SAND2013-7129P

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Using Molecular Simulation to Study Gas Uptake with Metal-Organic Frameworks: Diffusion and Adsorption

Marie V. Parkes

29 August 2013

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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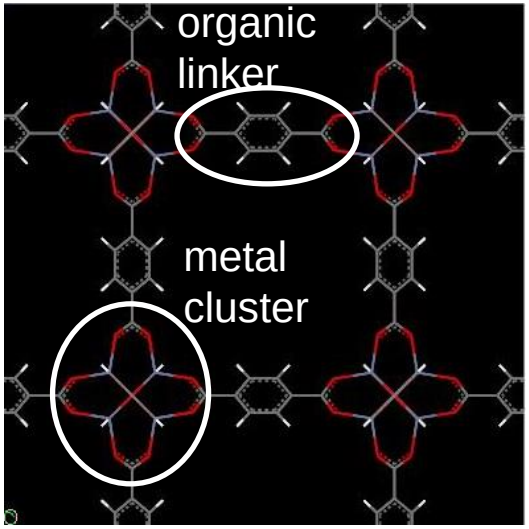
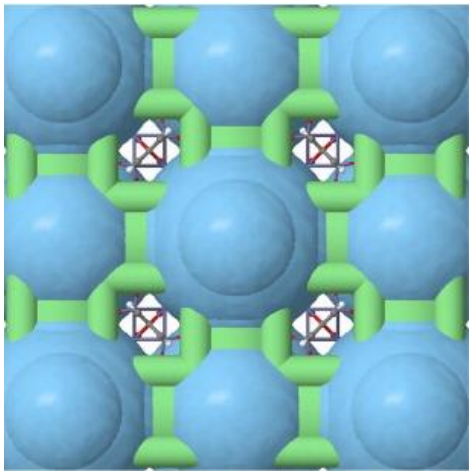
Agenda

- Diffusion of noble gases in MOFs
  - Background
  - Methods
  - MD simulations
  - Self-diffusivity calculated
  - Window size calculations
  - Conclusions
- Separation of oxygen and nitrogen
  - Background
  - Methods
  - Binding energies calculated
  - Conclusions

Metal-Organic Frameworks

- Porous solids made of an extended network of metal clusters coordinated to multidentate organic linkers
- Surface areas up to 5900 m^2g^{-1}
- "Crystalline sponges"





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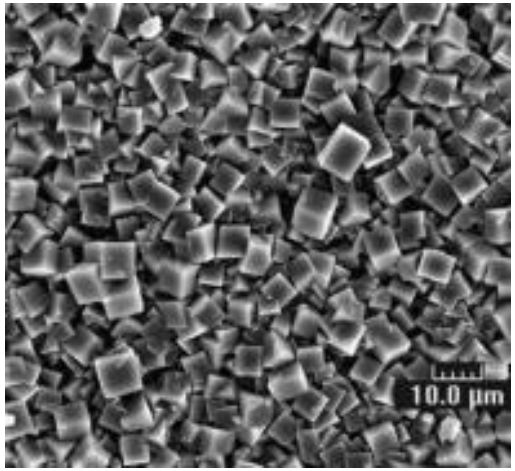

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Noble Gas Separations

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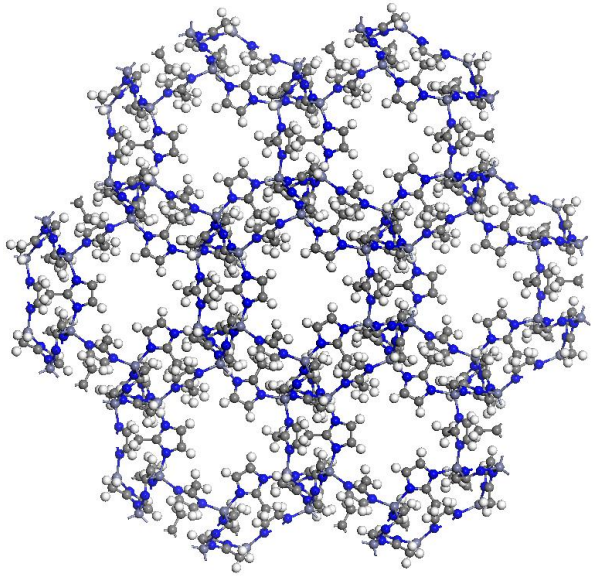
Noble gas uses:

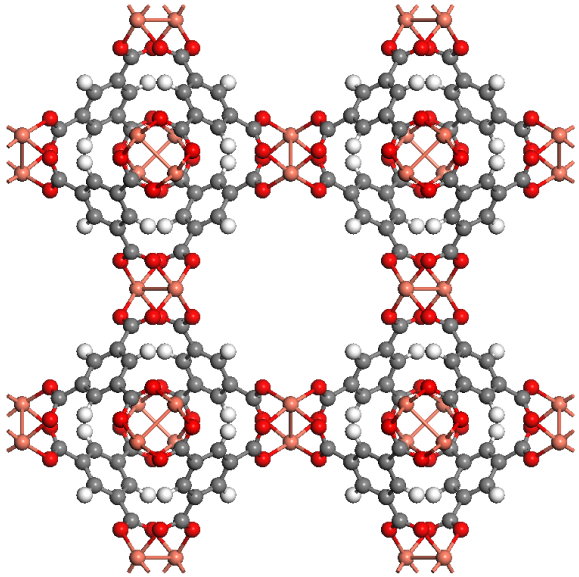
- Cryogenic refrigerants
- Carrier gases
- Lighting
- Laser applications

Capture and separation are challenging:

- Low natural abundance
- Relatively inert

Noble Gas Diffusion



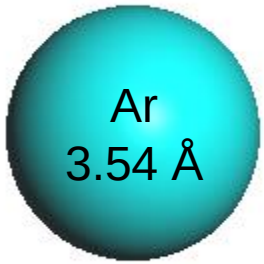


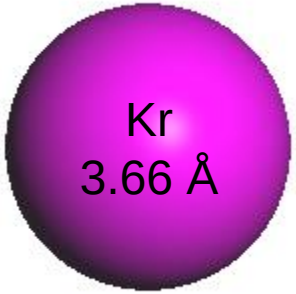
ZIF-8

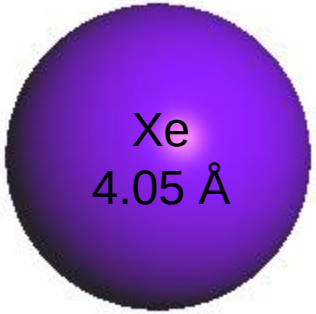
- Window diameter 3.4 Å

HKUST-1

- Window diameters 4.1 Å, 6.9 Å







Molecular Dynamics Simulations

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LAMMPS software

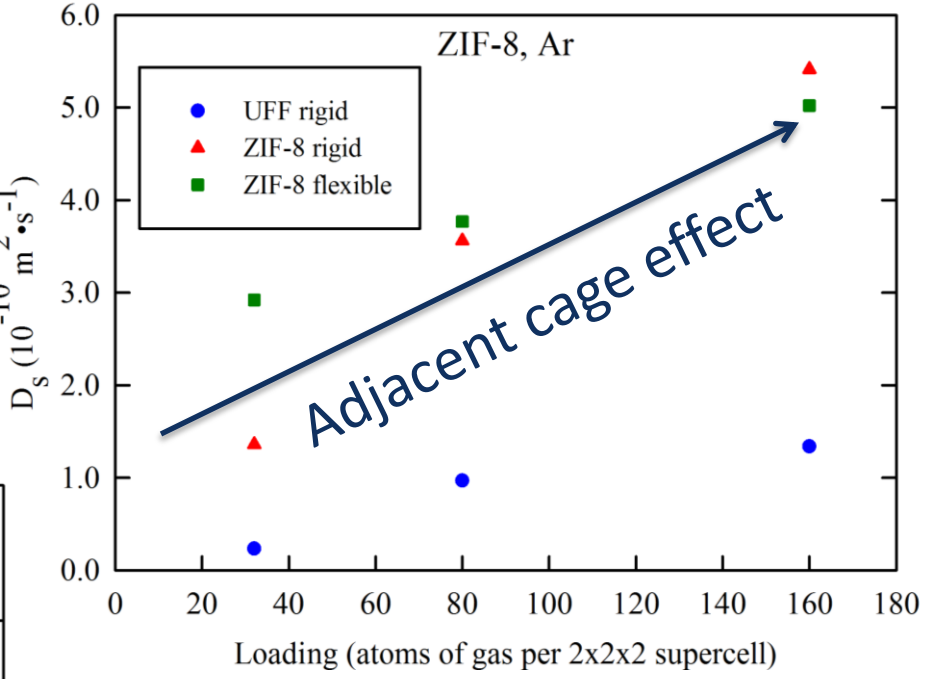
- MOF
  - ZIF-8
  - HKUST-1
- Gas
  - Ar
  - Kr
  - Xe
- Gas loading (0.3 to 65 bar)
  - 16/40/80 gas atoms (HKUST-1)
  - 32/80/160 gas atoms (ZIF-8)
- Force fields
  - UFF (rigid)
  - ZIF-8 FF[1] (flexible and rigid)
  - HKUST-1[2] FF (flexible and rigid)
- Initial structures
  - Published crystal structure
  - Force-field-optimized structure
  - DFT-optimized structure

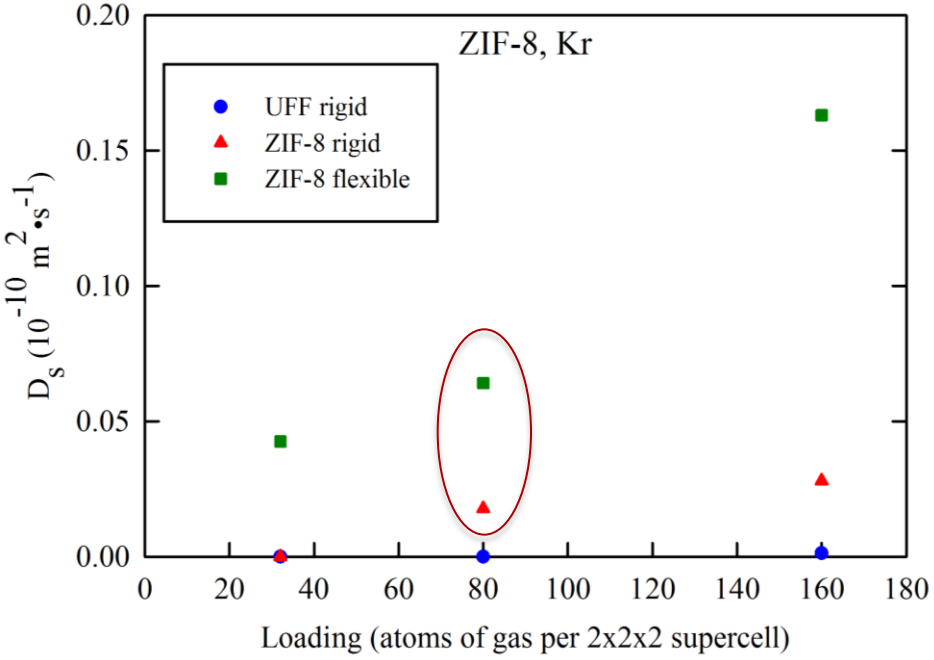
Equilibration (NVT, NVE) followed by data-gathering (20 ns NVE)

1. ZIF-8 FF: Zheng, B.; Sant, M.; Denontis, P.; Suffritti, G, B. *J. Phys. Chem. C* **2012**, *116*, 933-938.
2. HKUST-1 FF: Zhao, L.; Yang, Q.; Ma, Q.; Zhong, C.; Mi, J.; Liu, D. *J. Mol. Model.* **2011**, *17*, 227-234.

Diffusion in ZIF-8

- Diffusion is greatest with flexible force field
- Diffusion increases as loading increases (adjacent cage effect)





- Ar diffusion greater than Kr diffusion
- No diffusion seen for Xe

Kr Diffusion in ZIF-8

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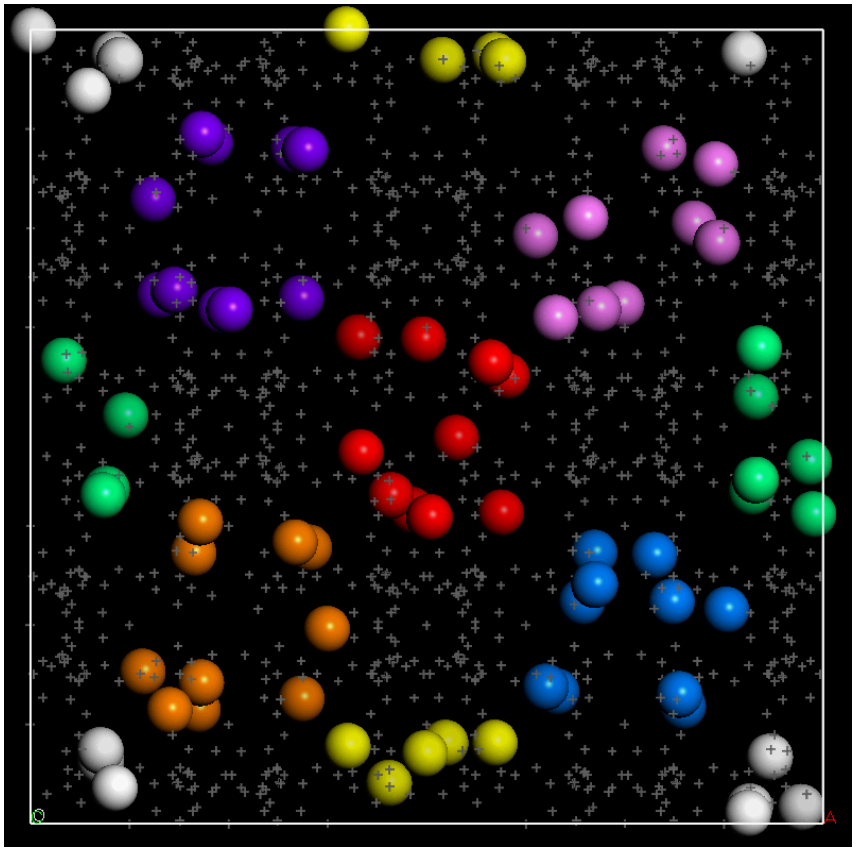
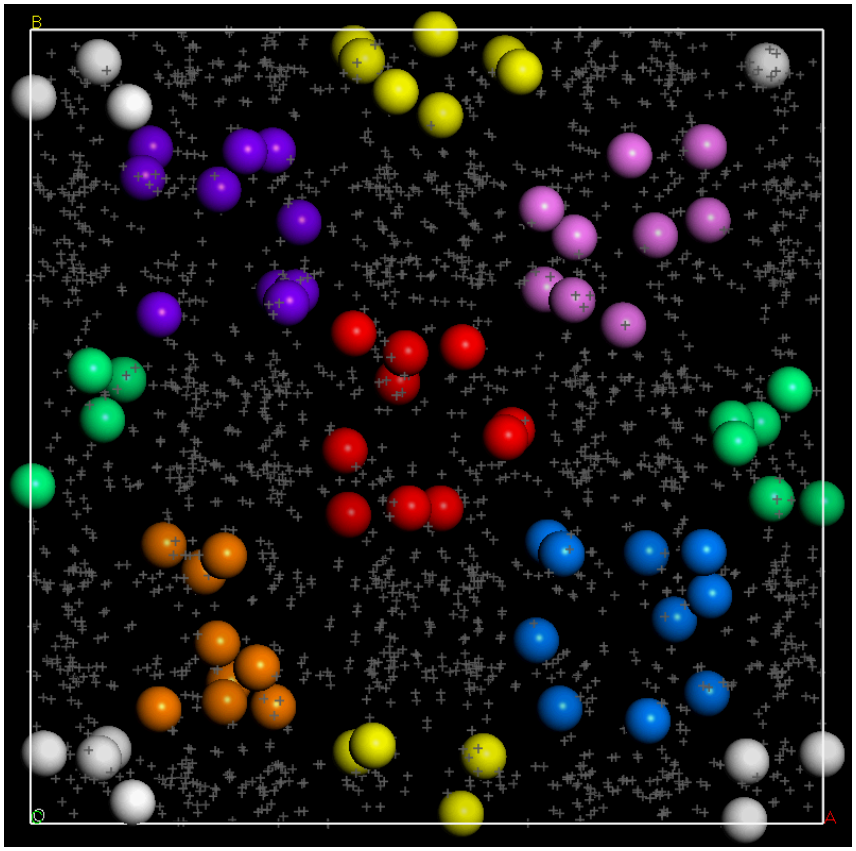
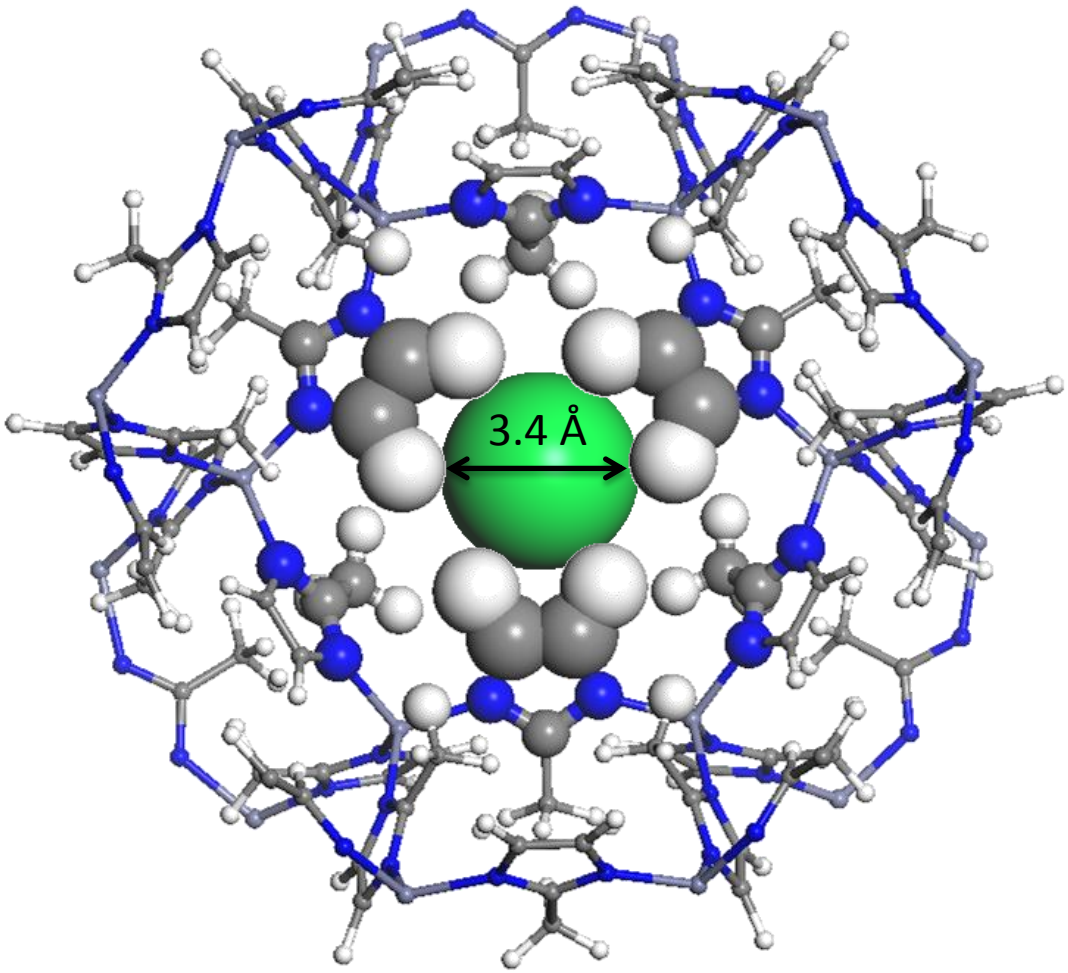
Rigid



Flexible



Kr Diffusion in ZIF-8

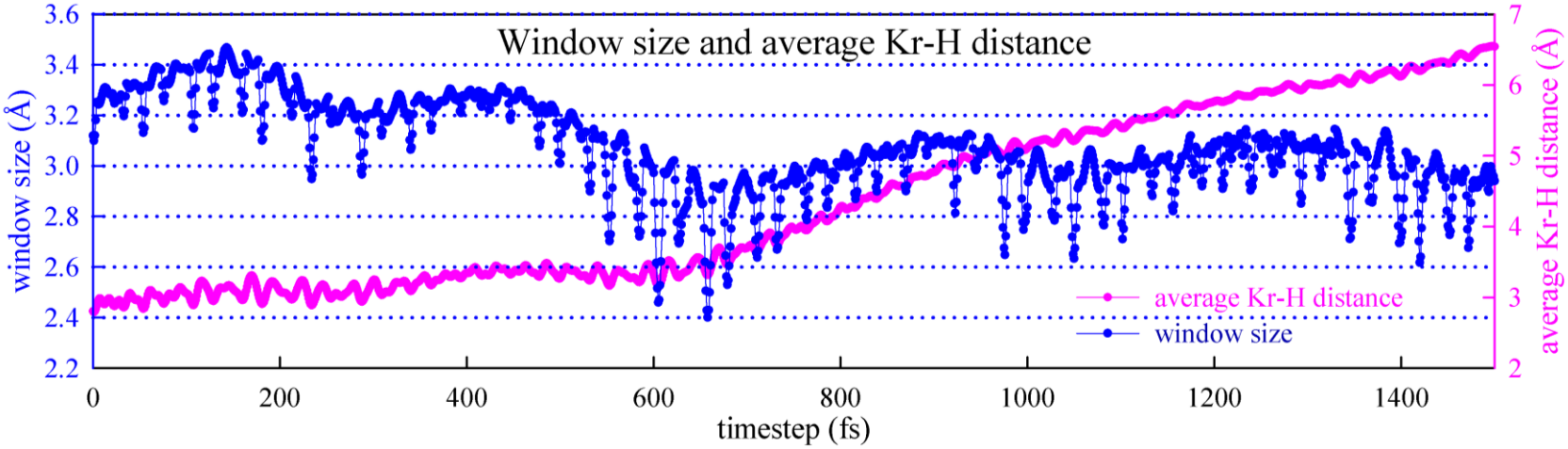


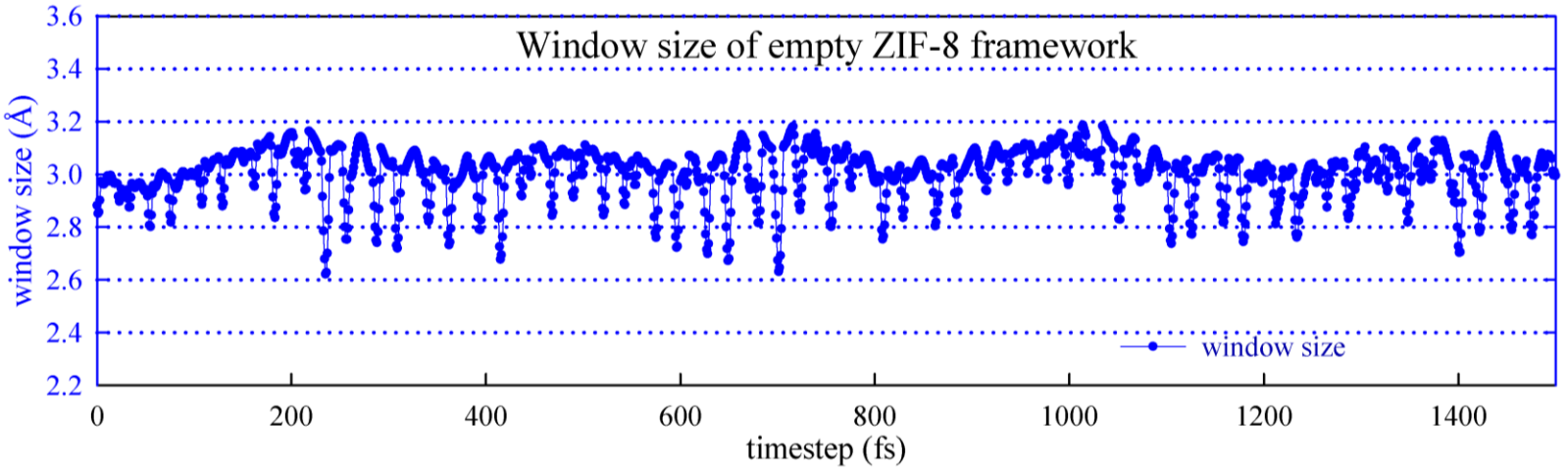
Fast diffusion — Ar 3.54 Å

Limited diffusion — Kr 3.66 Å

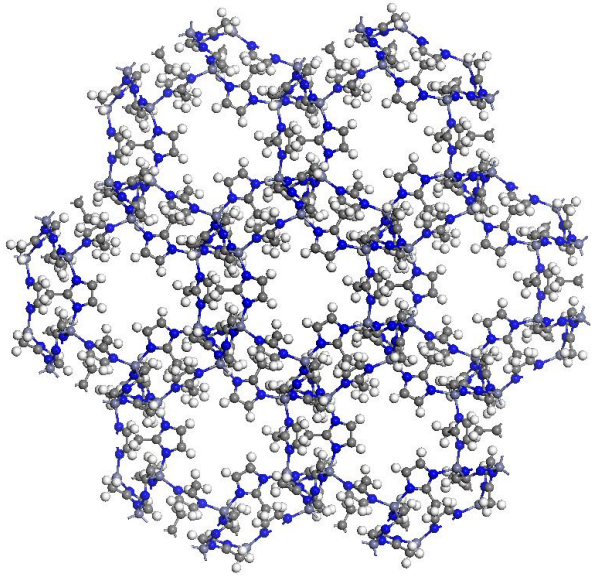
No diffusion — Xe 4.05 Å

Kr Diffusion in ZIF-8



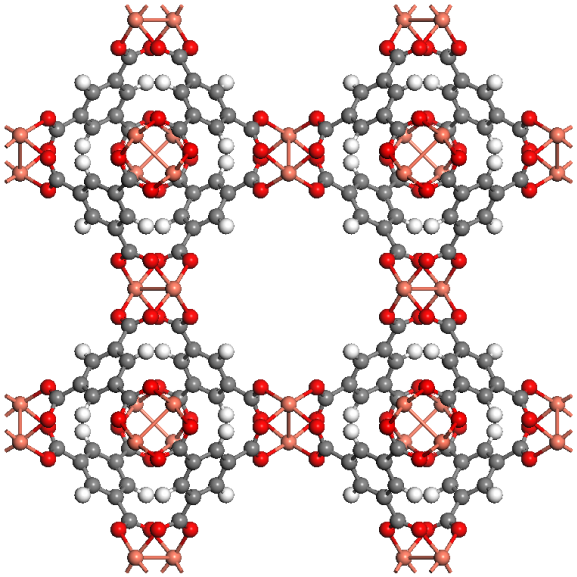


Noble Gas Diffusion



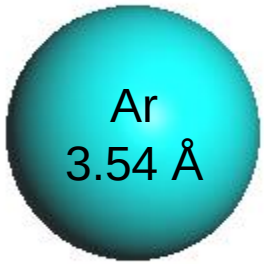
ZIF-8

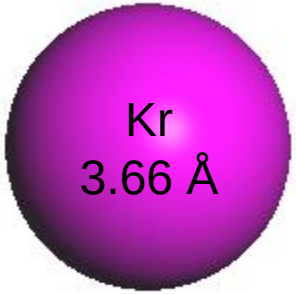
- Window diameter 3.4 Å

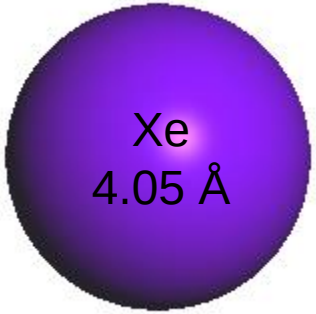


HKUST-1

- Window diameters 4.1 Å, 6.9 Å

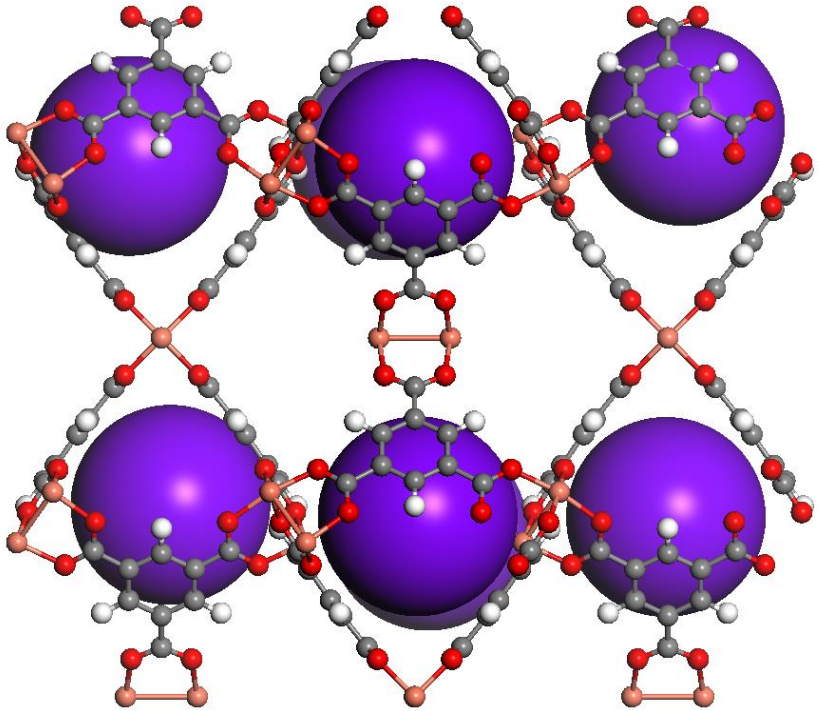


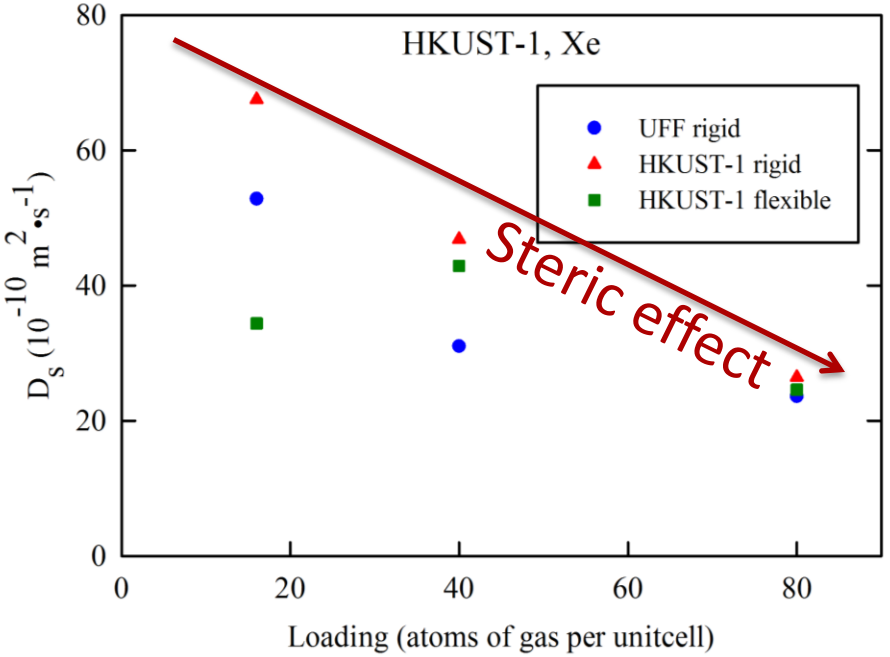




Xe Diffusion in HKUST-1

- Diffusion decreases as loading increases (steric effect)

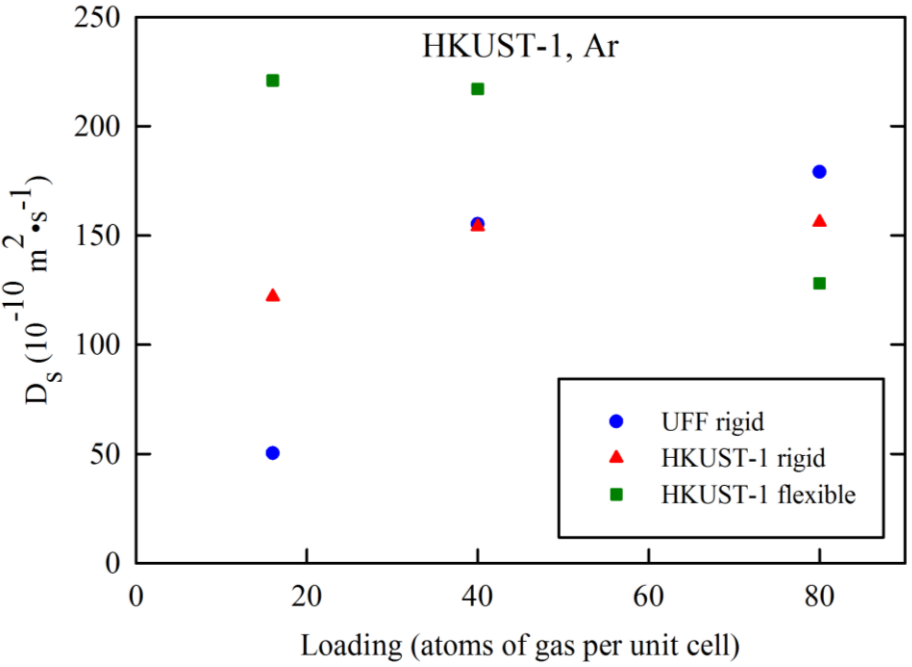


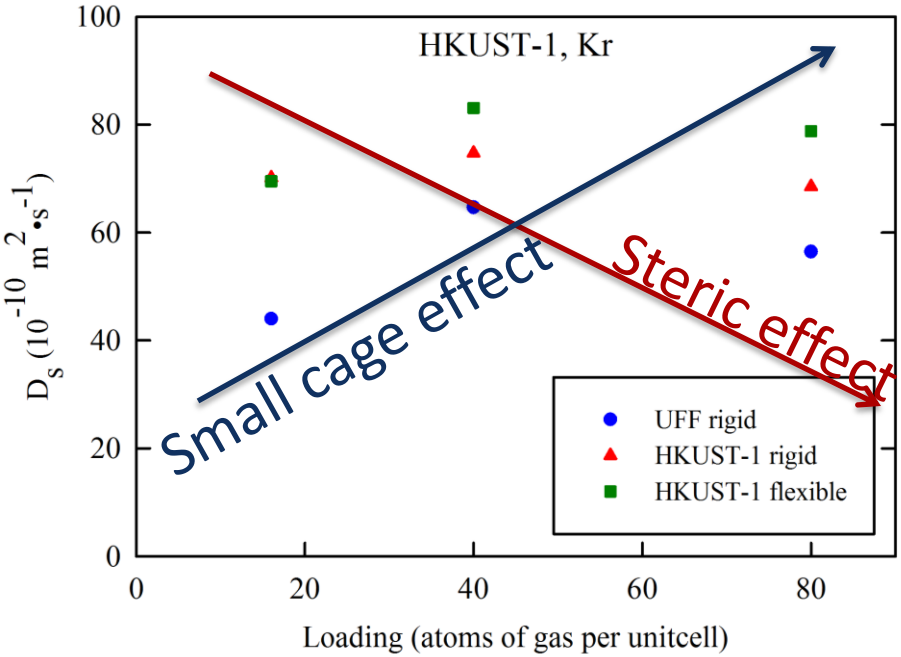


- Eight gas atoms strongly adsorbed in octahedral cages with small windows (small cage effect)

Kr/Ar Diffusion in HKUST-1

- Diffusion is greatest with flexible force field





- Loading dependence: steric effect and small cage effect compete

Conclusions

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- Generic force fields and rigid frameworks not sufficient to accurately describe guest diffusion in MOFs
- Diffusion dependence on loading is greatest when MOF windows are similar in size to guest
- ZIF-8
  - Gas diffusion increases as loading increases (adjacent cage effect)
  - Kr diffusion strongly dependent on flexible framework
  - ZIF-8 window expands as Kr passes through
- HKUST-1
  - “Small cage effect” due to strong adsorption sites and small windows
  - Small cage effect and steric effect compete

Agenda

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- Diffusion of noble gases in MOFs
  - Background
  - Methods
  - MD simulations
  - Self-diffusivity calculated
  - Window size calculations
  - Conclusions
- Separation of oxygen and nitrogen
  - Background
  - Methods
  - Binding energies calculated
  - Conclusions

Oxyfuel for Cleaner Power Plants

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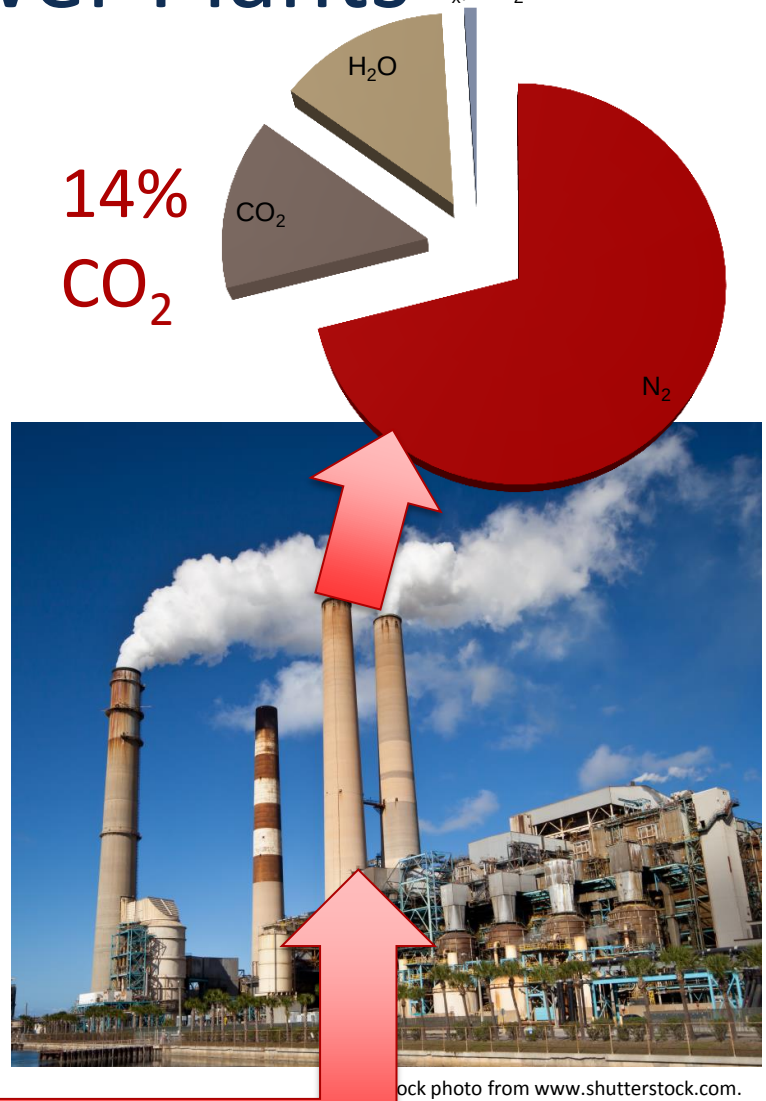
- Coal-burning power plants major source of carbon dioxide emissions
- Interest in capturing CO_2 emissions
  - What comes out depends on what goes in!

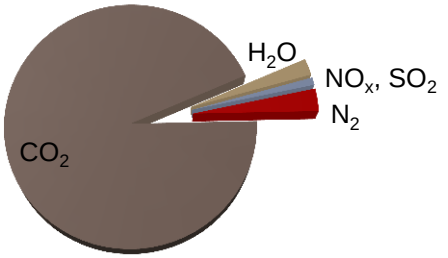


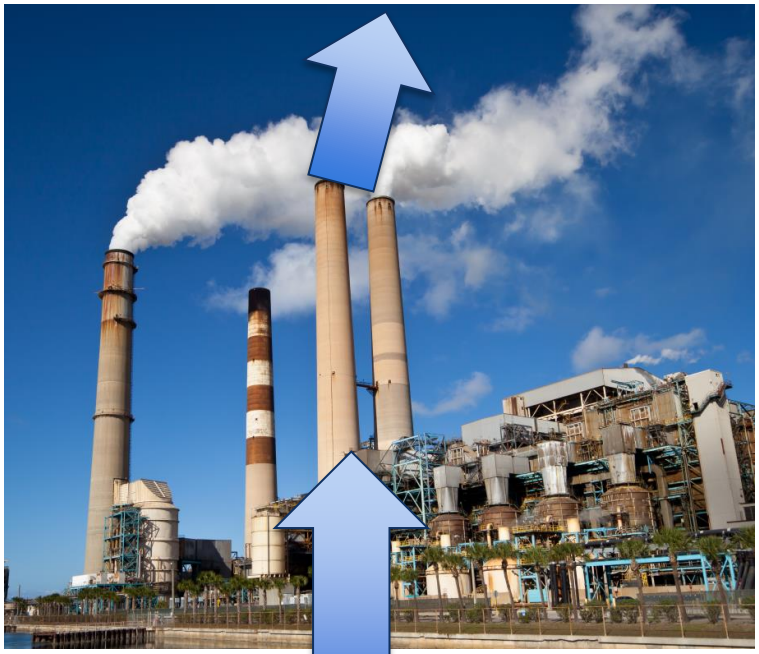
ock photo from www.shutterstock.com.

Oxyfuel for Cleaner Power Plants

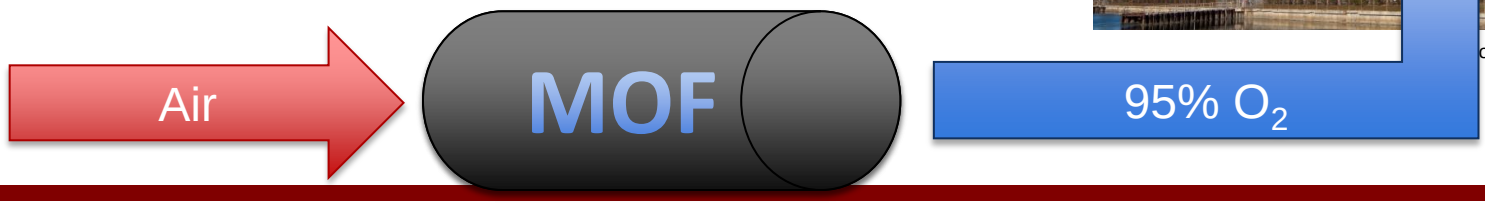
- Oxyfuel advantages
  - Flue gas volume decreased by 75%
  - Decreased NO_x emissions
  - Greater thermal efficiency
  - Easier to capture CO_2
  - More energy efficient (not using energy to heat N_2)

94% CO_2





ock photo from www.shutterstock.com.



MOFs for O_2/N_2 Separation

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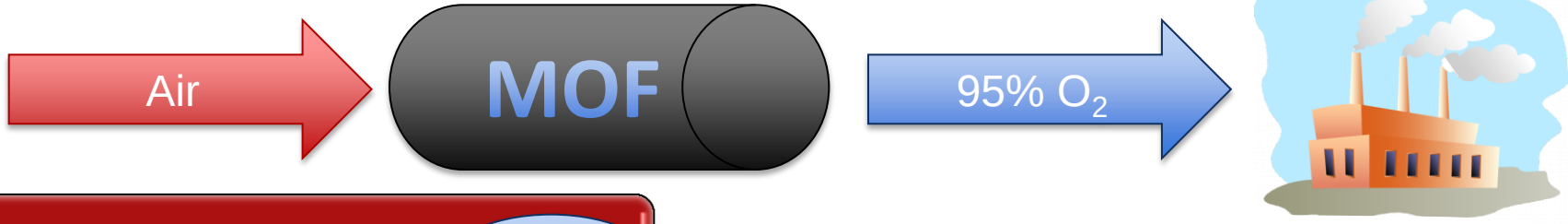


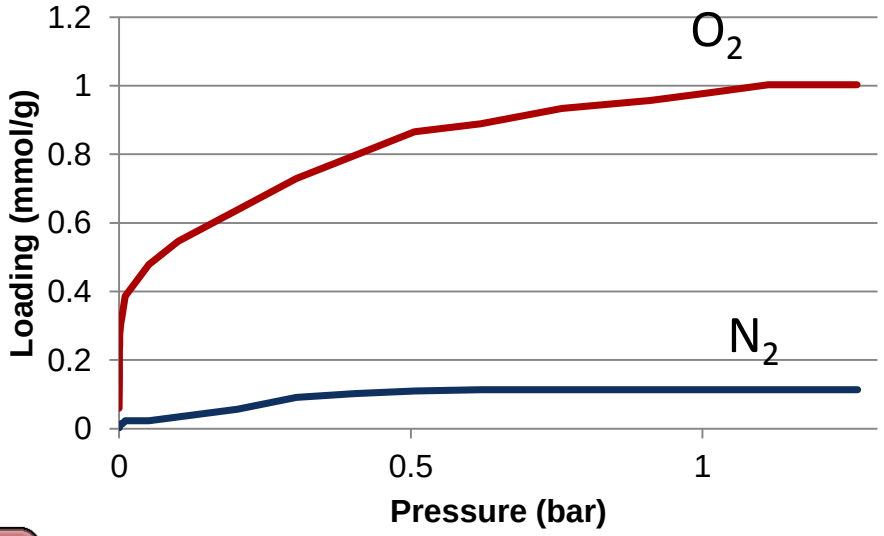
Clean crystal structures — 2855

Initial screening based on known properties — 554

Screening based on O_2/N_2 Henry's constants — 75

Sarkisov, L. *J. Phys. Chem. C* **2012**, *116*, 3025-3033.

Classical modeling of uptake with standard force fields — 0



MOFs for O_2/N_2 Separation

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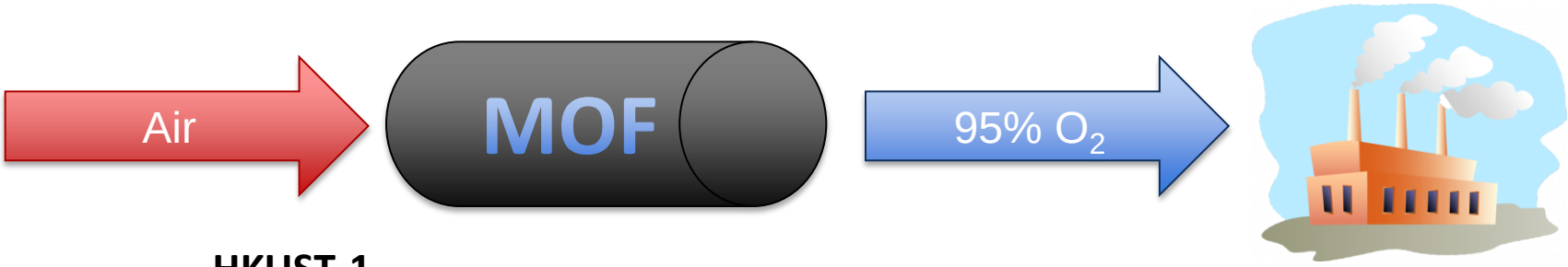
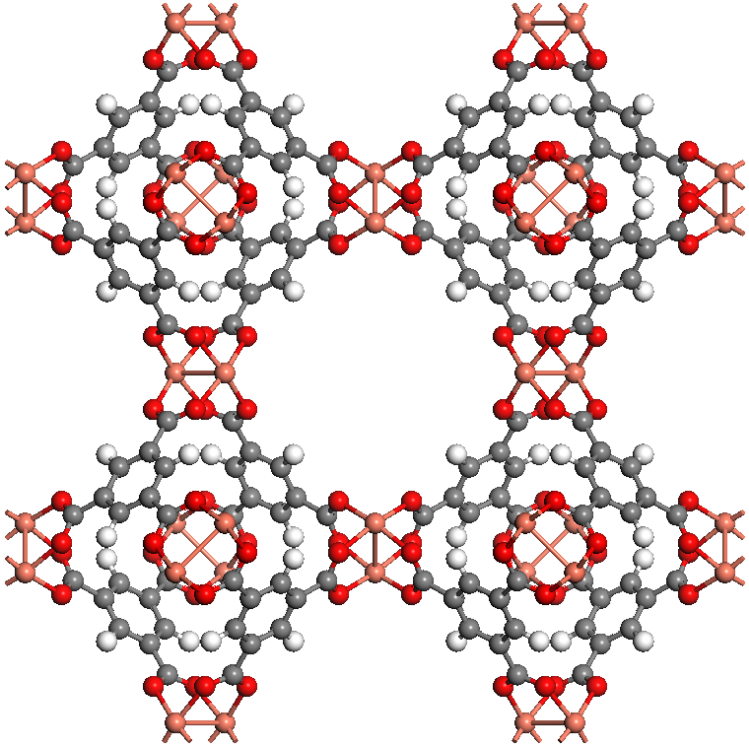
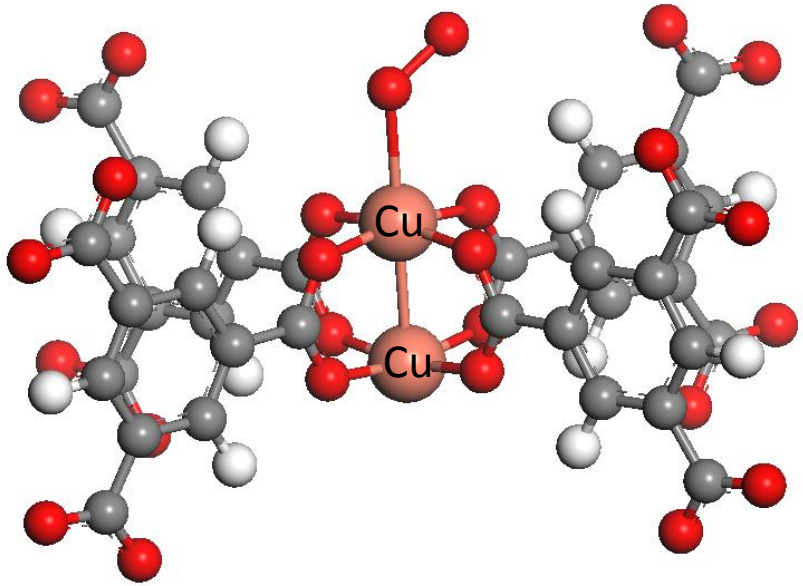


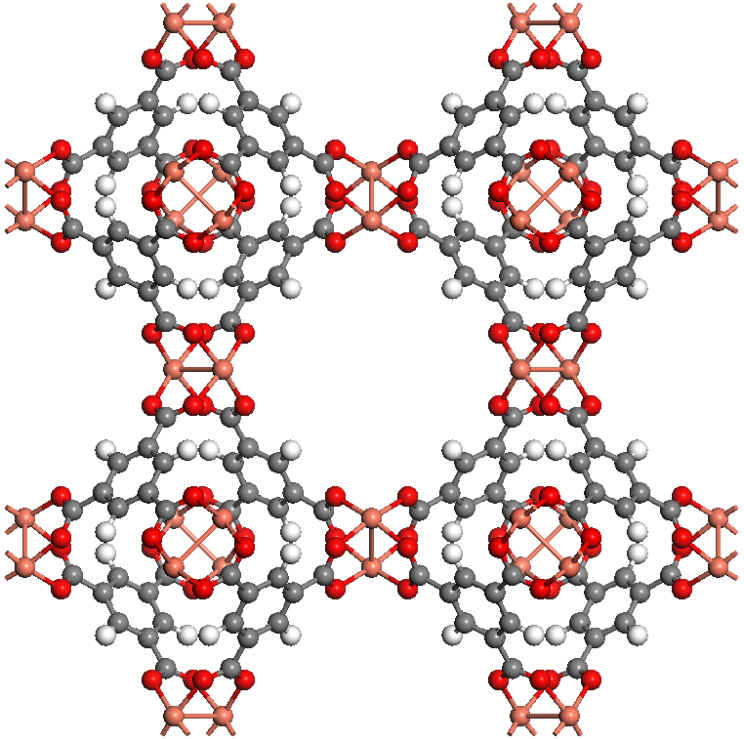
HKUST-1





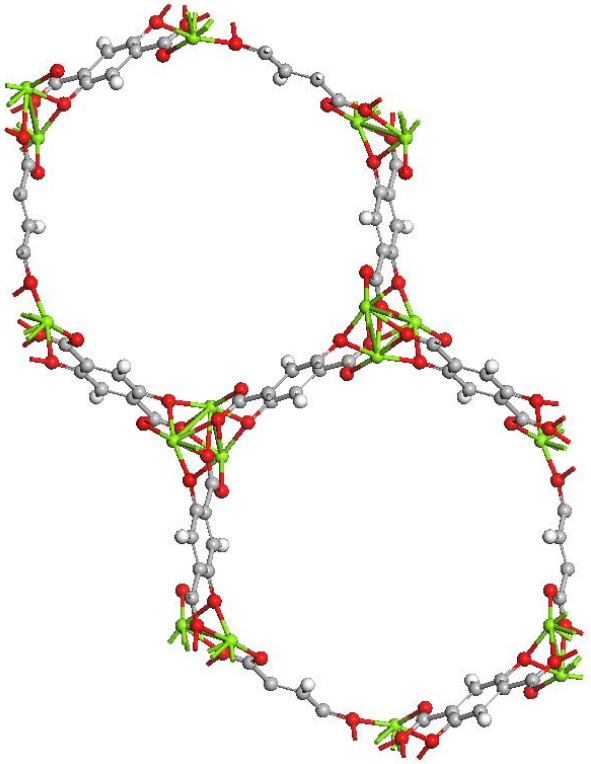
MOFs for O_2/N_2 Separation

HKUST-1



Cages: 6.9 Å, 11.1 Å, 13.2 Å
Windows: 6.9 Å, 4.1 Å

MOF-74



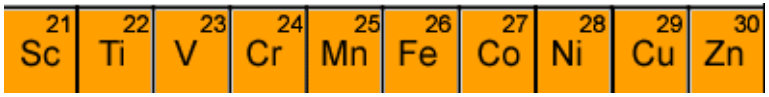
Pores: 10.8 Å

21	22	23	24	25	26	27	28	29	30
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn

DFT Calculations

Vienna *ab initio* simulation package (VASP)

- MOF
  - HKUST-1 analogs
  - MOF-74 analogs
- Metals



- Gas (one molecule per simulation cell)
  - O_2
  - N_2

- Plane wave DFT geometry optimizations, periodic structure
- PBE density functional with dispersion correction (PBE-D2), PAW potentials for core electrons
- Spin polarization

$$E_{binding} = E_{MOF+O_2} - \left(E_{MOF} + E_{O_2}\right)$$

O_2, N_2 Binding Energies (ΔE)

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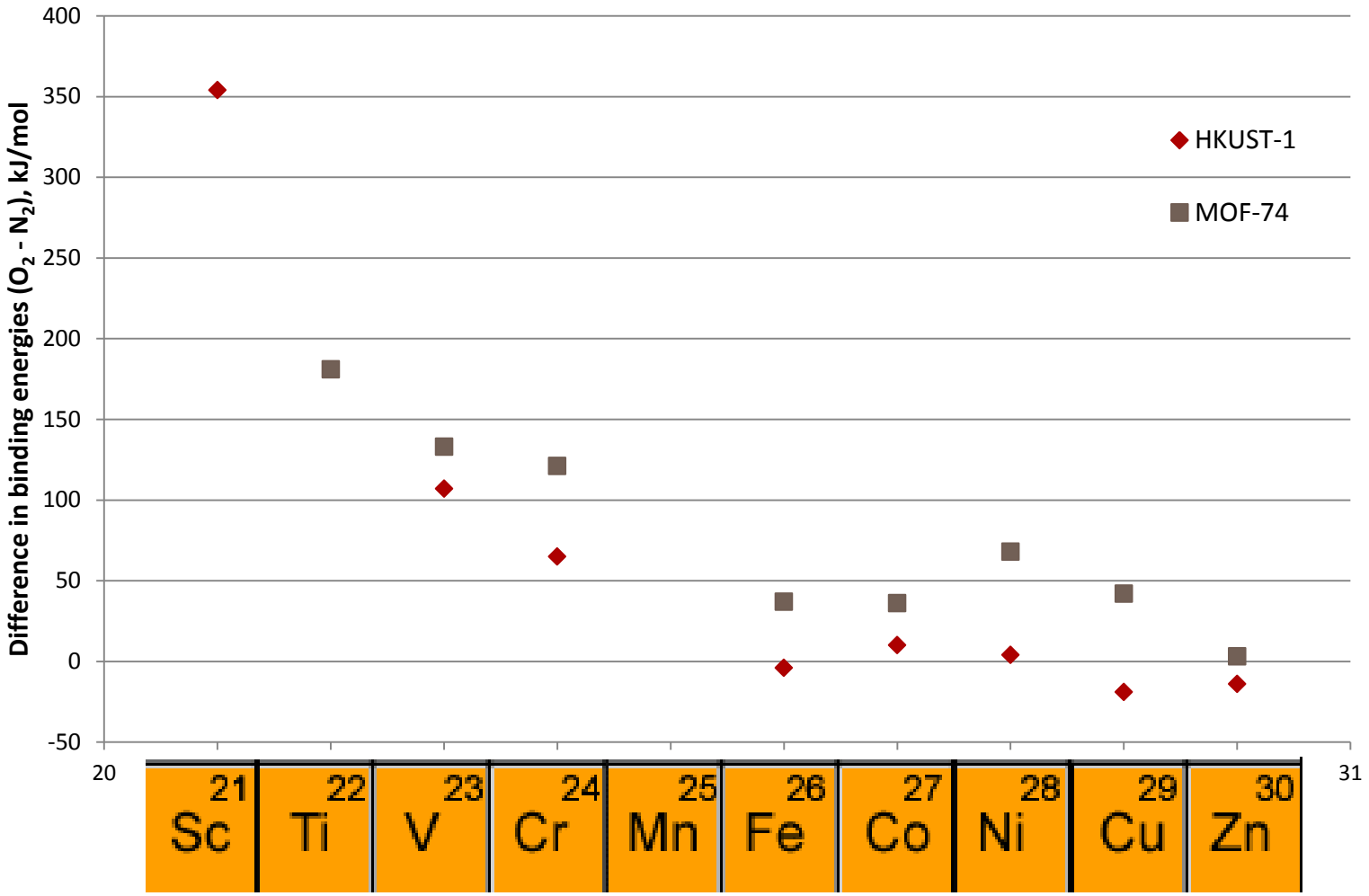
metal	HKUST-1 binding energy (kJ/mol)			MOF-74 binding energy (kJ/mol)		
	O_2	N_2	ΔΔE	O_2	N_2	ΔΔE
Sc	-401	-47	354	(O_2 added)	-41	
Ti	(failed)	-24		-255	-74	181
V	-127	-20	107	-229	-96	133
Cr	-106	-41*	65	-132	-11	121
Mn	(failed)	-11		(failed)	(failed)	
Fe	-41	-45	-4	-52*	-15*	37
Co	-67	-57	10	-81	-45	36
Ni	-54	-50	4	-85	-17*	68
Cu	-85	-104	-19	-60	-18*	42
Zn	-24	-38	-14	-24	-21*	3

* Gas atom not adsorbed on metal

Difference in Binding Energies (ΔΔE)



Conclusions

- Metal matters!
- Trend consistent in two MOFs
- Focus on early transition metals
- Other metals
  - First-row vs second-row transition metals?
  - Main group metals?
  - Alkaline earth metals?
- Develop force fields
  - Classical simulations to model O_2 and N_2 adsorption
- Synthesis, apply to separation of air for oxyfuel production

Acknowledgments

Noble gas project

- Jeffery Greathouse
- Mark Allendorf
- Stephanie Teich-McGoldrick

Oxyfuels project

- Jeffery Greathouse
- Tina Nenoff
- Dorina Sava Gallis

- David Sholl
- Hakan Demir