NATIONAL ENERGY TECHNOLOGY LABORATORY

Investigation of the Effect of Framework Flexibility on Adsorption in SIFSIX-3-Cu Using a Machine-Learned Force Field

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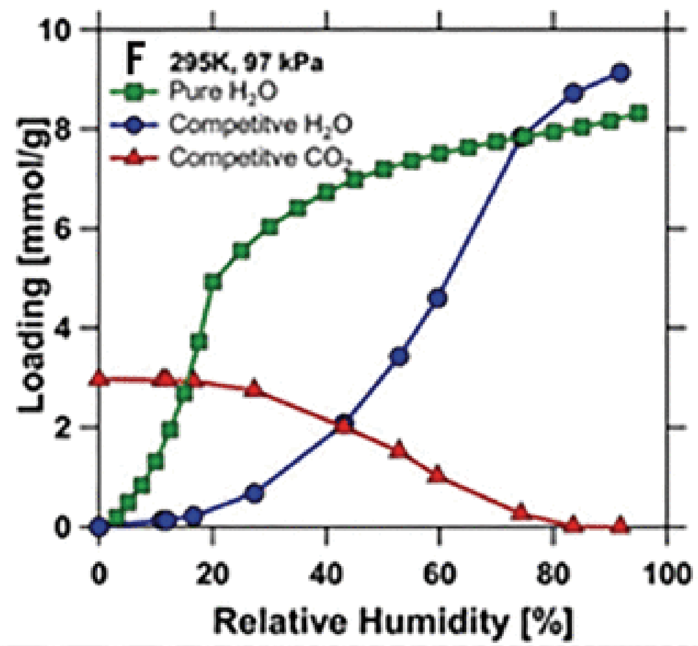
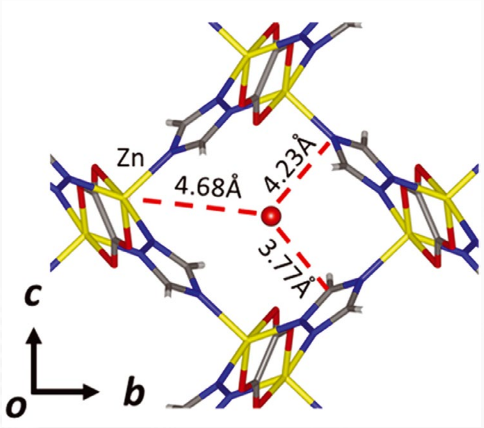
Physisorbent Materials for Gas Separations

Characteristics of a Good Physisorbent

- Characteristics of an economically viable sorbent
  - Selective: more efficient gas separations
  - Stable: lower material costs
  - Regenerable: reduced cost of power consumption





Lin et al., *Science* (2021).

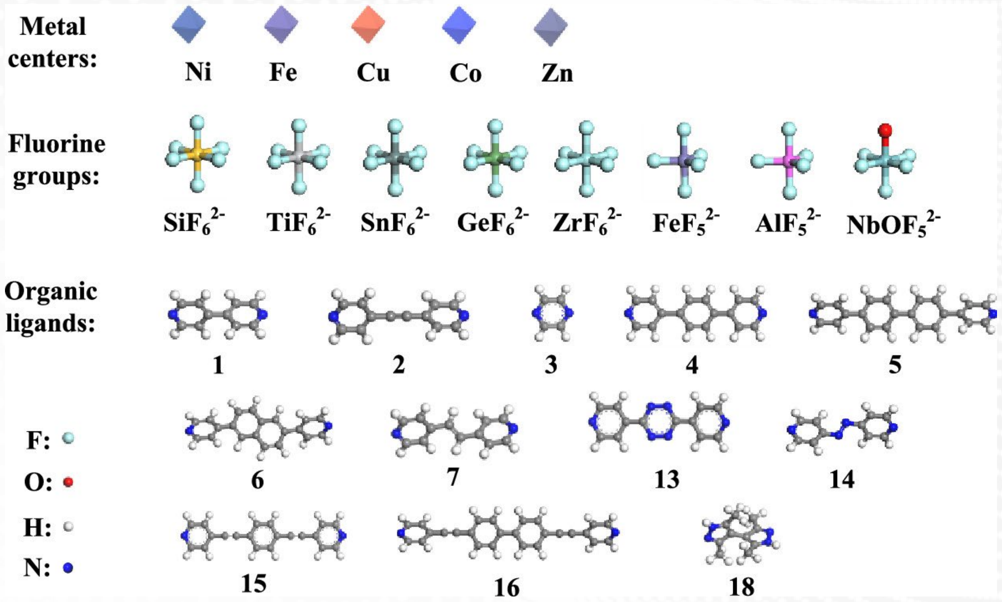
- Metal-organic frameworks (MOFs)
  - Metal nodes connected by organic linkers
  - Highly tunable for adsorption

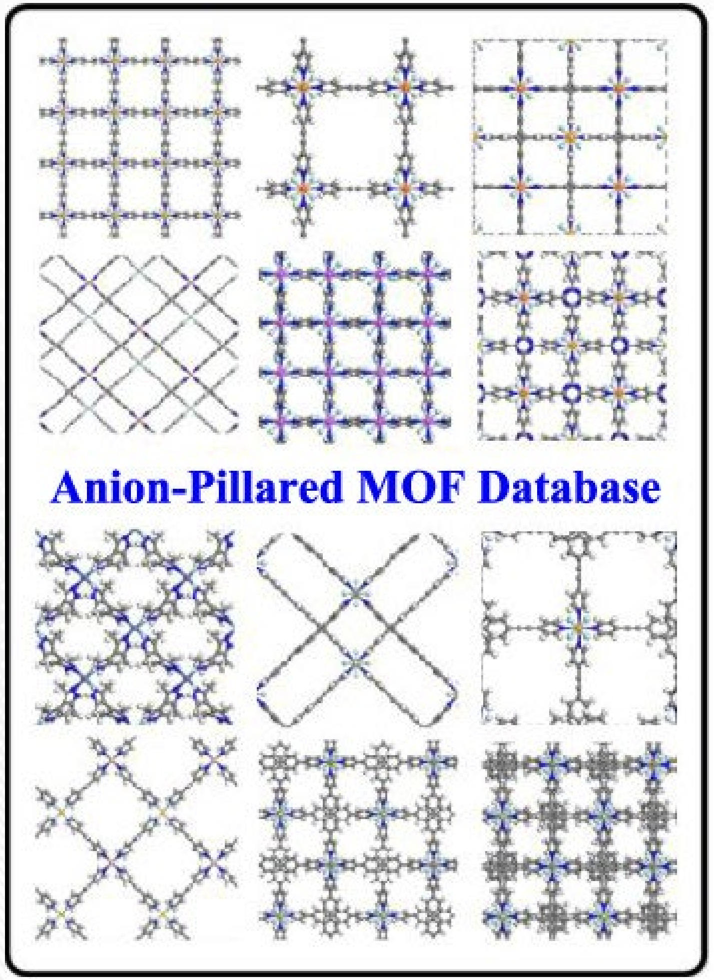
- Example: CALF-20
  - Successfully demonstrated for enhanced resource utilization in industrial processes (e.g., cement plants) and optimizing emissions from traditional power generation assets
  - Little effect of humidity up to 30% RH
    - Strong **dispersion** interactions

Screening for Strong Physisorbing MOFs

Screening Anion-Pillared MOFs

- **Goal:** Identifying MOFs with high selectivity
  - Database from Gu and Sholl (2021)
    - Tunable metal center, fluorine groups, linkers
    - Systematic dataset: easy to obtain structure-property correlations





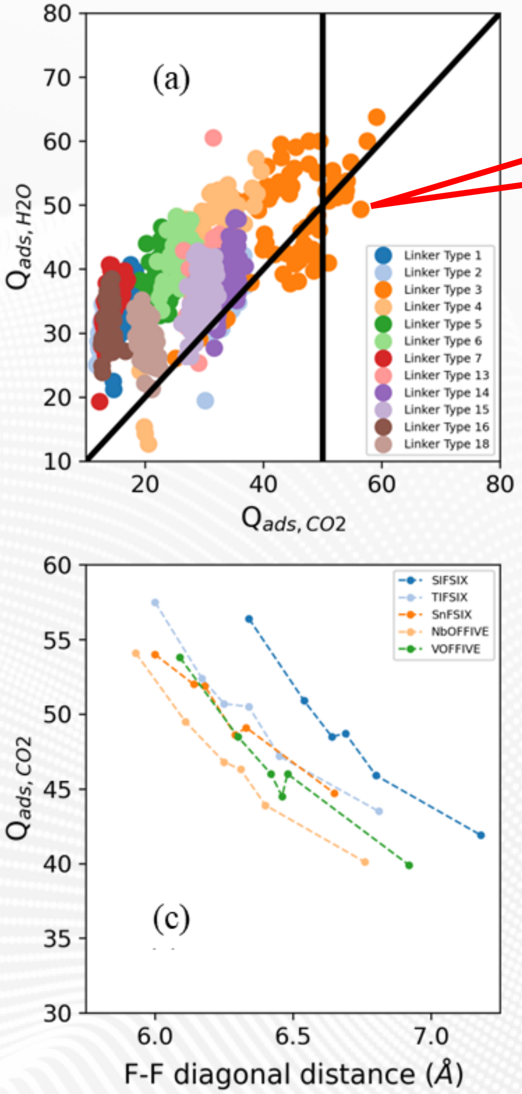
Gu et al., *ACS Appl. Mater. Interfaces* (2021).

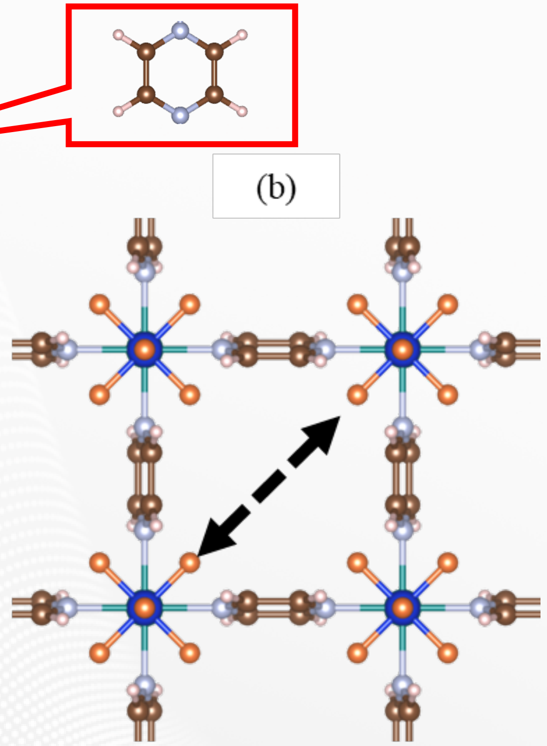
Screening for Physisorbent MOFs

MOFs with Pyrazine Linkers Show High Selectivity

- Screened database for MOFs based on zero-loading heats of adsorption
  - **Pyrazine** shows high selectivity
  - **Pyrazine** gives optimal F-F spacing

Fluorine Group	Linker	Metal	$Q_{ads, CO2}$ (kJ/mol)	$Q_{ads, H2O}$ (kJ/mol)
SIFSIX	Pyrazine	Cu	56.4	49.3
NbOFFIVE	Pyrazine	Cu	54.1	53.8
TIFSIX	Pyrazine	Ni	52.4	51.2
SIFIX	Pyrazine	Ni	50.9	41.0



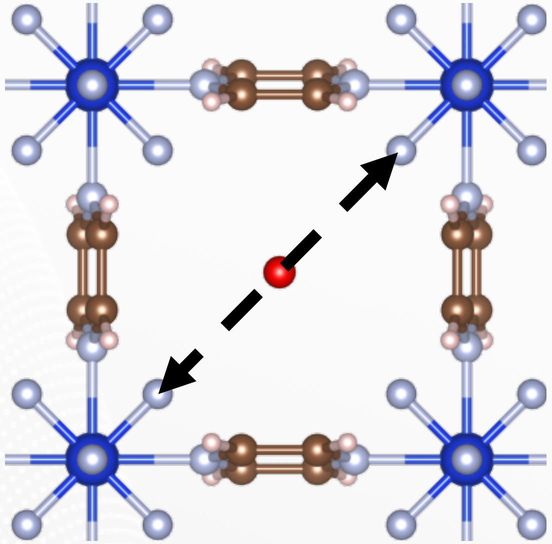


Findley et al. *J. Phys Chem C.* (2025).

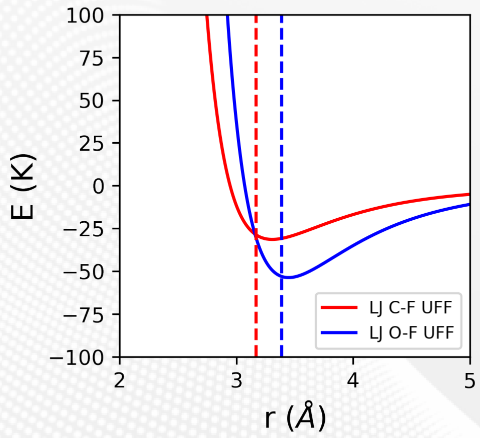
Importance of the Window

"Tug-of-War" Adsorption Sites

- Rigid, classical models showed strong adsorption in SIFSIX-3-Cu
  - Well-known material: good for benchmarking
- Adsorption site: Between four fluorine groups
- Correlation between window size and Q^0_{ads}
  - Optimal Van der Waals distances
- Flexibility of window can affect adsorption properties



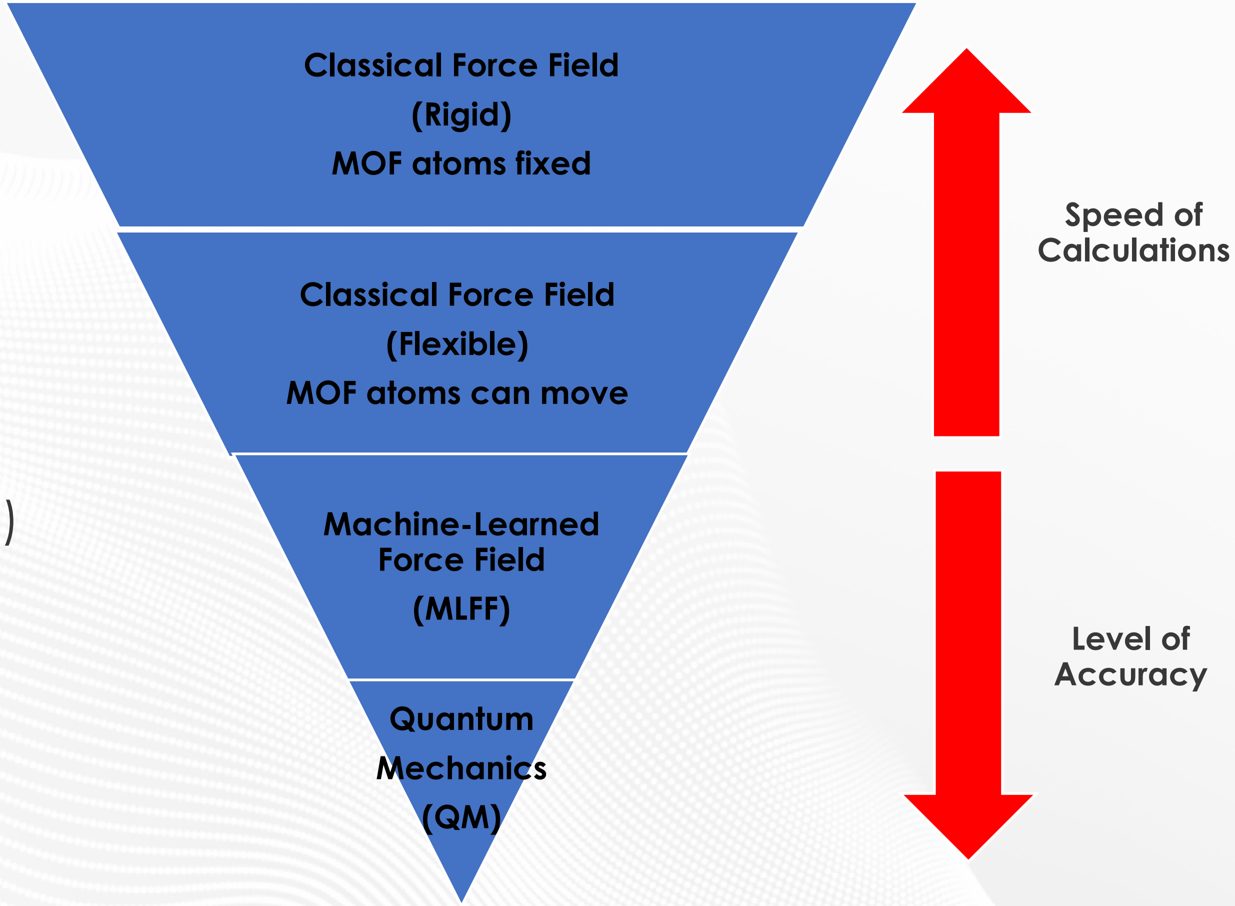
UFF Lennard-Jones



Levels of Calculations

Machine-Learned Force Fields (MLFF) Connect Classical and Quantum Simulations

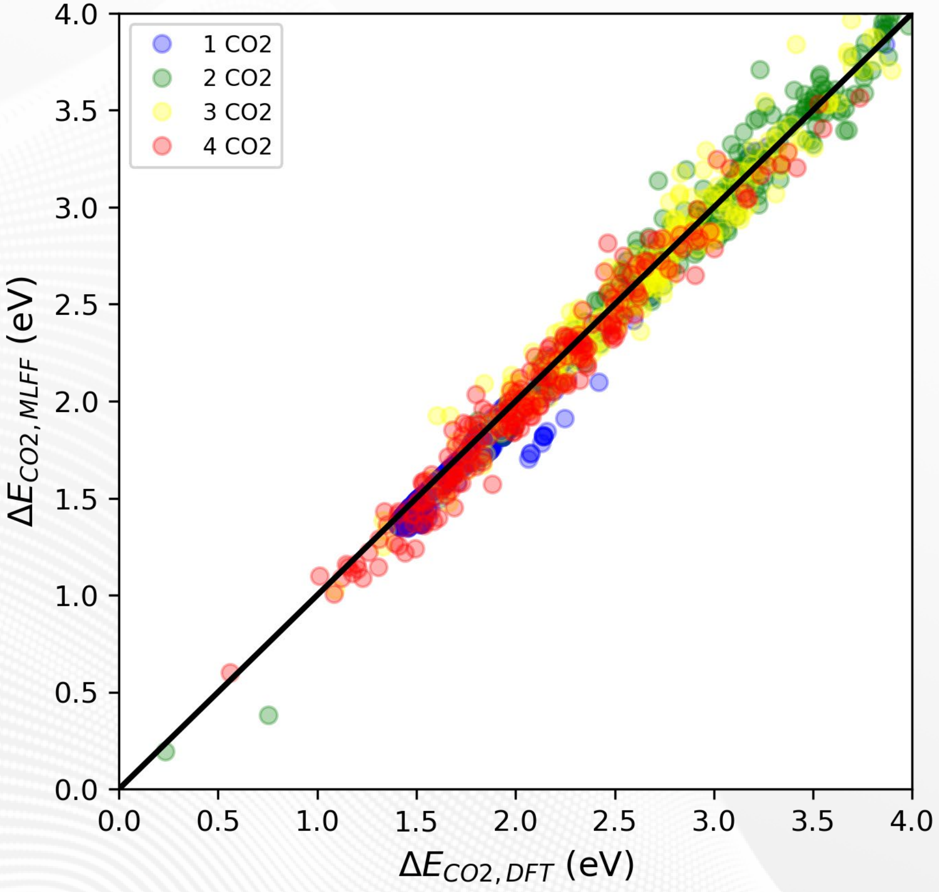
- **Classical Force Field (speed):**
  - **Rigid:** MOF atoms fixed during simulation
  - **Flexible:** MOF atoms can move
  - Energy, force from analytical function
  - Can calculate adsorption, diffusion
- **MLFF:**
  - Energy, force from ML model
    - Better fitting to quantum mechanical (QM) calculations
- **QM methods (accuracy):**
  - Such as density functional theory (DFT)
  - Accurate, slow
  - Compute energy, forces, determine structures



MLFF Fitting Procedure

Train → Simulate → Compare (to DFT) → Retrain & Repeat

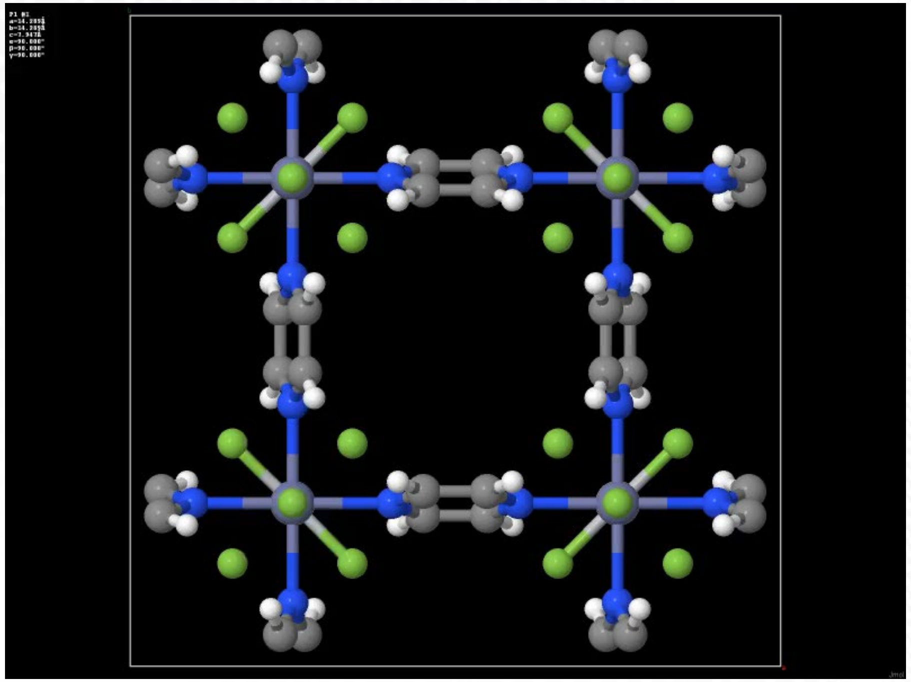
- Initial Training data from DFT
  - Optimization
  - Ab initio molecular dynamics
  - Empty to fully saturated sorbent
- Fit MLFF (DeePMD)
  - Deep learning potential
  - $\Delta E = E_{MOF+nads} - E_{MOF, opt} - n_{ads} * E_{ads}$
- Molecular dynamics (MD) using MLFF
  - 1 ns trajectory
  - Loadings of empty to fully saturated
- Compute energy, force, stress of snapshots using DFT
- Retrain if $R^2 < 0.9$
  - Converged after two cycles



Generation of a Robust Dataset for Deep Learning

Generation of Initial Training Dataset

Sample Framework Dynamics (both with and without adsorbates)

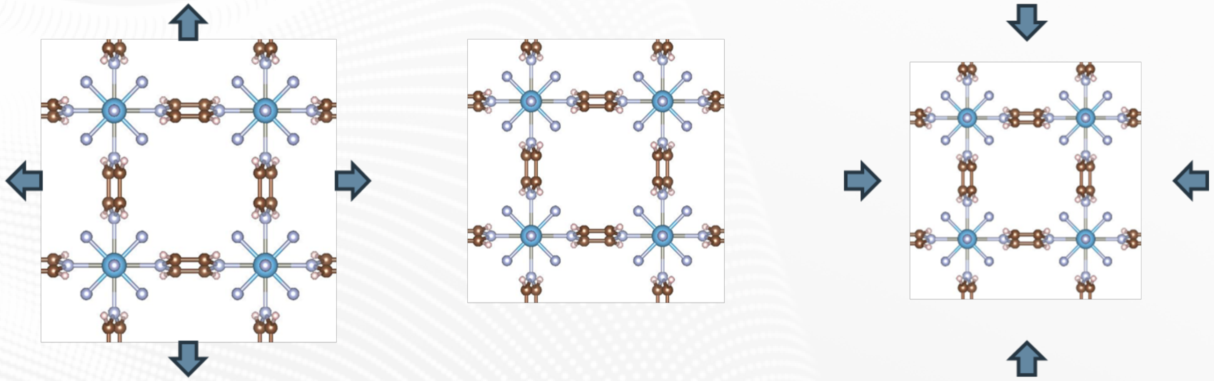


Sample Volume Changes

Expanded MOF

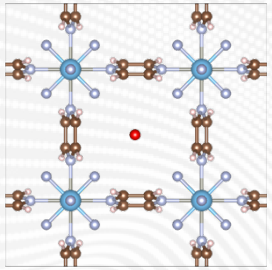
Optimized MOF

Compressed MOF

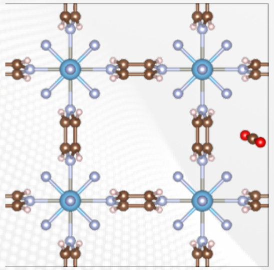


Sample CO_2 Adsorption

Lower Energy CO_2



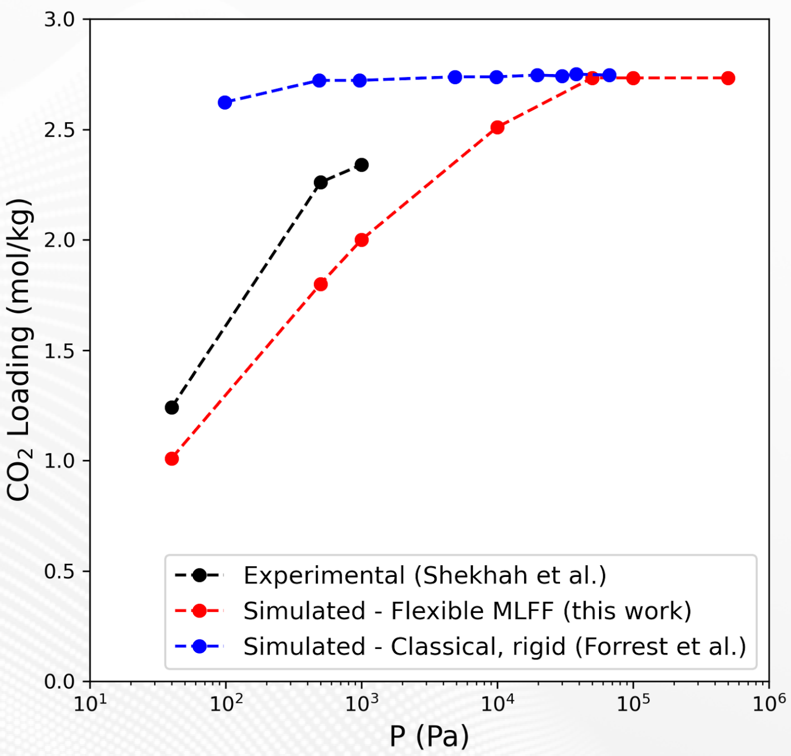
Higher Energy CO_2



Performance of MLFF Model

New Model Agrees Better with Experiments

- MLFF used for hybrid Grand Canonical Monte Carlo (GCMC)/MD calculations
- Low pressure agreement improved significantly
- Why does framework flexibility have a larger effect at low pressure for this MOF?

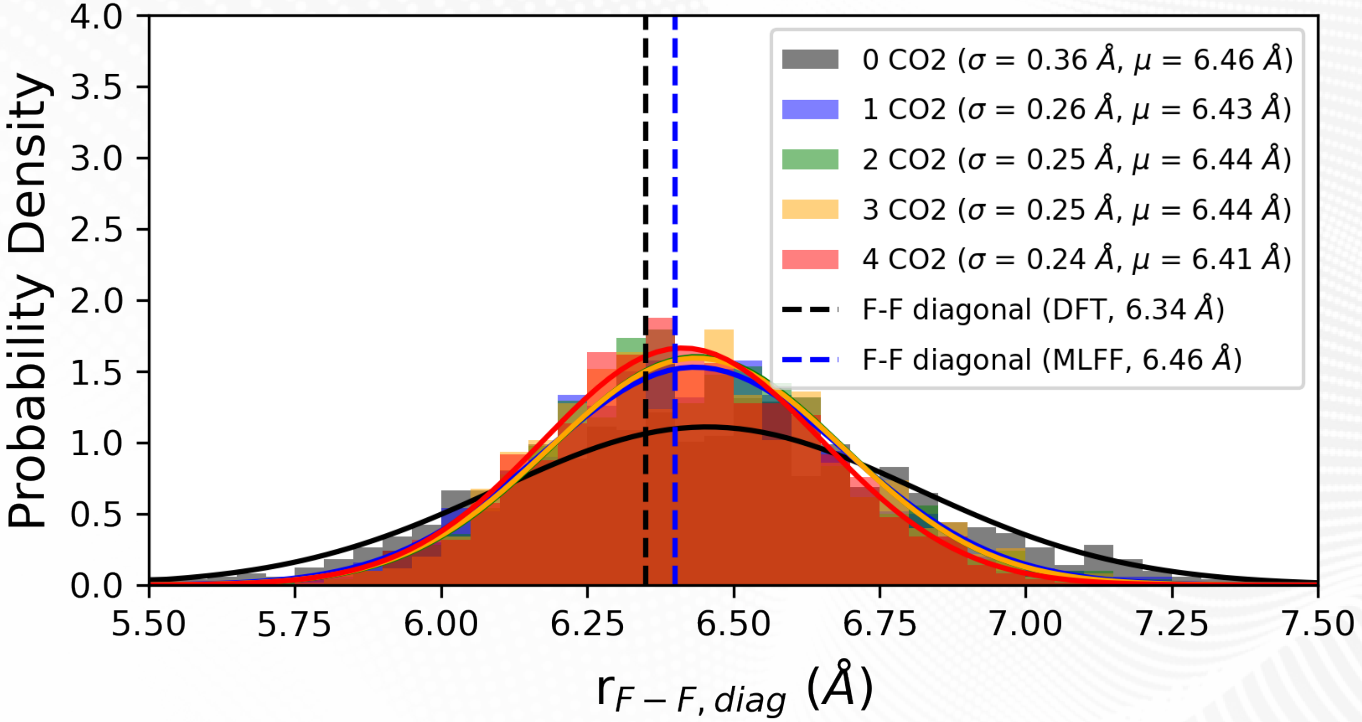


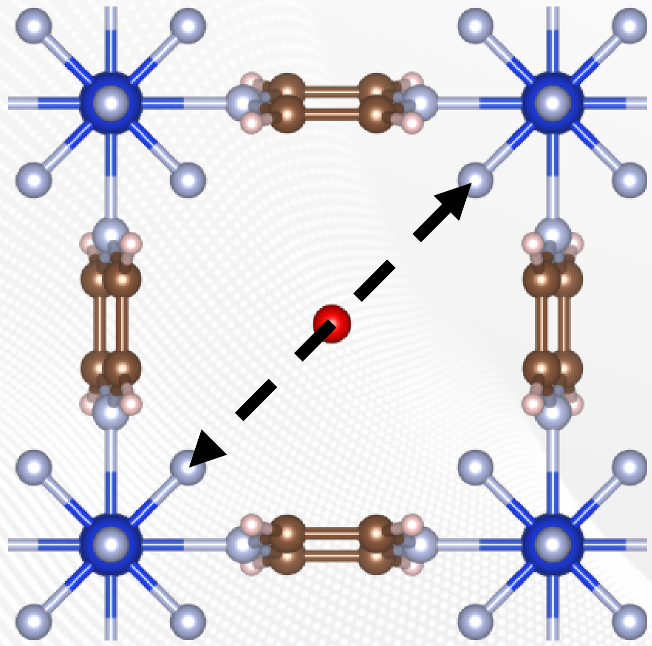
Findley et al. *J. Phys Chem C.* (2025)
Shekhah et al. *Nature Communications* (2014)
Forrest et al. *Crystal Growth and Design* (2019)

Flexibility in SIFSIX-3-Cu

Window Size Varies Significantly (T = 300 K)

- MLFF used for MD at five different adsorbate loadings (0-4 molecules per unit cell)
- Strong adsorbate-framework interactions reduce framework flexibility
  - Reduction in flexibility is observed at loadings expected under industrial point source capture conditions
- Adding adsorbates slightly decreases average window size





Water: First Approximation – Classical Models

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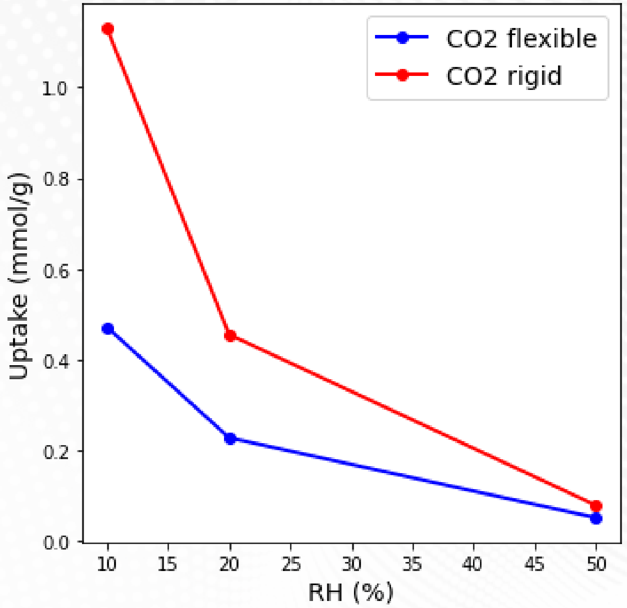
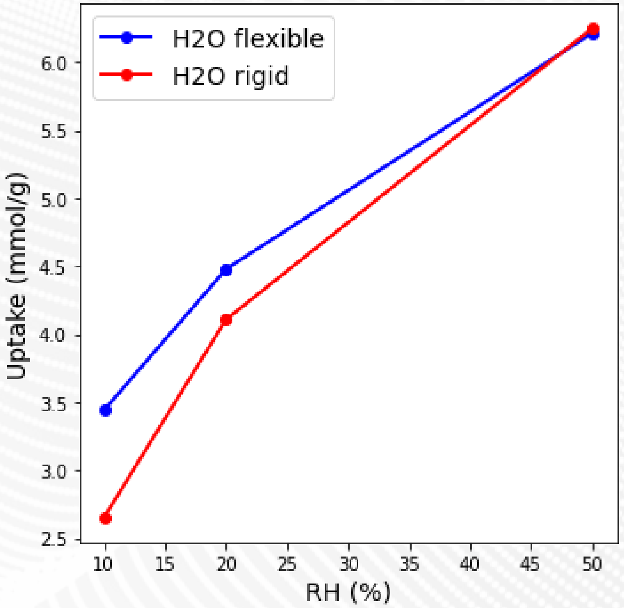
Binary GCMC of CO_2/H_2O Shows Competition

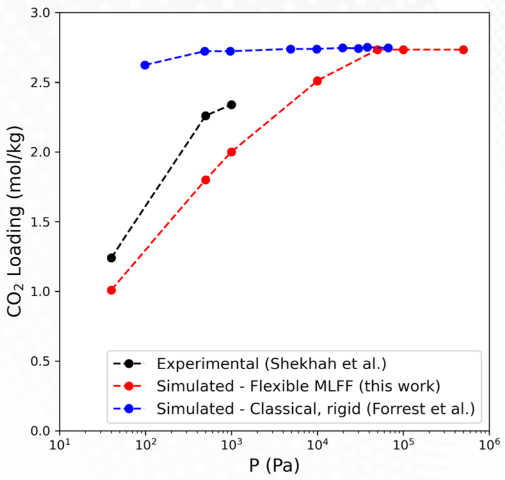
- Selective adsorption of CO_2 over H_2O assists in maintaining operational efficiency and reliability of gas processing units at power generation facilities
  - Accurate predictions of competitive adsorption result in more robust sorbent design
- Same images from MLFF-dynamics run
  - Two-component GCMC for each run, took average to get “flexible” approximation
- CO_2 and H_2O have similar affinities for SIFSIX-3-Cu, but different symmetries
  - Selectivity for CO_2 over H_2O decreases with flexibility, more prominent at low RH

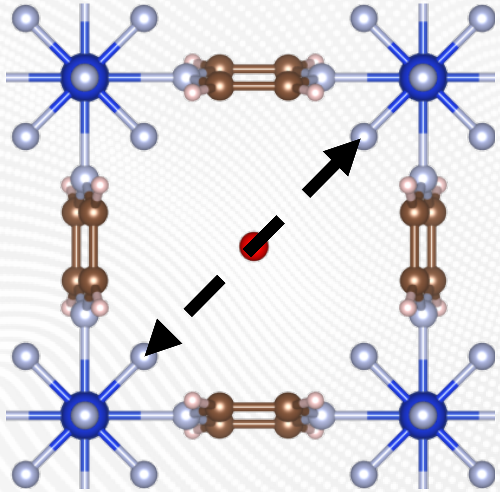




Conclusions

- Optimized material design through precise control of fluorine group spacing is critical for maximizing efficiency and throughput in industrial gas separation for reliable energy production.
- Machine Learning techniques significantly enhance our ability to predict material performance, accelerating the development of next-generation sorbents for American energy infrastructure.
- Understanding framework flexibility is key to designing robust, high-performance materials capable of sustained operation in demanding industrial environments associated with domestic energy production."

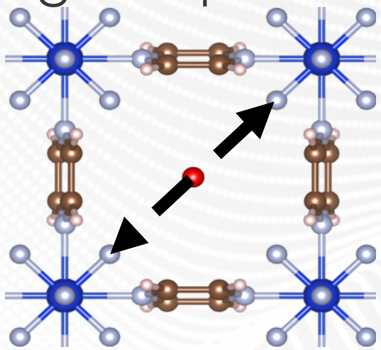




Next Steps

Thermal Conductivity, Water, Transferability

- **Thermal Conductivity:**
  - Quantifying the thermal management requirements to optimize energy efficiency and reduce operational costs in next-generation gas separation technologies for American industries
  - Does the presence of water or CO_2 affect thermal conductivity?
- **Water Adsorption:**
  - Investigating long-term material stability and performance under realistic operating conditions, especially with water, to ensure the reliability and economic viability of domestic energy utilization.
- **Transferability:**
  - Exploring synergistic impacts of flexibility and water on material performance to unlock new designs for robust and efficient gas separation in critical energy applications



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