

Quantum Mechanical Point Charges to Analyze Adsorption Differences Between MOF-505 and MOF-1

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Abstract

Two similarly structured metal-organic framework (MOF) samples, MOF-505 and MOF-1, showed significantly different H₂ and C₂H₂ uptakes experimentally. We extracted a variety of fragments from the crystal structure of MOF-1 and calculated point charges on the of each fragments using quantum mechanical calculations. We used the point charges to find the differences in the charges between the two MOFs at the ab initio level of theory; in order to analyze the differences in uptake of H₂ and C₂H₂ gases.

MOFs

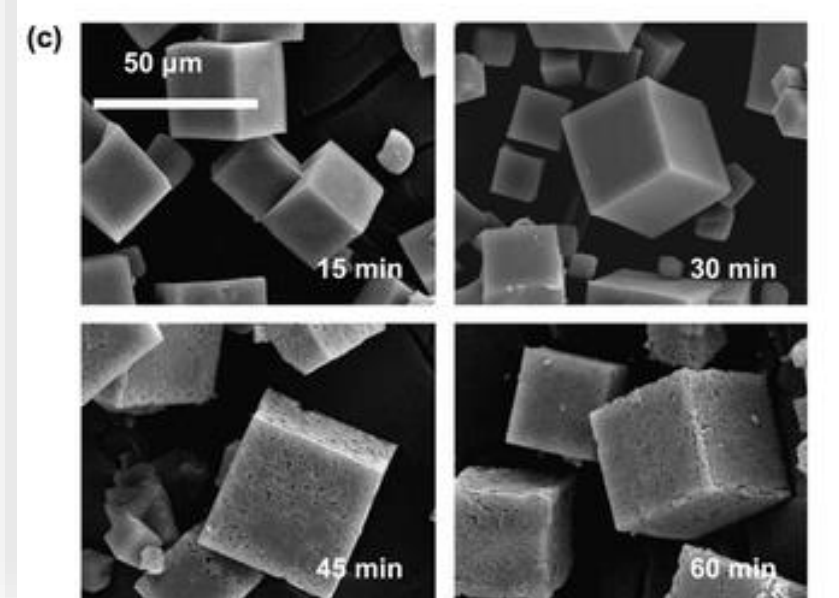
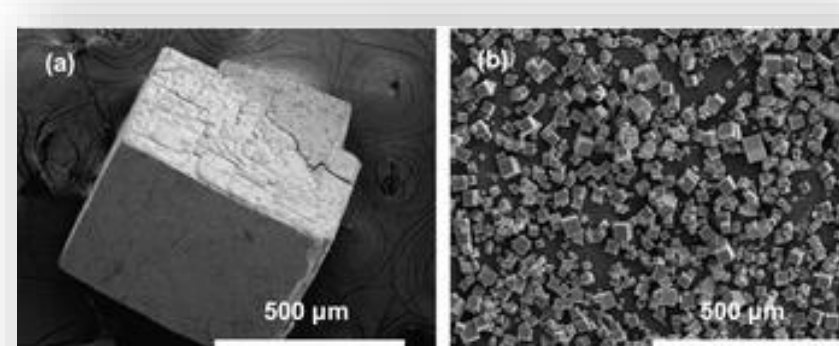
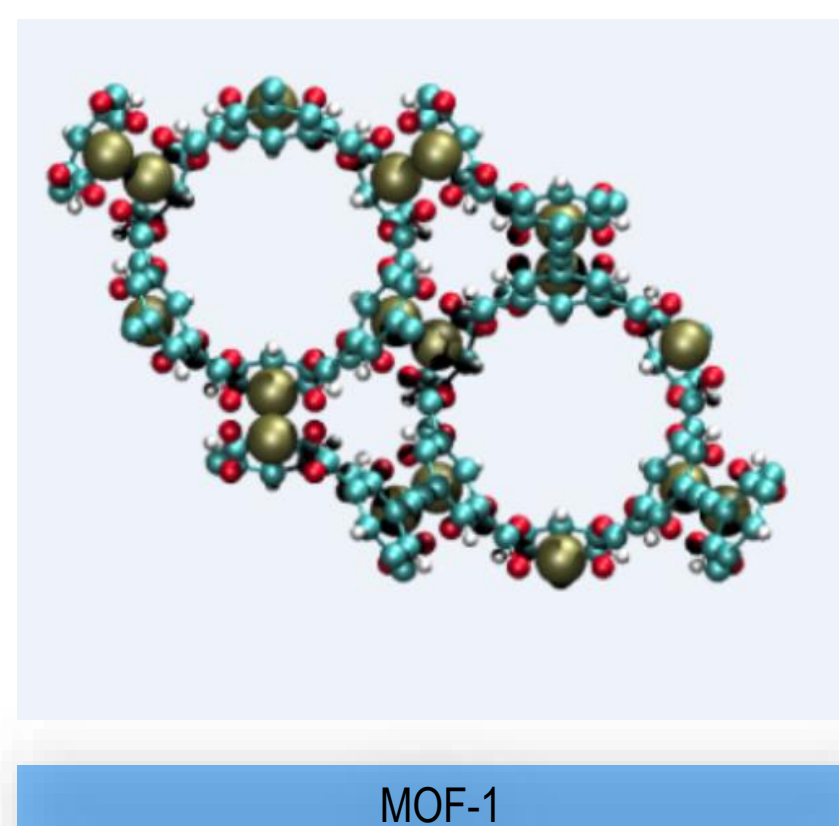
Background

Metal-organic frameworks (MOFs) are an emerging class of crystalline compounds that are made up of metal cations linked together by organic ligands. These MOFs have extremely unique shapes due to their repeating structure and metal sites creating a larger variety of bond structures. Some of these MOFs have extremely large open spaces, up to 90% free space.¹

MOF-505 and MOF-1 are two extremely similarly structured MOFs, with the main difference being their organic ligand. The ligand in MOF-1 has an additional set of carbons with a triple bond in between. MOF-1 also displays much higher H₂ and C₂H₂ adsorption² which is the source of interest in these two MOFs for this experiment.

Applications & Synthesis of MOFs

- Hydrogen storage
- Clean energy
- Safer storage
- CO₂ extraction
- Coal plants/car exhausts
- C₂H₂ storage
- Safer and cheaper storage.
- MOFs are synthesized through self-assembly
- Post synthetic modification is also possible

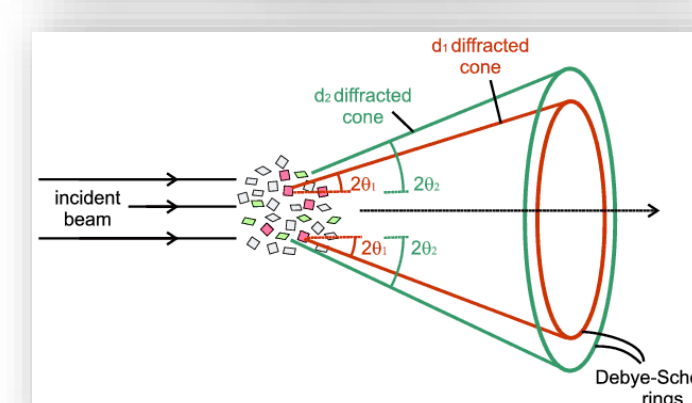
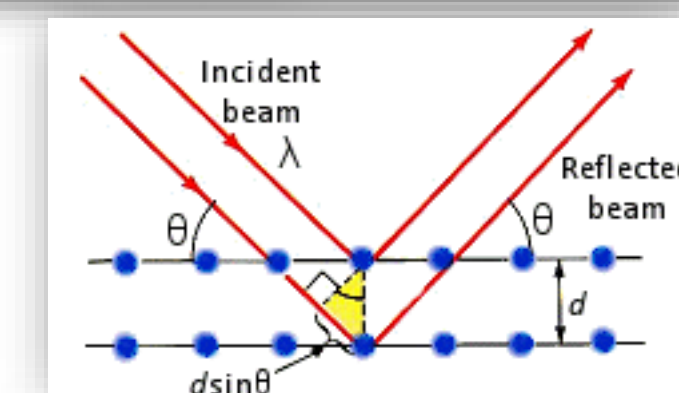


MOF5 crystals³

Preliminary experimental work

X-ray Powder Diffraction

- Used to characterize crystalline structures
- Powder samples contain almost every crystalline orientation
- Bragg's law gives a relation between the lattice spacings of a crystal and the angles at which there are maximum reflection of radiation
- X-rays scatter by interaction with the electron cloud of the sample
- Single crystal x-ray data was supplied and used to create xyz coordinate files for complete unit cells of MOF-505 and MOF-1



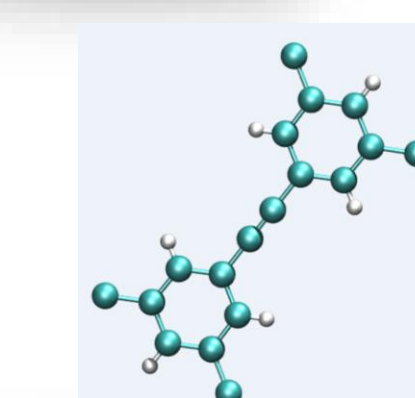
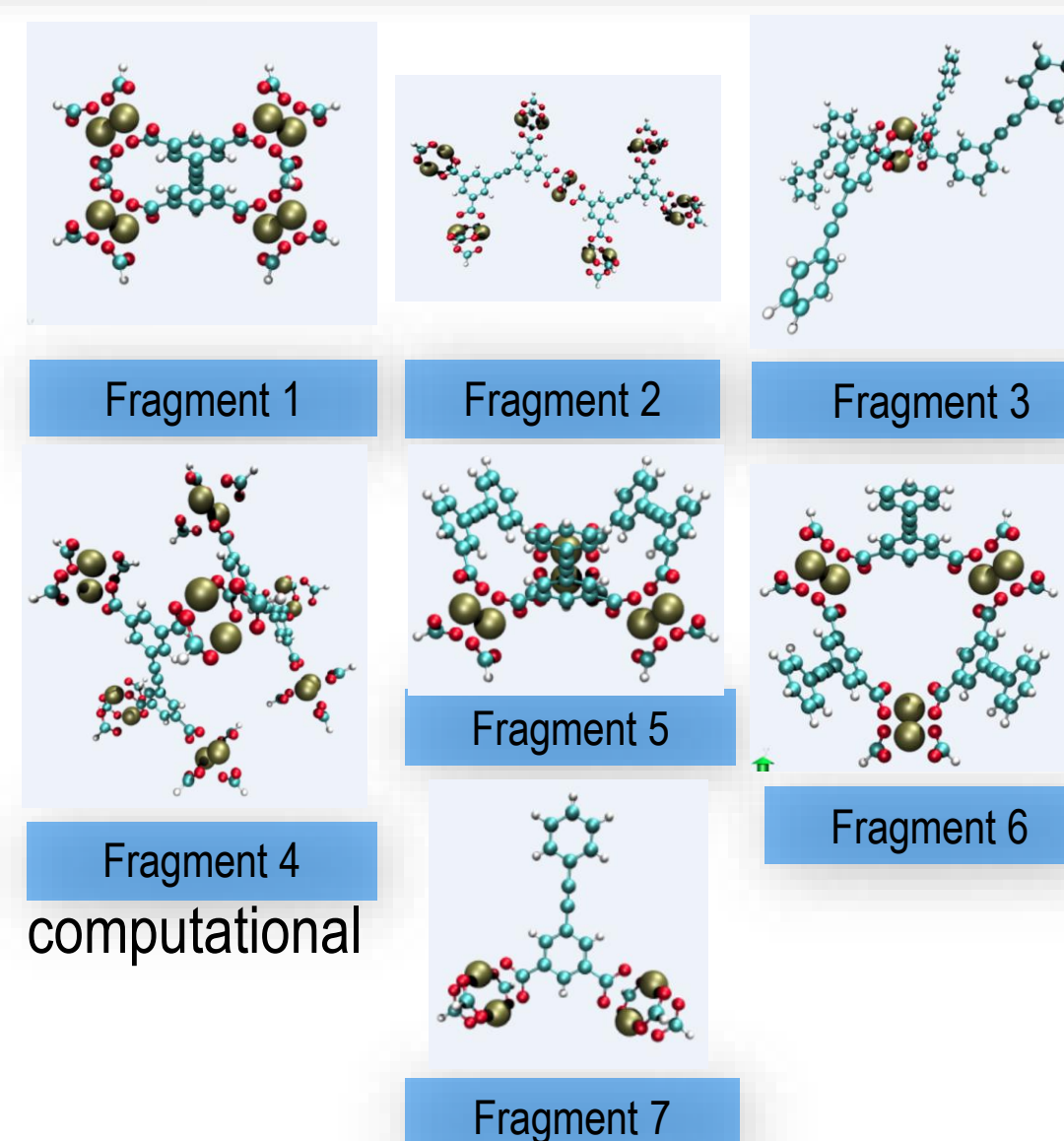
Methods

Pre-Computational Work

- Original x-ray diffraction xyz atom coordinates were taken from experimental groups, and were shifted and duplicated due to the non-orthogonal shape, in order to get a full picture of the MOF lattice.
- Fragments of the MOF were isolated with MOLDEN

Computational Methods

- NWCHEM (using USF CIRCE computational resources)⁷
- Geometry Optimization
 - designated atoms that were adjusted, or cut in the fragmentation process were set to be optimized.
 - Total energy of the fragment was calculated, and the atoms set to be optimized were adjusted until total energy was at a minimum.
- Charge Potential Calculation
 - Established grid of potential energy calculation points for each optimized fragment structure
 - Calculated potential energy at each point
 - Then fit atom charges to accommodate exact energies on the grid



Ligand for MOF-1 (above)
Ligand for MOF-505 (below)

Results

Atom Type	Name	MOF505			MOF1			Difference (q)
		Charge(q)	# Atoms (n)	q*n	Charge(q)	# Atoms (n)	q*n	
1	C1	N/A		N/A	-0.16604	18	-2.98872	N/a
2	C2	0.01371	18	0.24678	0.21352	18	3.84336	-0.19981
3	C3	-0.13845	36	-4.9842	-0.15431	36	-5.55516	0.01586
4	C4	-0.14194	36	-5.10984	-0.13736	36	-4.94496	-0.00458
5	C5	0.97684	36	35.16624	0.9694	36	34.8984	0.00744
6	C6	-0.08026	18	-1.44468	-0.092	18	-1.656	0.01174
7	O1	-0.75507	36	-27.1825	-0.75413	36	-27.1487	-0.00094
8	O2	-0.74172	36	-26.7019	-0.74529	36	-26.8304	0.00357
9	H1	0.18228	36	6.56208	0.19082	36	6.86952	-0.00854
10	H2	0.19382	18	3.48876	0.18042	18	3.24756	0.0134
11	CU	1.10888	18	19.95984	1.12585	18	20.2653	-0.01697
Total			288	0.00054		306	0.00018	

Table of atom type charges (q) and sum of charge throughout each entire unit cell for MOF-505 and MOF-1, as well as differences in charge for each distinct atom type. When scaled, the total charge will be ~0.00

Conclusion / Future Work

- Both MOFs have total charges close to zero and can be scaled to prepare them for simulations.
- Slightly higher charges in MOF-1 for Copper and the outer carbons on each linker, which can be related to higher H₂ and C₂H₂ adsorption.
- Hydrogen and Acetylene gas adsorption simulations can be performed to gather adsorption data for MOF-505 and MOF-1 using Visual Molecular Dynamics software (VMD) and Massively Parallel Monte Carlo (MPMC).
- Hydrogen and/or other gases absorbed (calculation of Q_{st} etc.) can be quantified to compare the adsorption simulations to experimental data to confirm an accurate model.
- The model charges can be further analyzed to explain the adsorption differences between the two MOFs, once an accurate model is confirmed.

References & Acknowledgements

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