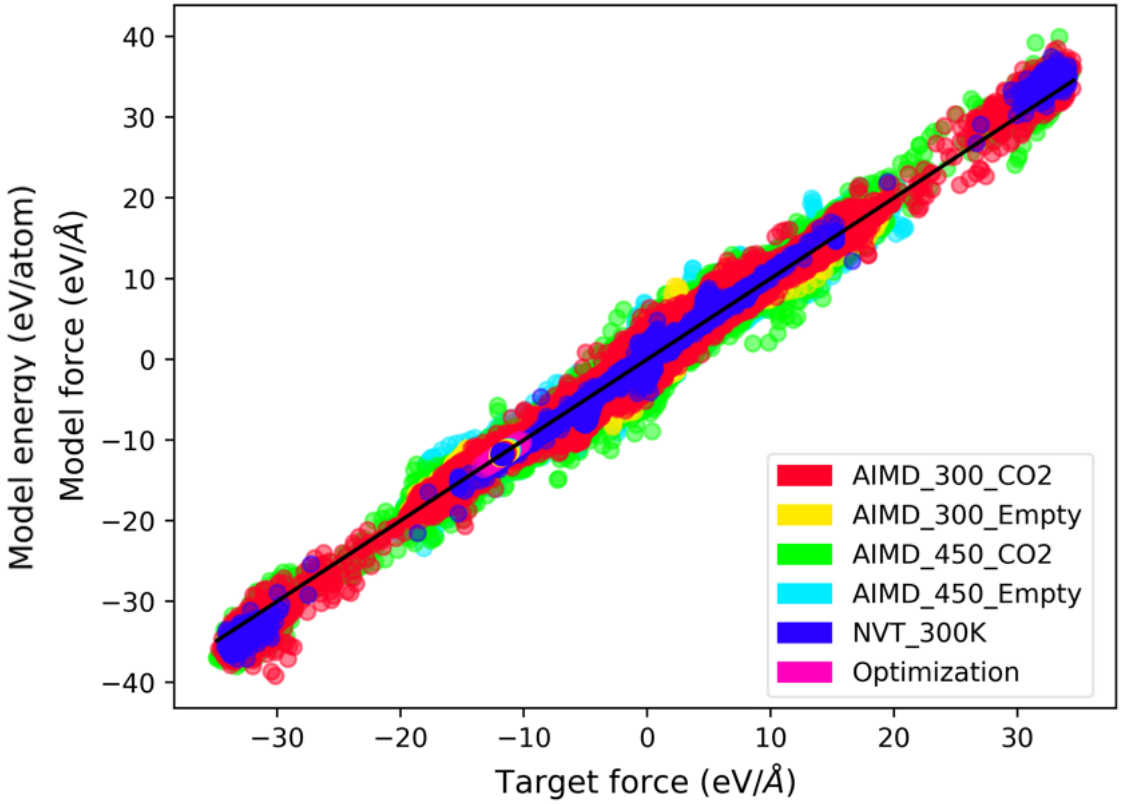

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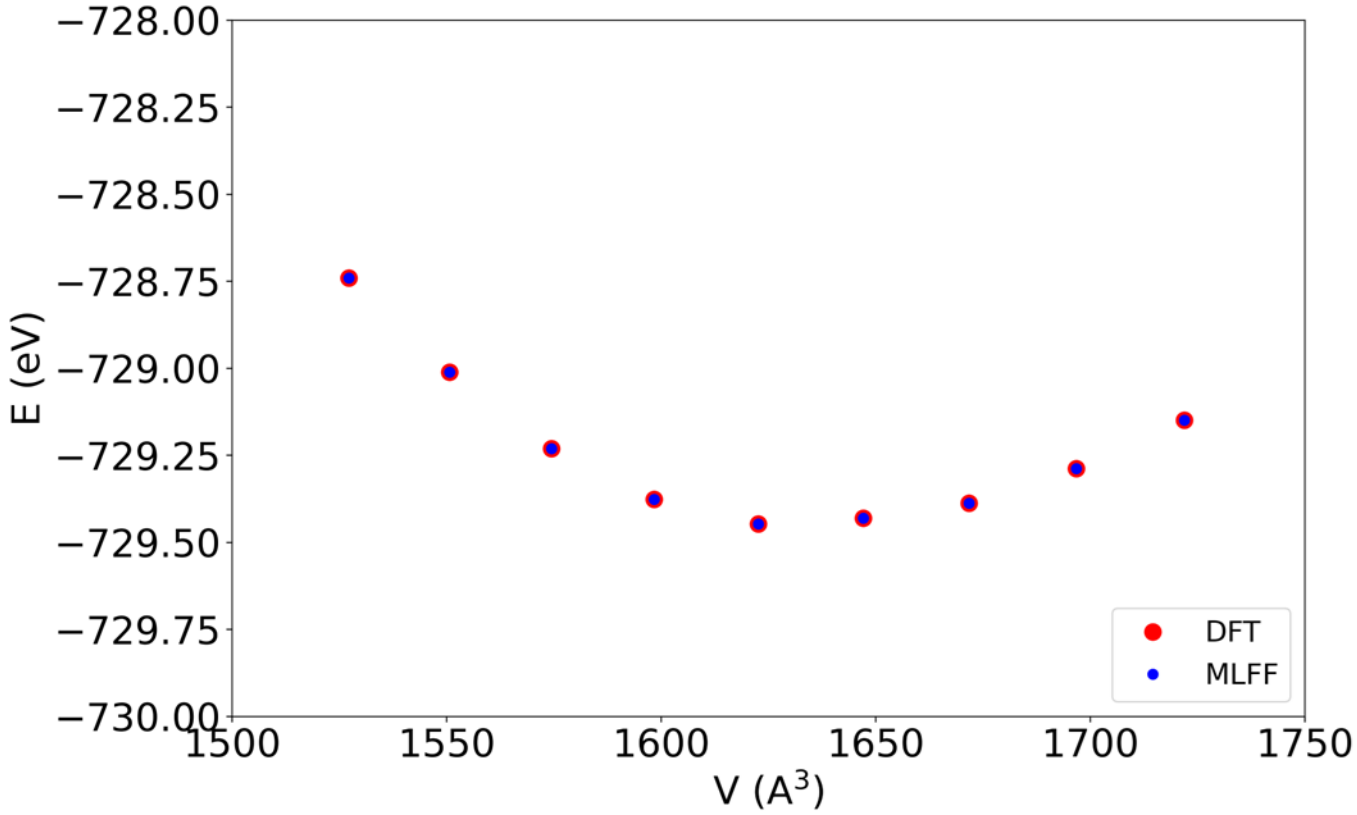


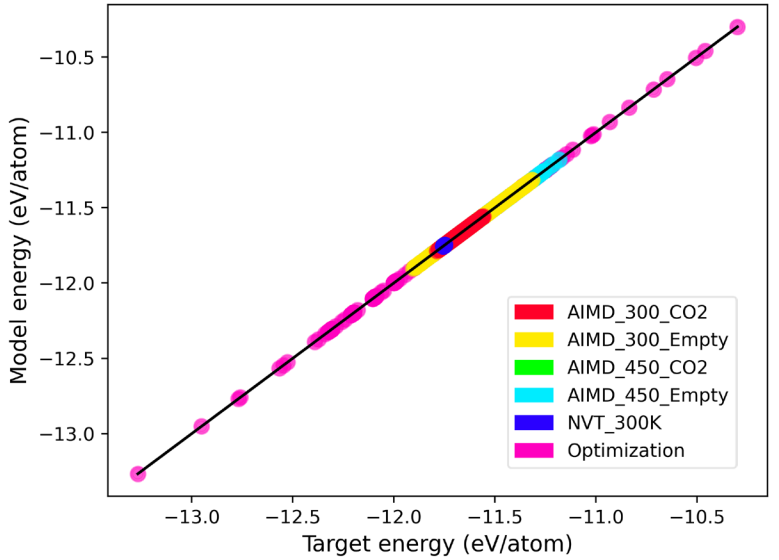
Performance of MLFF Model (CO_2 Adsorption)

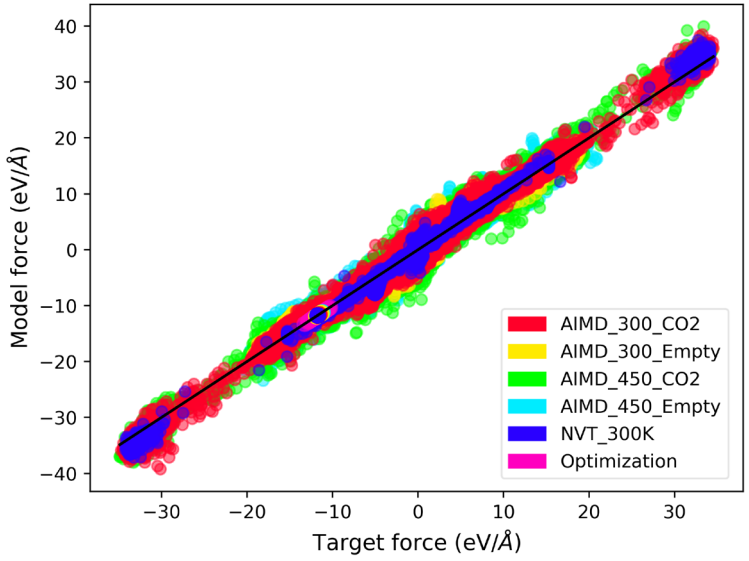
MLFF Describes Force, Energy for CO_2 (TIFSIX_3_Zn)

- MLFF model accurately describes energies and forces MOF loaded with CO_2
- Training on the error of the classical force field rather improves the model fit
  - $\Delta E_{ads, CO2, MLFF}$ = -52.9 kJ/mol

Data (Testing set)	R^2 Energies	R^2 Forces
AIMD – 300K	0.990	0.983
AIMD – 450K	0.990	0.978
MC – 300K	0.975	0.995

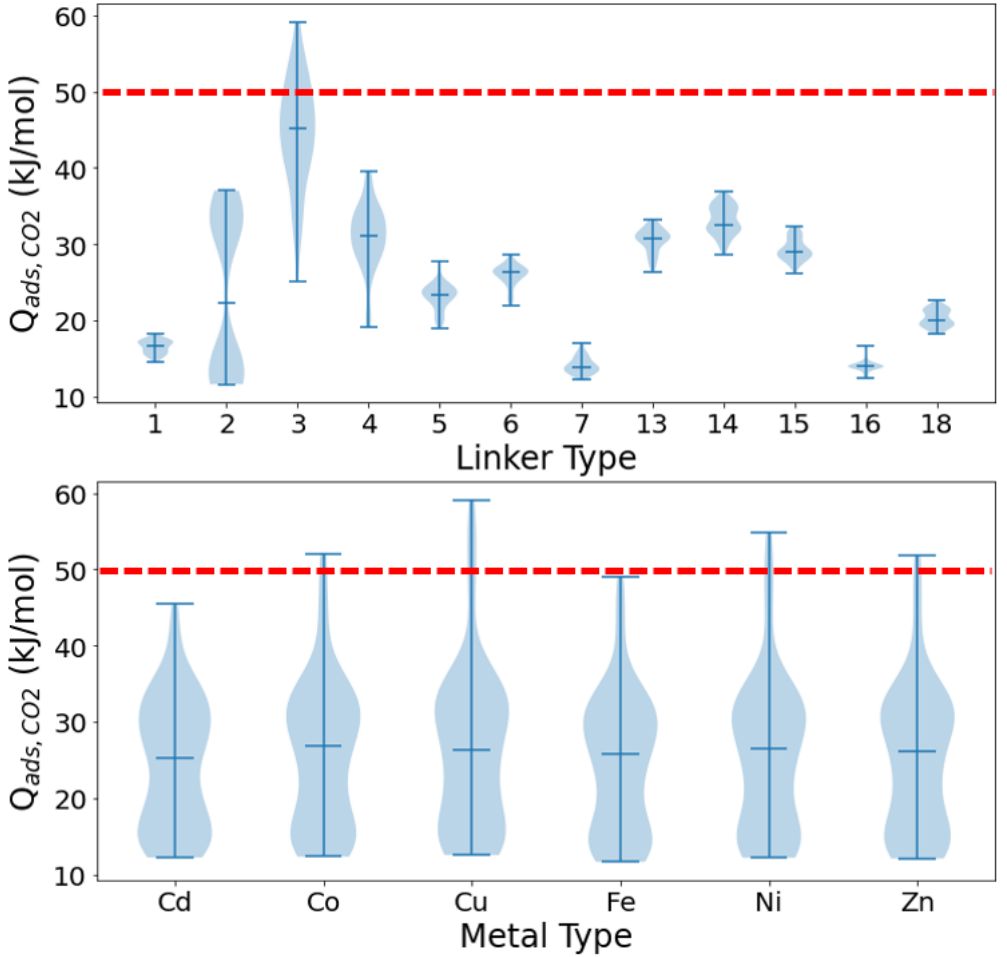
- **Prediction:** TIFSIX-3-Zn adsorbs1.08 mmol/g*
  - 400 ppm, 298 K
- **Next:** Validate other MOFs
  - TIFSIX(Ni) and SIFSIX (Cu)





Conclusions

- Screened MOFs for CO_2 capture
  - Strong dispersion interactions are important!
- Flexibility is important for CO_2 adsorption at low pressure
- Developed flexible MLFF for TIFSIX MOFs for CO_2 capture
  - **Next:** Further benchmarking MLFF methods
  - **Next:** How much of a role does humidity play?



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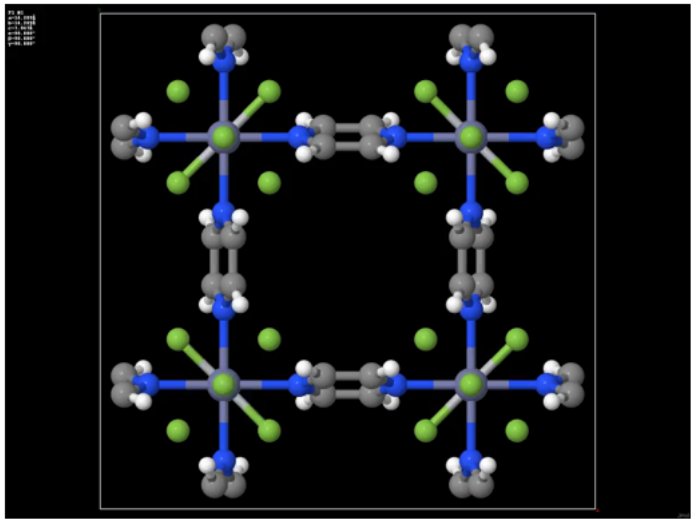

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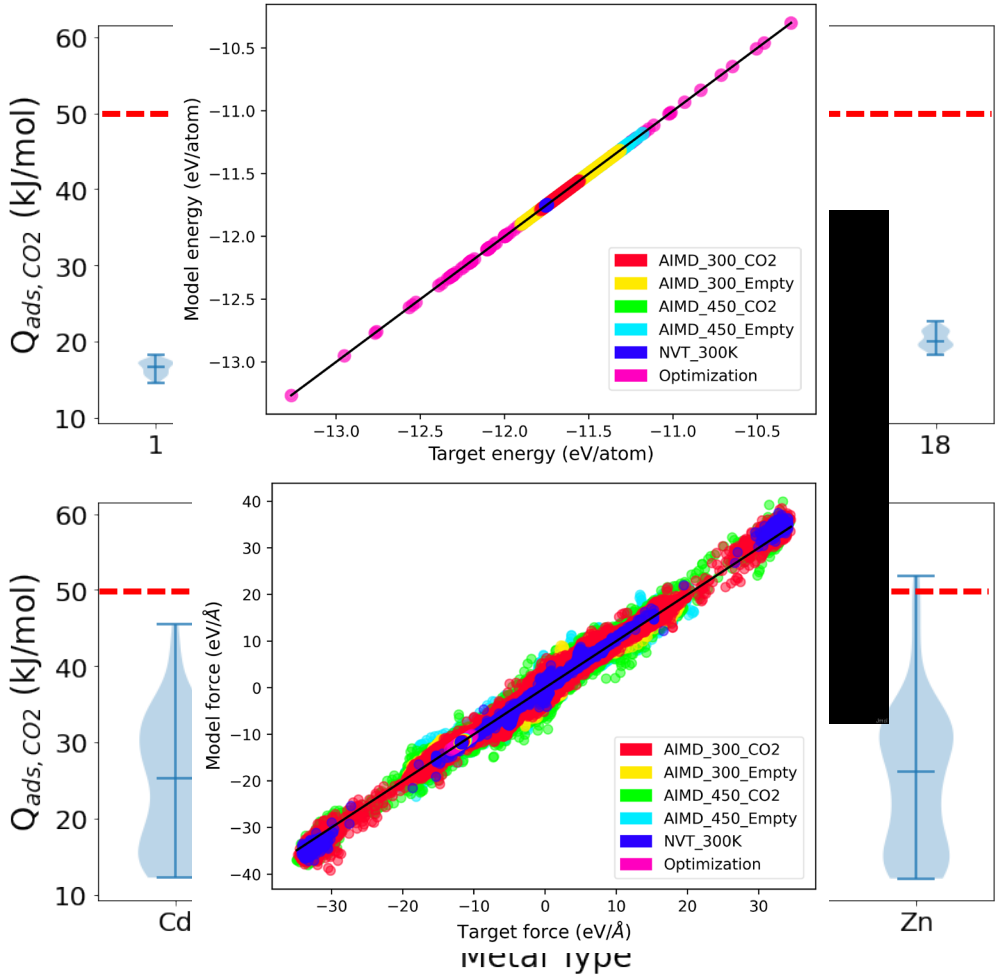

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