

The Design of Metal Organic Frameworks for the Separation of Carbon Dioxide From Flue Gas and Gasification Streams

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Project Objectives

Develop a low cost novel adsorbent to remove CO₂ from flue gas and gasification streams

- High selectivity
- High adsorption capacity
- Good adsorption/desorption rates
- Adsorbent has low enough binding energy for regenerability

Scope of Work

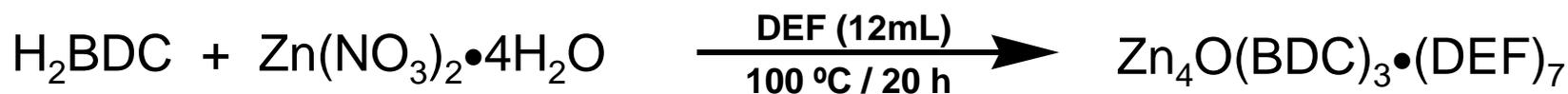
- Evaluate adsorption properties of MOFs for CO₂
- Single component and binary gas adsorption isotherm data will be generated for existing MOFs to allow parameterization of theoretical model.
- Develop a theoretical model for Virtual High Throughput Screening of existing and hypothetical MOF frameworks for the application.
- Prepare functionalized MOFs based on VHTS model
- Detailed characterization will elucidate nature of adsorption sites.
- Process integration and economic analysis for the use of MOFs in flue gas and gasification streams

Phases

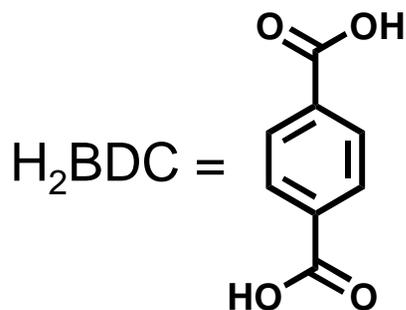
- Phase 1
 - Generate single component and binary isotherms for existing MOF's to populate database
 - Develop theoretical adsorption model and VHTS generation of candidate materials
- Phase 2
 - Prepare MOFs predicted to have high CO₂ affinity by VHTS modeling
 - Optimize promising MOFs from Phase 1, including tailoring of adsorption reversibility
- Phase 3
 - Select best MOF for further optimization and scale up materials for commercial testing
 - Thermal, oxidative and contaminant tolerance testing of MOFs
 - Commercial analysis of economics and integration of MOFs into both flue gas and gasification streams

Synthesis and Structure of IRMOF-1

IRMOF \equiv Isoreticular Metal Organic Framework

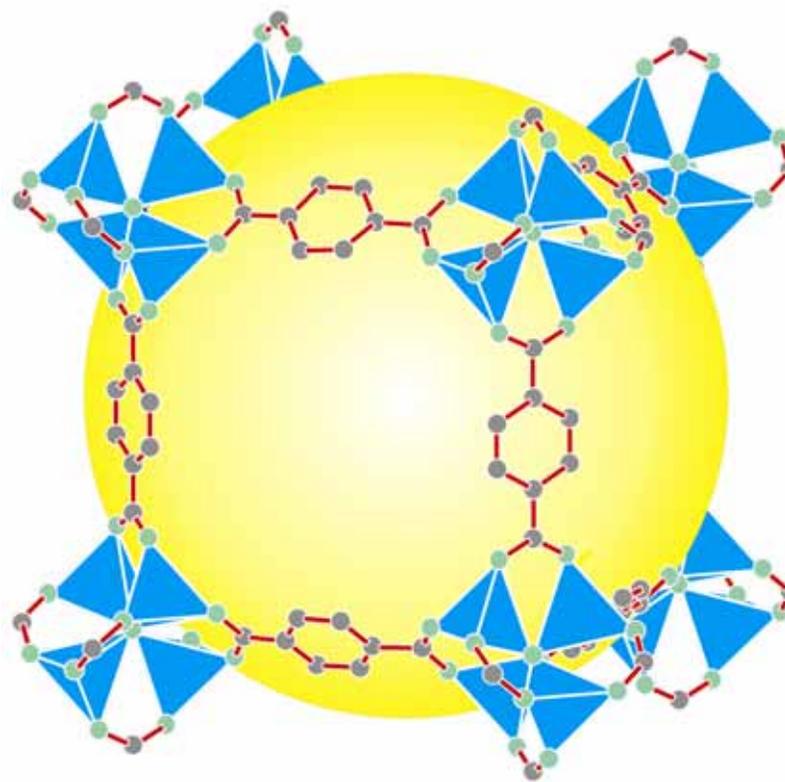


0.033 g 0.156 g
0.20 mmol 0.60 mmol

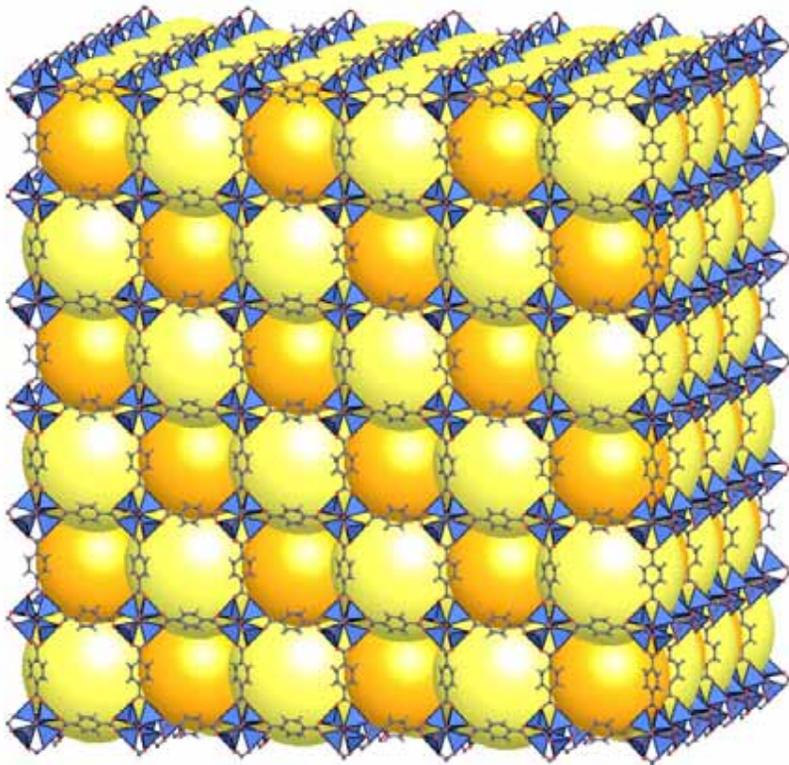


Benzenedicarboxylic acid

Cubic *Fm-3m*
 $a=25.6990(3)\text{\AA}$
 $V=16972.61\text{\AA}^3$



Crystal Structure of IRMOF-1

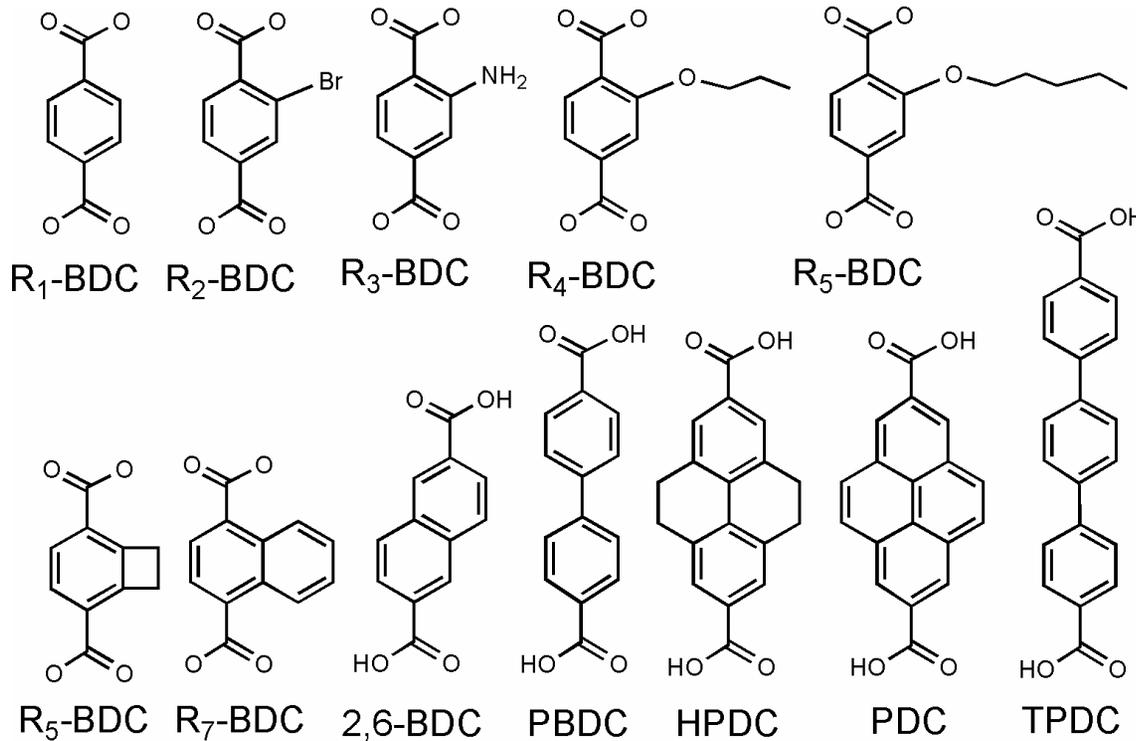


- The IRMOF-1 crystal structure is a cubic array of Zn₄O units bridged by benzenedicarboxylate.
- Large cages separated by large apertures.
- Can adsorb large amounts of gases with easy diffusion.

Isorecticular

(Having The Same Network Topology)

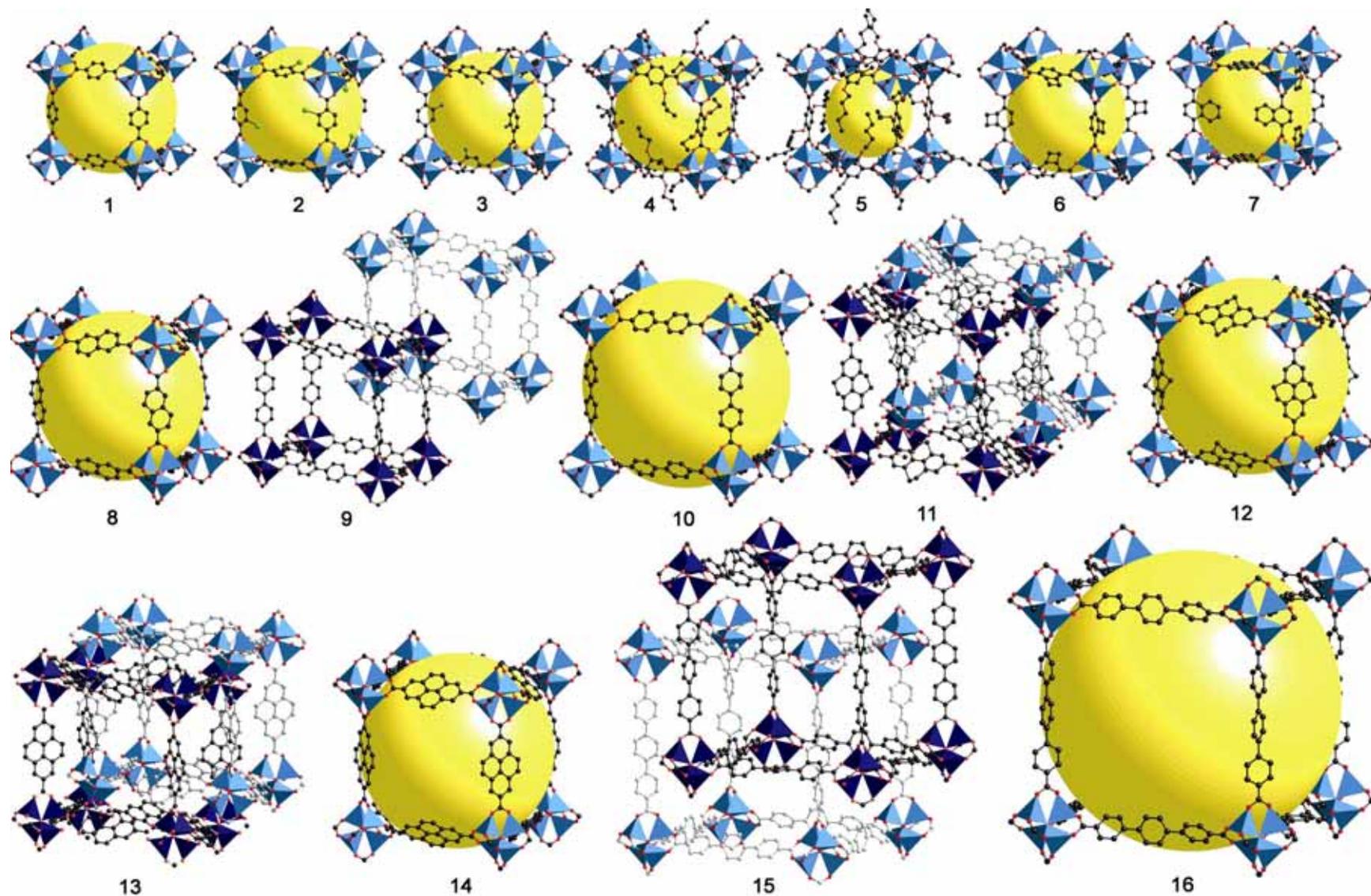
IRMOF Series



IRMOF-*n*

- IRMOF-1
- A large series of materials can be designed and synthesized by changing the organic linker.
- IRMOFs have a wide range of pore volumes and chemistry.

Systematic Design of Functionality and Metrics



■ Fixed diameter (Å) is the size of guests which are trapped in pores.

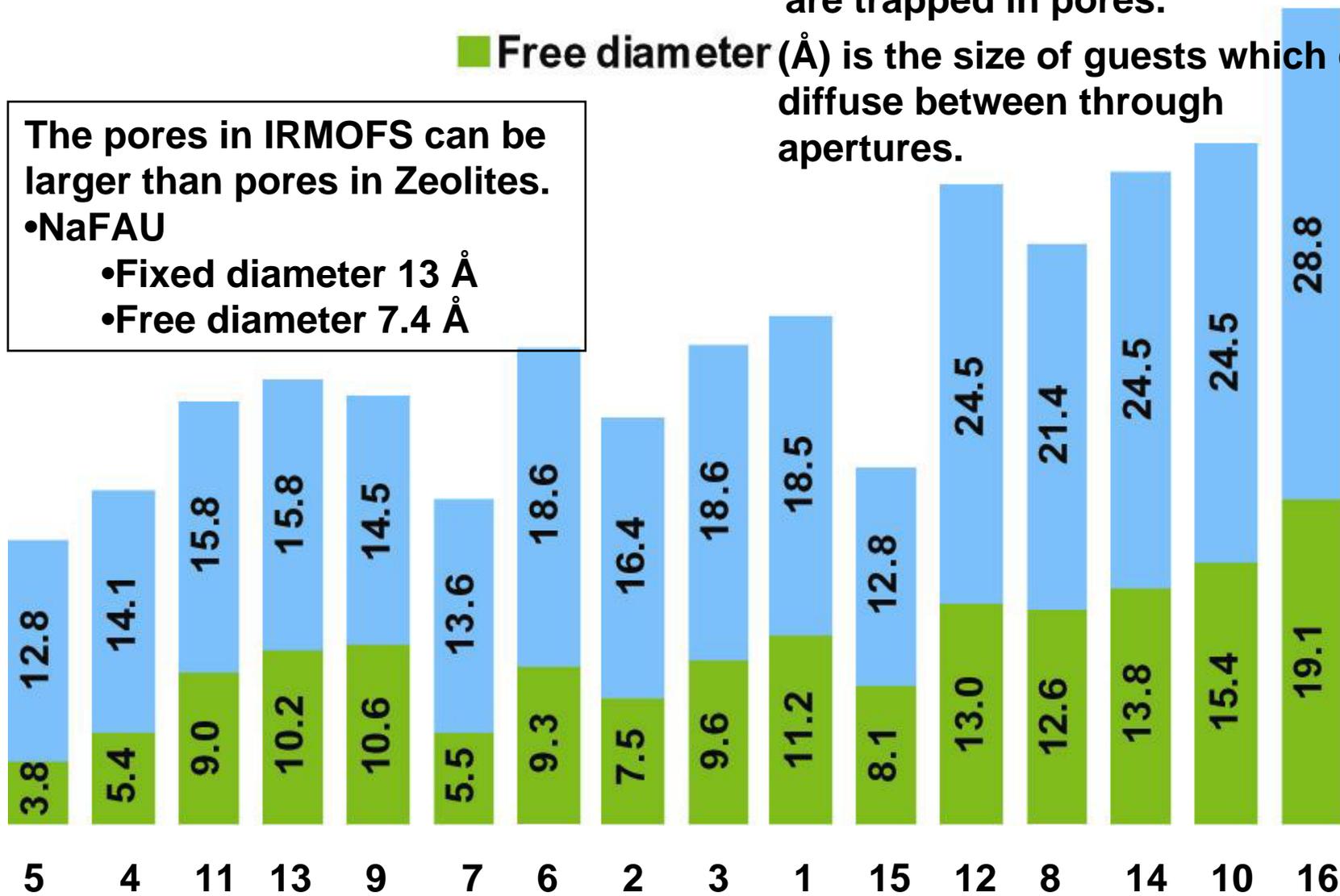
■ Free diameter (Å) is the size of guests which can diffuse between through apertures.

The pores in IRMOFS can be larger than pores in Zeolites.

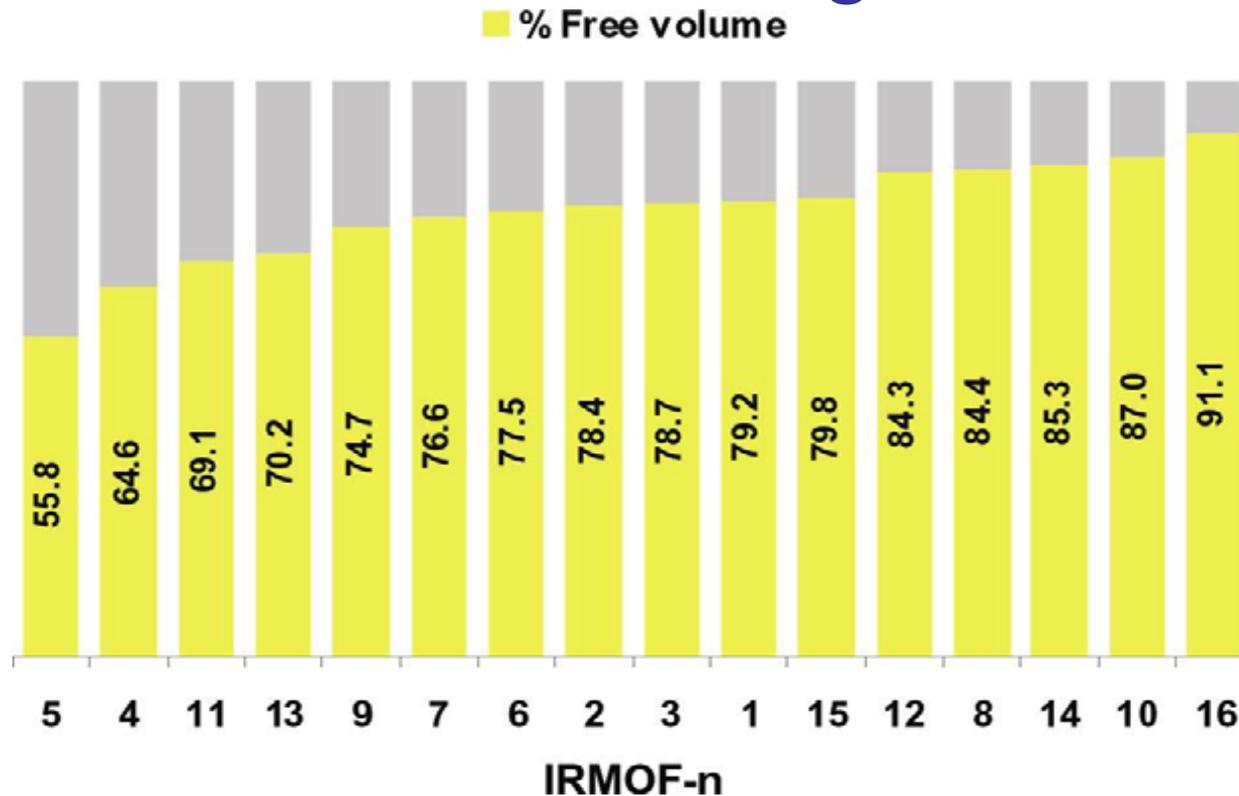
• NaFAU

• Fixed diameter 13 Å

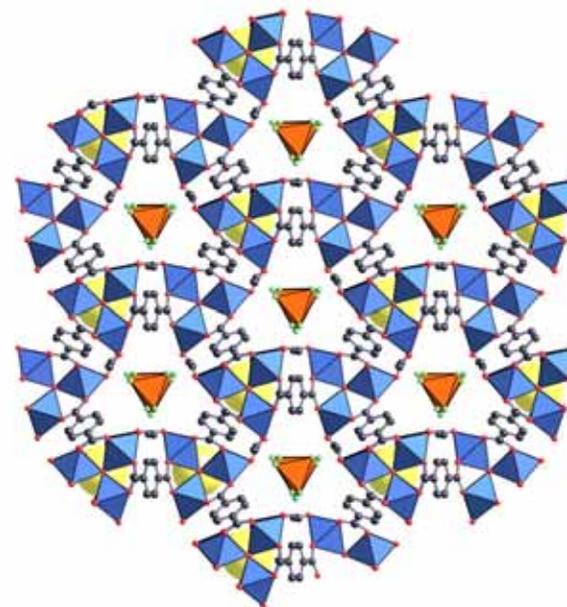
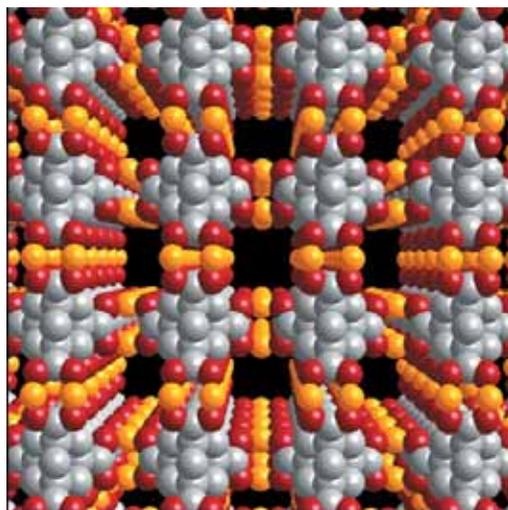
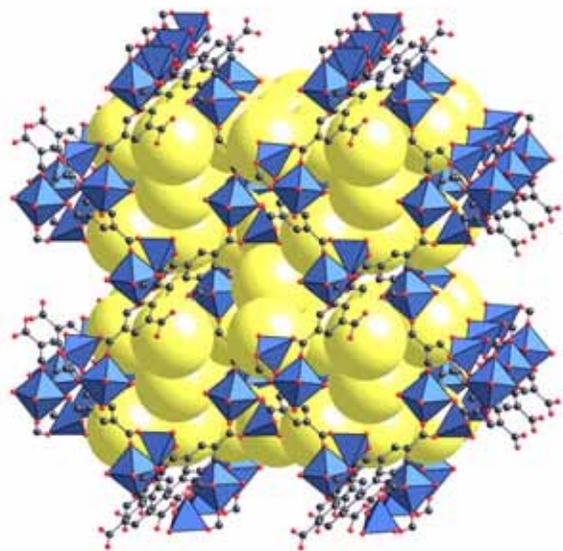
• Free diameter 7.4 Å



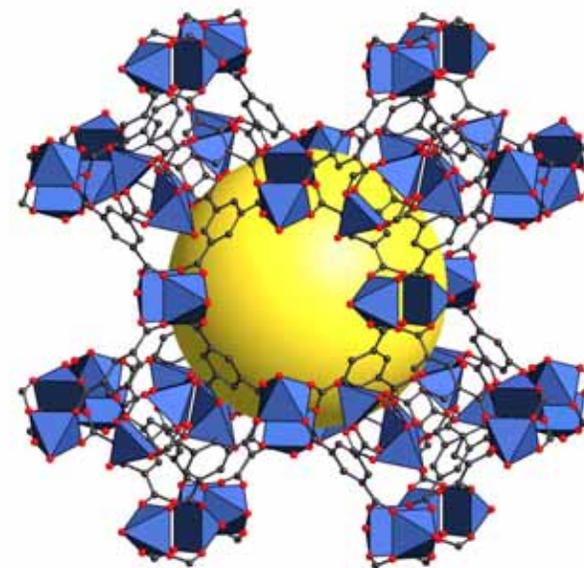
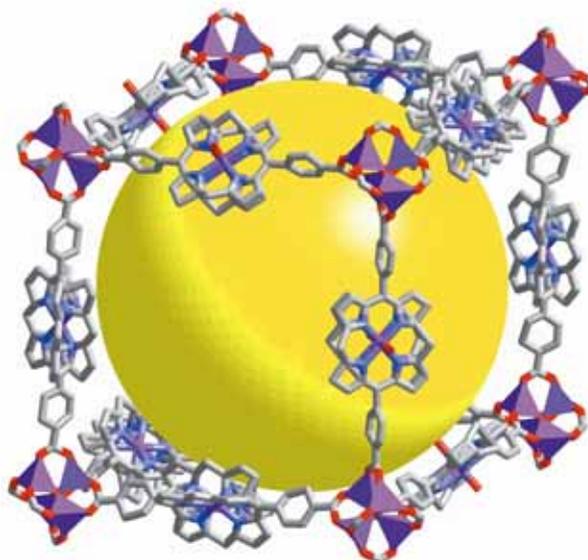
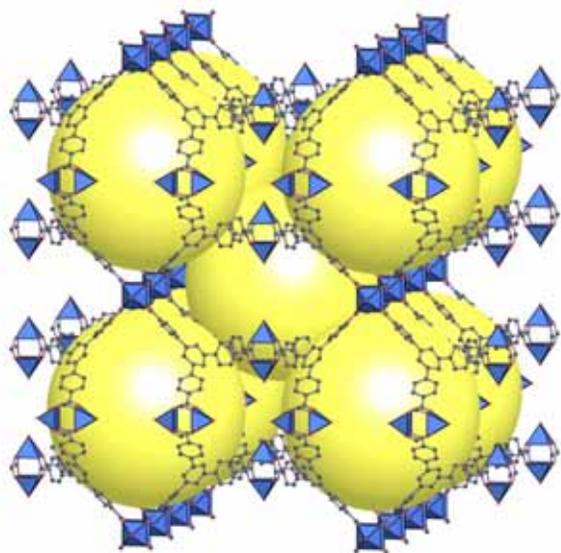
There is a Lot of Nothing in IRMOFS



- IRMOFS have a Large Void Fraction.
 - Larger than Zeolites (NaFAU 0.47 cc/cc)
- Sorbents with Large Capacities.



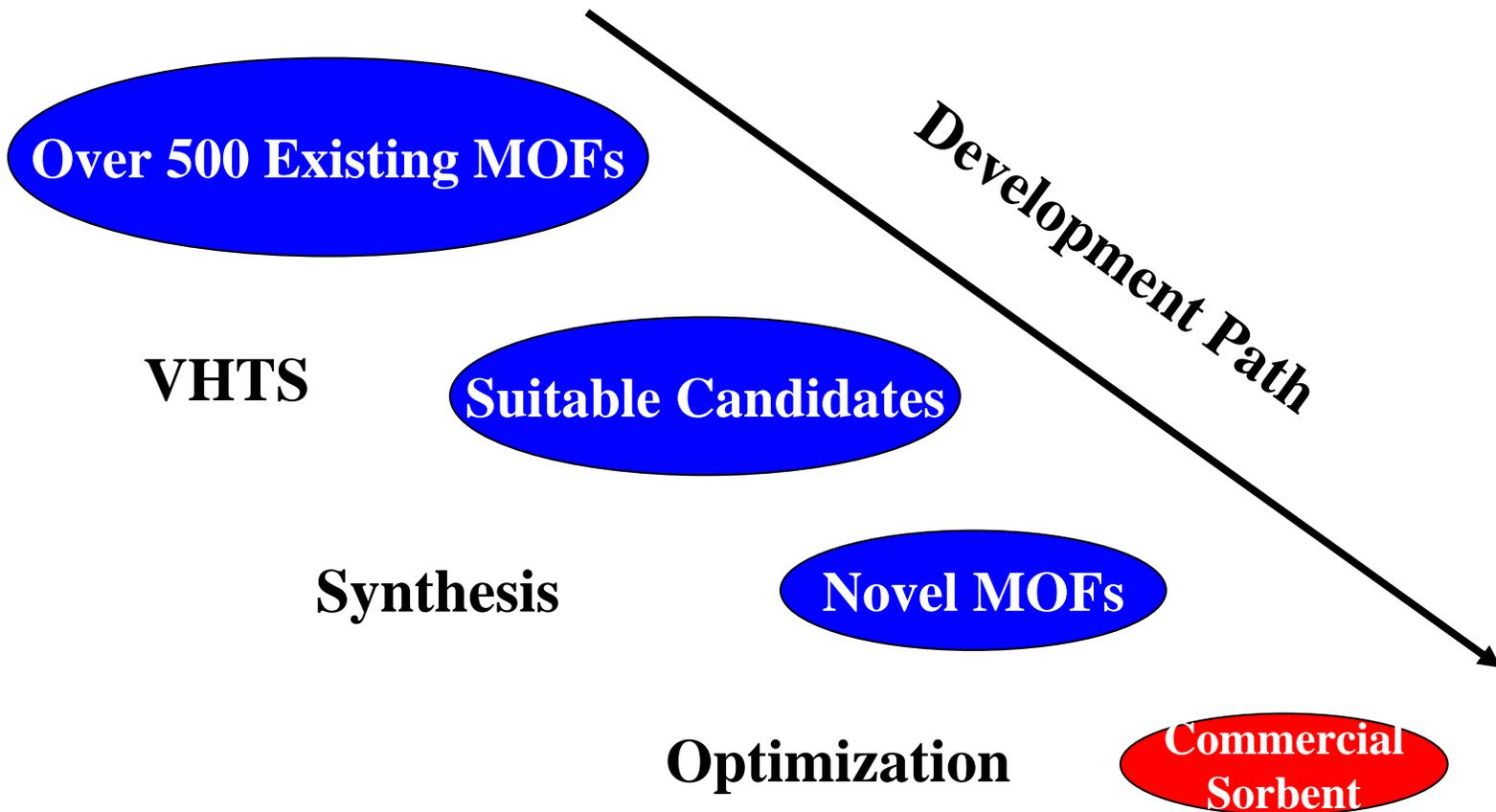
>500 MOFs prepared!



Role of Molecular Modeling

- The synthesis routes are very predictable. So, if we dream up a new “wall” ligand, there is a good chance that the material can be synthesized.
- Molecular modeling may allow for screening of new candidate materials before they are synthesized.
For example,
 - Monte Carlo simulations to predict adsorption isotherms and heats of adsorption
 - Molecular dynamics simulations to predict diffusion coefficients
 - Docking calculations to predict “fit” of guest molecules within pores or cavities

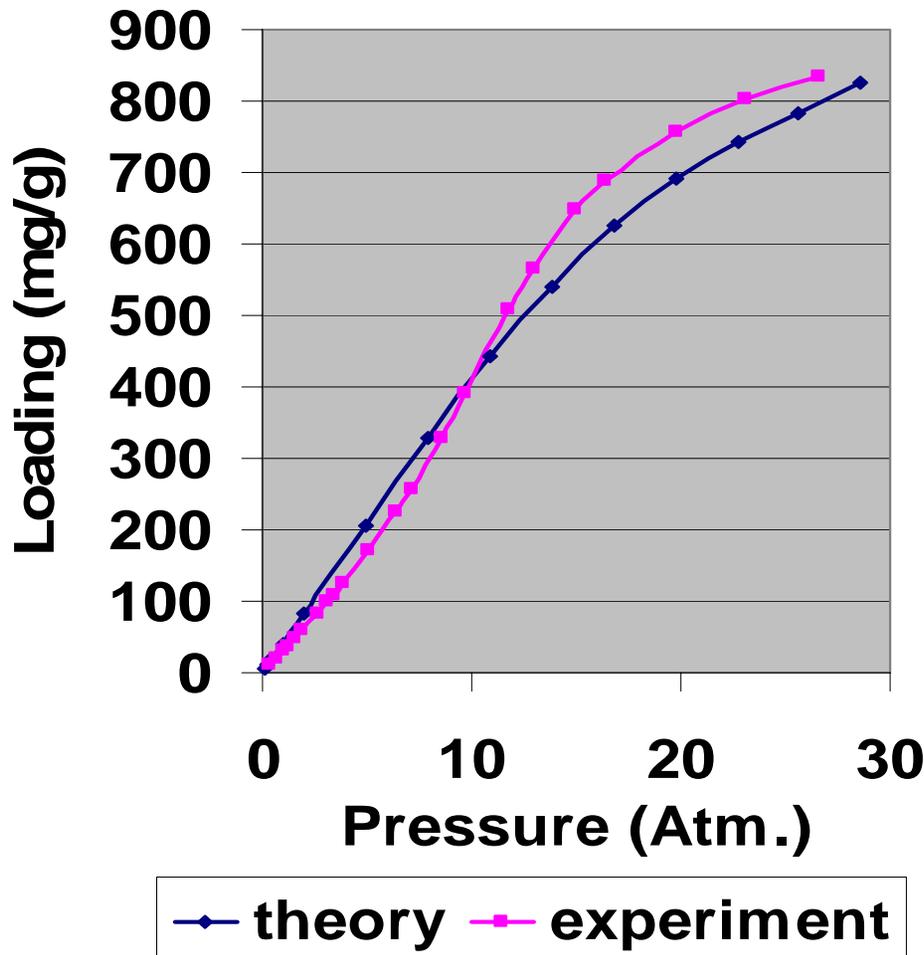
Investigate MOFs for CO₂, N₂, H₂



Isotherm Model

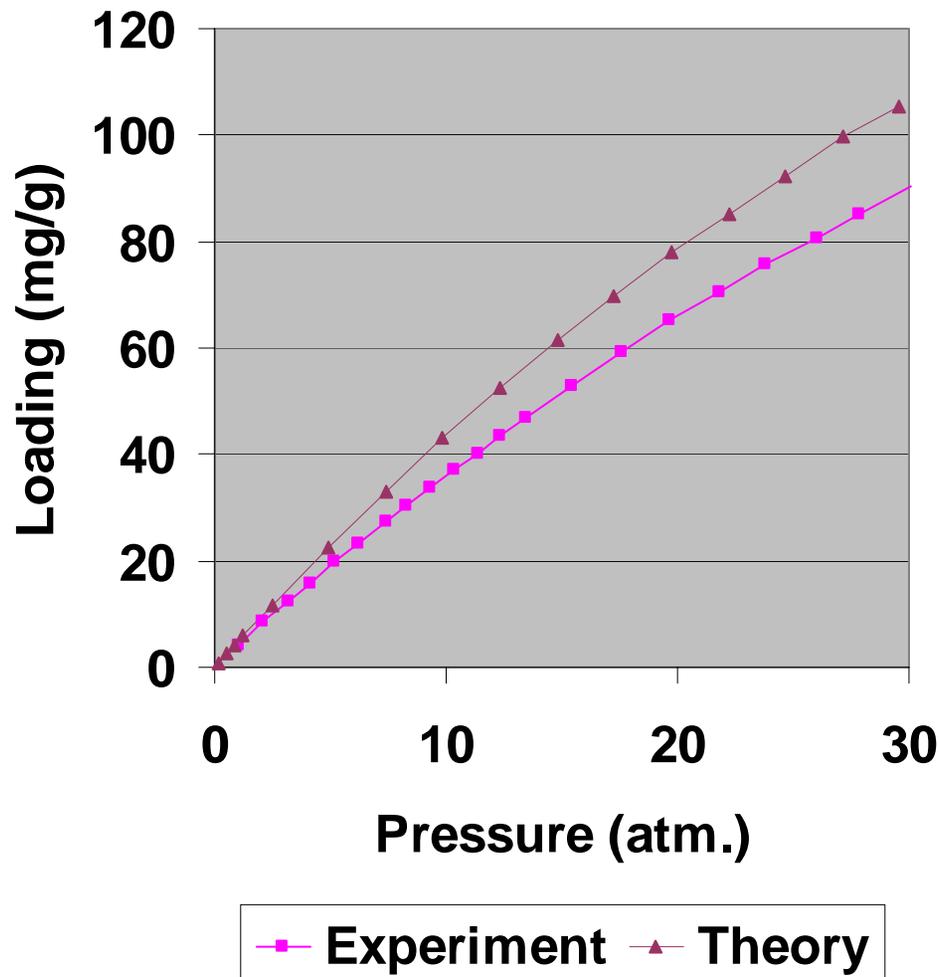
- UOP version of MUSIC sorption modeling software to calculate isotherms.
 - Charge distribution of MOF represented by a multipole expansion up to quadrupoles.
 - Very accurate predictions of Electrostatic Potential in Pores.
 - Multipole moments derived from DMOL3 (Accelrys, Inc.)
 - A. Gupta, S. Chempath, M. J. Sanborn, L. A. Clark, R. Q. Snurr, Mol. Sim. 29(2002)29
 - J.J.Low, J.D.Sherman, L.S.Cheng, R.L.Patton, A.Gupta, R.Q.Snurr, FOA7 Proceedings, 2002.
- Intermolecular Potentials
 - MOF– W.A.Goddard, et al. J.Phys.Chem 94(1990)8897
 - CO₂ – J.I. Siepmann, et al. AIChE J. 47(2001)1676
 - N₂ – C.S. Murthy, et al. Mol.Phys. 41(1980)1387
 - Lorentz-Berthelot mixing rules used to estimate sorbate-sorbent interactions.

Comparison of Experiment and Theory for CO₂ on IRMOF-1 at 300K



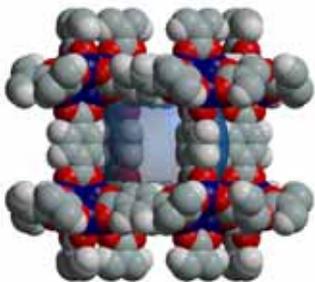
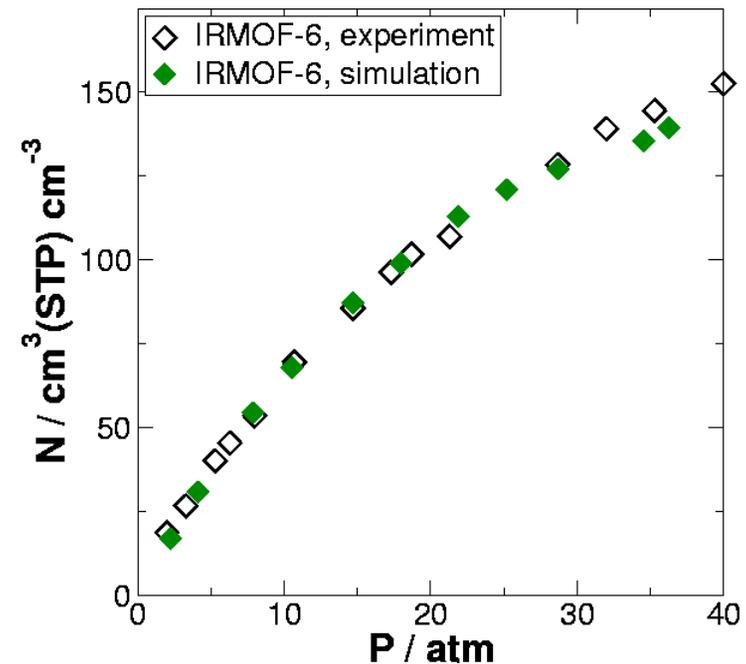
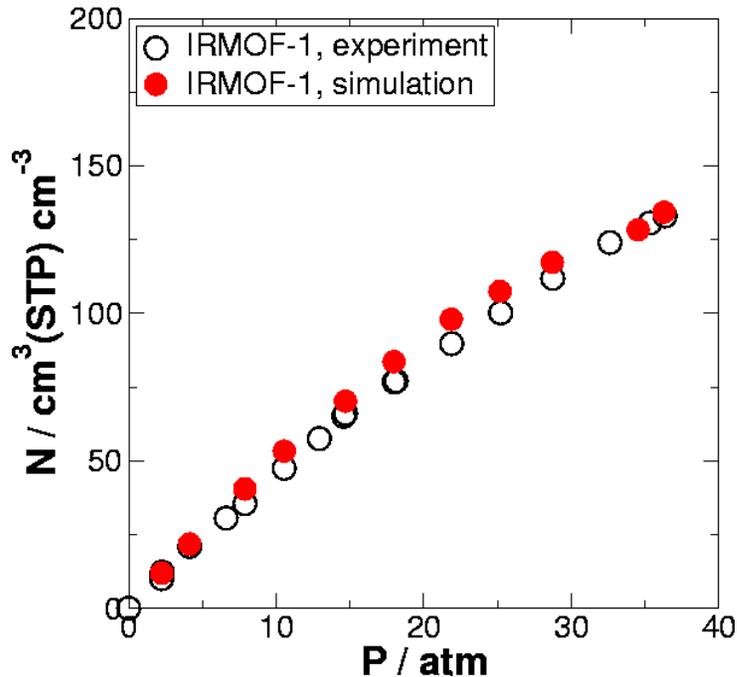
- Fair agreement with no adjustment of parameters!!!!
- Good enough for initial screening of sorbents.
- Need to adjust parameters to get isotherm shape right.

Comparison of Experiment and Theory for N₂ on IRMOF-1 at 300K

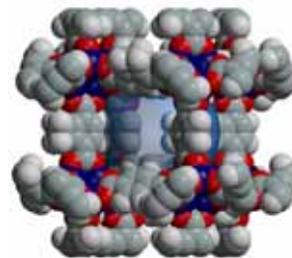


- Good agreement with no adjustment of parameters!!!!
- Good enough for initial screening of sorbents.
- Capacity for N₂ 10X less than CO₂.

CH₄ Adsorption in IRMOFs ~10X less than CO₂



IRMOF-1
128 cm³ (STP) / cm³
at 35 bar

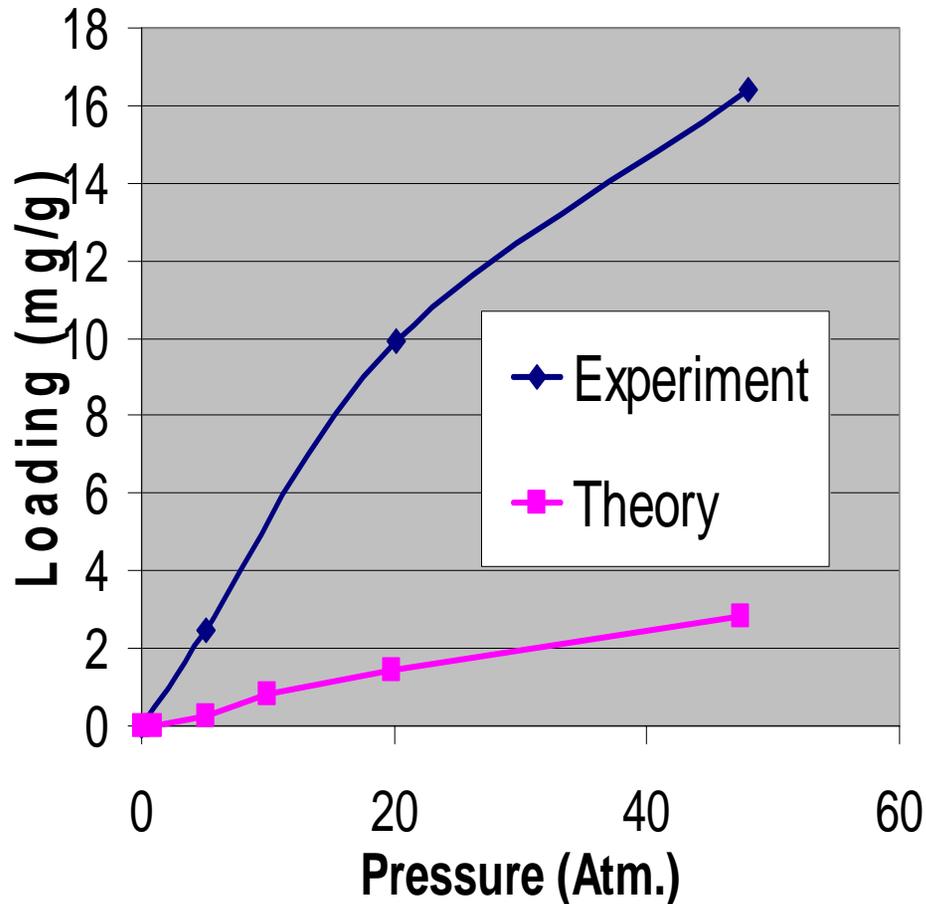


IRMOF-6
136 cm³ (STP) / cm³
at 35 bar

DOE target: for onboard storage: 150 cm³(STP) / cm³ at 35 bar

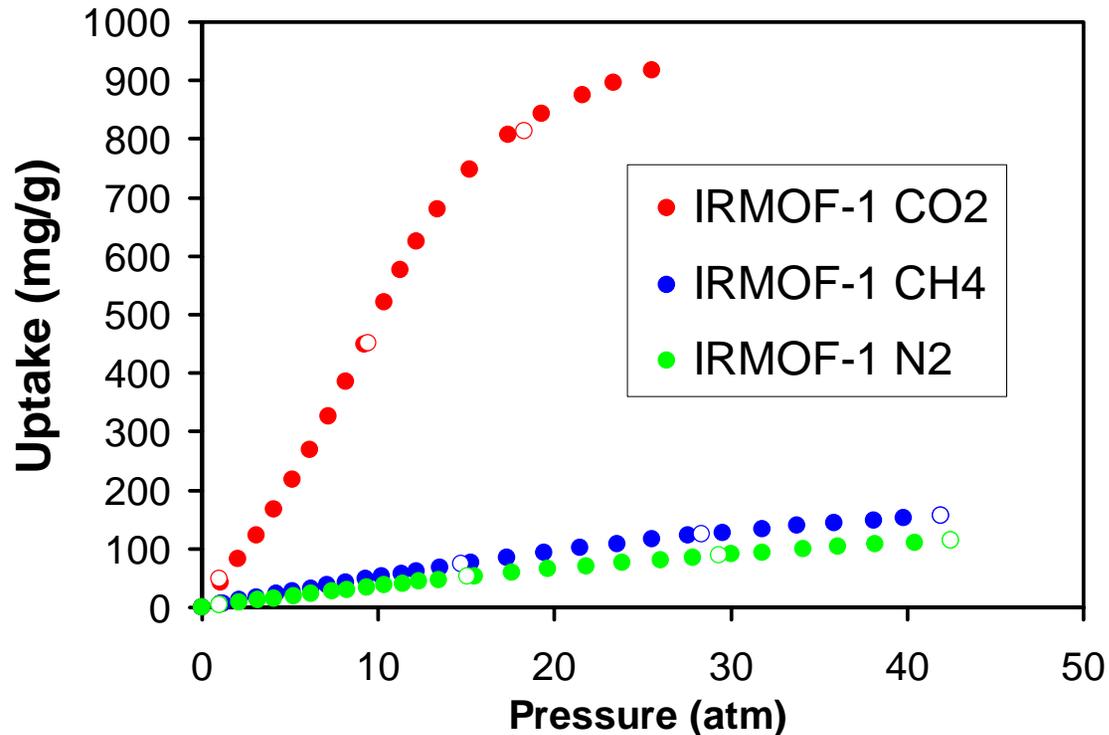
Düren, Sarkisov, Yaghi, Snurr, *Langmuir*, 2004

H₂ Adsorption in IRMOF5



- Large discrepancy between experiment and theory
 - Chemical sorption not included in theory?
- Experiment and theory agree that H₂ capacity is ~100 times lower than CO₂ capacity.
- T. Sagara, J. Klassen, E. Ganz, J.Chem.Phys. 121(2004)12453

Experimental Isotherms for MOFs



- CO₂, N₂ and CH₄ isotherms have been measured at 300 K for IRMOF-1, IRMOF-3 and MOF-74.
- Currently under review for patent applications.

Conclusions

- IRMOF-1 is >10X more selective for CO₂ over less polar gases like N₂, CH₄ and H₂.
- We have successfully modeled the sorption isotherms for gases on IRMOFS.
 - Modeling results should allow us to design IRMOFs with good selectivity for CO₂ versus other gases in flue gases and gasification streams.
- We are confident that we can synthesize the designed MOF.
- Funded by DOE grant DEFG26-04NT42121