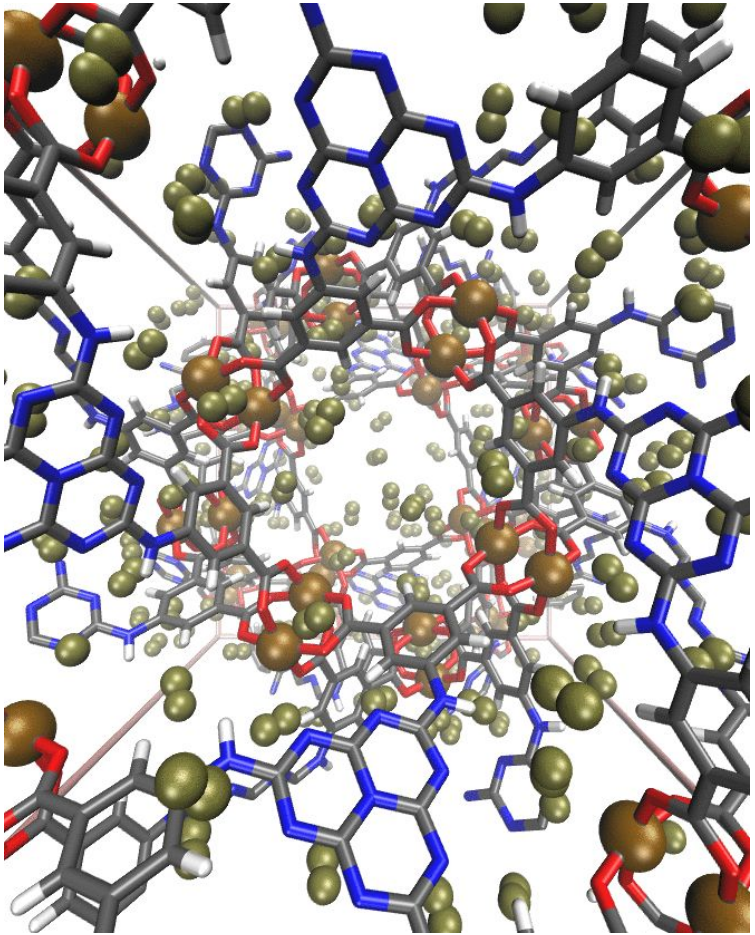
Simulations of gas sorption in rht-MOF-9

Or,

Monte-Carlo molecular-mechanical simulations of H_2, CO_2, CH_4, C_2H_2, C_2H_4, and C_2H_6 sorption in the metal-organic framework Cu_3[2,5,8-tris(3,5-dicarboxyphenylamino)-1,3,4,6,7,9,9b-heptaazaphenalene]

H_2 (tan diatomics) in rht-MOF-9 @ 77K, 1.0 atm →



Douglas M. Franz, University of South Florida

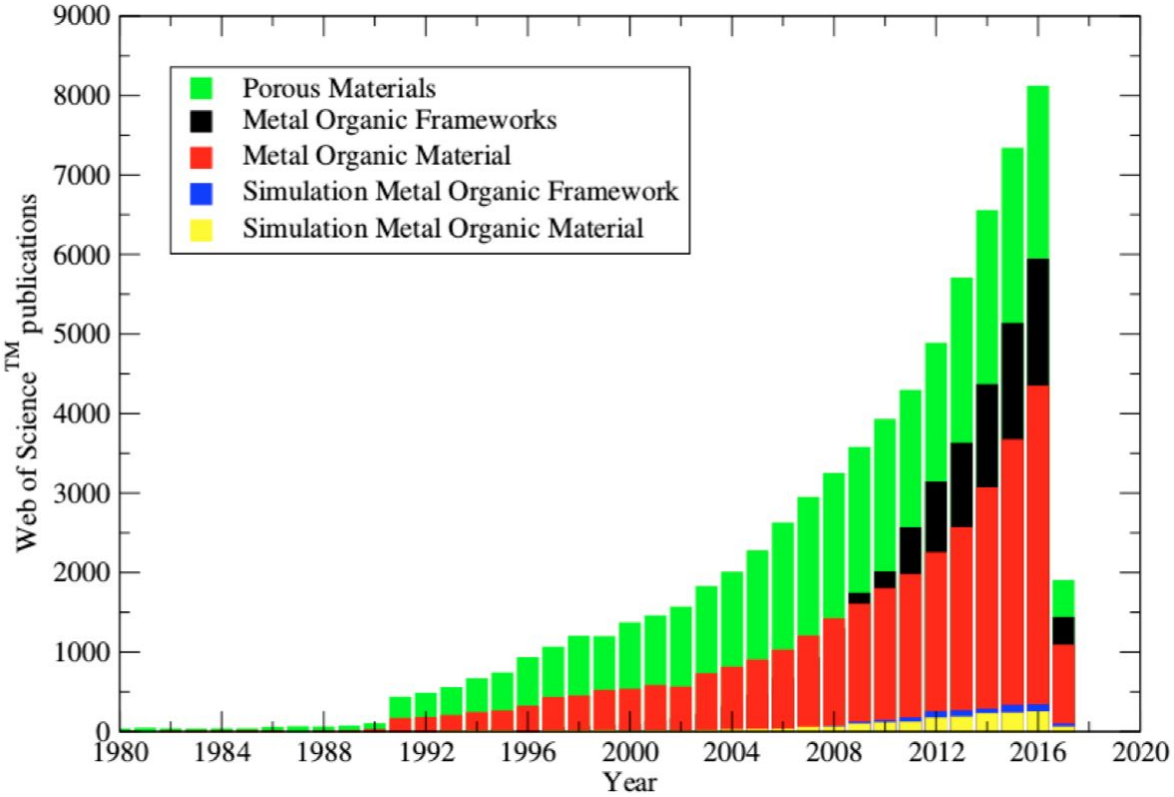
The Space group

Cadets from left → right:
Brant Tudor, Adam Hogan, Dr. Tony Pham, Dr. Chris Cioce (warped to Sandia NL), Prof. Brian Space, Dr. Sameh Elsaidi + Mona Mohamed + young-one (warped to PNNL), Douglas Franz, Taylor Harris (changed space-station), Katherine Forrest

What we’re going to look at

1. What is rht-MOF-9?
2. Gas uptake modeling compared w/experiment
3. Gas uptake mechanism of sorption discovered from simulation

Growing interest metal-organic frameworks

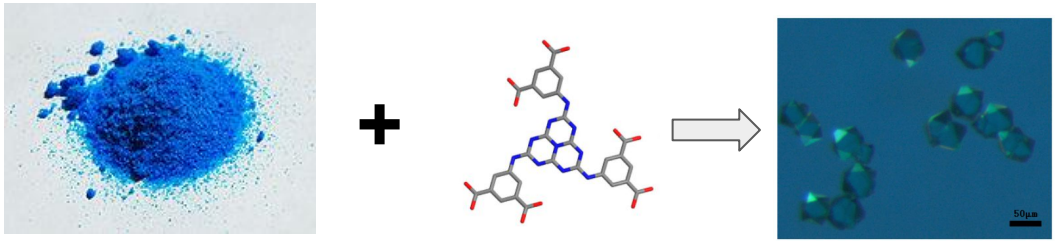


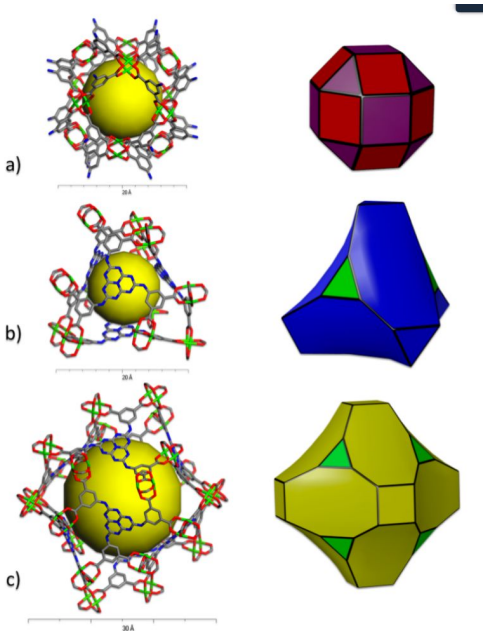
*2017 bars as of April 13.

← Simulation of porous materials is relatively new

A profile of rht-MOF-9

- Being in the *rht*- geometry class of crystals, it has 3 distinct cages:
  - a) rhombicuboctahedral (~20 Å)
  - b) truncated tetrahedron (~20 Å)
  - c) augmented rhombic dodecahedron (~30 Å)
- Blue octahedral macro-crystals
- Reported in early 2014
- One of the best CO_2 and H_2 “nanosponges” to-date.
- Synthesized from Cu (II) nitrate and TDCPAH





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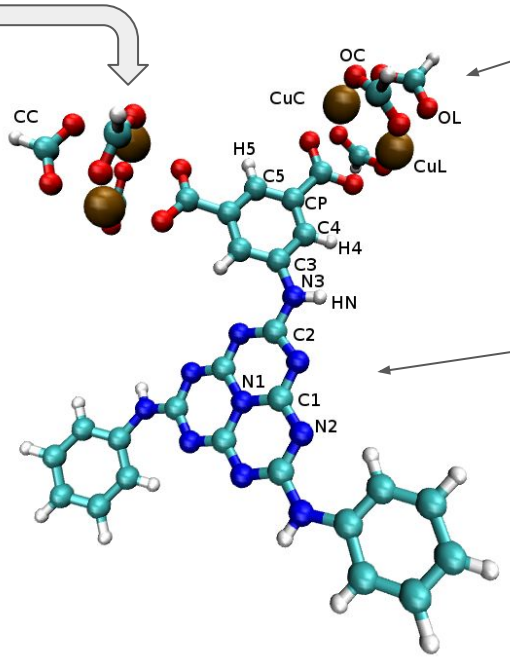
rht-MOF-9 : the building blocks

Charges:
CuC: 1.31
CuL: 1.43
(HF 6-31G*)

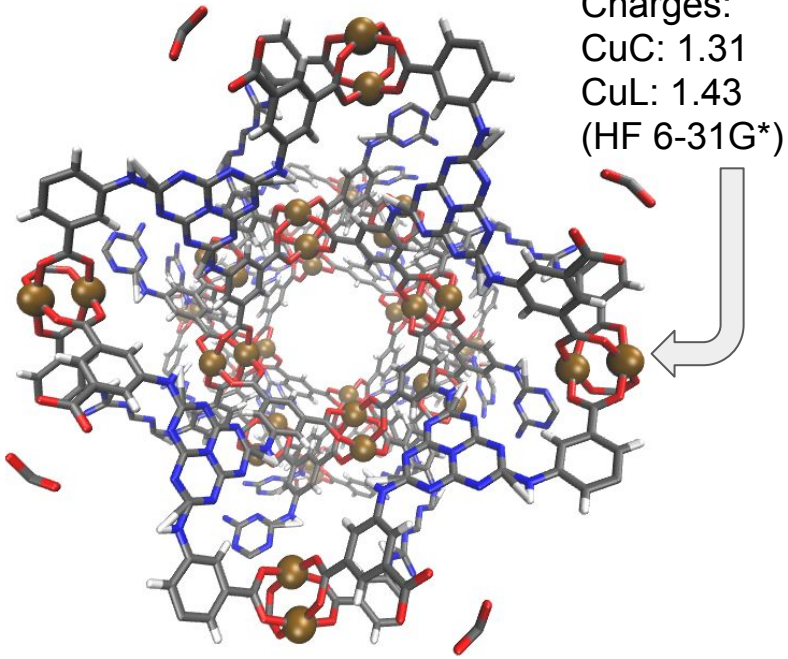


Cu paddlewheel cluster

TDCPAH (organic linker)

rht-MOF-9 > NOTT-112

- 2.6 wt% H_2 uptake at 77K / 1atm
  - 6.9 kJ/mol Qst at zero-loading



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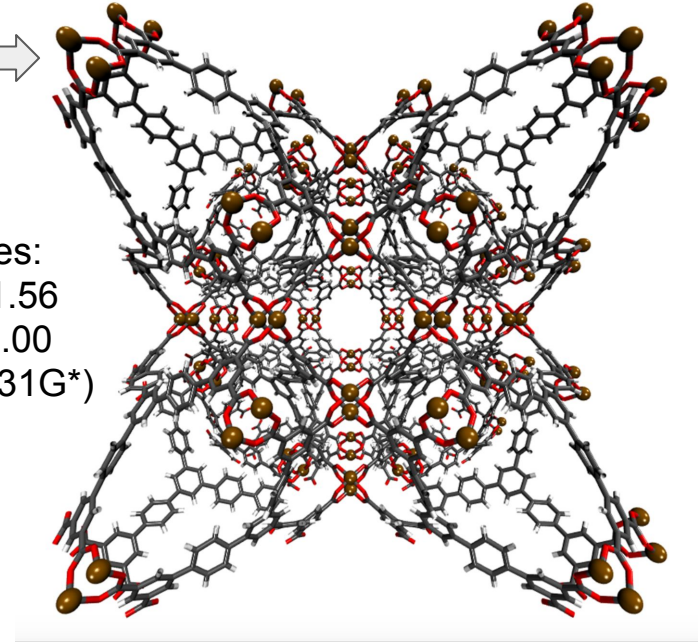
- 2.3 wt% H_2 uptake at 78K / 1atm
  - 5.7 kJ/mol Qst at zero-loading

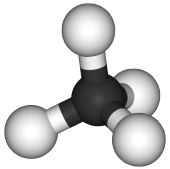
Charges:
CuC: 1.56
CuL: 1.00
(HF 6-31G*)



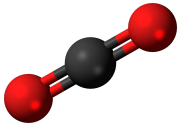
Franz, Douglas, et al. "Accurate H2 Sorption Modeling in the rht-MOF NOTT-112 Using Explicit Polarization." *Crystal Growth & Design* 16.10 (2016): 6024-6032.

Yan, Yong, et al. "Exceptionally high H 2 storage by a metal–organic polyhedral framework." *Chemical Communications* 9 (2009): 1025-1027.

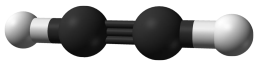
Gases of interest



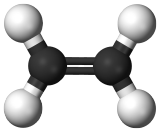
CH_4: The major component (80-95%) of natural gas; useful for production of chloromethanes, acetylene, etc.



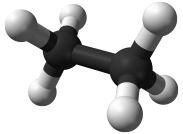
CO_2: Poisons the Li/MgO catalyst for methane to ethane/ethylene (separation from CH_4 is desirable)



Acetylene



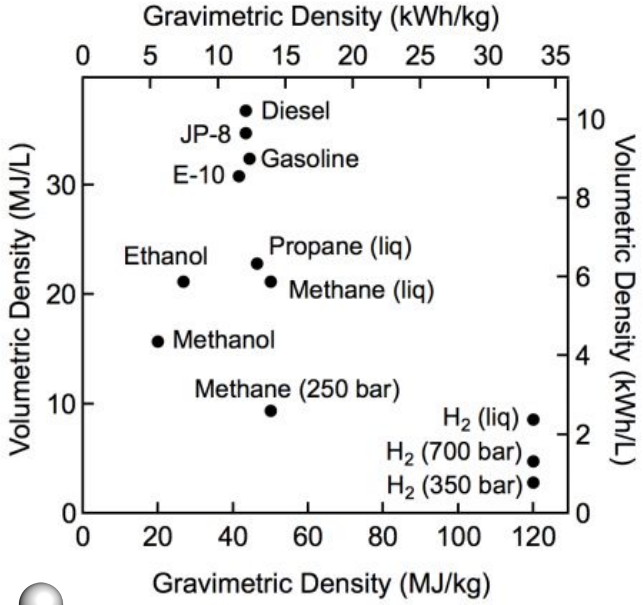
Ethylene



Ethane

Main impurities in naturally occurring methane.

rht-MOF-9 has high selectivity of CO_2, C_2H_2, C_2H_4, C_2H_6 over methane.

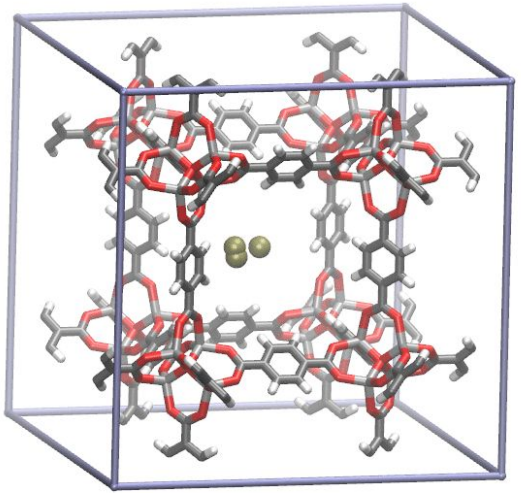


H_2 is the highest-energy producing fuel by mass but not by volume, so we want to densify it.

https://energy.gov/eere/fuelcells/hydrogen-storage

Classical Grand Canonical (GC) Monte Carlo (MC) Simulations

- MC is not Molecular Dynamics
- Time is not a part of equations
- μVT (GC) simulation has constant:
  - Chemical potential $\mu = \delta E/\delta N$
  - Volume
  - Temperature
- Energy is calculated by:
  - $U = U_{rd} + U_{es} (+ U_{pol})$
    - Like this...



How energy is calculated for each system state

$$U_{FH} = U + \frac{\beta\hbar^2}{24\mu}\left(U'' + \frac{2}{r}U'\right) + \frac{\beta^2\hbar^4}{1152\mu^2}\left(\frac{15}{r^3}U' + \frac{4}{r}U''' + U''''\right)$$

$$U_{LJ} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

U_{rd}

$$U_{Coulomb} = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{r}$$

U_{es}

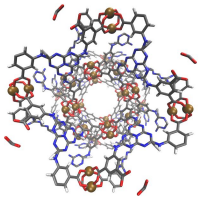
U_{pol}

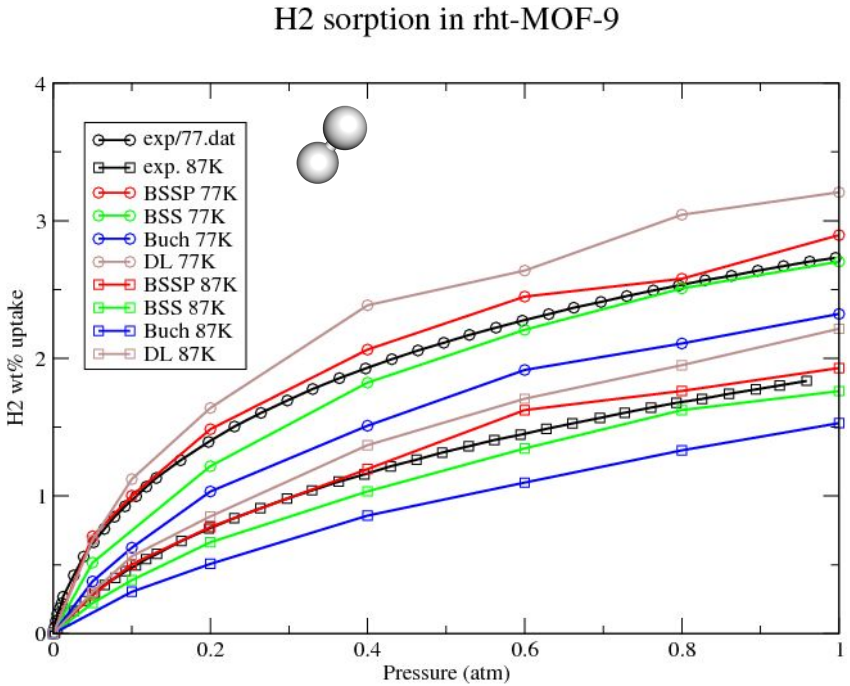
$$\vec{\mu}_i = \alpha_i^{\circ}\left(\vec{E}_i^{stat} - \sum_{j\neq i}^{N}\mathbf{T}_{ij}\vec{\mu}_j\right)$$

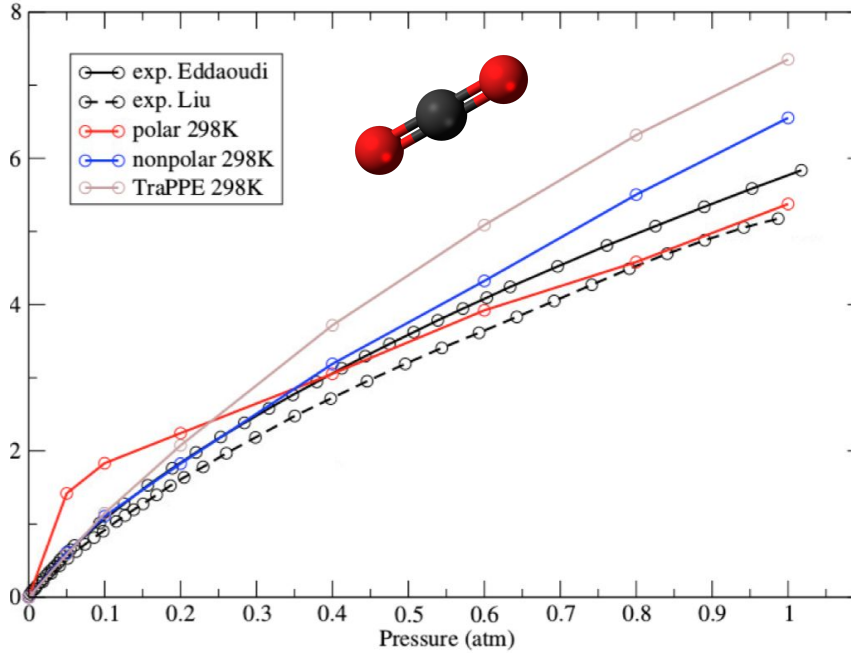
$$U_{pol}^{k} = -\frac{1}{2}\sum_i \vec{\mu}_i^{k}\cdot\vec{E}_i^{stat} - \frac{1}{2}\sum_i \vec{\mu}_i^{k}\cdot\vec{E}_i^{k+1}$$

$U_{tot} = U_{rd} + U_{es}$ (+ U_{pol})

Gas uptake: Experiment vs. Simulation







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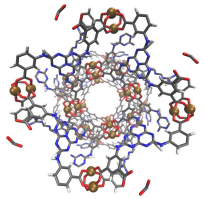

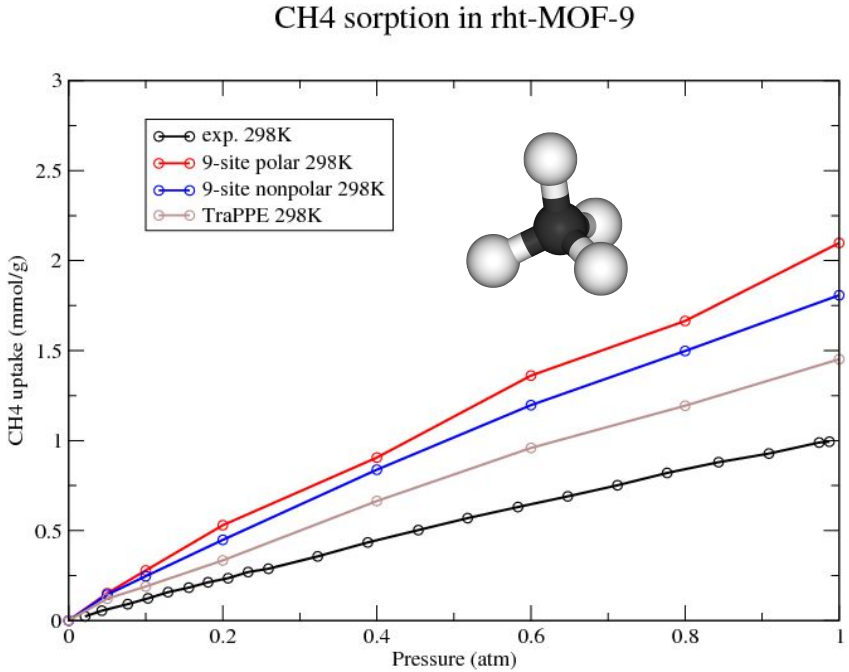

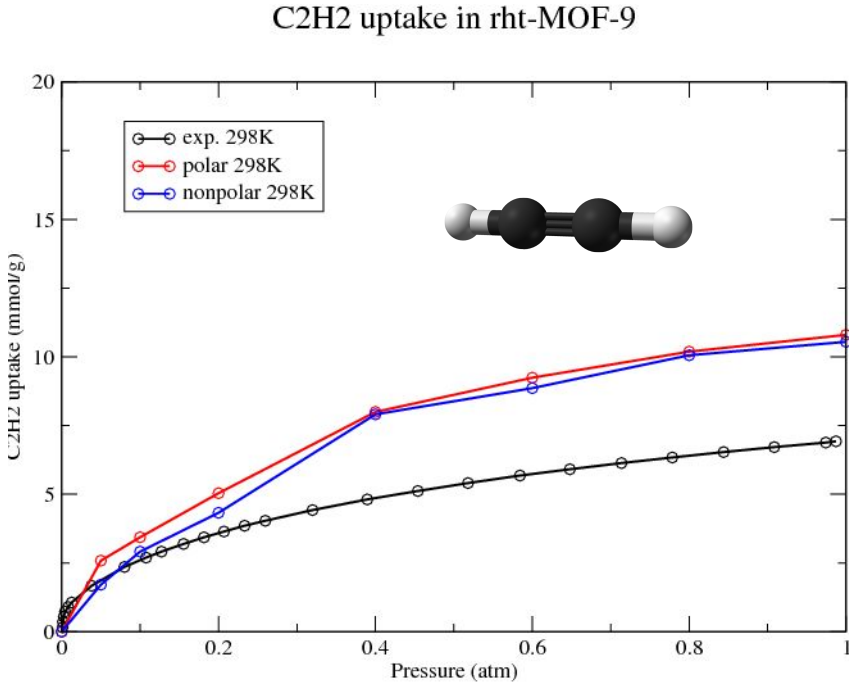

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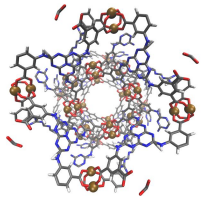

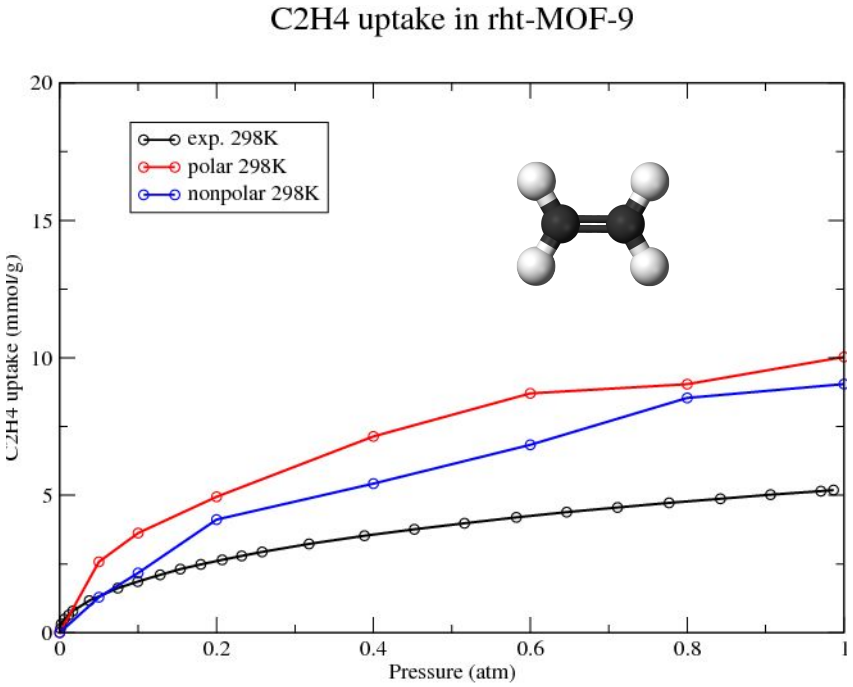

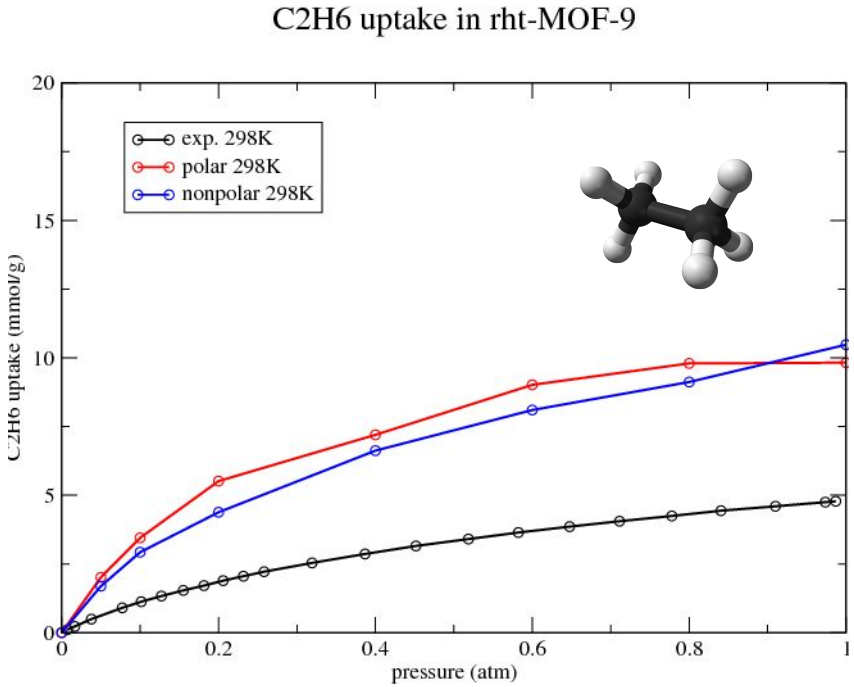

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Q_{st} (the heat of sorption; or, the isosteric heat)

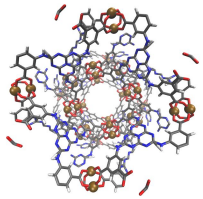
How experimentalists calculate:

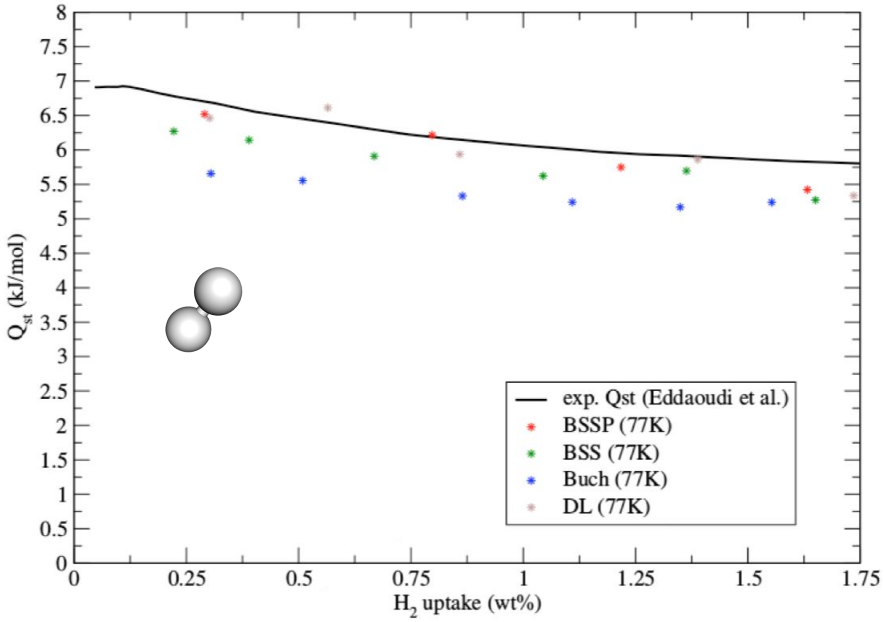
$$Q_{st} = kT^2 \frac{\partial ln P}{\partial T}$$

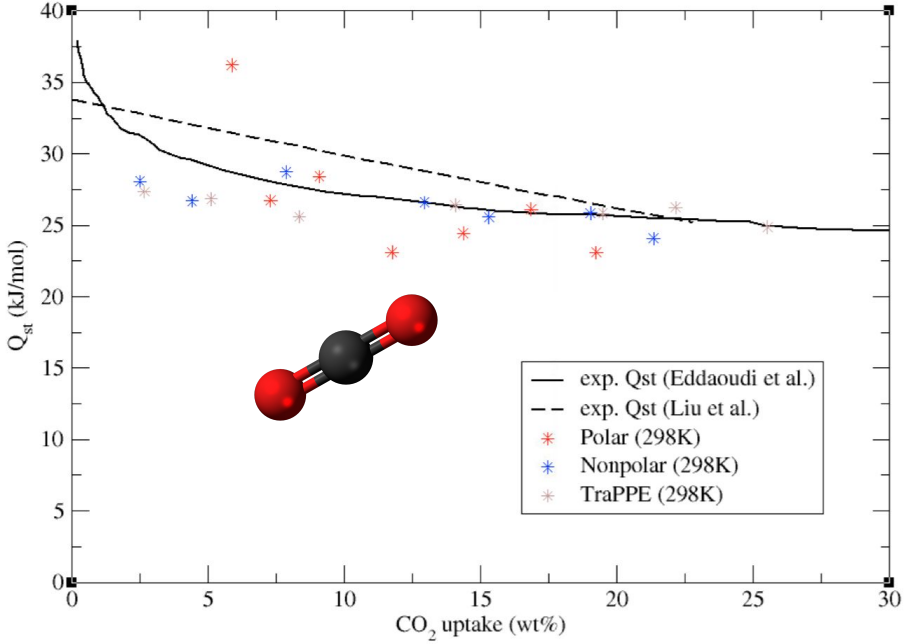
How we calculate (in GCMC):

$$Q_{st} = -\frac{\langle NU \rangle - \langle N \rangle \langle U \rangle}{\langle N^2 \rangle - \langle N \rangle^2} + kT$$

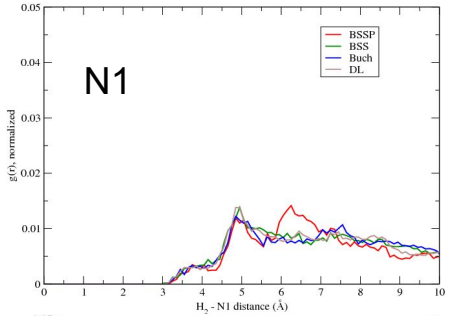
Qst (the heat of sorption)

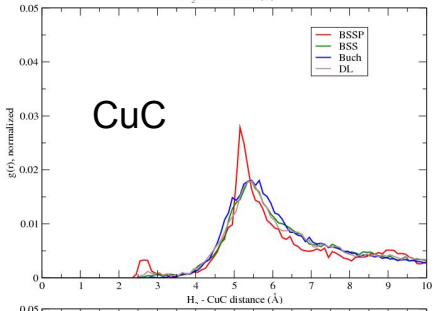


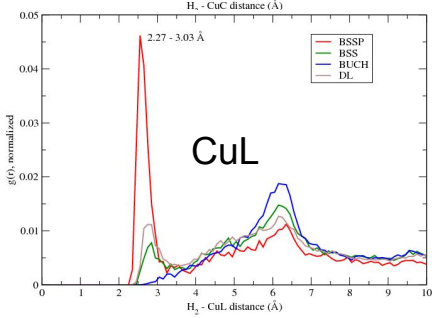


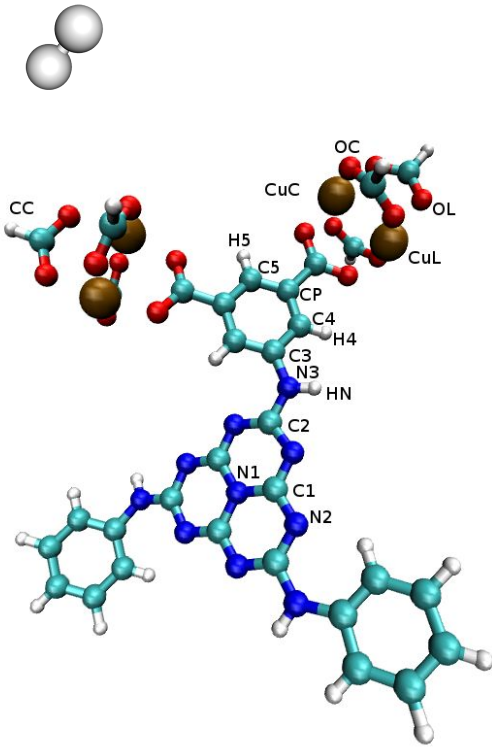


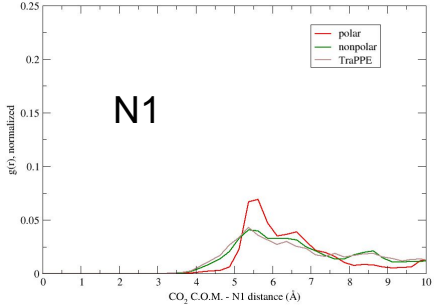
Radial distribution *g*(**r**) studies

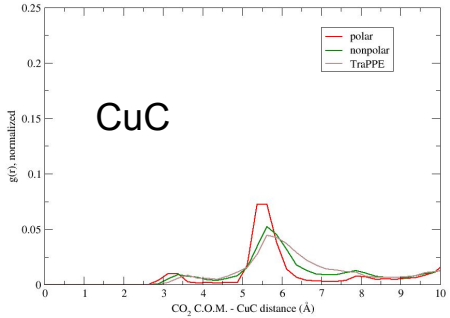


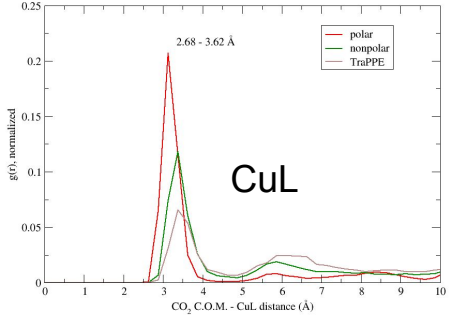


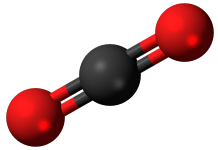












All graphs depict sorbate C.O.M. distance with labeled MOF atom, at 0.05atm.

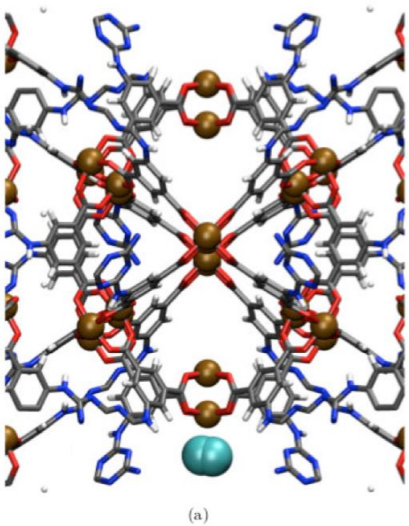
77K for H2
298K for CO2

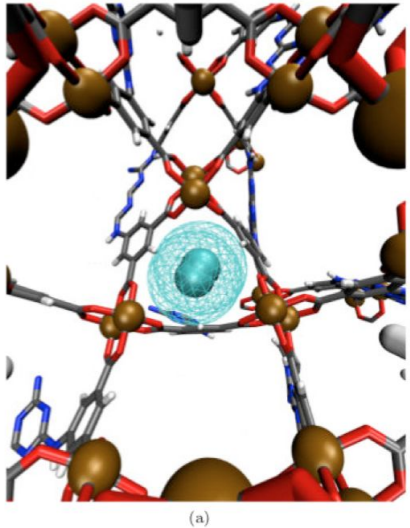
Main sorption sites

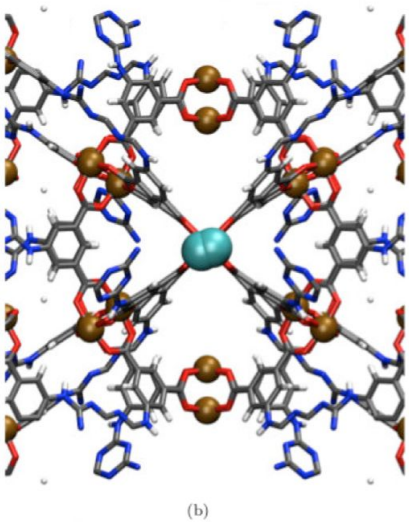
1) **Left:** physisorption to CuL
2) **Right:** The “window-cage” or “corner site” the shell around atoms represents the width of the broad peak in g(r) studies. (~ 2.0 Å)
3) (not shown): physisorption to CuC

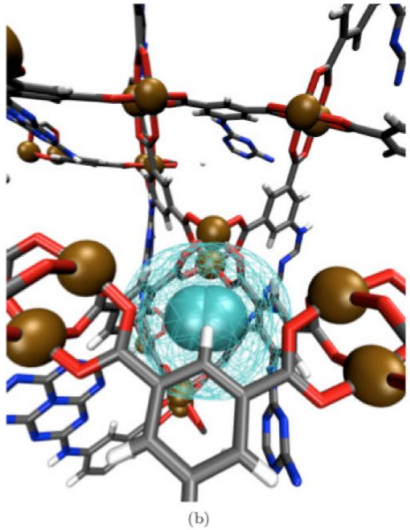
Discovered by radial distribution and simulated annealing.

All of these sites have been observed extensively in both simulation and experiment (e.g. neutron powder diffraction, X-ray, etc.)



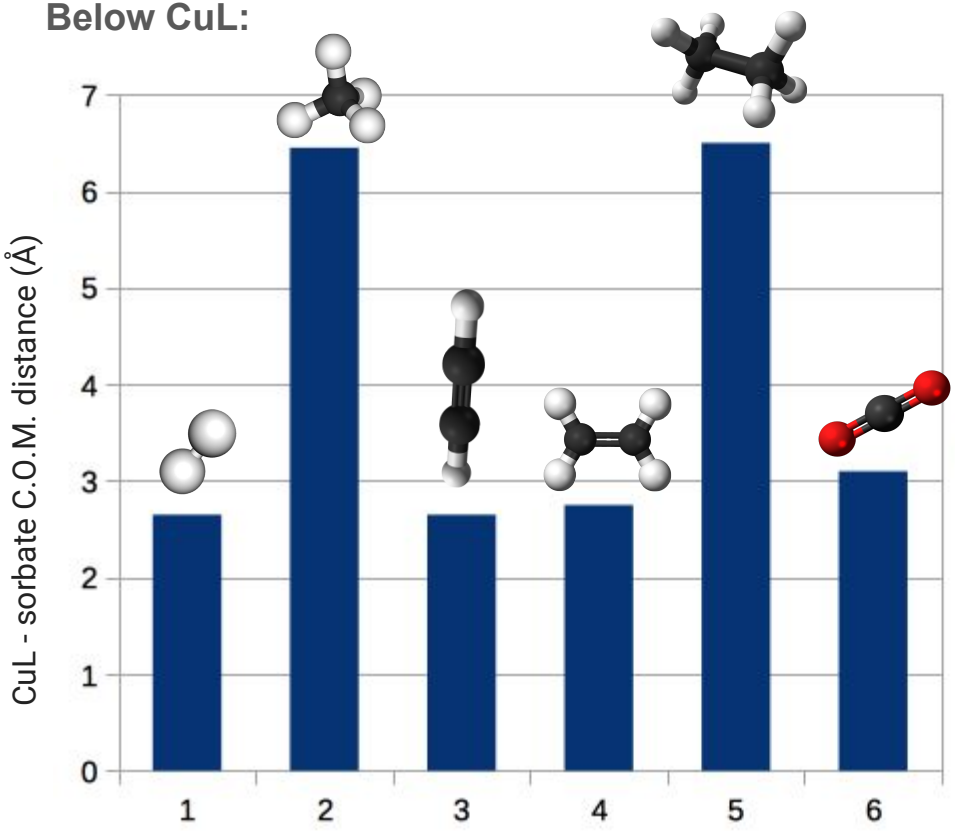


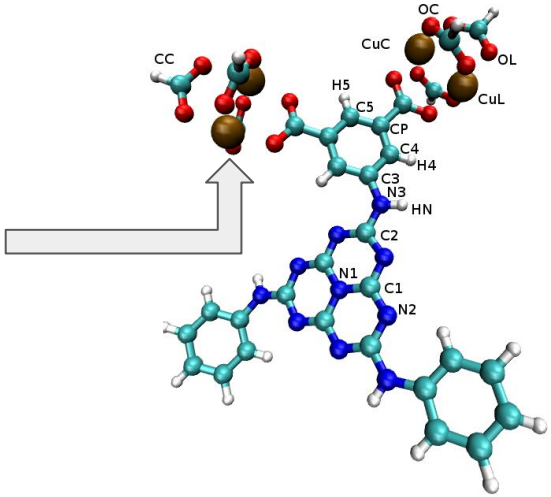




More g(r): Where do the gases sorb?

Below CuL:





Steric effects hinder methane and ethane sorption to open-metal sites

Summary

- Our models validate experimental data and supplement it with atomistic detail on the mechanism of sorption
  - rht-MOF-9 (and other rht-MOFs) are robust and probably have relatively few defects
- We can do so with minimal quantum-mechanical energy calculations, which are prohibitively expensive (e.g. for the entire unit-cell).

Future work

- Further development of polarizable hydrocarbon potentials
- Predictive simulations in new materials
- MCMD: a new software for MC and/or MD simulation of materials
  - https://github.com/khavernathy/mcmd

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NSF MRI CHE-1531590

The Space fam.

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Thanks also to undergraduates Zac Dyott, Matthew Mostrom, and Sean Carter.

MPMC code:
https://github.com/mpmccode/mpmc

MCMD code:
https://github.com/khavernathy/mcmd

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