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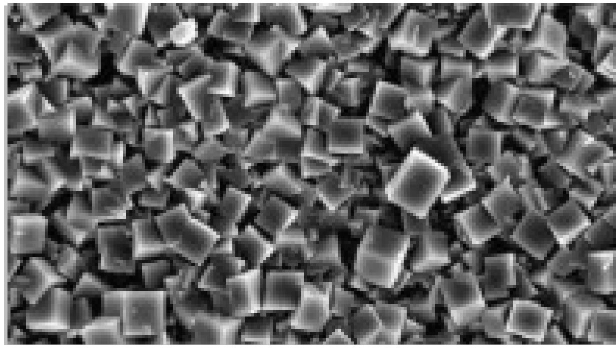

Importance of Flexibility in Simulating Gas Diffusion through Metal-Organic Frameworks

Marie V. Parkes,* Hakan Demir, David S. Sholl, Jeffery A. Greathouse, Mark A. Allendorf

Sandia National Laboratories, Georgia Institute of Technology

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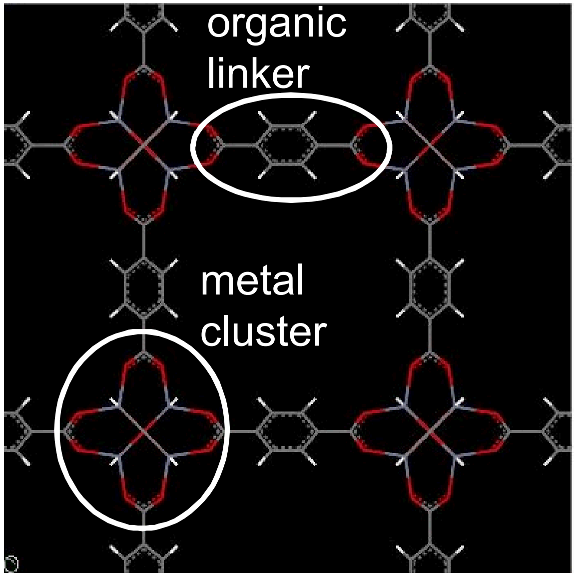
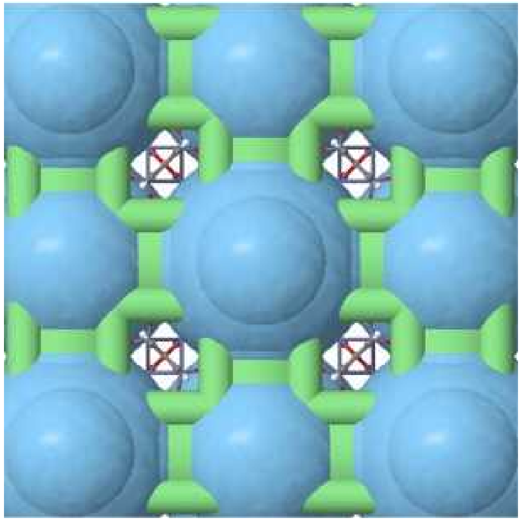
Metal-Organic Frameworks (MOFs)

- 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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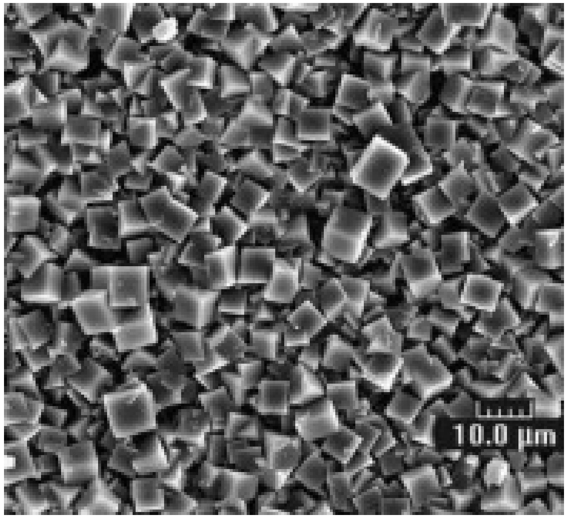

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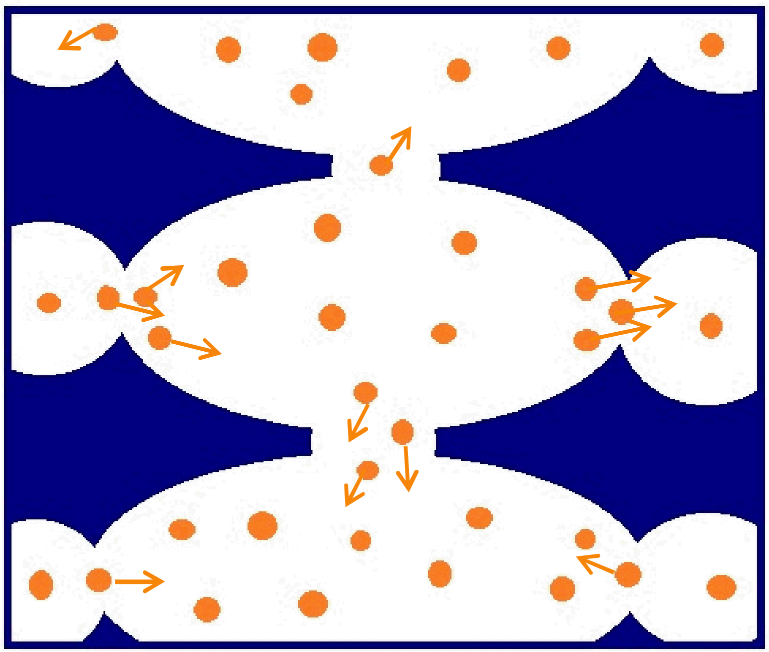
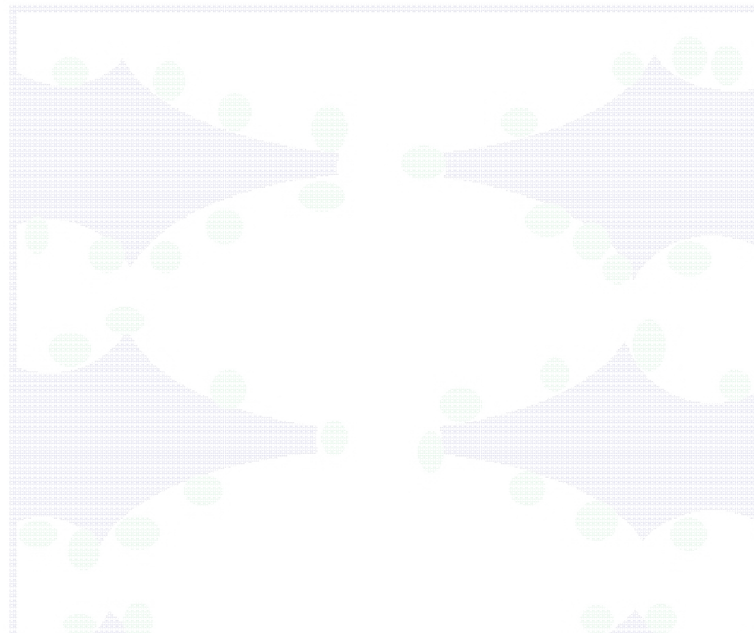
Separation of Gases in MOFs

Diffusion between MOF cages



Adsorption on MOF surface



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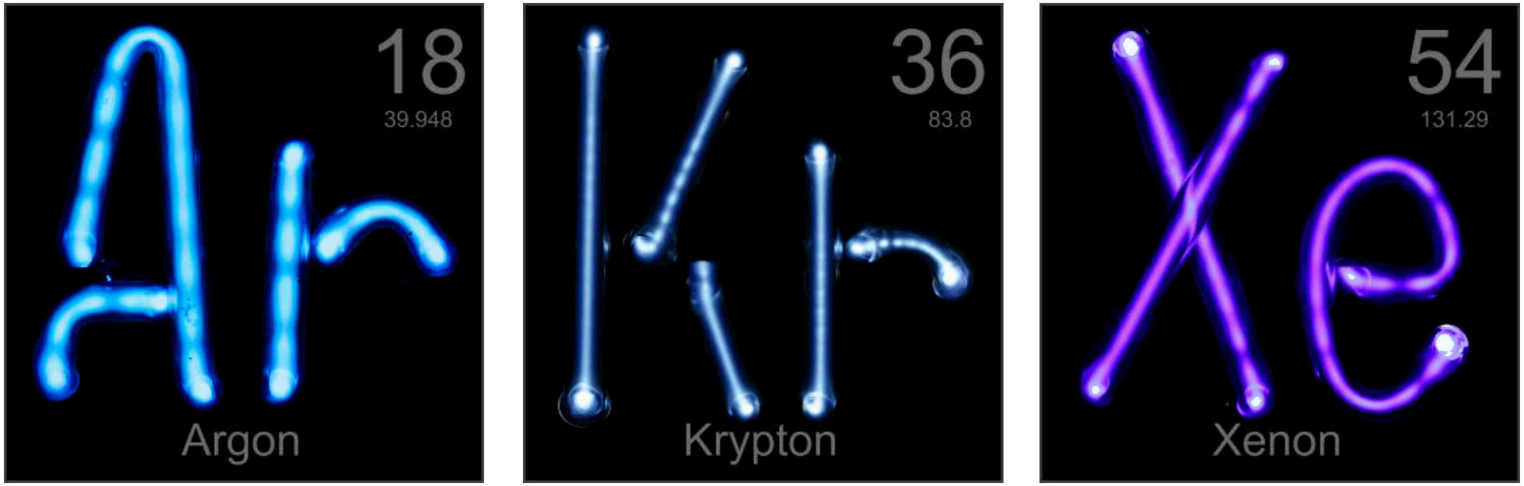
Noble Gas Separations



Stock photos from www.periodictable.com.

Noble gas uses:

- Cryogenic refrigerants
- Carrier gases
- Lighting
- Laser applications

Capture and separation are challenging:

- Low natural abundance
- Relatively inert

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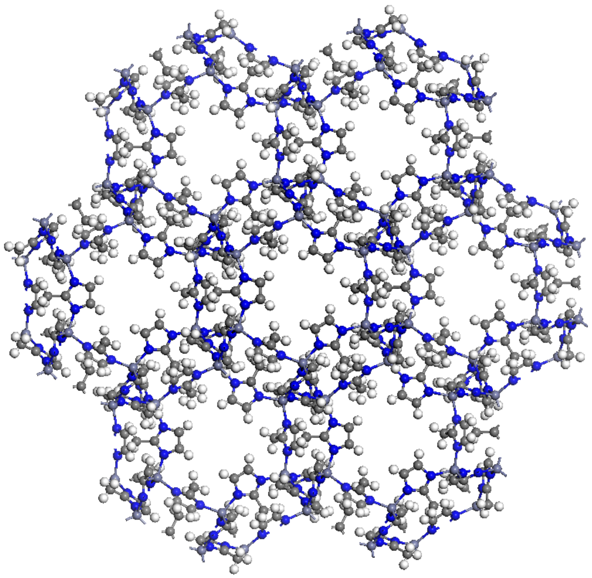
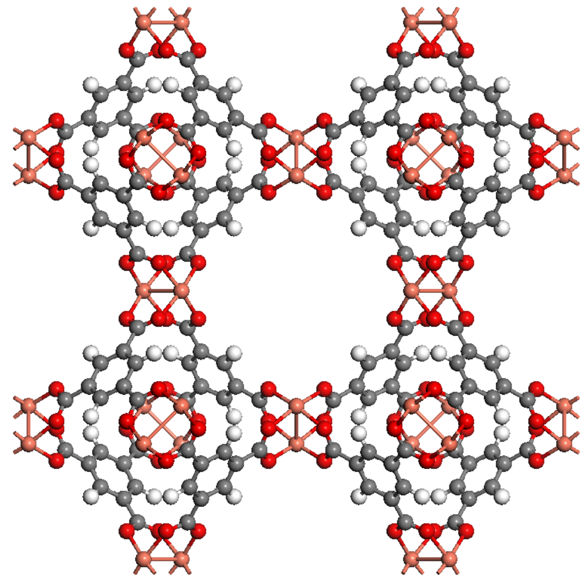
Noble Gas Diffusion



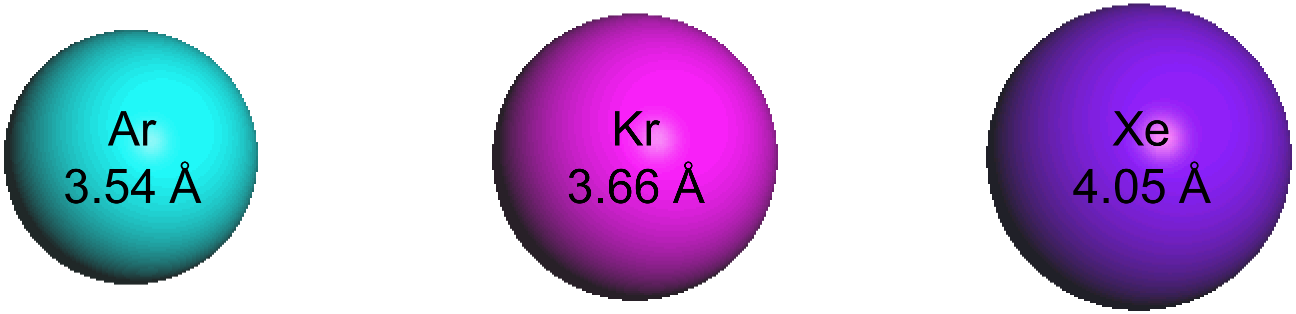


ZIF-8

- Window diameter 3.4 Å

HKUST-1

- Window diameters 4.1 Å, 6.9 Å



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Molecular Dynamics Simulations

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.

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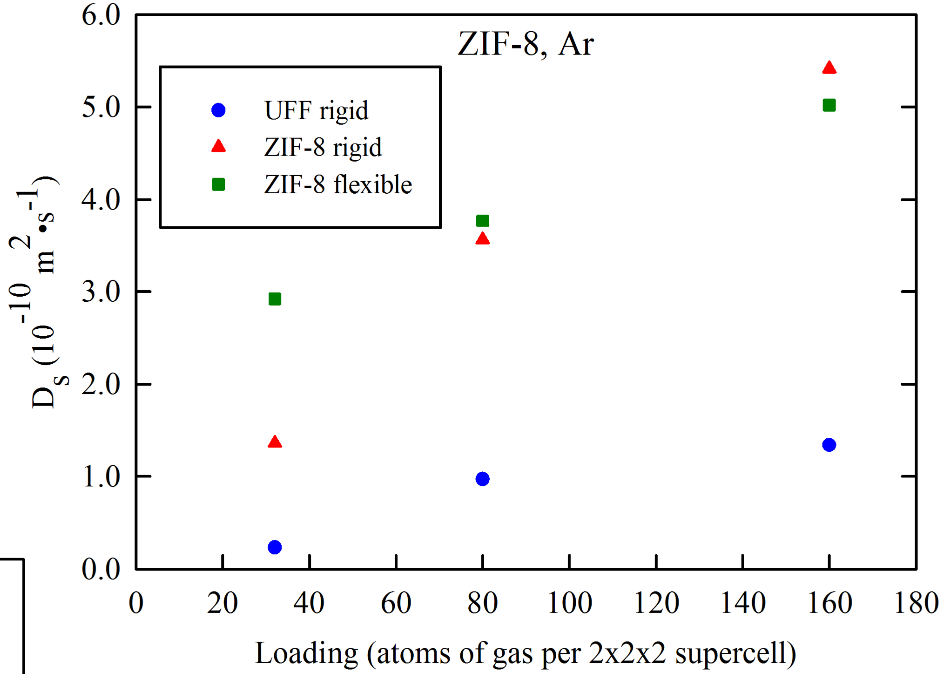
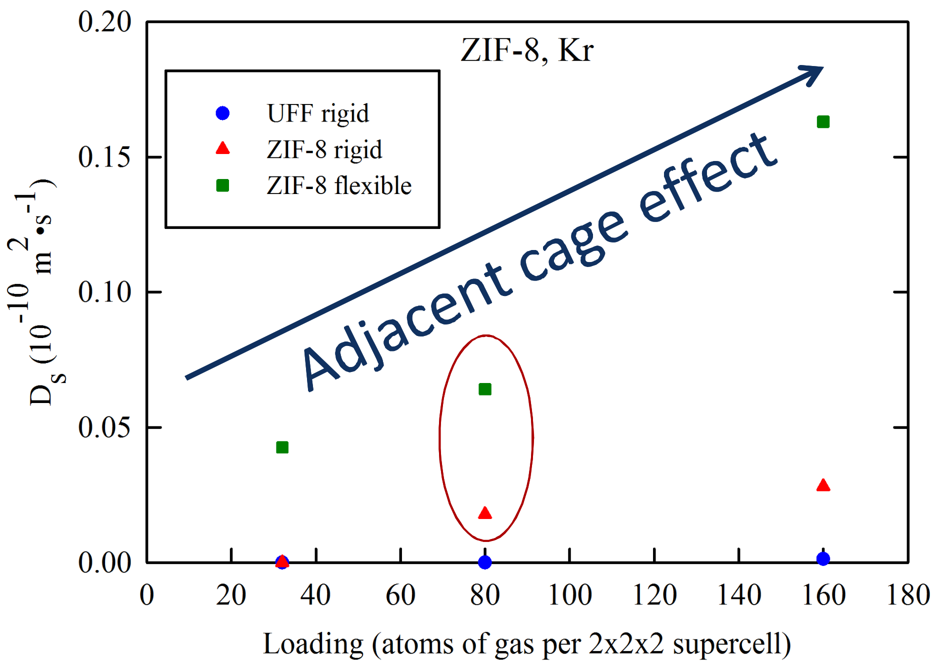
Diffusion in ZIF-8

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

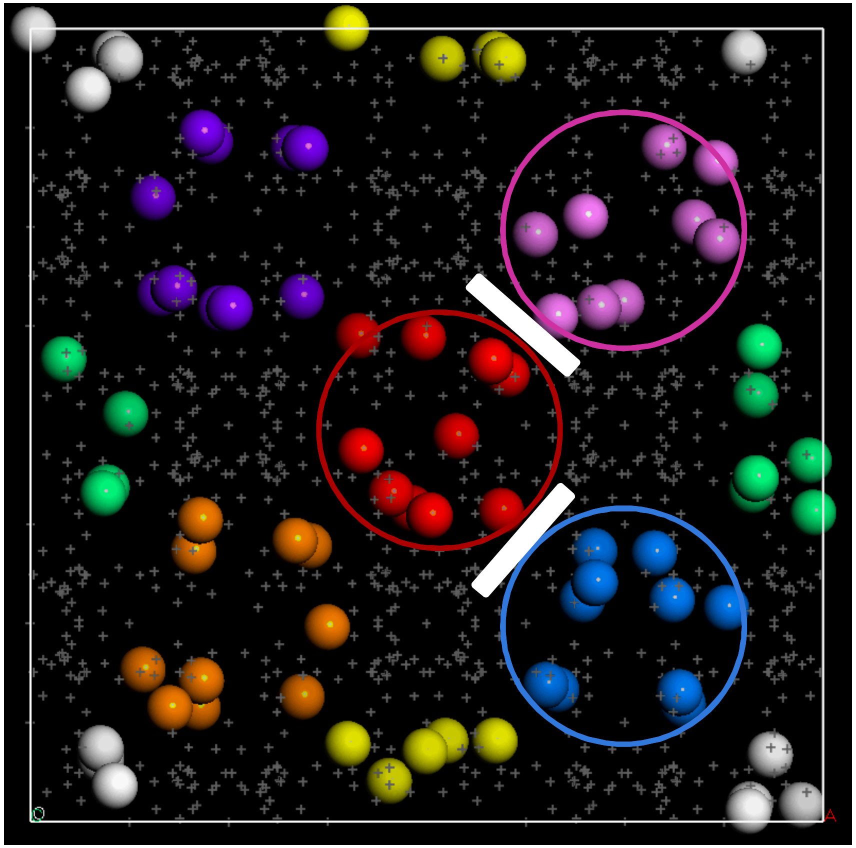




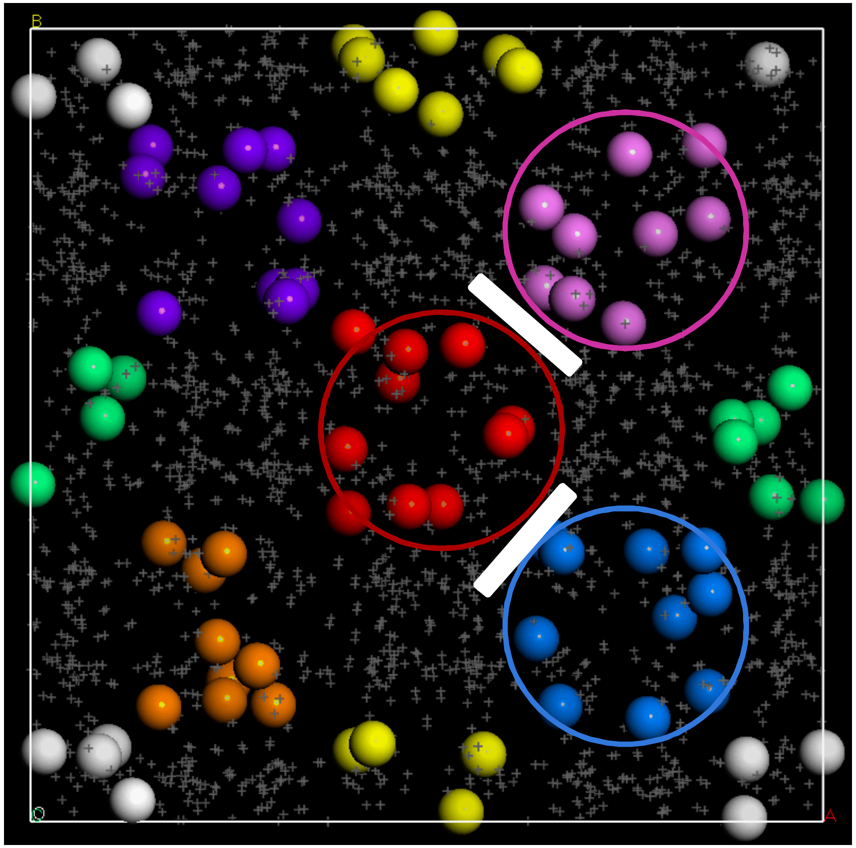
- Diffusion increases as loading increases (adjacent cage effect)
- Diffusion is greatest with flexible force field

Kr Diffusion in ZIF-8

Rigid



Flexible



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Kr Diffusion in ZIF-8

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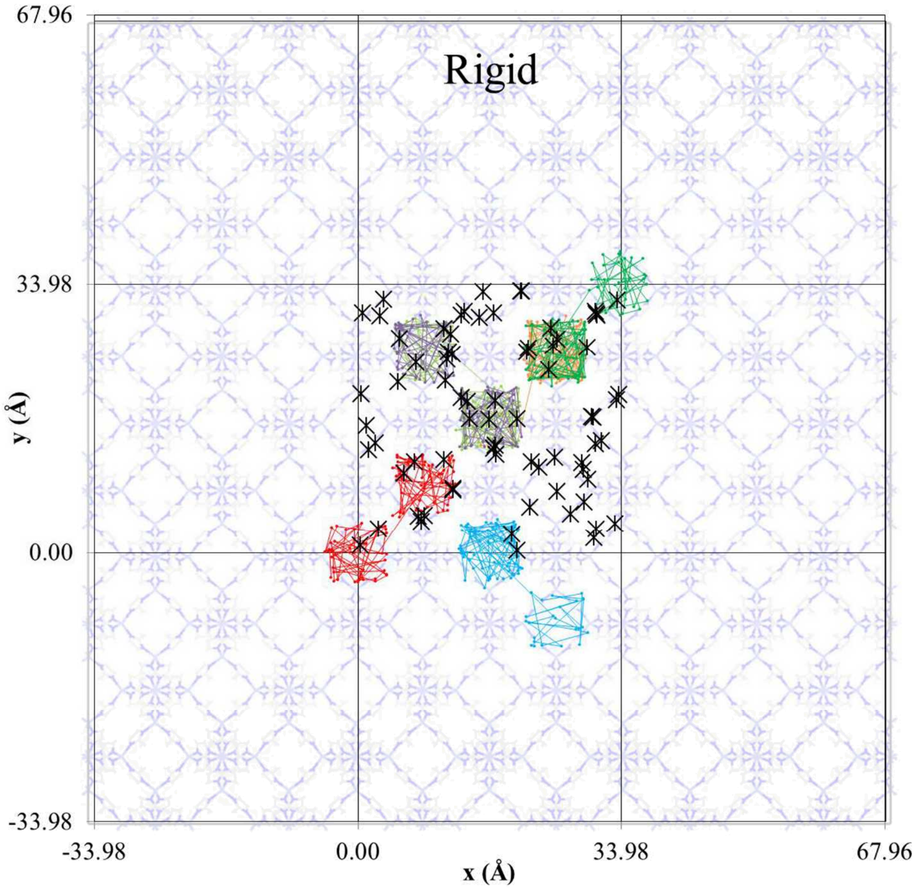
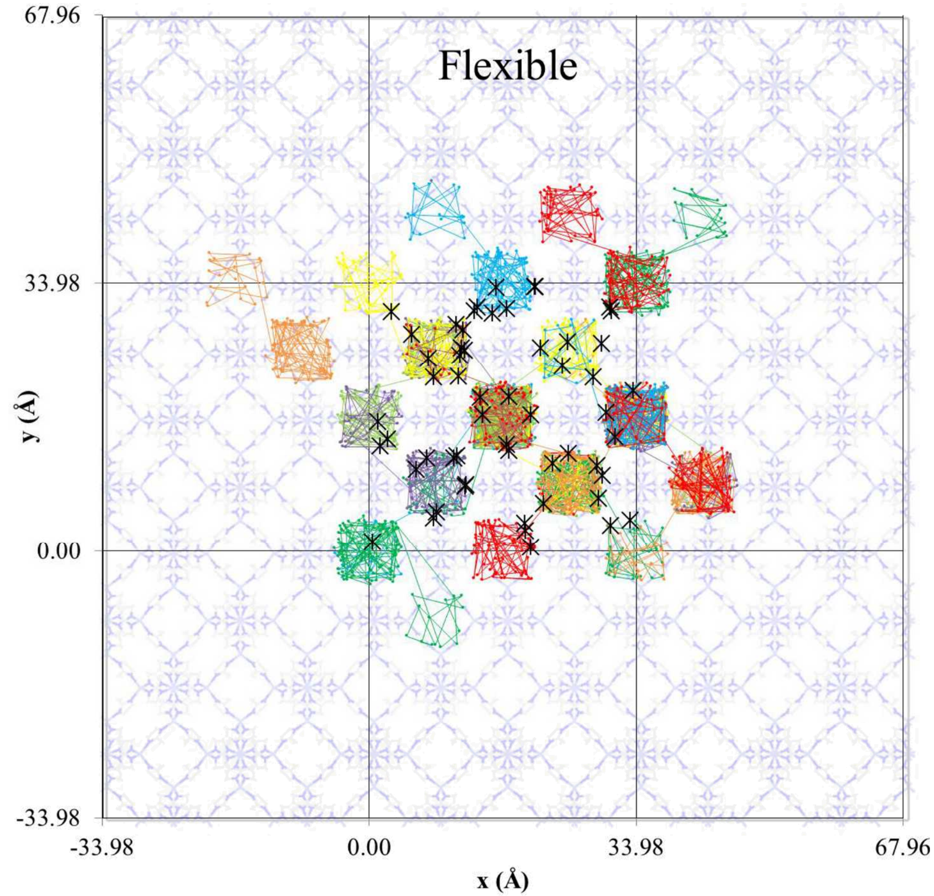
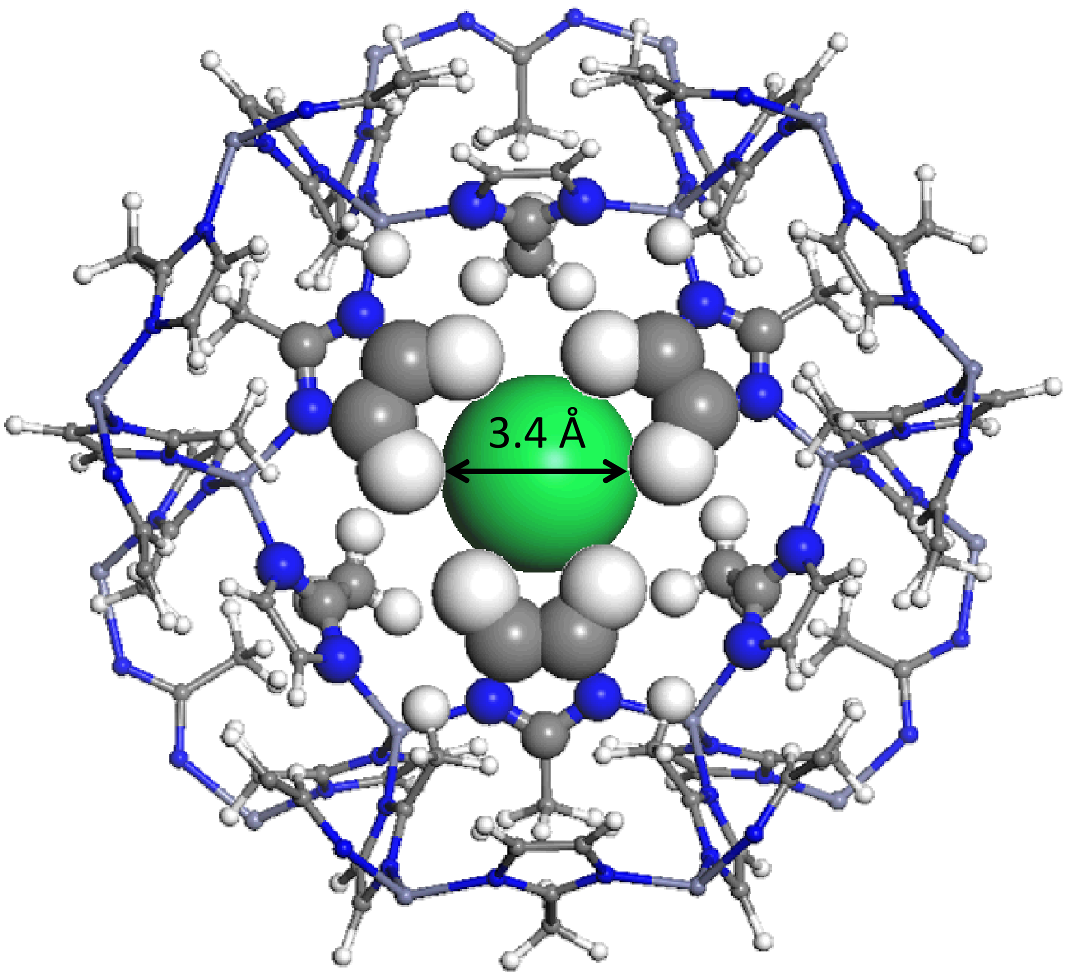
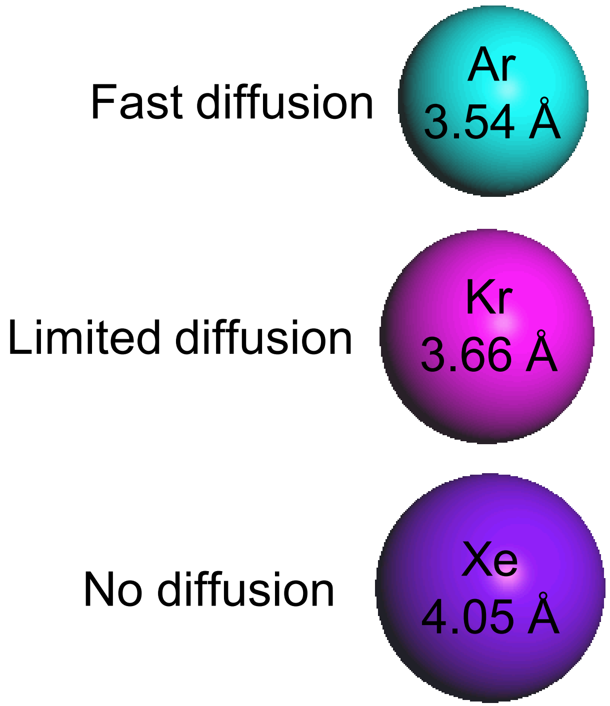




Kr Diffusion in ZIF-8





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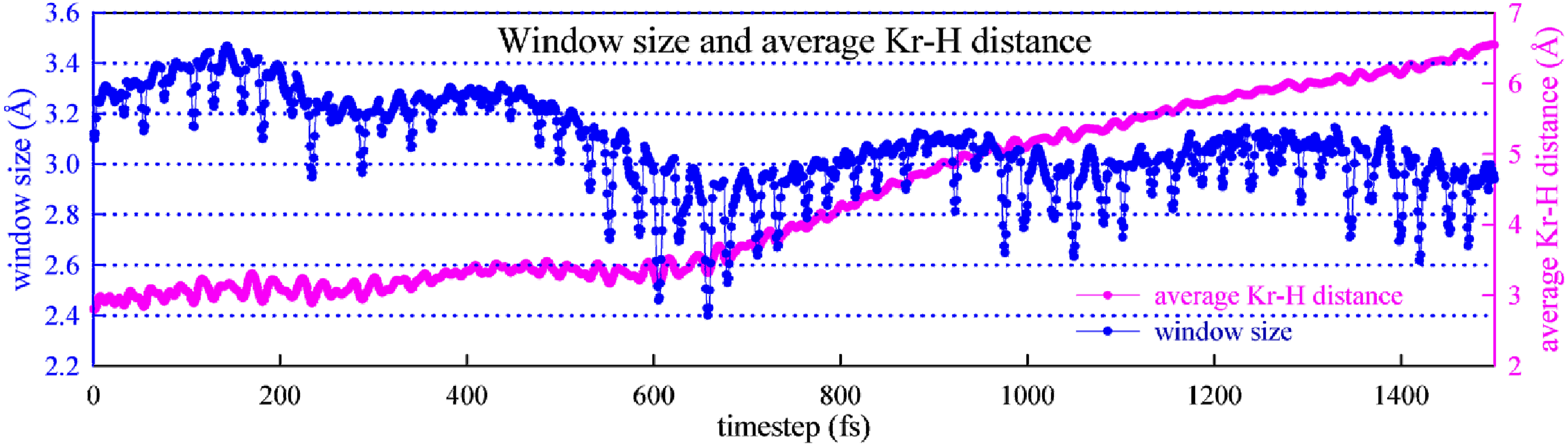
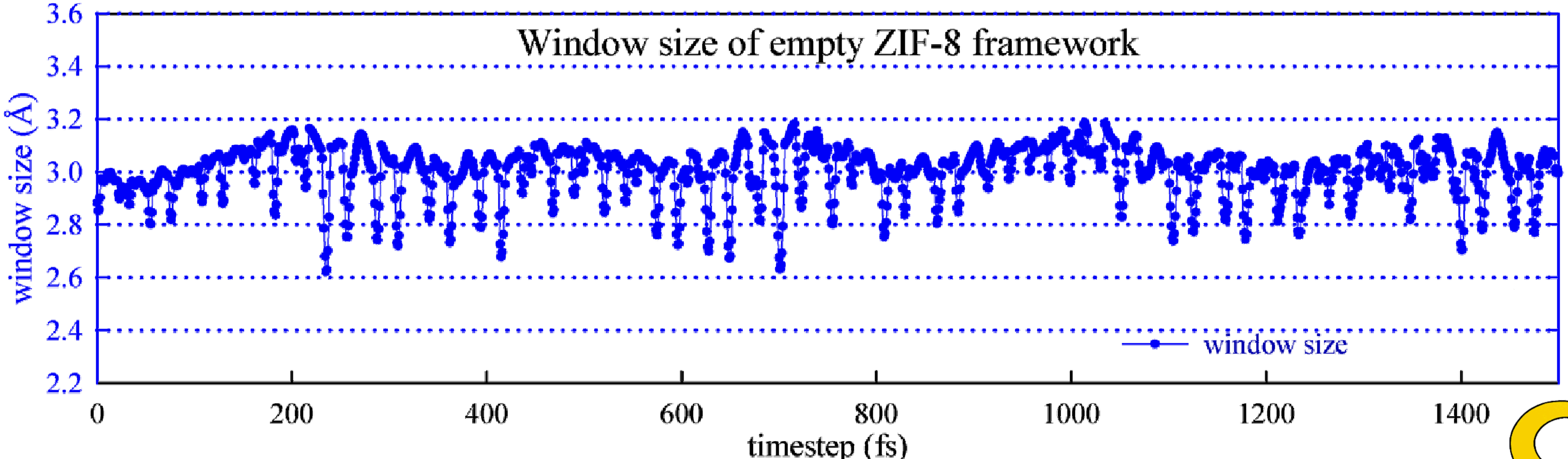
Kr Diffusion in ZIF-8





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Conclusions

- Accurate description of guest diffusion in MOFs requires
  - MOF-specific force fields
  - Flexible frameworks (when MOF windows and guests are similar in size)
- 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

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Acknowledgments

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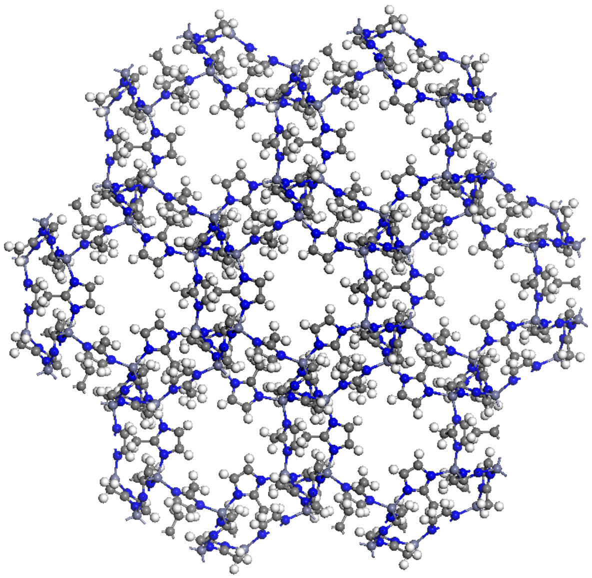
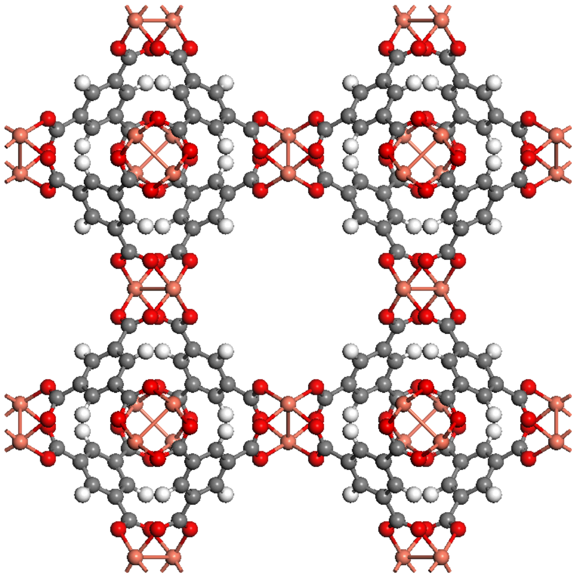
Noble Gas Diffusion



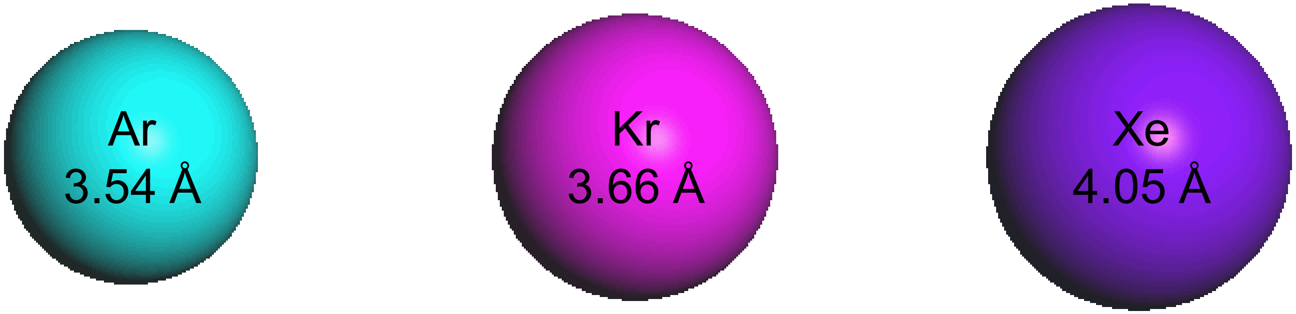
ZIF-8

- Window diameter 3.4 Å



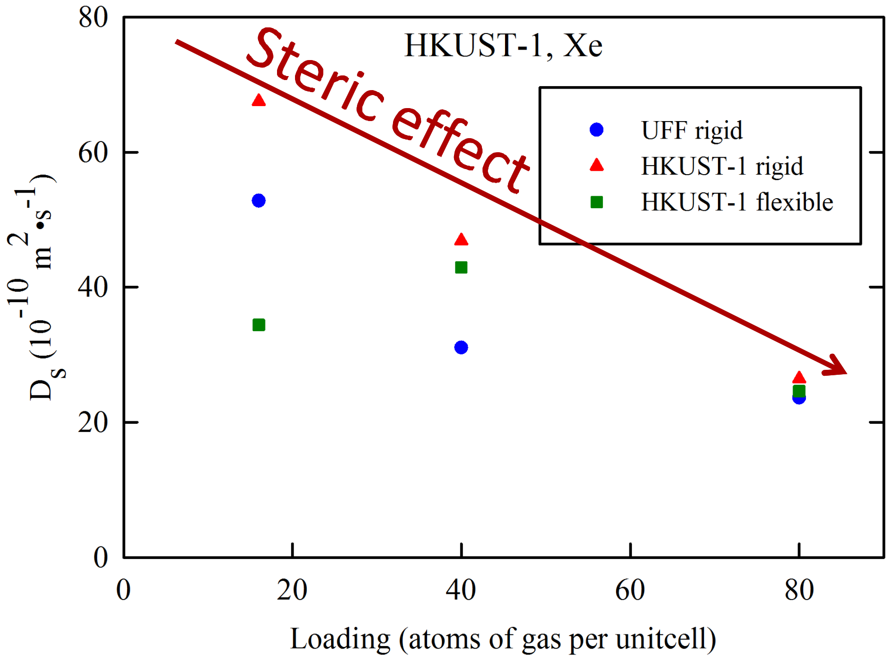
HKUST-1

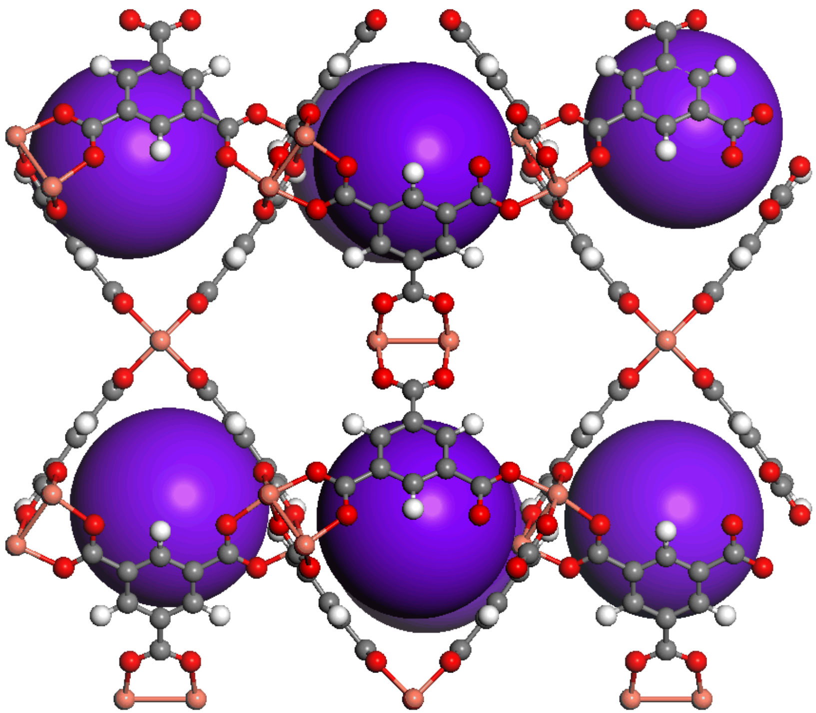
- Window diameters 4.1 Å, 6.9 Å



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)

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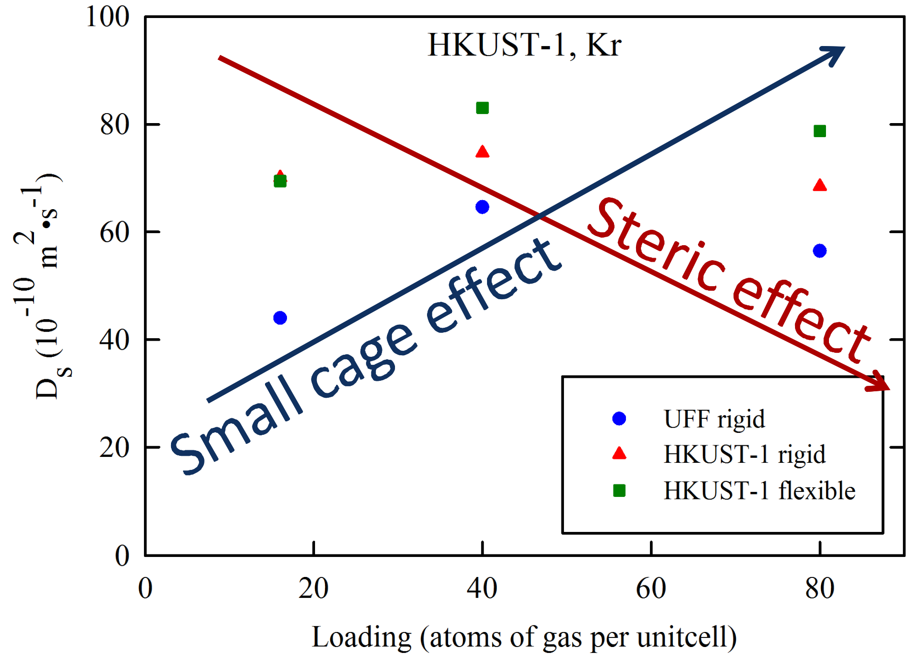
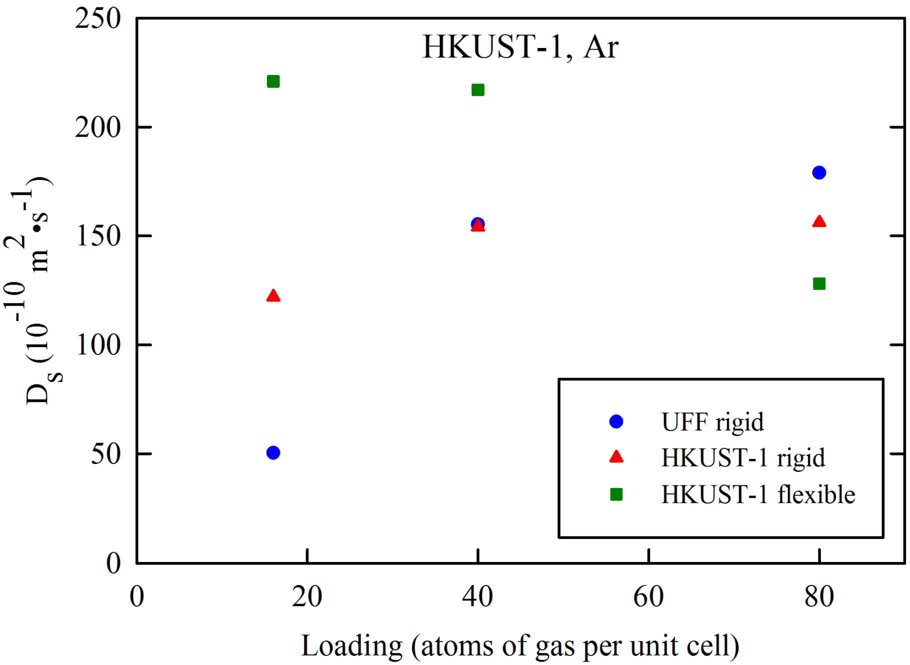
Kr/Ar Diffusion in HKUST-1

- Diffusion is greatest with flexible force field





- Loading dependence: steric effect and small cage effect compete

Conclusions

- Accurate description of guest diffusion in MOFs requires
  - MOF-specific force fields
  - Flexible frameworks (when MOF windows and guests are similar in size)
- 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

Acknowledgments

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