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

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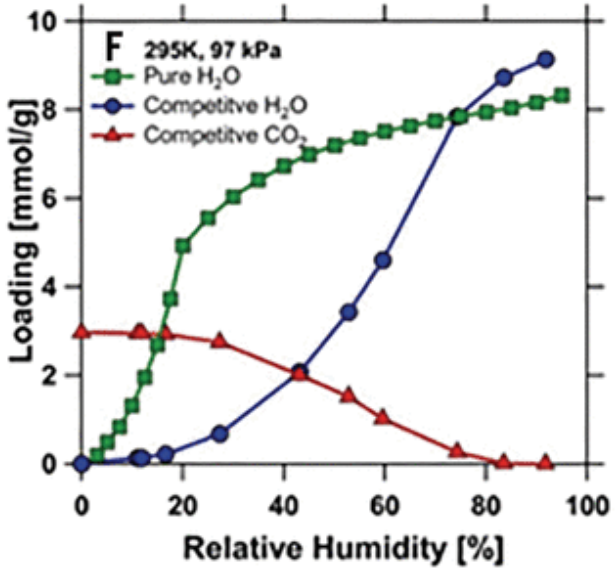
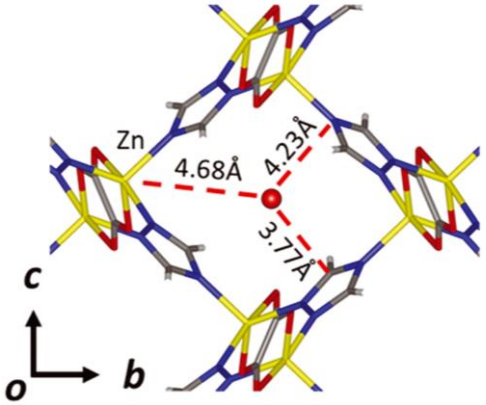
Physisorbents for CO_2 Capture

Characteristics of a Good Physisorbent

- Characteristics of a good direct air capture (DAC) sorbent
  - High CO_2 uptake at low partial pressures
  - Performance not hindered by humidity
    - Strong electrostatics leads to selectivity for H_2O
  - Regenerable
- Example: CALF-20
  - Successfully used for capture applications
    - No chemical bonds formed
    - Easier to regenerate sorbent
  - Not hydrophilic
    - Humidity has little effect on performance (up to 30% RH)
    - $\Delta E_{ads,\ CO2}$ = -36.5 kJ/mol[1]
    - $\Delta E_{ads,\ H2O}$ = -29.1 kJ/mol[1]
    - Humidity is often an issue for other CO_2 physisorbents
      - CALF-20 exhibits strong **dispersion interactions** with CO_2
- Metal organic frameworks (MOFs) have a diverse set of pore structures and adsorption sites.
  1. Need stronger CO_2 binding (preferably $\Delta E_{ads,\ CO2}$ < -50 kJ/mol)
  2. Need comparable H_2O adsorption to CALF-20



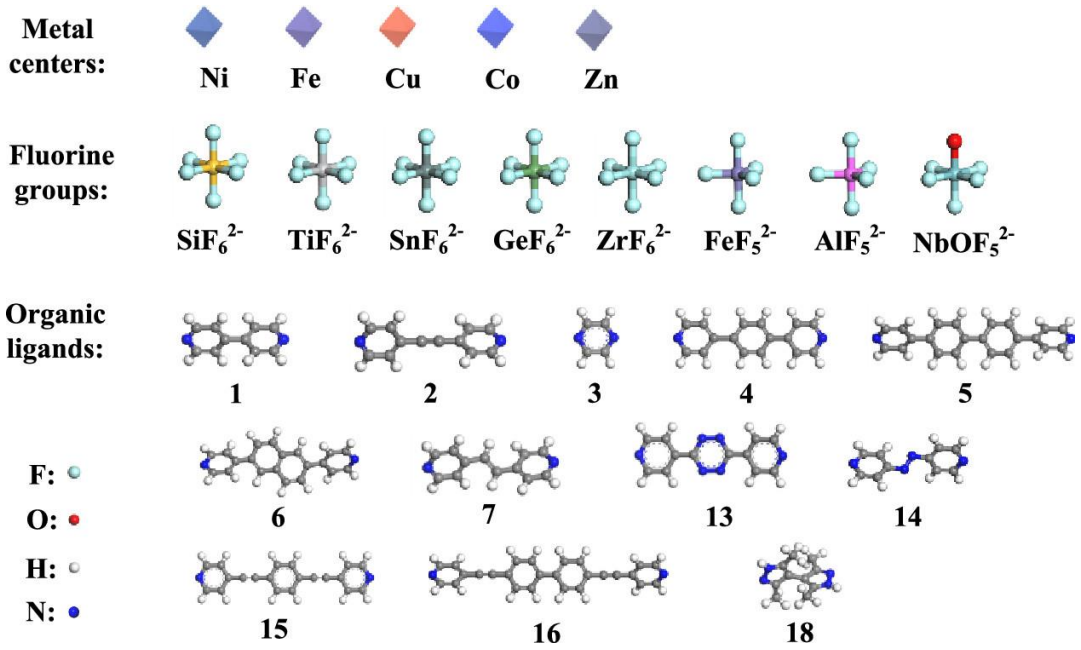


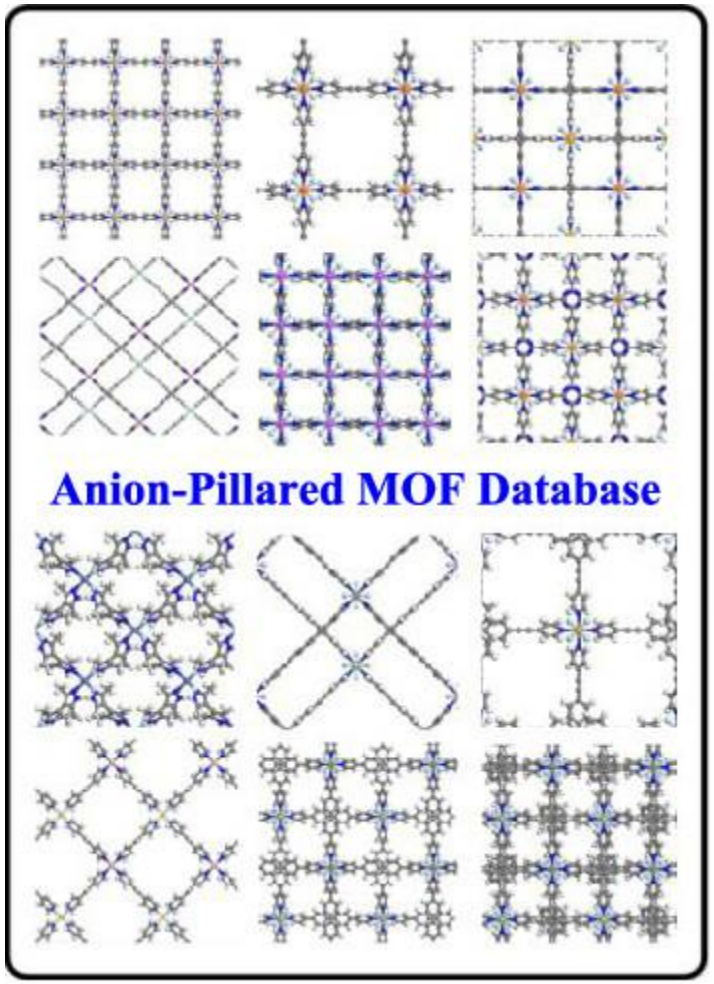
[1]Lin et al., *Science* (2021)

Screening for Strong Physisorbing MOFs

Anion-Pillared MOFs for Capture

- **Goal:** Identify MOF with adsorption energy higher than 50 kJ/mol
- Database from Gu and Sholl (2021)[2]
  - Metals not exposed – expect weaker humidity effects
  - Systematically tunable metal center, fluorine groups, linkers



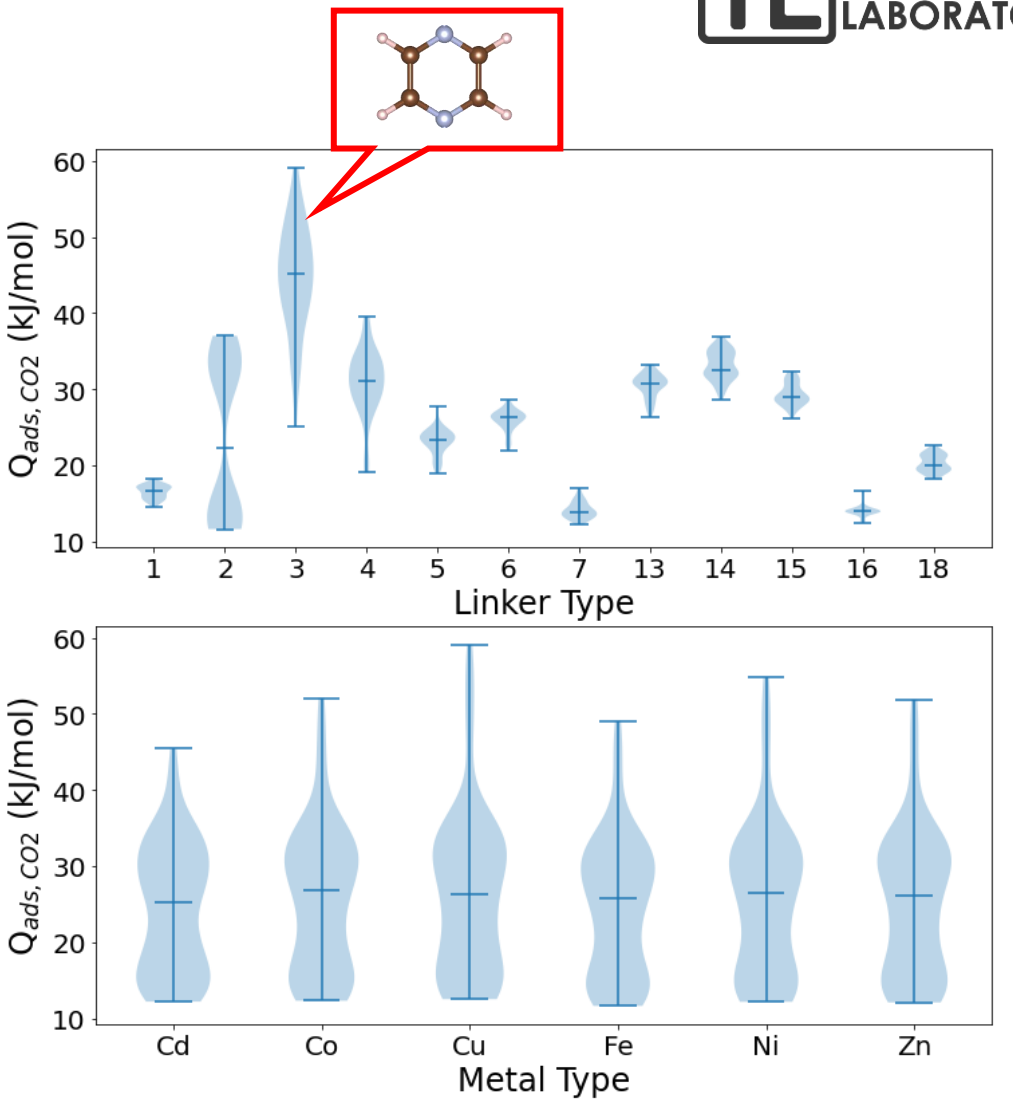


[2]Gu et al., *ACS Appl. Mater. Interfaces* (2021)

Screening for Physisorbent MOFs

MOFs with Pyrazine Linkers Perform Best

- Computed zero loading heats of adsorption for CO_2 in each MOF in the database
- Some high CO_2 heats of adsorption observed
  - Up to ~58 kJ/mol
- Heat of adsorption more associated with **linker** than with the metal center present
  - Linker #3 (pyrazine) outperforms all others – why?
  - Why is there little association with metal center?

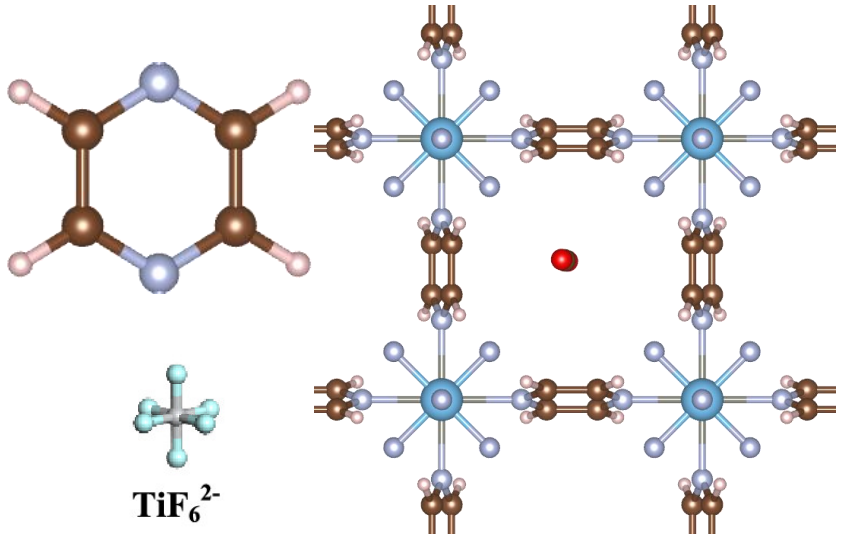


Screening for Physisorbent MOFs

MOFs with Pyrazine Linkers Perform Best

- TIFSIX MOFs are the most represented in the Q_{ads} > 50 kJ/mol range
- Two of these MOFs (TIFSIX_3_Ni[3], SiFSIX_3_Cu[4]) have been previously synthesized
  - TIFSIX_3_Ni adsorbs 1.2 mmol/g CO_2 at 500 ppm CO_2
  - Stronger binding of CO_2 than H_2O ($\Delta E_{ads, CO2} > \Delta E_{ads, H2O}$)
  - Water stable up to 80% RH
- Stronger CO_2 adsorption than CALF-20 shown by density functional theory (DFT)
  - $\Delta E_{ads, CO2, TIFSIX\_3\_Ni}$ = -52.1 kJ/mol[3]
  - $\Delta E_{ads, CO2, CALF\text{-}20}$ = -36.5 kJ/mol
- Performance warrants more advanced simulation methods
  - What does CO_2 uptake look like at 400 ppm?
  - How does co-adsorption of CO_2 and H_2O affect this capacity?

MOF	$\Delta H_{ads, CO2}^{0}$ (kJ/mol)
TIFSIX_3_Cu	-57.5
SIFSIX_3_Cu	-56.5
TIFSIX_3_Ni	-52.4
TIFSIX_3_Zn	-50.5



A TIFSIX MOF with CO_2 adsorbed

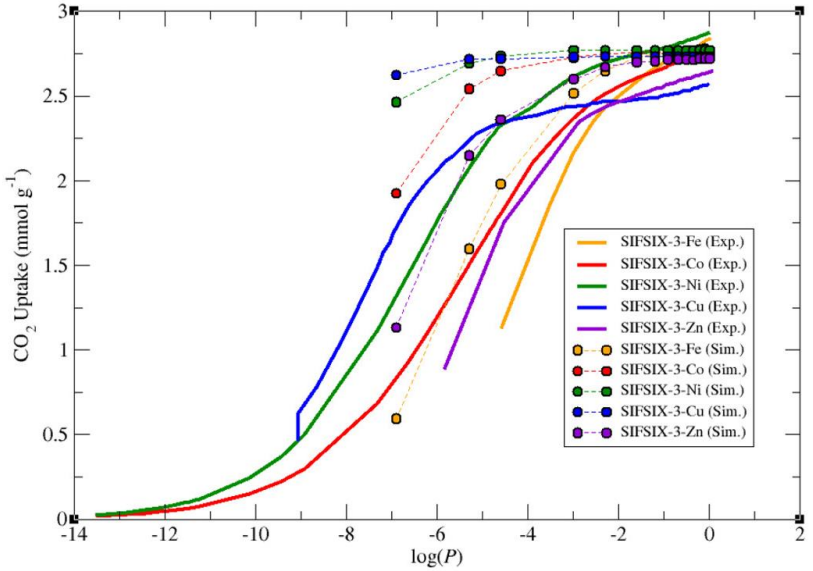
[3]Ullah et al., *Angewandte Chemie* (2022)
[4]Forrest et al., *Crystal Growth and Design* (2019)

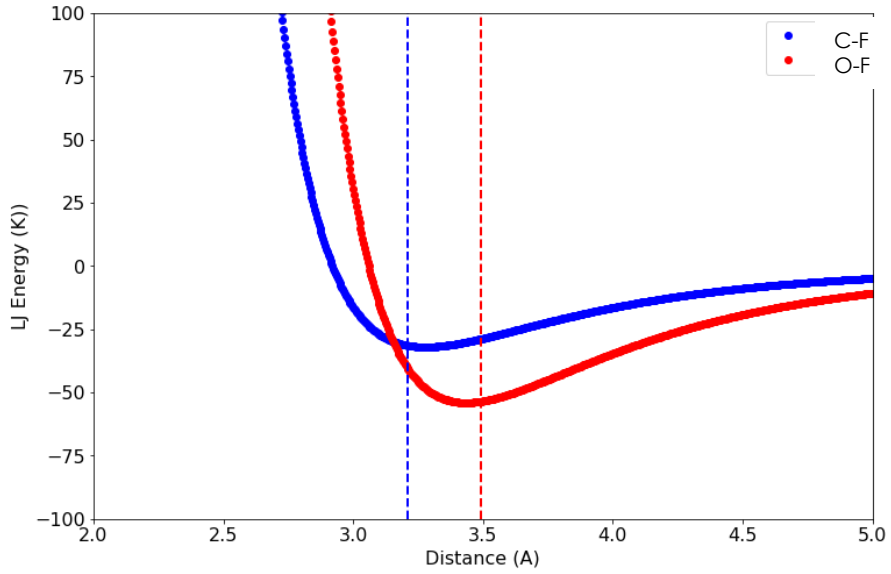
CO_2 Adsorption Sites

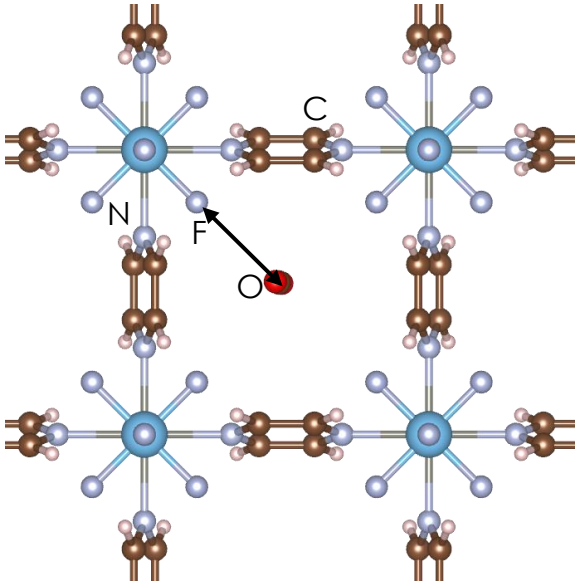
CO_2 Adsorbs at Fluorine Ring Centers

- CO_2 adsorbs at the center of 4 fluorine
  - Agreement with previous observations
  - Near optimum distance for CO_2 – F dispersion interactions – TIFSIX_3_Zn
  - Good agreement for interaction energies
- Previous work by Forrest et al. for SIFSIX-3-M[4]
  - Agreement with description of adsorption site
  - Classical force field (dotted) did not predict experimental isotherm (solid) at low P_{CO2}

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





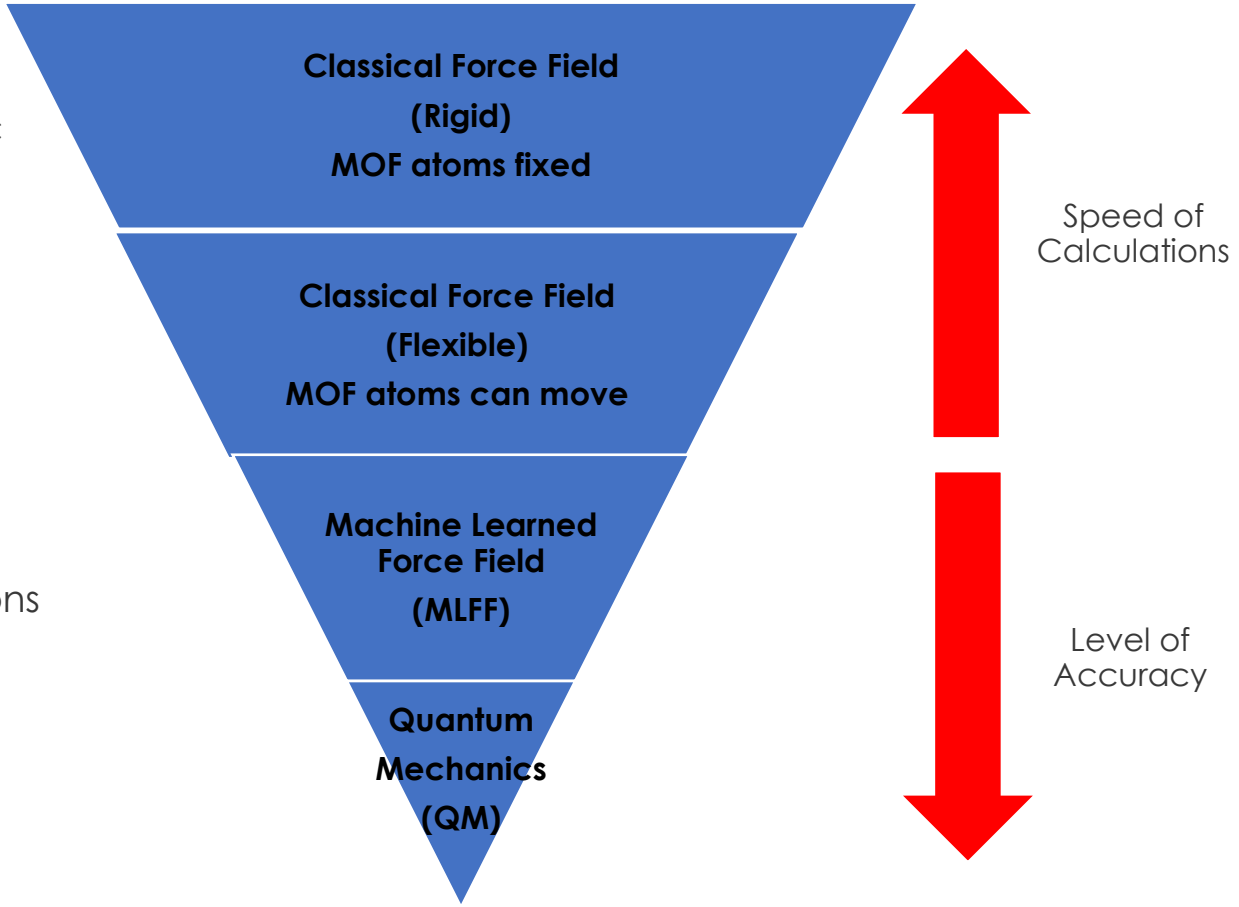


[4]Forrest et al., *Crystal Growth and Design* (2019)

Levels of Calculations

Machine Learned Force Fields Connect Classical and Quantum Simulations

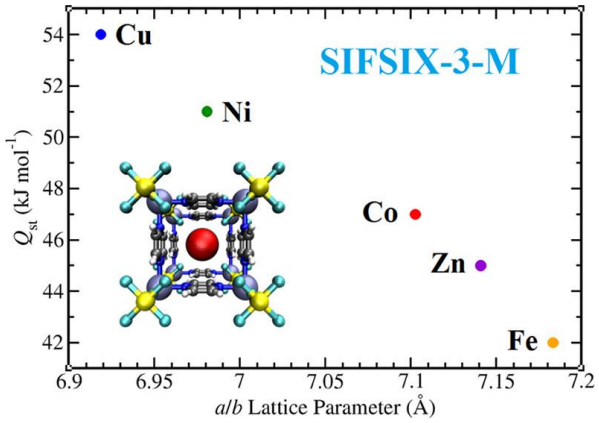
- **Classical Force Field:**
  - **Rigid:** MOF atoms fixed before simulation
  - **Flexible:** MOF atoms can move during simulations
  - Describes energy, force as analytical functions of atomic positions
    - Coulomb's Law ($E = k\frac{q_1 q_2}{r^2}$)
    - Harmonic oscillators ($E = \frac{K}{2}(r - r_0)^2$)
  - Simple form, fast calculations
  - Can be used to calculate thermodynamic quantities
    - **Adsorption isotherms**
    - Diffusivity
- **Machine Learned Force Field (MLFF):**
  - Describes energy, force as ML functions of atomic positions
    - Better fit to Quantum Mechanical (QM) data
    - Faster than QM calculations
    - Can predict measurable quantities such as adsorption isotherms
- **Quantum Mechanical (QM) methods:**
  - Accurate, slow
  - Compute energy, forces, determine structures



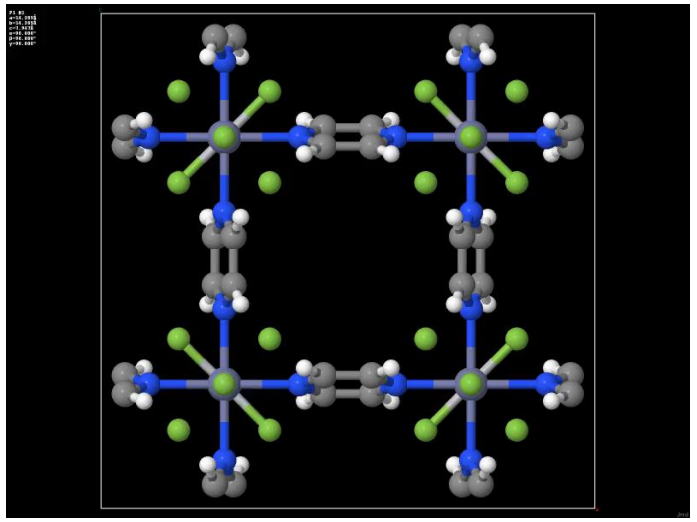
Why Do We Need MLFFs?

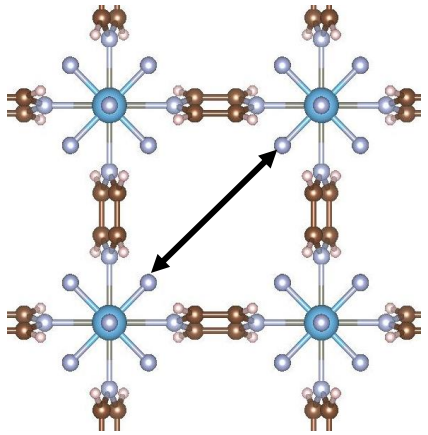
Flexible SiF_6 and TiF_6 can Cause Changes in Window Size

- Classical rigid force field performs poorly for SIFSIX_3_Cu, TIFSIX_3_Ni isotherms
- F-F diagonal distance has a strong effect on CO_2 adsorption[4]
  - How much can this change?
- Ab initio molecular dynamics:
  - Significant window diameter changes for empty MOF (F-F diagonal)
  - Significant Ti-F, Si-F bond stretching/compressing, linker rotation observed
  - Need to include flexibility

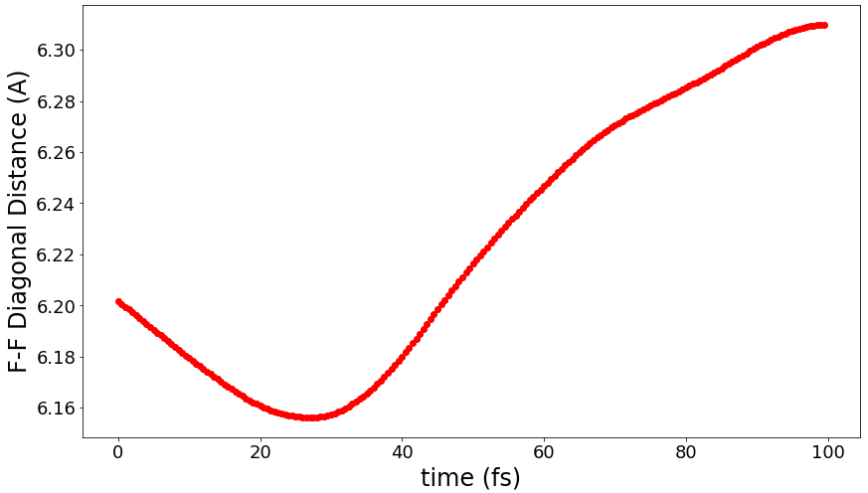


[4]Forrest et al., *Crystal Growth and Design* (2019)





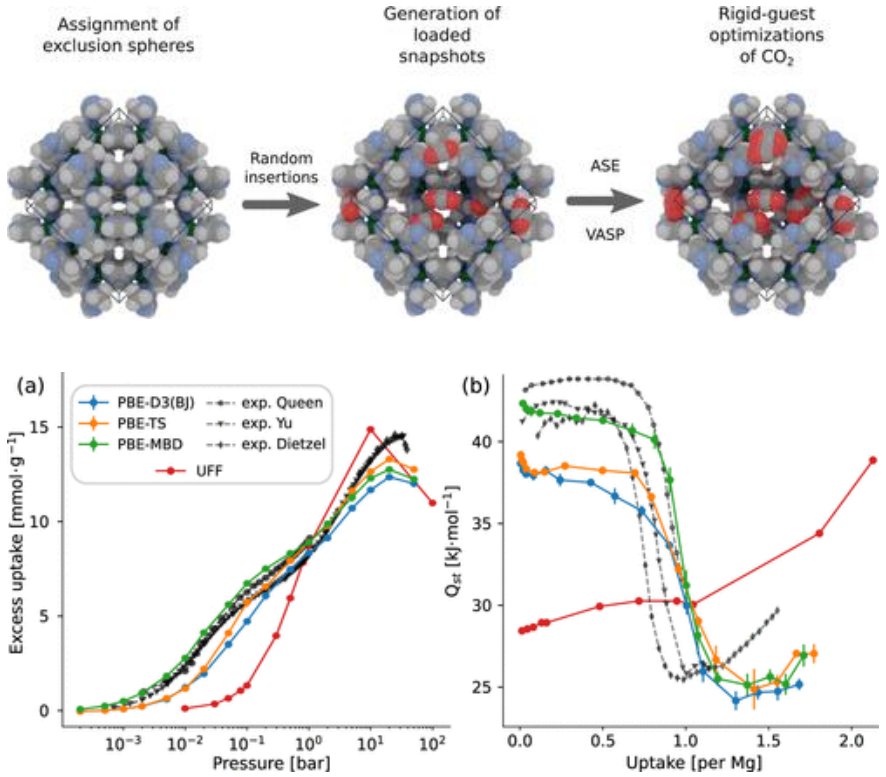
F-F diagonal



MLFF Training Recipe

MLFFs Trained on Accurate DFT Data

- **Sampling of Configurations**
  - Sampling needs to reflect adsorption process
    - Vary amount of CO_2 in MOF
    - Vary CO_2 locations (both favorable/unfavorable)
    - Compressed/expanded MOF
    - MOF dynamics with and without CO_2 present
- **DFT Calculations**
  - Perdew-Burke-Ernzerhof (PBE) functional
  - D3 dispersion correction
- **MLFF Method**
  - Defines the descriptors (atom identities, local geometries)
  - Determines number of fitting parameters, form of the model
  - **This work:** Spectral Neighbor Analysis Potential (SNAP)
    - Trained on the **error** in the classical force field

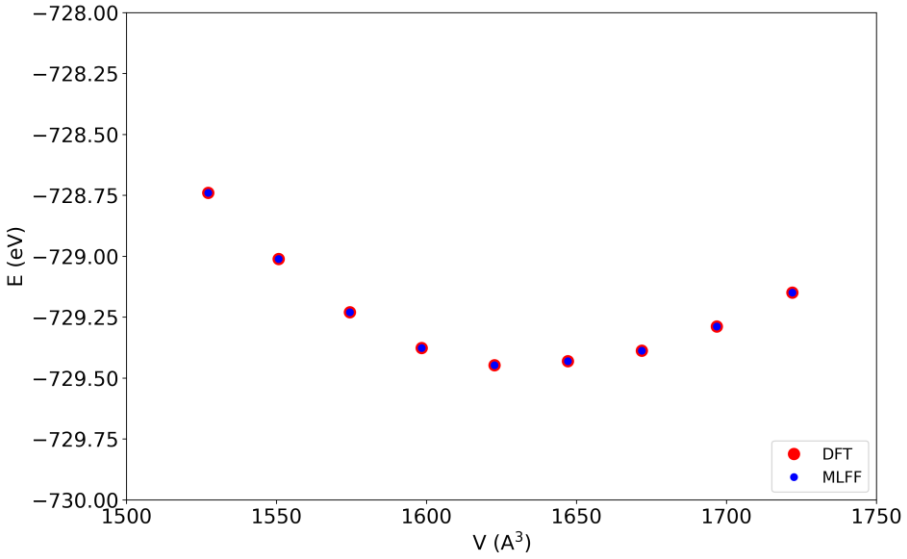


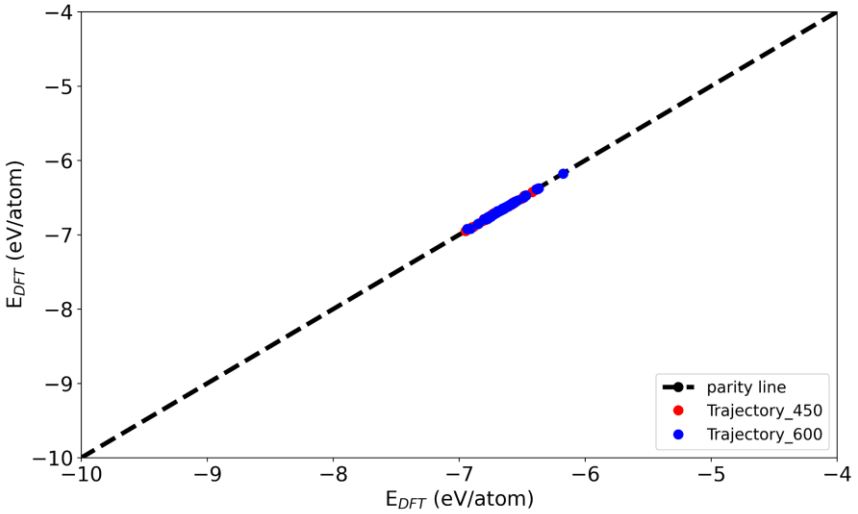
Goeminne et al., *JCTC* (2023)

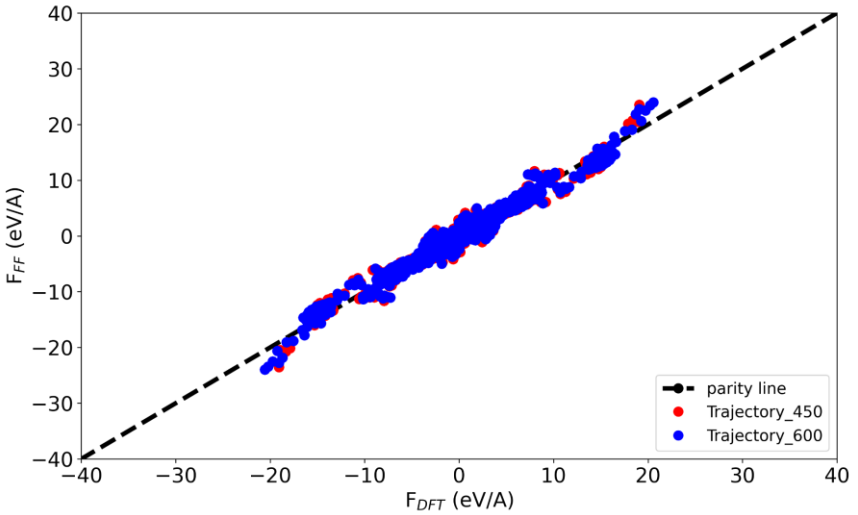
Performance of MLFF Model

MLFF Describes MOF Structure and Flexibility

- 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
  - $R^2 > 0.99$ for energy, $R^2 \approx 0.99$ for force for **testing** data (held out of model training)



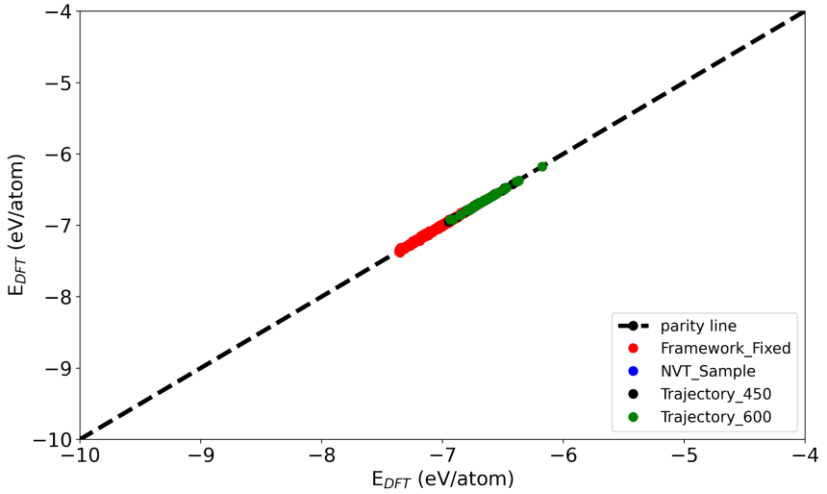


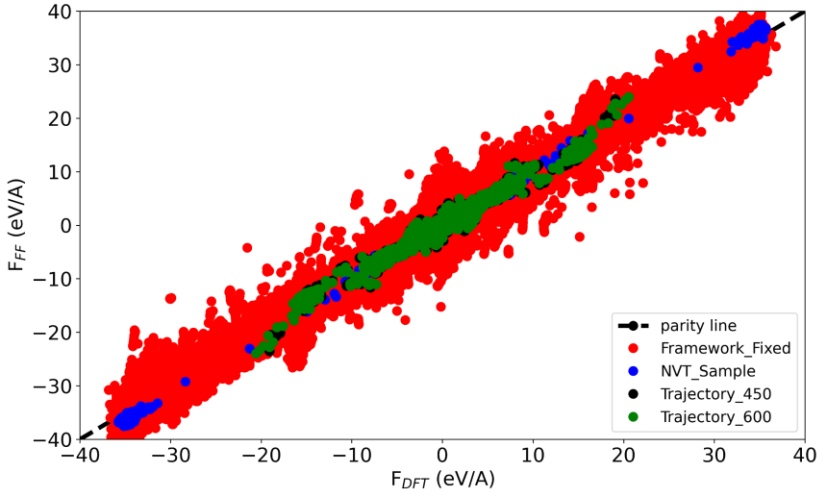


Performance of MLFF Model (CO_2 Adsorption)

MLFF Describes Force, Energy for CO_2 in TIFSIX_3_Zn

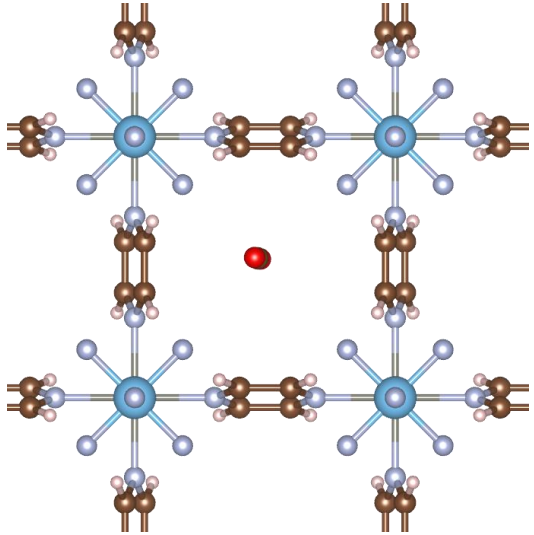
- MLFF model accurately describes energies ($R^2 > 0.99$) and forces ($R^2 = 0.98$) MOF loaded with CO_2
- Training on the error of the classical force field rather improves the model fit
  - $\Delta E_{ads,\ CO2,\ MLFF}$ = -52.9 kJ/mol
- MLFF models can be used to compute isotherms
  - **Next:** Predict CO_2 sorption at 400 ppm





Next Steps

- How much CO_2 is adsorbed under DAC conditions?
  - MLFFs to simulate CO_2 adsorption (Grand Canonical Monte Carlo)
- How does N_2 affect CO_2 adsorption?
  - Compare energetics of N_2 vs. CO_2 adsorption (DFT)
  - Fit N_2 MLFF
  - Study co-adsorption
- How much of a role does humidity play?
  - Study energetics of H_2O adsorption (DFT)
  - Fit H_2O MLFF
  - Study co-adsorption of CO_2/H_2O



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