Ab Initio Molecular Dynamics: A Key to Unravel Microscopic Phenomena in Metal-Organic Framework Solids

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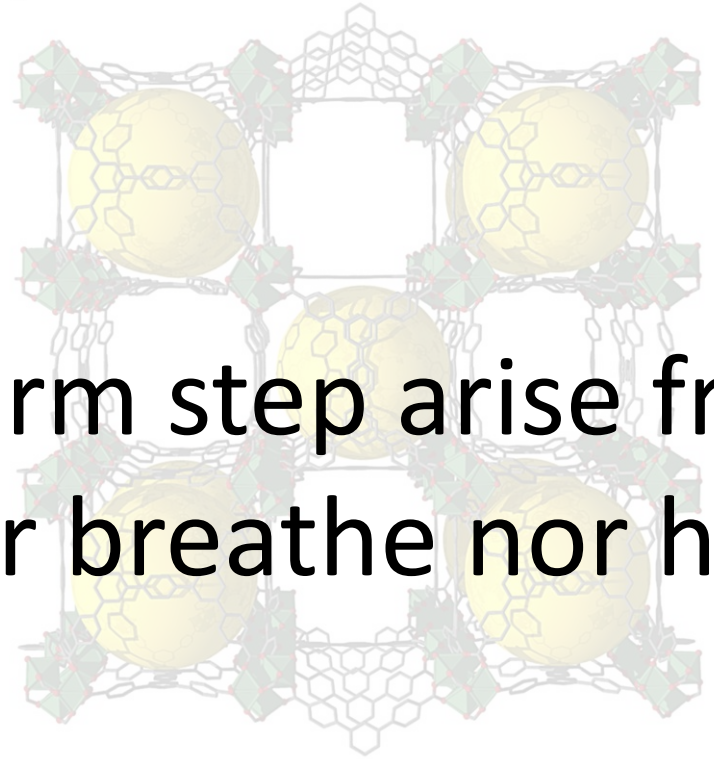
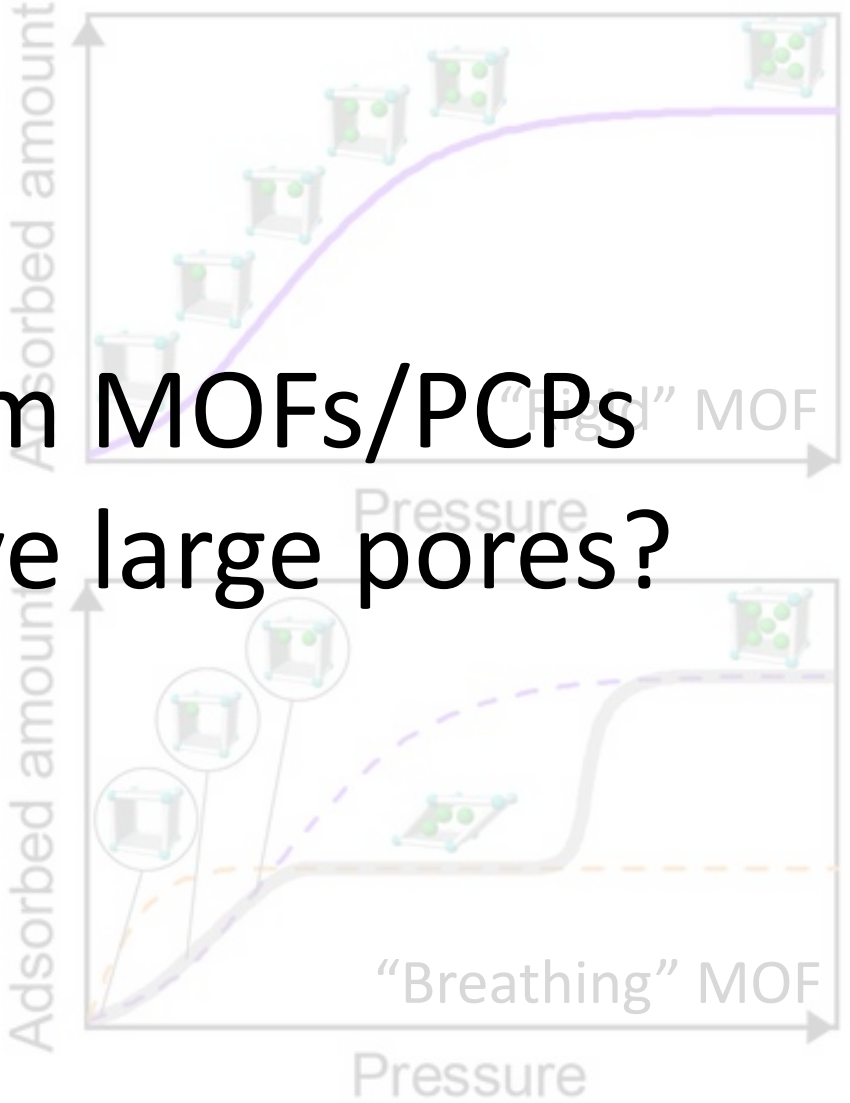
MOFs/PCPs and gas adsorption

oxo-centered trinuclear chromium(III) cluster



Cr-soc-MOF-1
S_{BET} = 4549 m^2/g

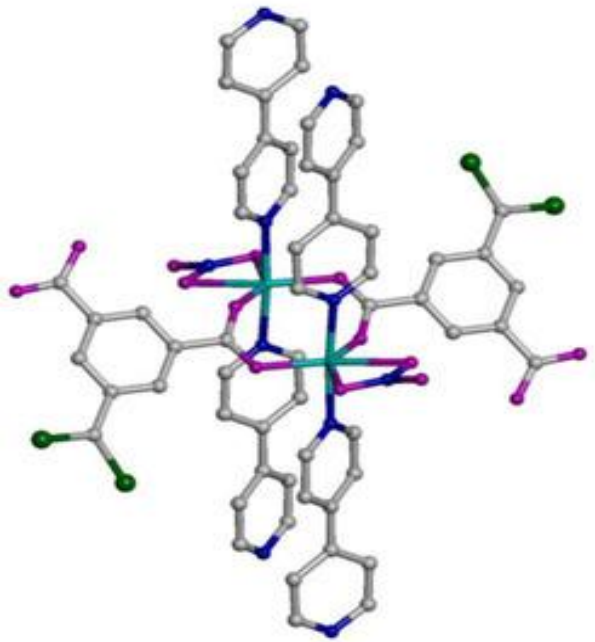


Can isotherm step arise from MOFs/PCPs that neither breathe nor have large pores?

Towsif Abtab *et al.*; *Chem* **2018**, *4* (1), 94–105
Otun, K. O.; *Inorganica Chim. Acta* **2020**, *507* (119563)
Krause, S. *et al.*; *Angew. Chem. Int. Ed Engl.* **2020**, *59* (36), 15325–15341

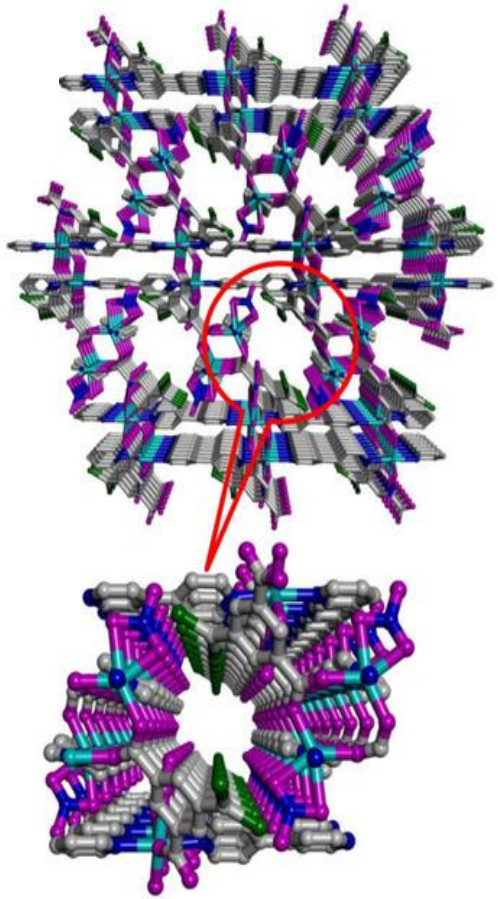
Experiment: synthesis, measurements & conjecture

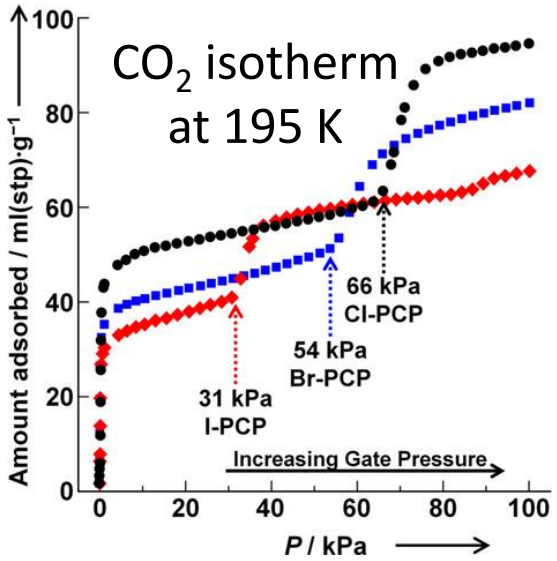
MOF constituents

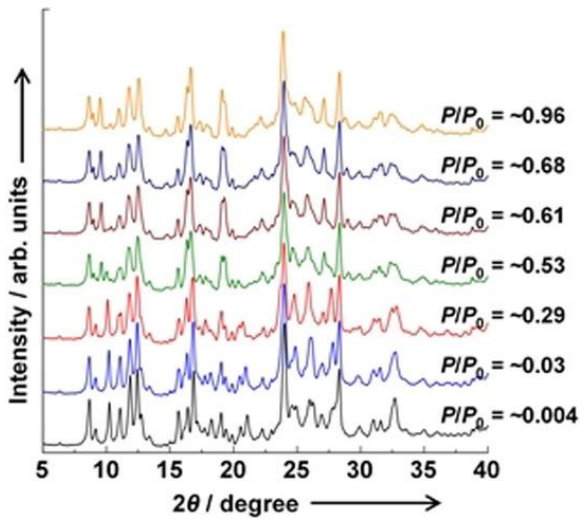


$Zn_2(ip\text{-}CH_2X)(NO_3)_2(bpy)_2 \cdot 4H_2O$
X = Cl, Br, or I

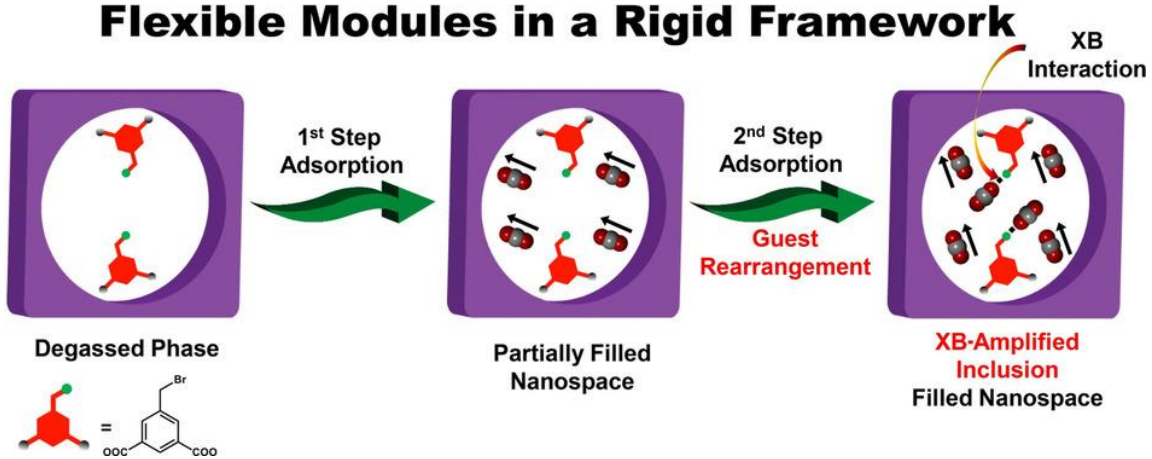
Pore channels







Mechanism for the second isotherm step:



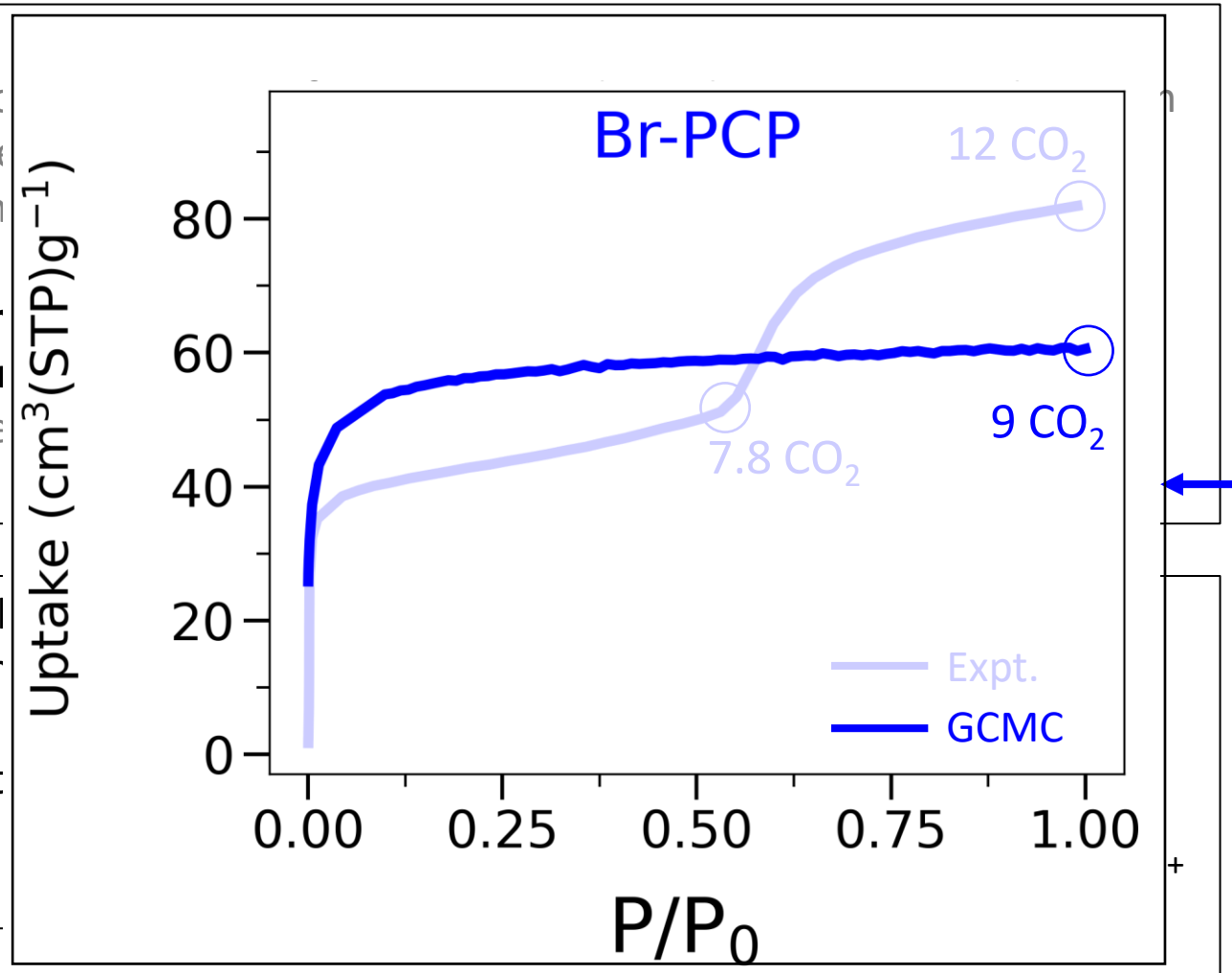
Kanoo *et al.*; *Chem. Eur. J.* **2020**, *26*, 2148--2153

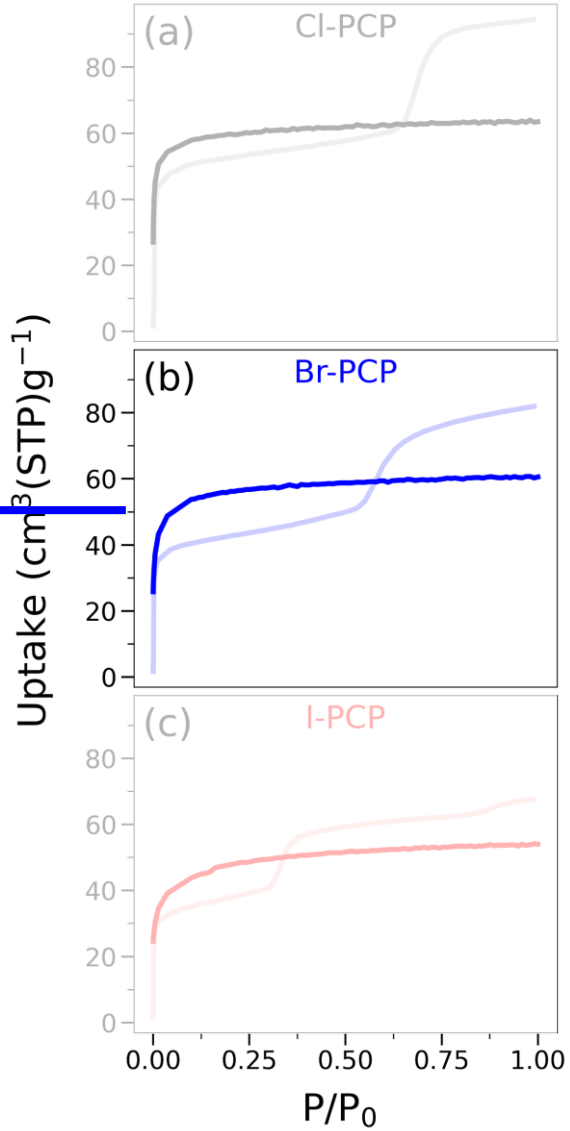
In this talk…

Summary of our work*:

- Halogen bonding interac
  the framework and solve
- Orientation of –CH_2Br m
  isotherm step
- **Propose the mechanism**
  phenomenon is peculia
- Explanation on the depe
  step w.r.t halogen atom

- Results from force field
  (GCMC) simulations usir
  crystal structures
- #CO_2 molecules per unit
  intuitive for the present



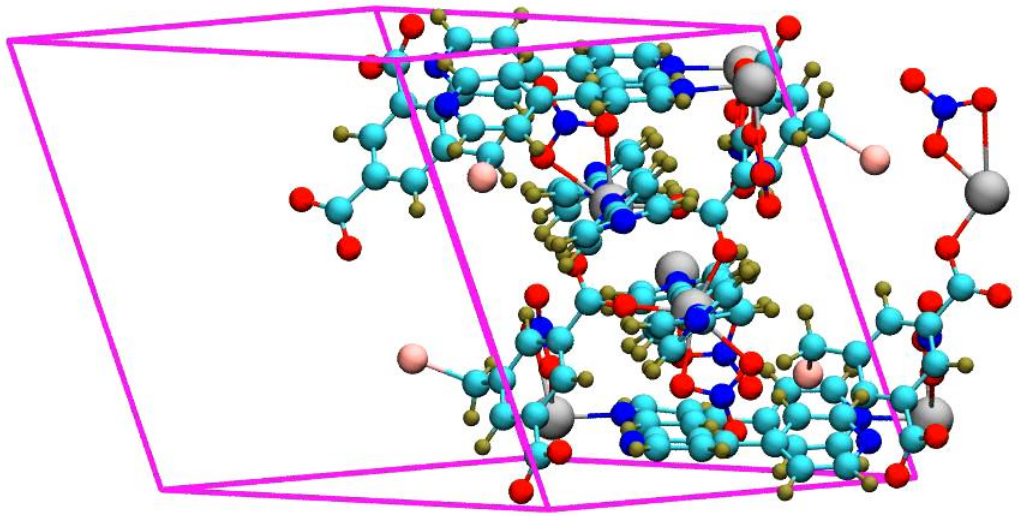


- TraPPE for CO_2

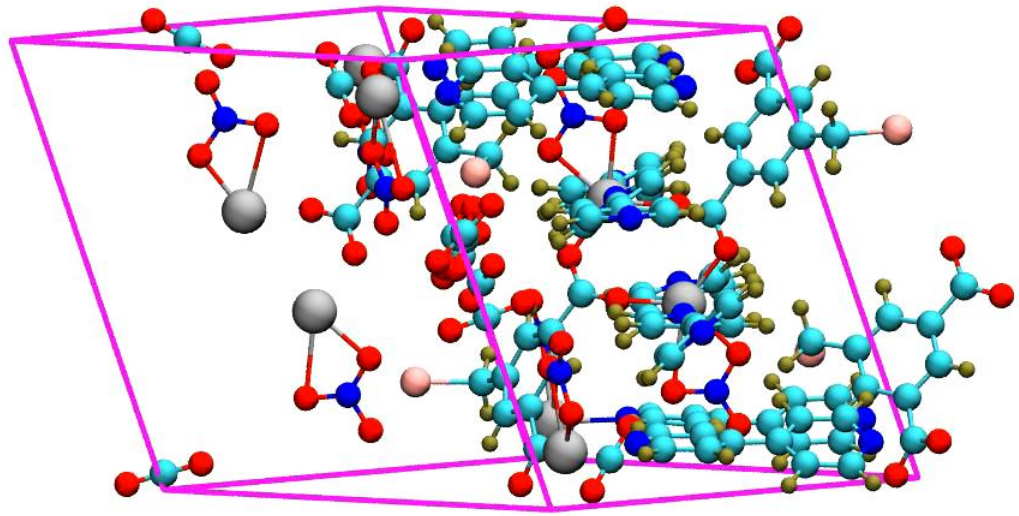
*N. Dwarkanath and S. Balasubramanian (manuscript under preparation)

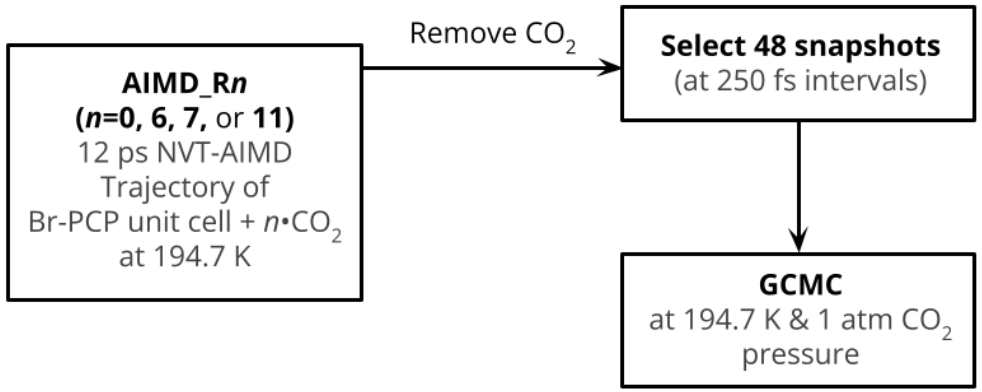
Simulation protocol

AIMD_R0



AIMD_R11

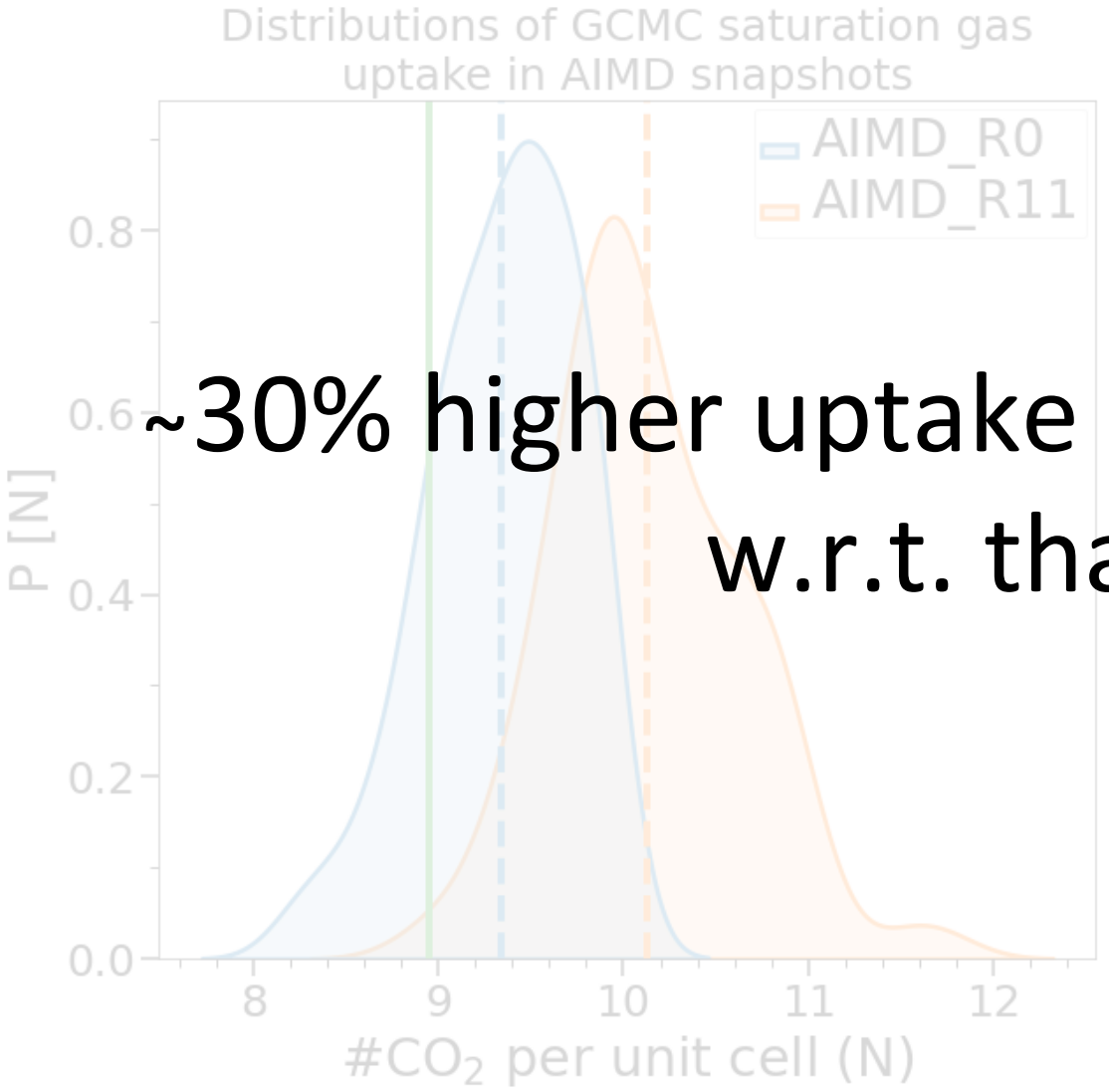




AIMD Details:

- CP2K-6.1 package
- NVT-MD @ 194. 7 K
- PBE+D3
- TZV2P BS + GTH PP
- Δt = 0.5 fs

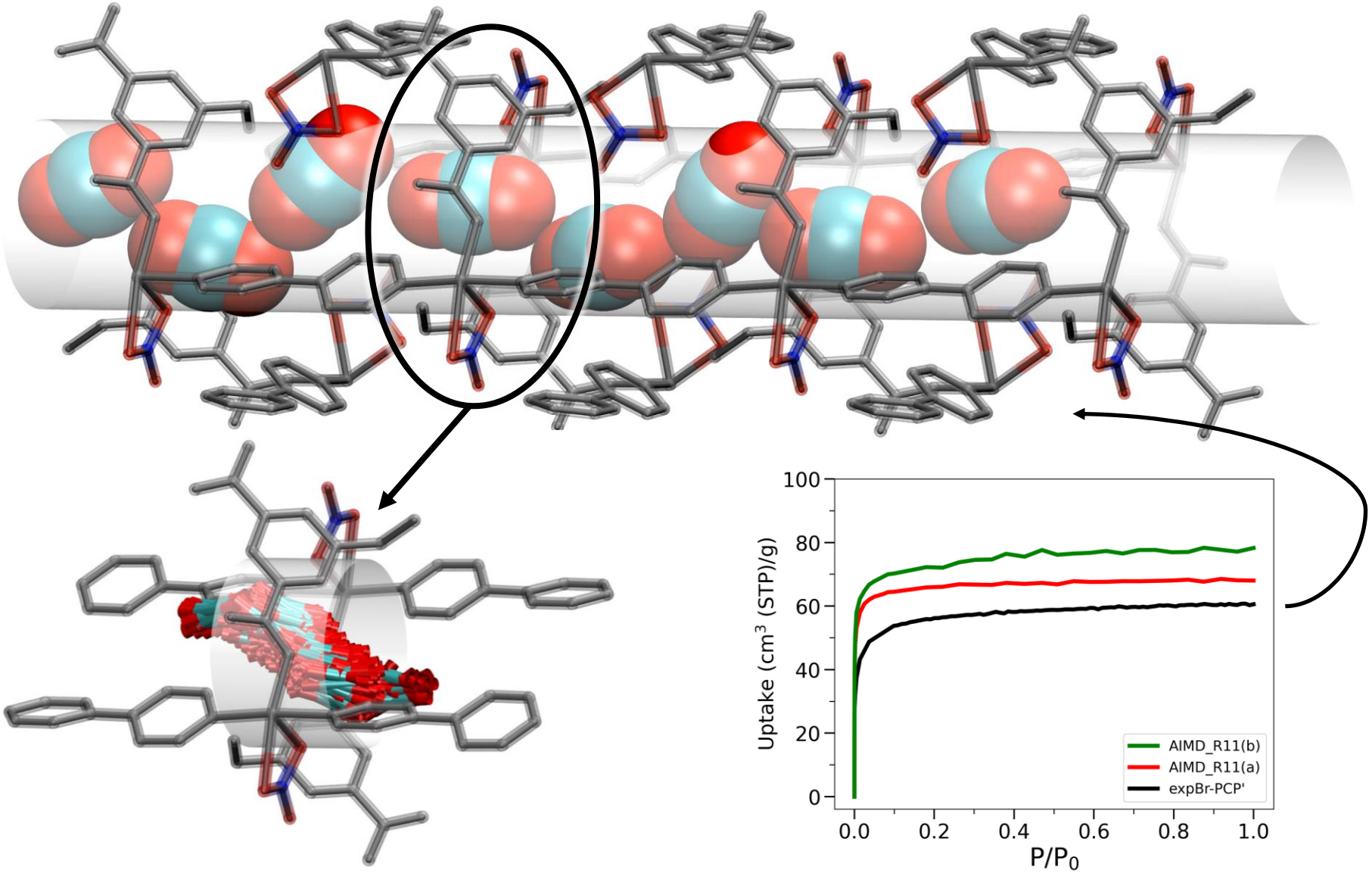
Results

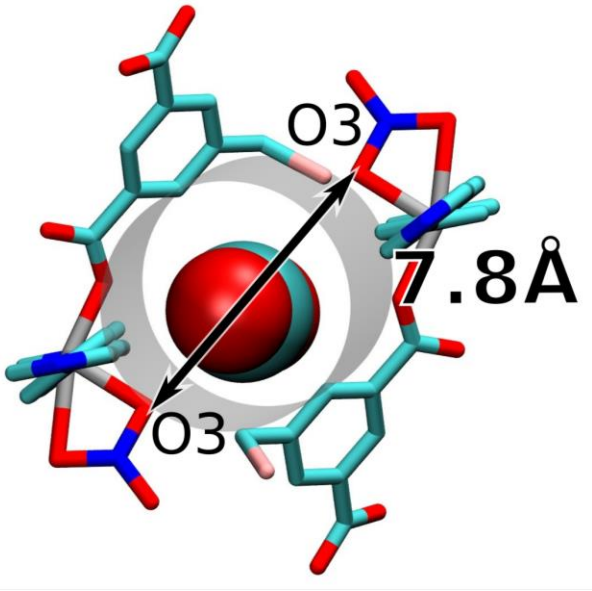


~30% higher uptake in a snapshot of AIMD_R11 w.r.t. that in expBr-PCP'!

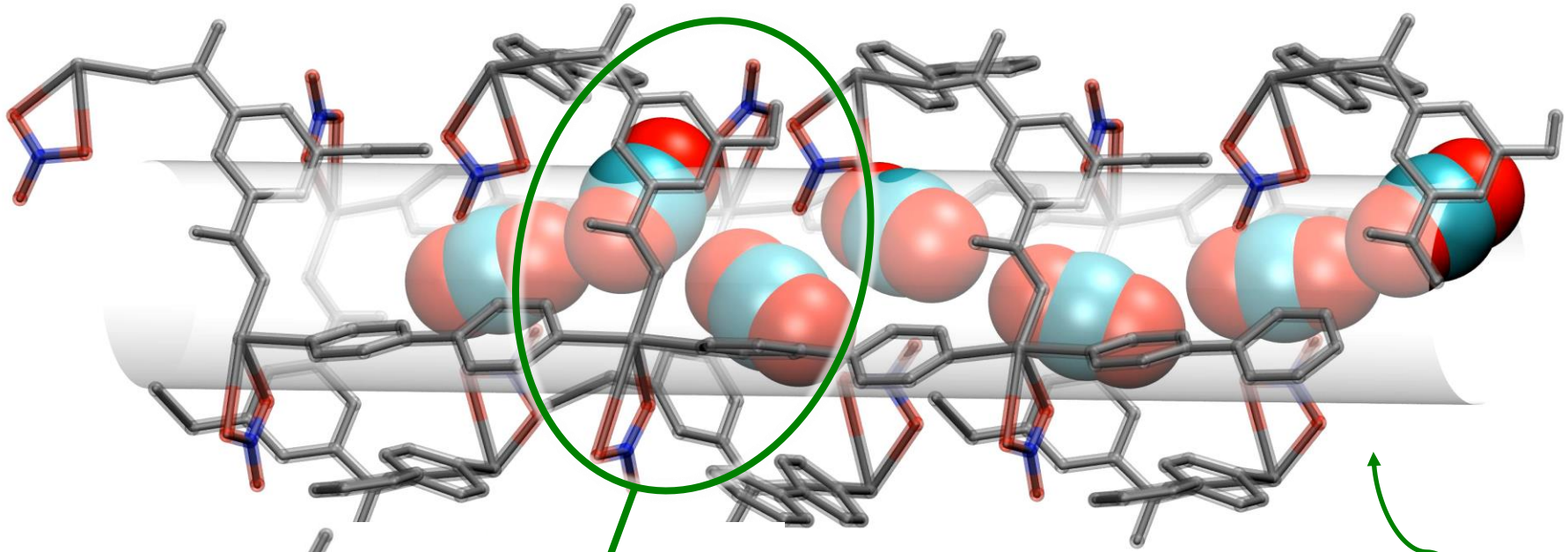
Why?

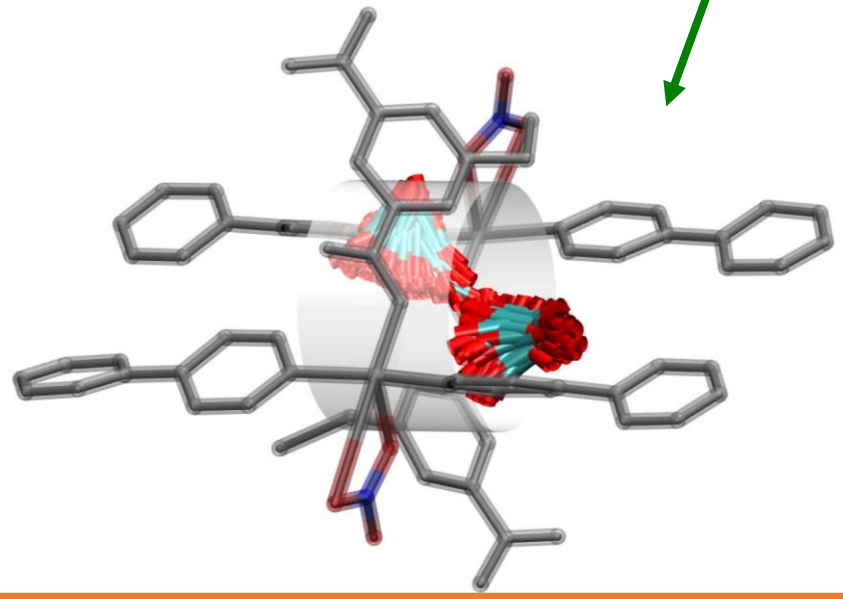
expBr-PCP’ pore channel

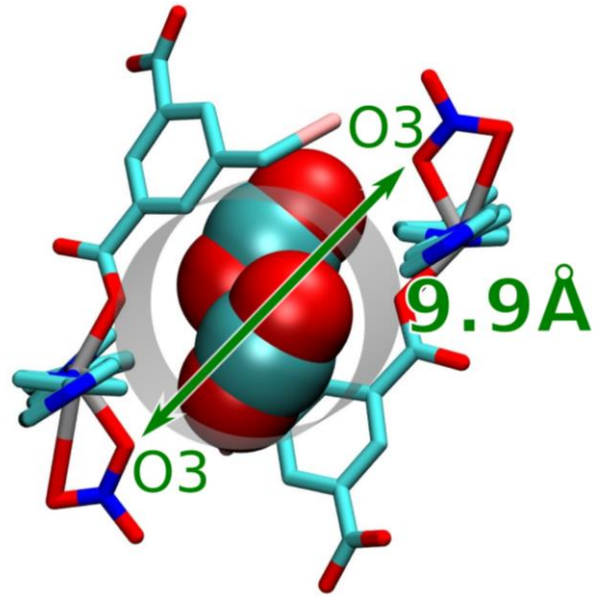


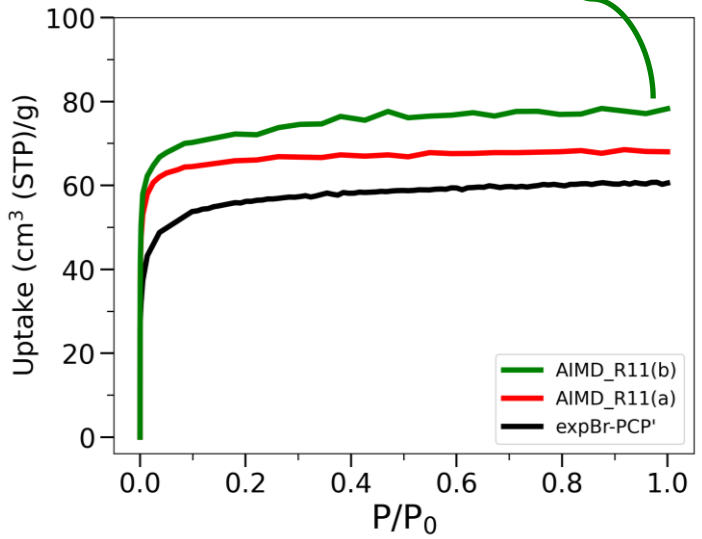


AIMD_R11 pore channel





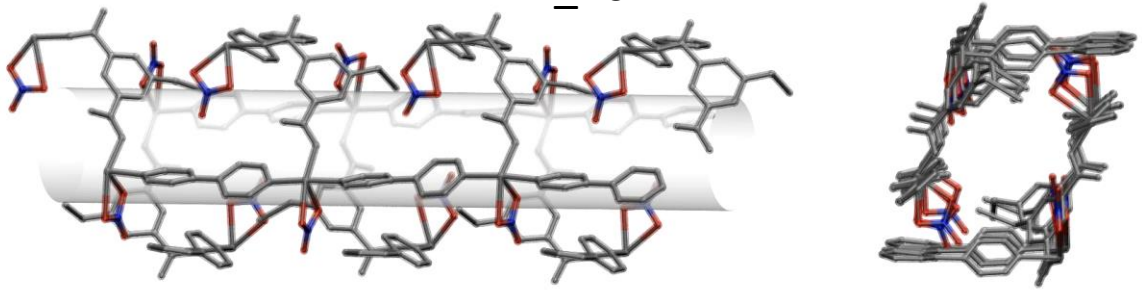




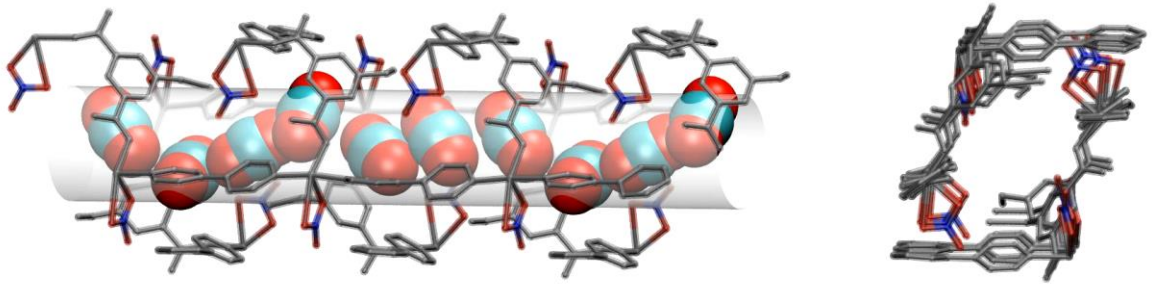
Summary

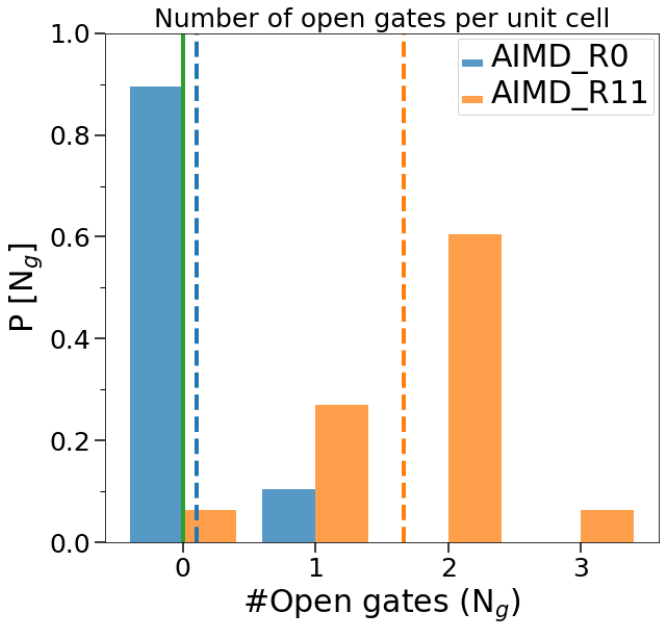
- AIMD+GCMC:
  - AIMD_R0: 0.1 gates & 9.3 CO_2
  - AIMD_R11: 1.7 gates & 10.1 CO_2
- 4 –NO_3 gates per unit cell & height of the second isotherm step is ~4 CO_2 per unit cell for all the three X-PCPs!

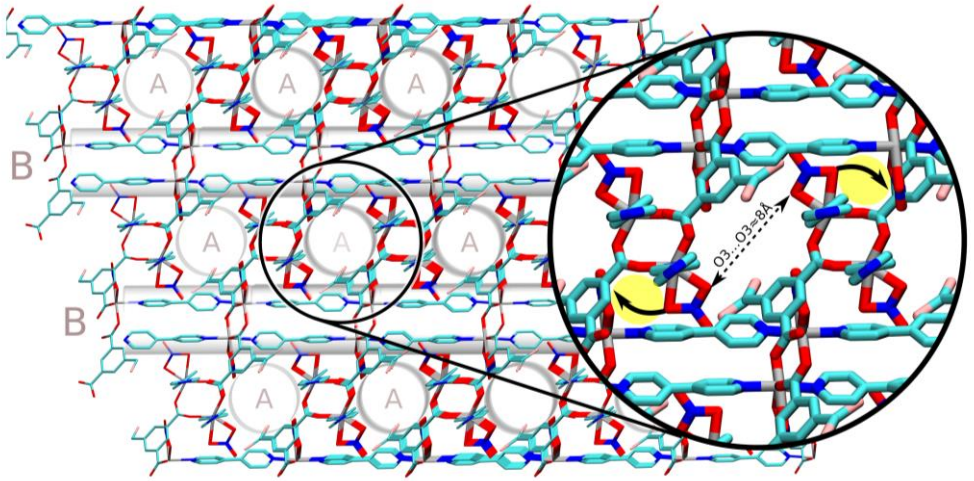
AIMD_R0



AIMD_R11





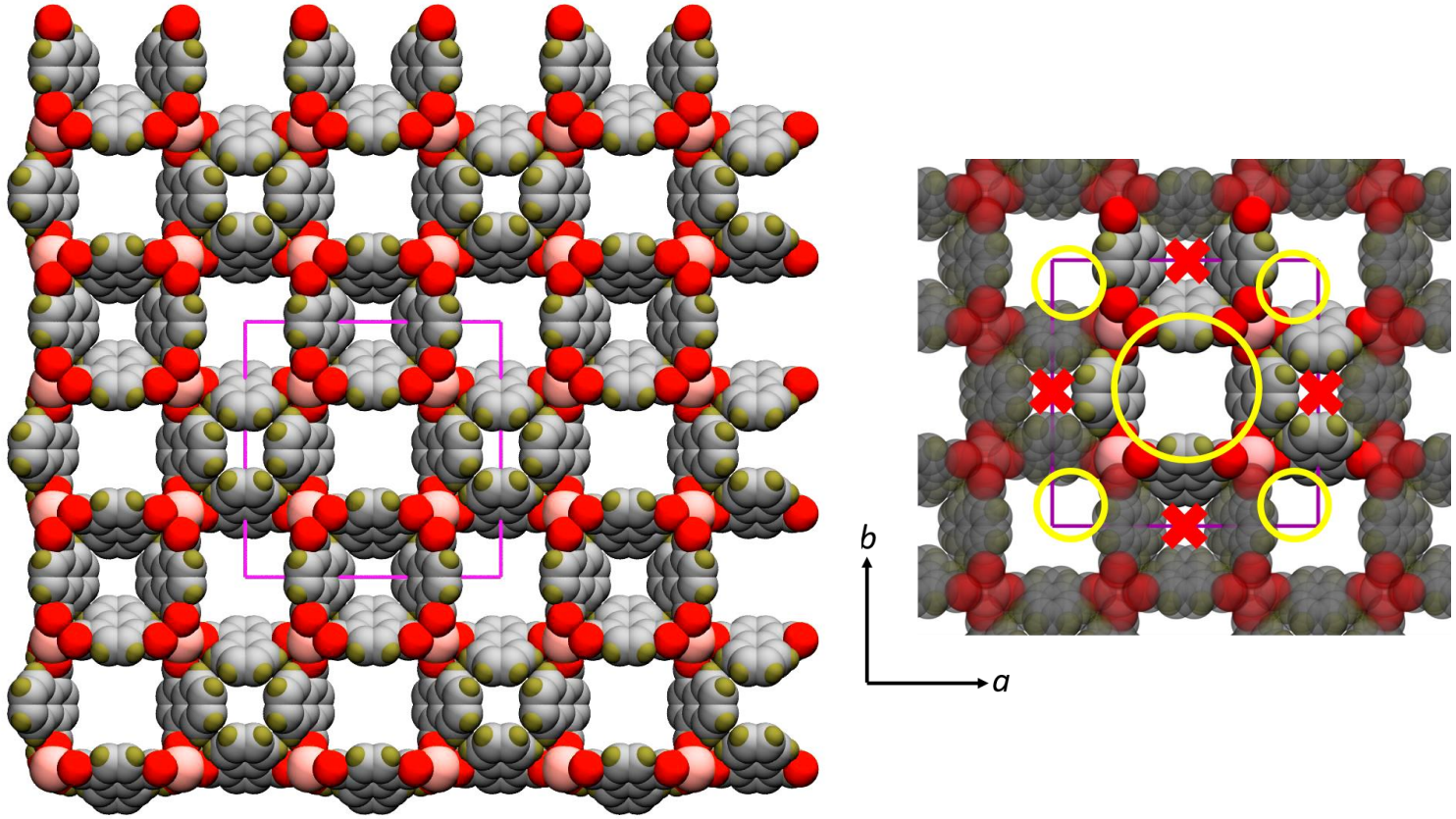


Al-MOF

Al-MOF (Al-NDC)

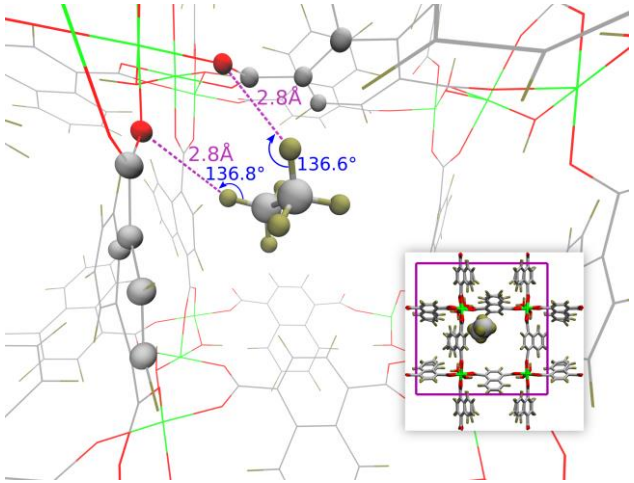
- Two kinds of Pore channels: Large & small
- Primary Binding sites are in the small pore channels
- Calculated binding energies overestimate Qst (0).

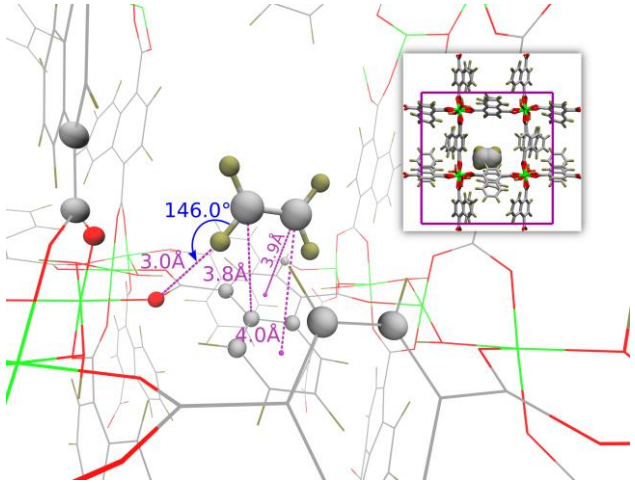
Remedy?

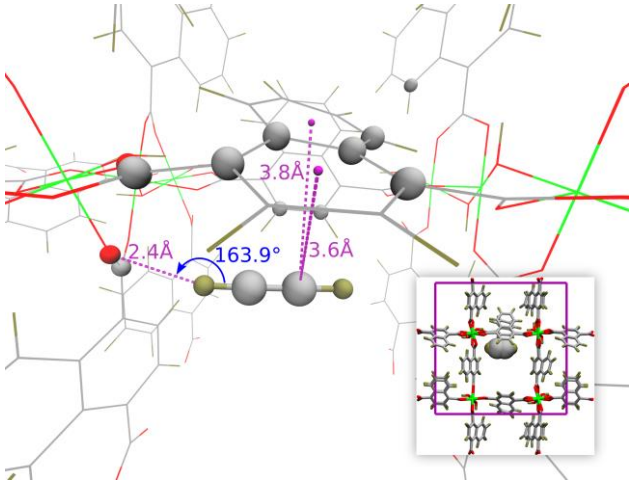


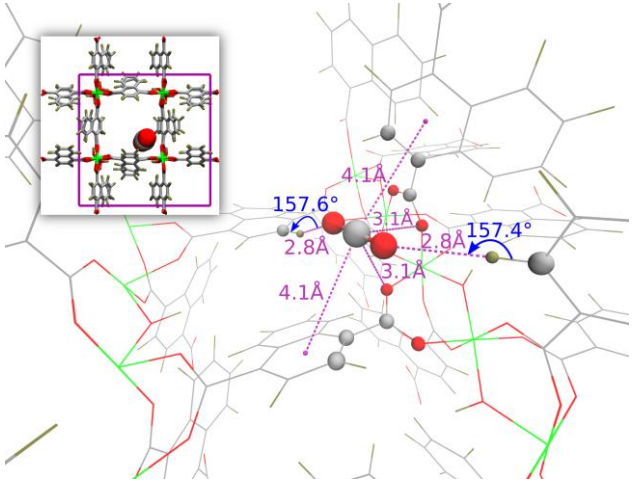
S. Laha, N. Dwarkanath, A. Sharma, D. Rambabu, S. Balasubramanian, T. K. Maji (Under review)

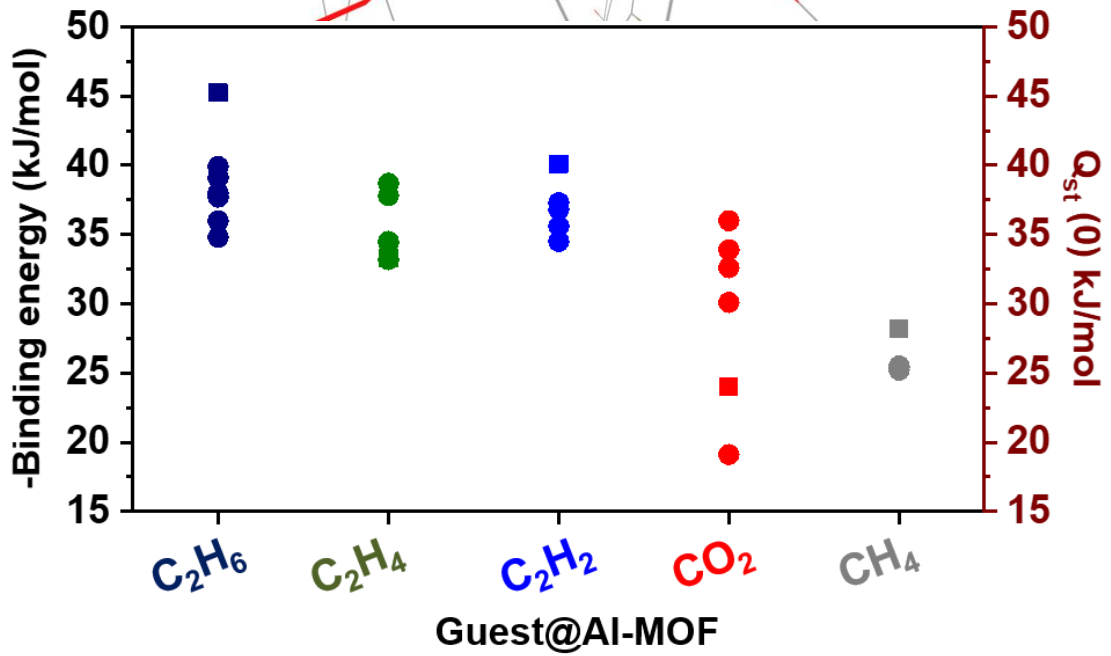
Results

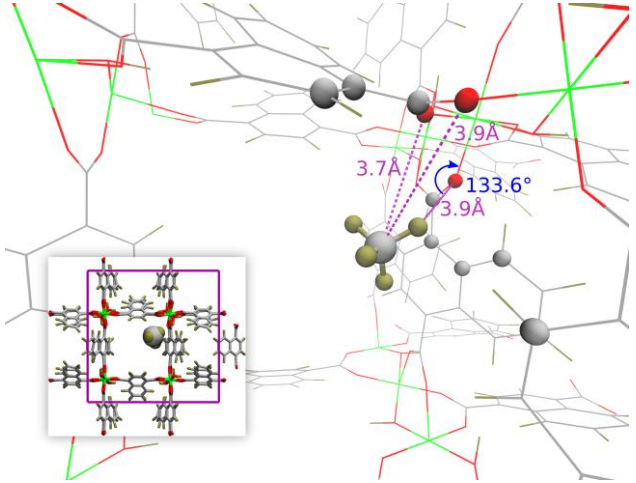

2.8Å
2.8Å
136.8°
136.6°


146.0°
3.0Å
3.8Å
3.9Å
4.0Å


3.8Å
2.4Å
163.9°
3.6Å

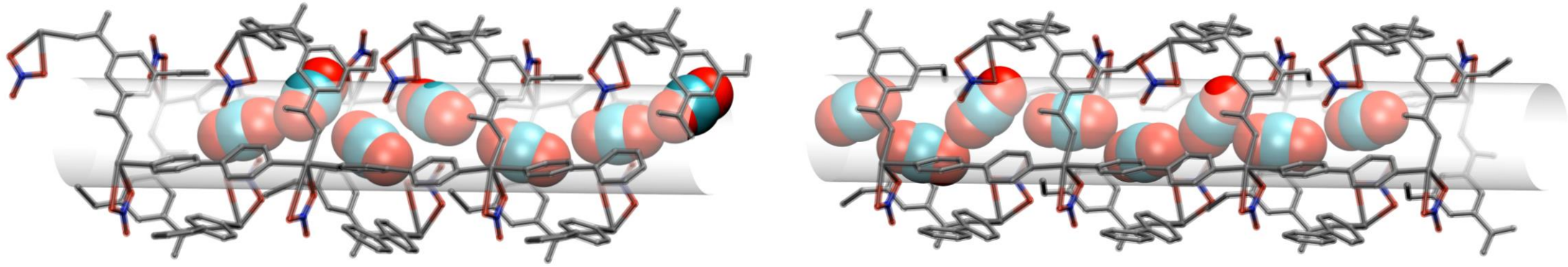

4.1Å
157.6°
3.1Å
2.8Å
2.8Å
157.4°
3.1Å
4.1Å


-Binding energy (kJ/mol)
Q_{st} (0) kJ/mol
50
45
40
35
30
25
20
15
C_2H_6
C_2H_4
C_2H_2
CO_2
CH_4
Guest@Al-MOF


3.9Å
3.7Å
133.6°
3.9Å

Conclusions

- Explained the mechanism of isotherm step in X-PCPs



- AIMD showed that the small pore channels of Al-MOF close spontaneously; indicating that the guest molecules go into the large pore channels