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# Using Metal-Organic Frameworks to Capture and Store Noble Gases

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*Sandia National Laboratories*

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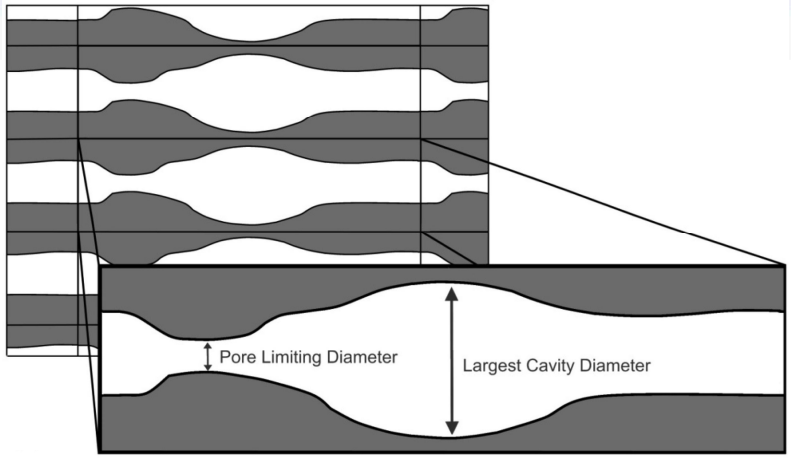
# Capturing noble gases

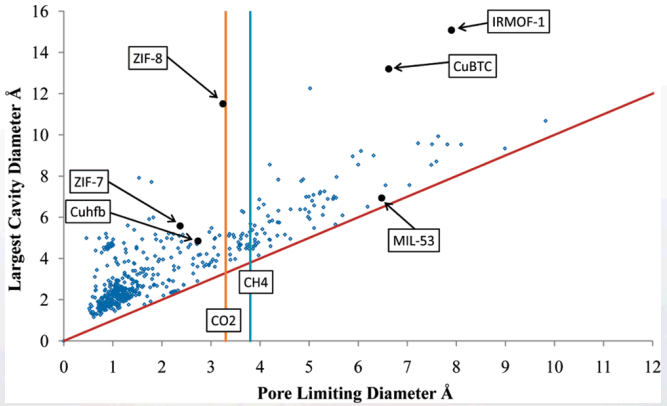
- Noble gases
  - Colorless
  - Odorless
  - Low natural abundance
  - Very low reactivity
- Weakly interacting noble gases adsorb onto MOFs by van der Waals interactions
- Use MOFs to capture and store noble gases

| Gas | Concentration in air | |
|---|---|---|
| Nitrogen | 78.09% | |
| Helium | 0.00052% | 5.2 ppm |
| Neon | 0.00182% | 18.2 ppm |
| Argon | 0.934% | 9340 ppm |
| Krypton | 0.00011% | 1.1 ppm |
| Xenon | 0.000009% | 0.09 ppm |
| Radon | | 6E-14 ppm |

# Screening MOFs

- Over 2000 MOFs known
  - Specific surface area
  - Pore-limiting diameter (2 to 47 Å)
  - Cavity volume
  - Flexibility
  - Metal (Zn, Cu, others)
  - Open metal sites
  - Reactive functional groups
  - Charge distribution




- How to rapidly screen MOFs for noble gas adsorption?

Haldoupis, E.; Nair, S.; Sholl, D. S. *J. Am. Chem. Soc.* **2010**, *132*, 7528-7539.

# Screening methods

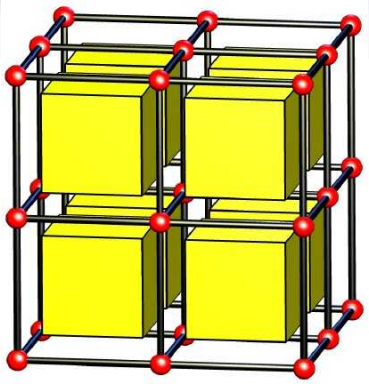
- Grand Canonical Monte Carlo simulations
  - Classical simulations implemented through Towhee code
  - Used to predict noble gas adsorption isotherms at room temperature
- 16 MOFs examined
  - **pcu** (5)
  - **nbo** (5)
  - **rht** (3)
  - **sod** (1)
  - **seh** (1)
  - **tbo** (1)

| Gases |
| --- |
| Nitrogen |
| Argon |
| Krypton |
| Xenon |
| Radon |

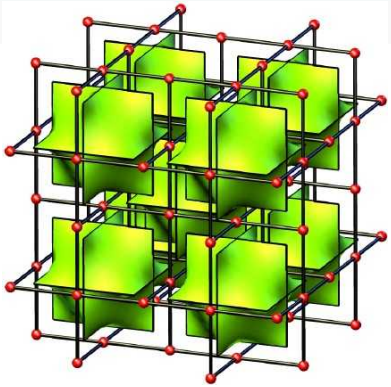
- Using simulations to guide synthetic work

http://towhee.sourceforge.net/

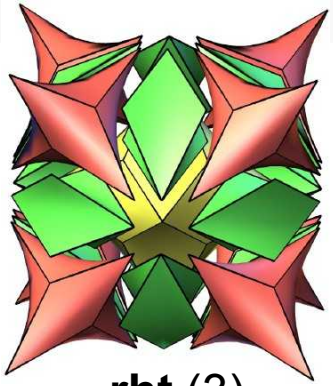
# MOFs examined



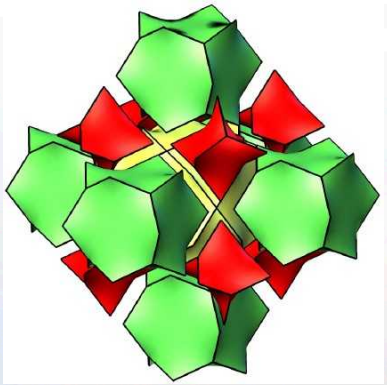
**pcu** (5)
IRMOF series
$Zn_4O$ cluster



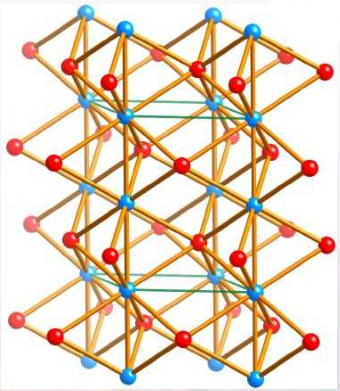
**nbo** (5)
NOTT-10x, PCN-14
$Cu_2$ cluster



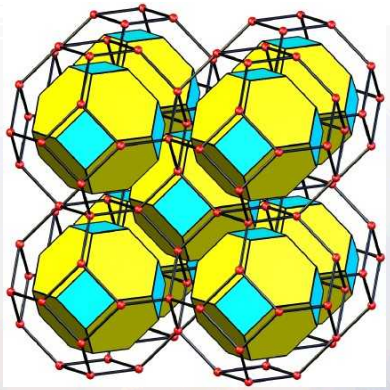
**rht** (3)
NOTT-11x, PMOF-2
$Zn_2$ or $Cu_2$ cluster



**tbo** (1)
HKUST-1
$Cu_2$ cluster



**seh** (1)
MIL-53(Al)
Al(OH) cluster

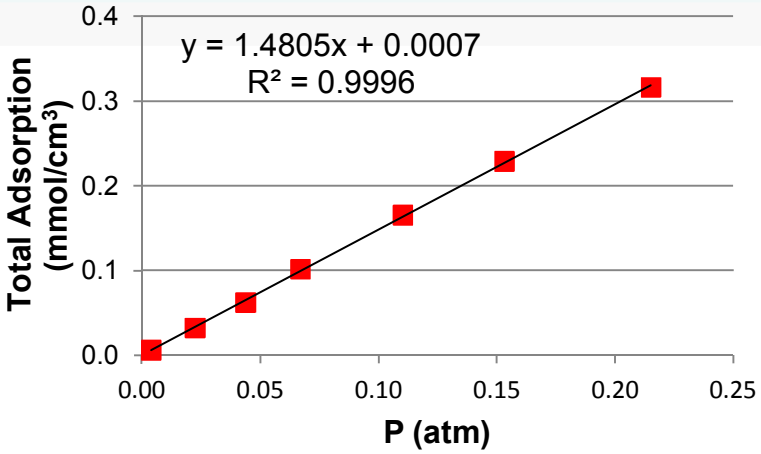


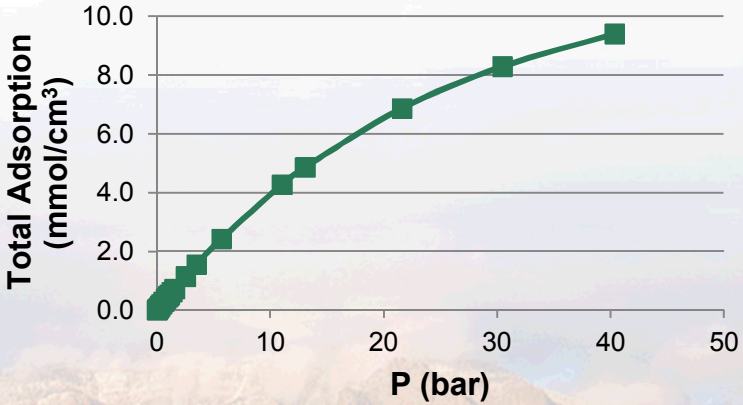
**sod** (1)
ZIF-8
Zn cluster

O'Keeffe, M.; Peskov, M. A.; Ramsden, S. J.; Yaghi, O. M. *Accts. Chem. Res.* **2008**, 41, 1782-1789.

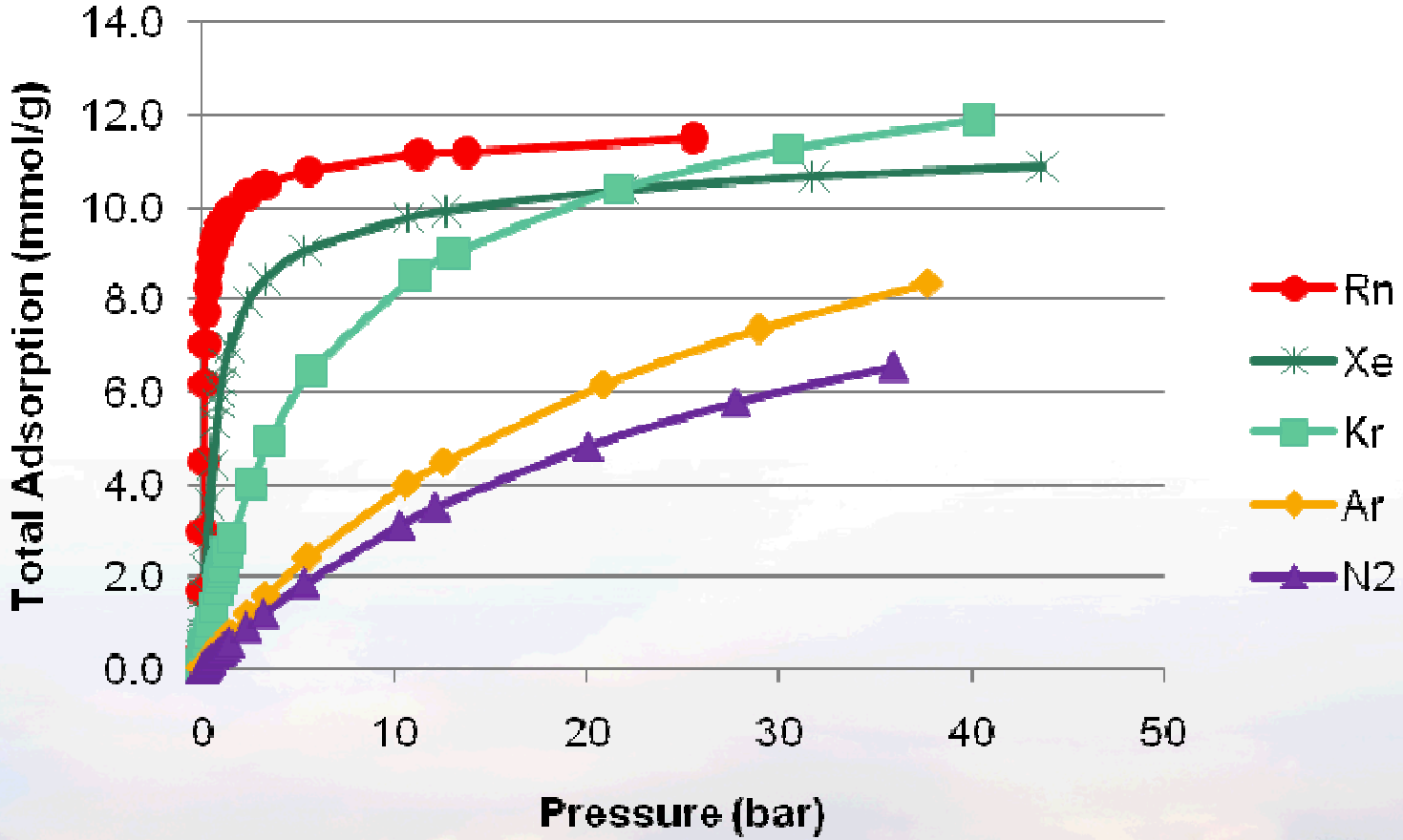
# Simulation results

- Henry's constant
  - Partitioning of gas between gas phase and gas adsorbed on the surface
- Adsorption energy
  - Energy released when first gas molecule adsorbs to the surface
- Isotherm plot
  - Plot of gas adsorbed on surface as a function of pressure, at a given temperature

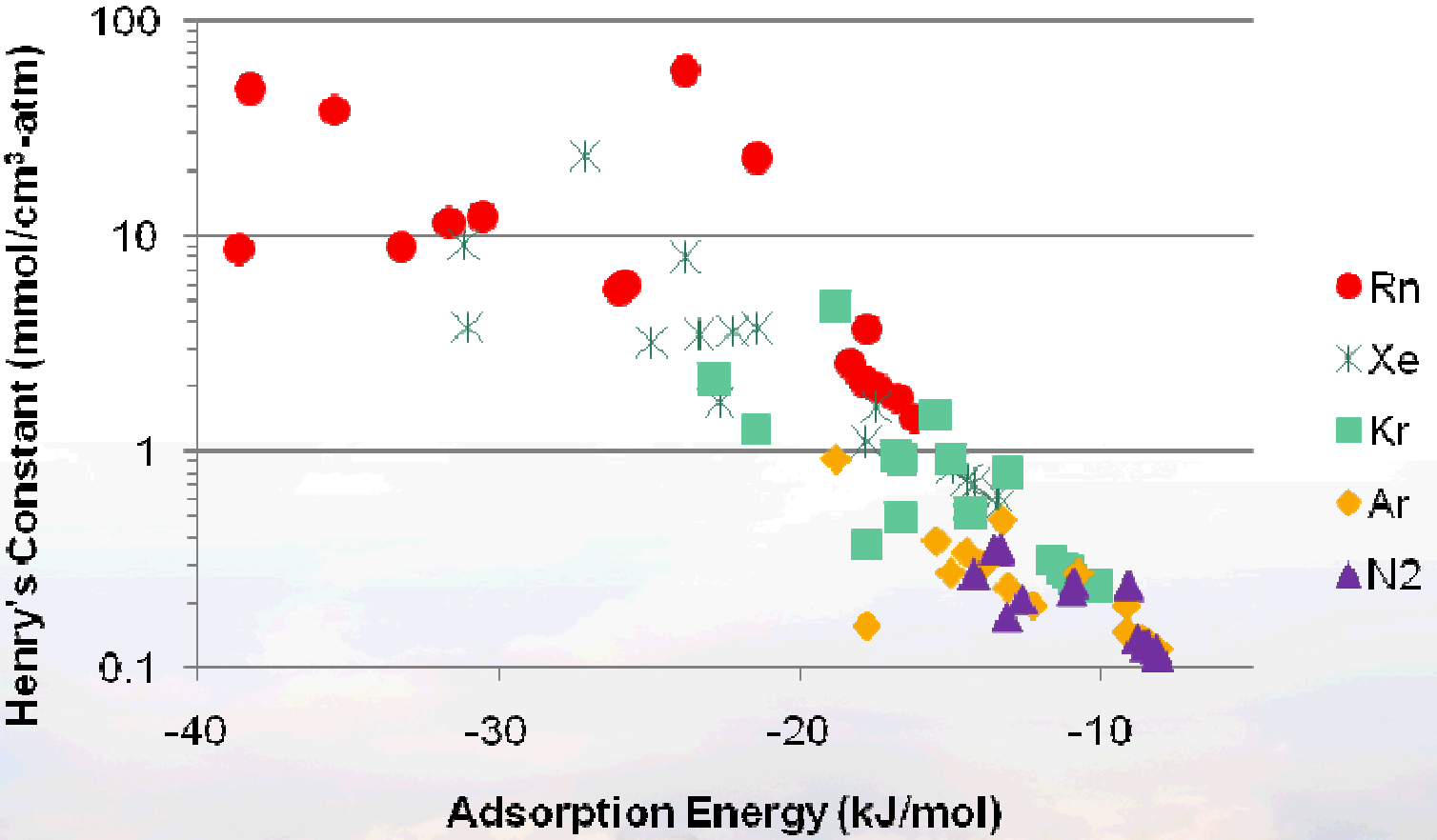


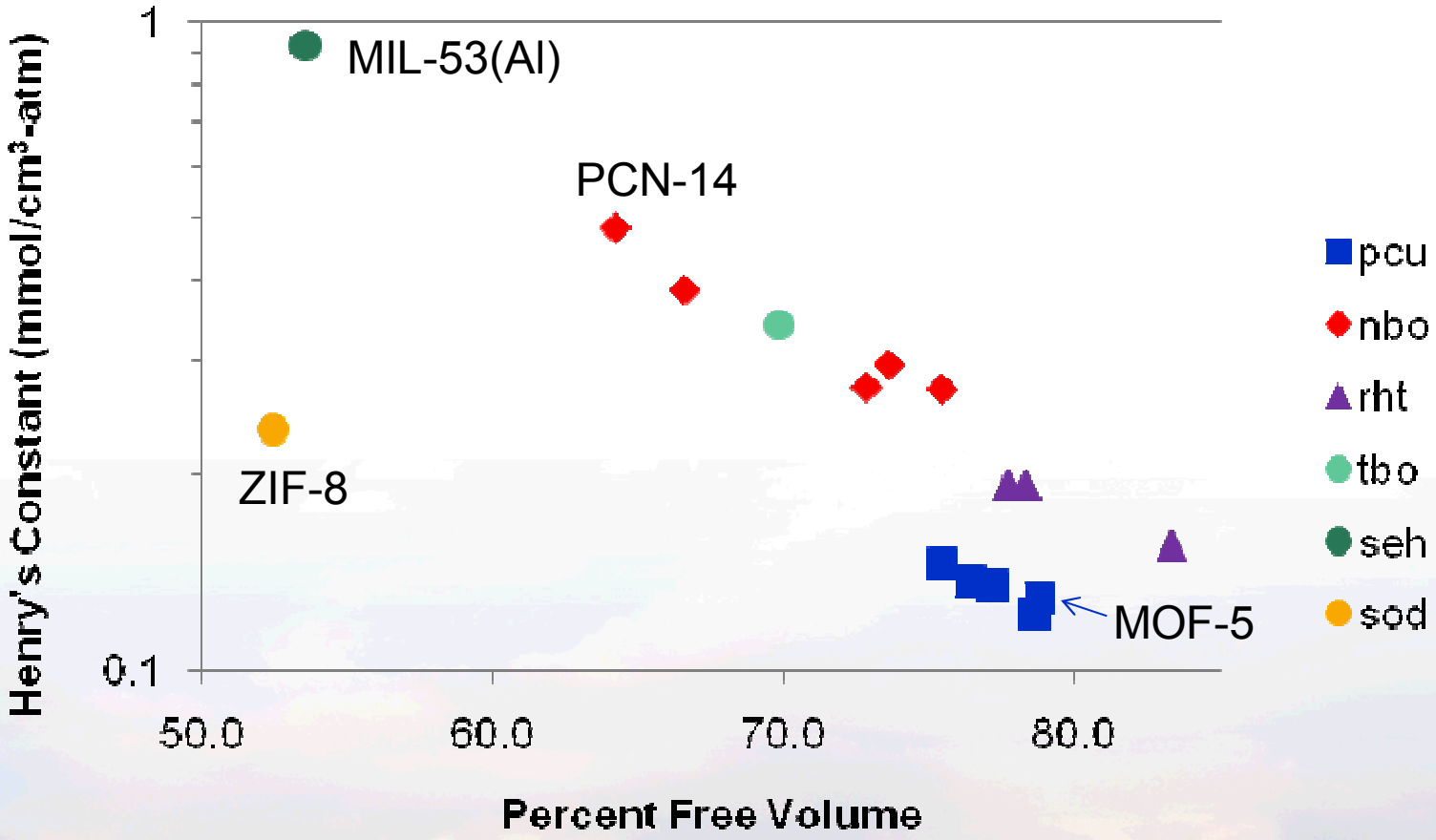
# Gas adsorption in PCN-14



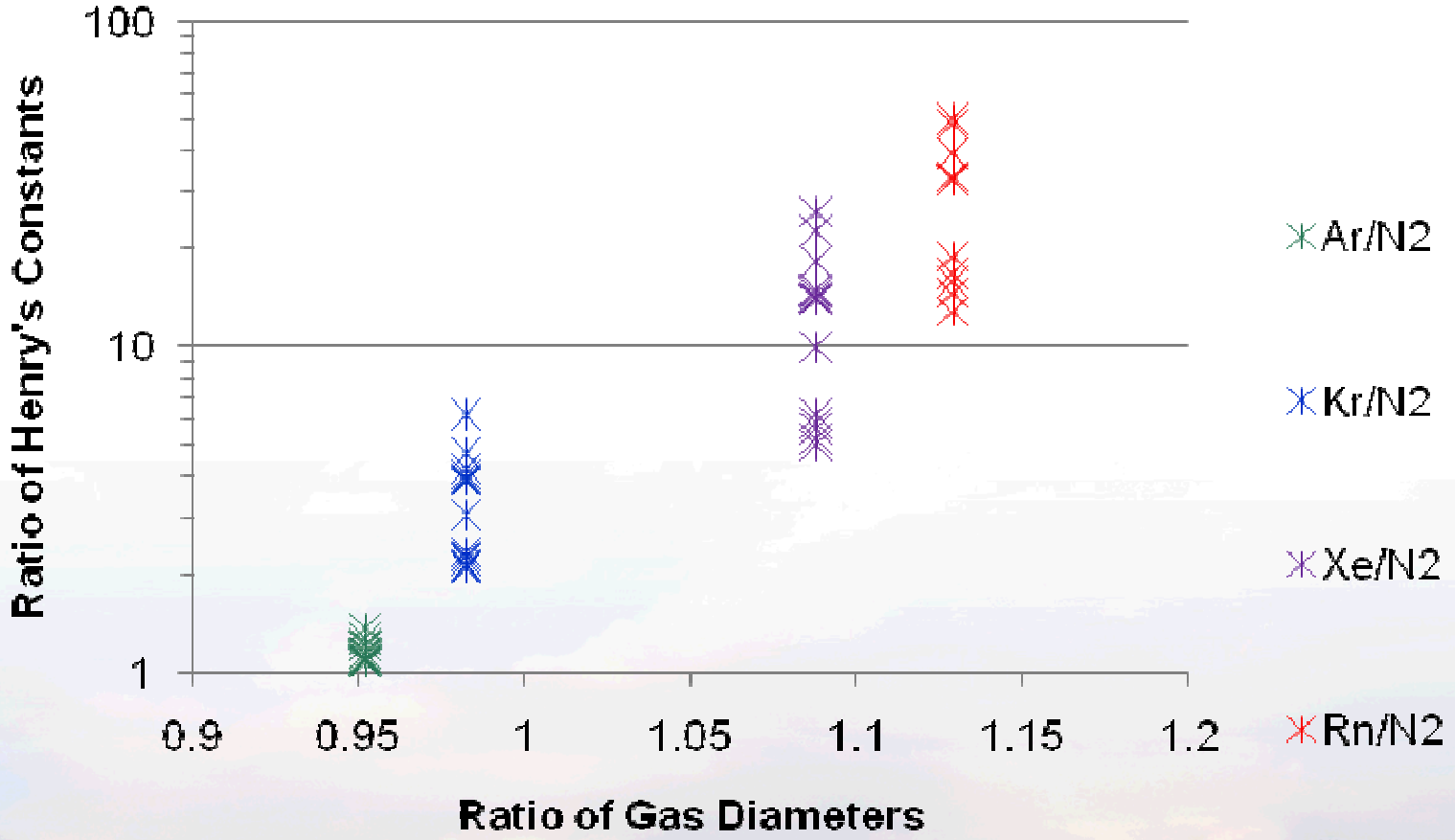
# Henry's constant and adsorption energy



# Gas adsorption trends, for argon



# Selectivity of noble gases over nitrogen



# Conclusions

- Simulated noble gas adsorption in 16 different MOFs
  - Henry's constants
  - Adsorption energies
  - Isotherm plots
- Heavier noble gases adsorb in MOFs more readily than lighter noble gases
- MOFs with smaller percent free volume have higher Henry's constants
- MOFs examined were selective for noble gases over nitrogen

# Acknowledgements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