Locating Adsorbed Hydrogen Molecules in $Cu_2(BTC)_{4/3}$ by Powder Neutron Diffraction

Sven C. Vogel[1], Jürgen Eckert[1,2], Jesse L.C. Rowsell[3]

[1]Los Alamos National Laboratory, Los Alamos, NM
[2]University of California, Santa Barbara
[3]University of Michigan

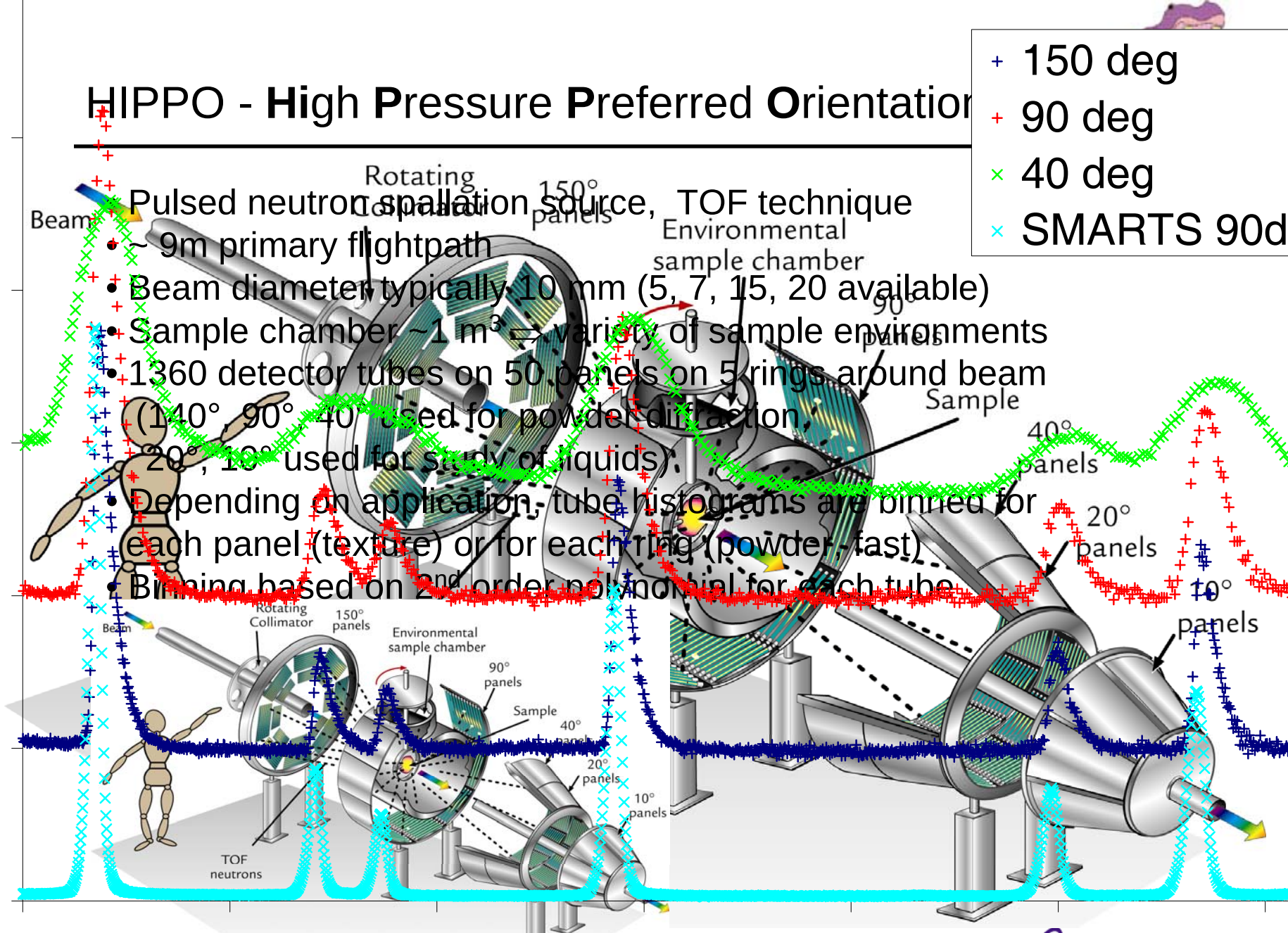
This work has benefited from the use of the Lujan Neutron Scattering Center at LANSCE, which is funded by the Department of Energy's Office of Basic Energy Science.
Los Alamos National Laboratory is operated by Los Alamos National Security LLC under DOE Contract DE-AC52-06NA25396.

Outline

- HIPPO –
  High Pressue/Preferred Orientation diffractometer at LANSCE
- Hydrogen related application examples
- Metal organic framework (MOF) materials
- Structure refinement of Cu-BTC as a function of hydrogen loading

HIPPO - **Hi**gh **P**ressure **P**referred **O**rientation

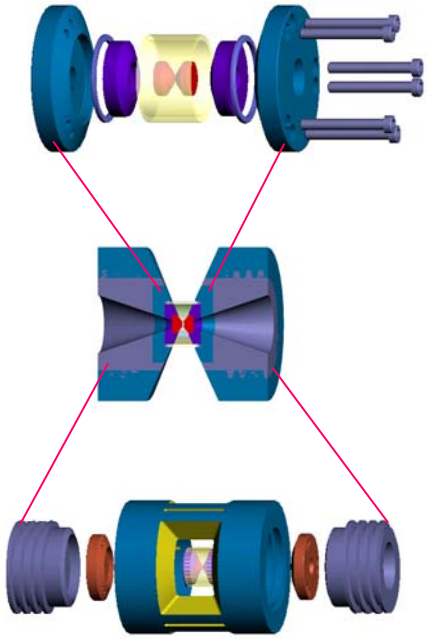
- Pulsed neutron spallation source, TOF technique
- ~ 9m primary flightpath
- Beam diameter typically 10 mm (5, 7, 15, 20 available)
- Sample chamber ~1 m^3 ⇒ variety of sample environments
- 1360 detector tubes on 50 panels on 5 rings around beam (140°, 90°, 40° used for powder diffraction, 20°, 10° used for study of liquids)
- Depending on application, tube histograms are binned for each panel (texture) or for each ring (powder, fast)
- Binning based on 2nd order polynomial for each tube



L. Wenk et al., NIM, **515** (2003) 575. Vogel et al., Powder Diffraction **19** (2004) 65.

Sample Environments

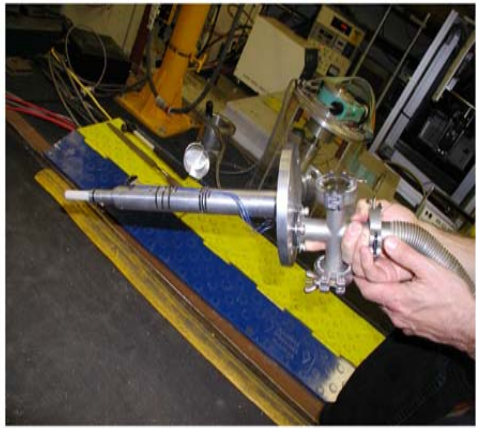
- Furnace: RT to 1473K, rotatable sample stick for texture (unique)
- New furnace: ~2700K, quenching, DSC, rotatable sample stick (commissioning phase)
- Sample changer: 16 texture, 50 powder samples
- Load frame: 100 kN, rotatable for texture (unique)
- Displex: 10K to RT
- Cryostat: 10K to 600K, rotatable sample stick for texture (unique)
- TAP-98 high pressure cell: 10 GPa, 2000K
- ZAP-01 pressure cell: Up to 30 GPa, 15-1500K
- Gas/liquid-cells: 2 kbar, 20K



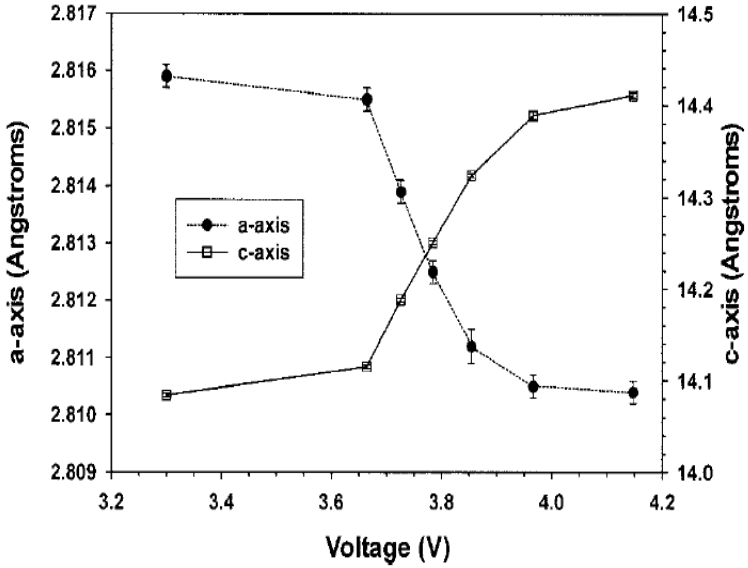
User supplied sample environments

Examples:

- Peltier stage to heat/cool rocks, combination of neutron diffraction and RUS/acoustic measurements TenCate, Darling et al., unpublished



- Battery charger/discharger Rodriguez et al., Electrochemical and Solid State Letters **7** (2004) A8-A10



- Gas loading of MOFs at 20K (this presentation)

Hydrogen related application examples:

- Xu et al., „Anisotropic thermal expansion and hydrogen bonding behavior of portlandite: A high-temperature neutron diffraction study”, J. Sol. State Chem. **180** (2007) 1519.
- Kim et al., „Pressure-Driven Phase Transitions in NaBH4: Theory and Experiments” J. Phys. Chem. B **111** (2007) 13873.
- Rodriguez et al., „X-ray and Neutron Diffraction of ErD2 Films”, Adv. X-ray Analysis **49**

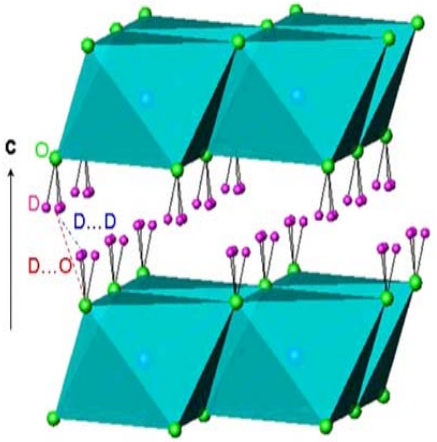
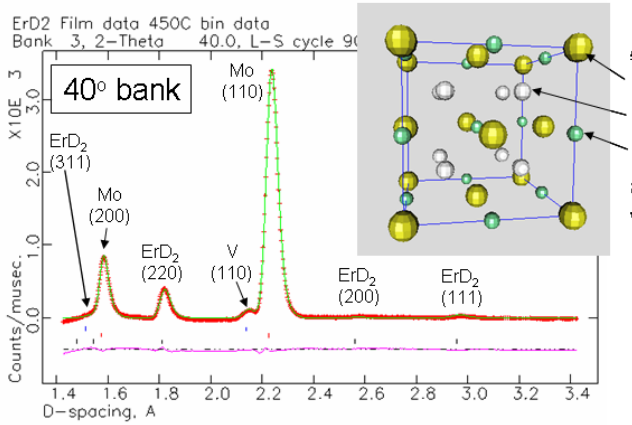


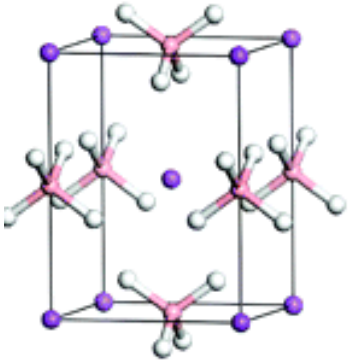
Fig. 1. Crystal structure of portlandite. Octahedra represent [CaO_6] units, green balls represent O atoms, and pink balls represent *H*(*D*) atoms. Note that each *H*(*D*) atom is disordered over three positions about the 3-fold rotation with occupancy of $\frac{1}{3}$. Red and blue dash lines indicate the interlayer D···O and D···D distances, respectively.

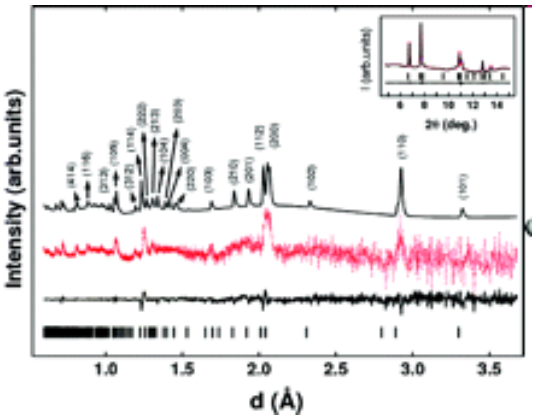


Crystal data

Atom	occ.	B_{iso}(Å^2)
Er	1.0	0.15
D_t	1.04(2)	1.01
D_o	0.15(3)	1.01

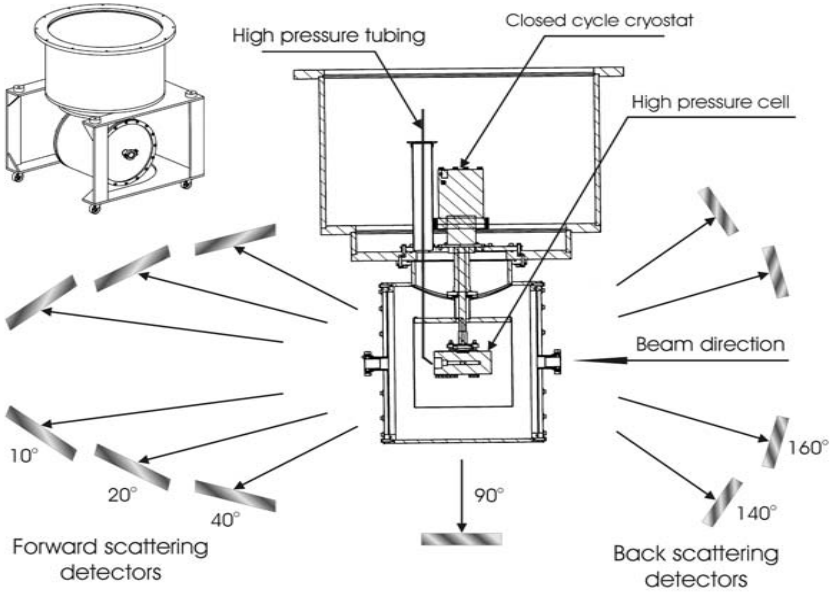
a = 5.119(1) Å
Vol = 134.2 Å^3
R_{wp} = 0.0087
R_p = 0.0073

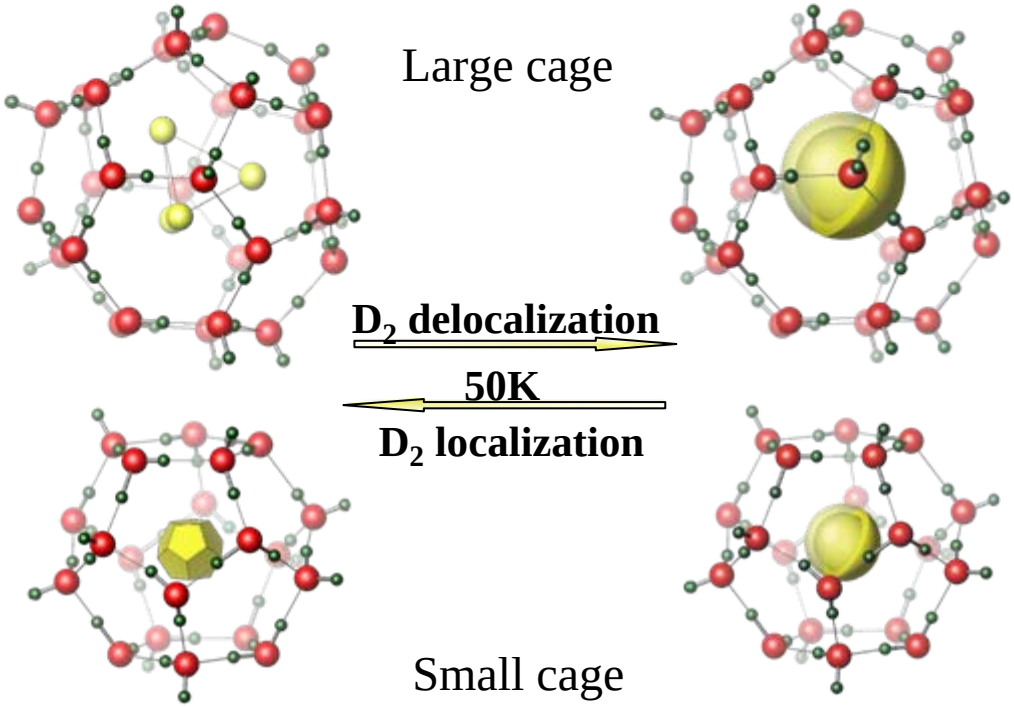




Application Example: H_2 Clathrate

- D_2 moldecules can be either localized or rotating
- Amount of localized D_2 moldecules decreases when temperature rises from ~70 to 120 K
- Clathrate structure is stable at ambient pressure but decays at 163(2) K





K. Lokshin et al., Phys. Rev. Lett, **93** (2004) 125503.

Outline

- HIPPO –
  High Pressue/Preferred Orientation
  diffractometer at LANSCE
- Hydrogen related application examples
- Metal organic framework (MOF) materials
- Structure refinement of Cu-BTC as a function of hydrogen loading

MOFs: Requirements for Hydrogen Storage

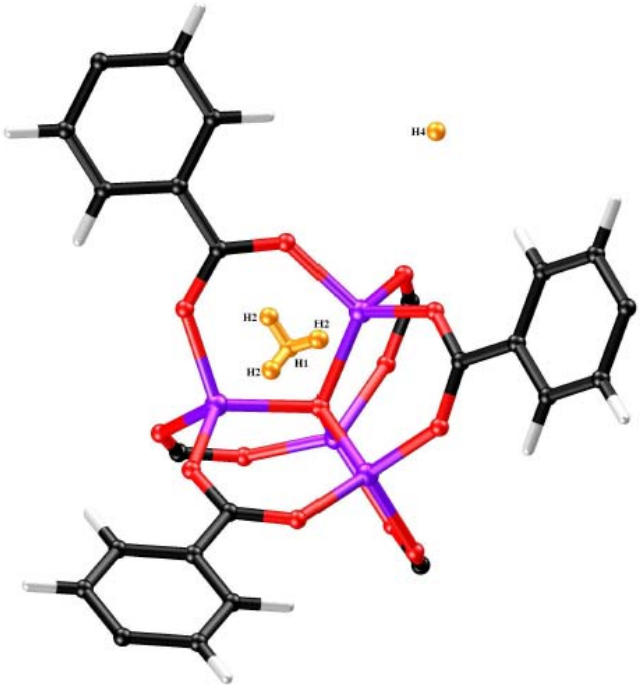
- Conventional high pressure storage requires heavy-walled vessels, which contribute to >90% of system mass
  $\Rightarrow$ framework structures may reduce these requirements
- Large gravimetric capacity (adsorbed molar amount per material mass)
  $\Rightarrow$ large pore volume
  $\Rightarrow$ composed of light elements
- Large volumetric capacity (adsorbed molar amount per material volume)
  $\Rightarrow$ efficient H_2 packing within pores
- Good uptake/release kinetics
- Appropriate heat of adsorption
- Multiple diffusion pathways (quick loading/unloading)
- Cheap, robust, non-toxic

Attributes of Metal-Organic Frameworks (MOFs)

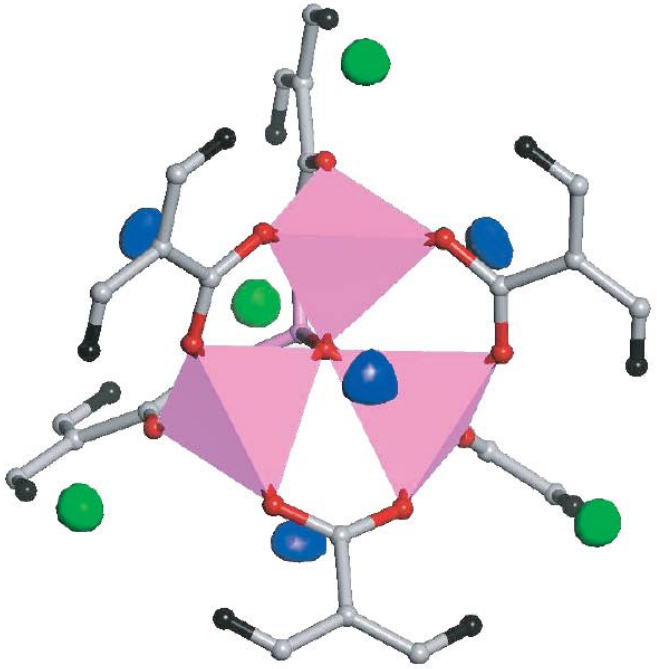
- Exhibit large uptake of gases: large pore volume
- Crystalline open frameworks with uniform pore array
- Purity can be monitored by microscopy and diffraction
- Both inorganic and organic components can be altered to optimize properties, including:
  - nature of binding sites
  - pore size
  - pore connectivity
- Straightforward and cost-effective “one-pot” synthesis from molecular precursors
- Lighter than zeolites (MOFs have larger gravimetric capacities)

H_2/D_2 in IRMOF-1 by Neutron Diffraction

- IRMOF-1/MOF5 is most widely studied MOF
- Consists of ZnO_4 clusters linked by 1,4-benzene-dicarboxylates (BDC)
- ZnO4 clusters are responsible for most of adsorption



data collected with VIVALDI (ILL) on
(0.5 mm)^3 single crystal sealed under H_2



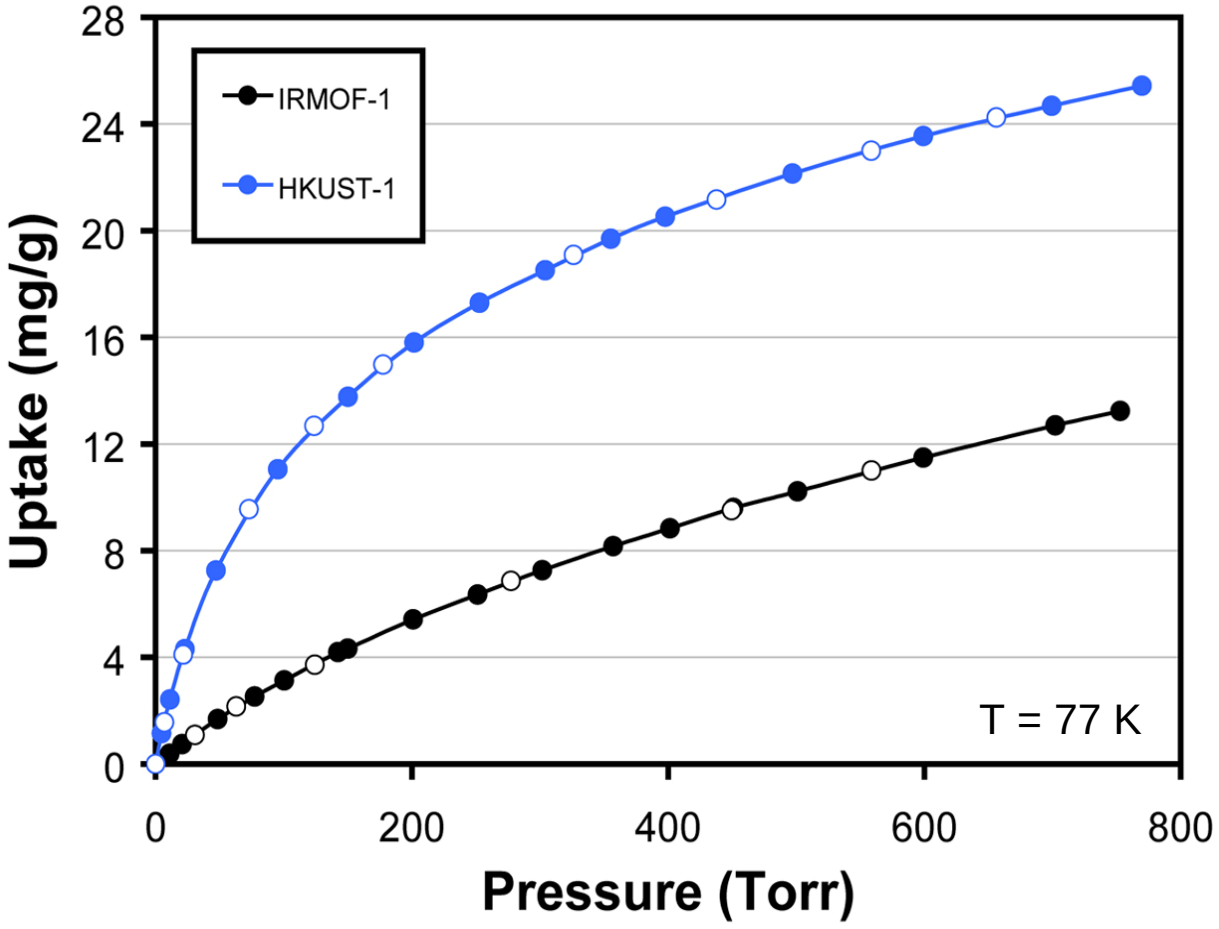
data collected with BT-1 (NIST) on
powder loaded with D_2

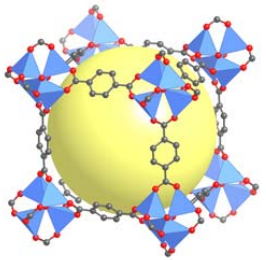
E.C. Spencer, J.A.K. Howard, G.J. McIntyre, J.L.C. Rowsell, O.M. Yaghi, *Chem Comm* **2006**, 278.

T. Yildirim, M.R. Hartman, *Phys Rev Lett* **2005**, 95, 215504.

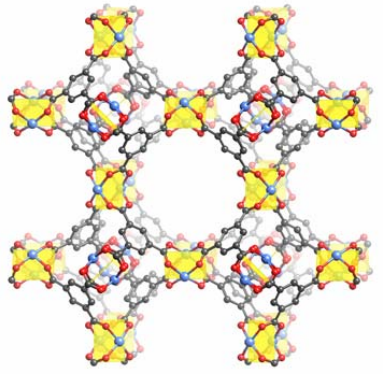
HKUST-1 shows improved H_2 uptake

- H_2 uptake at 77 K, 1 atm





IRMOF-1

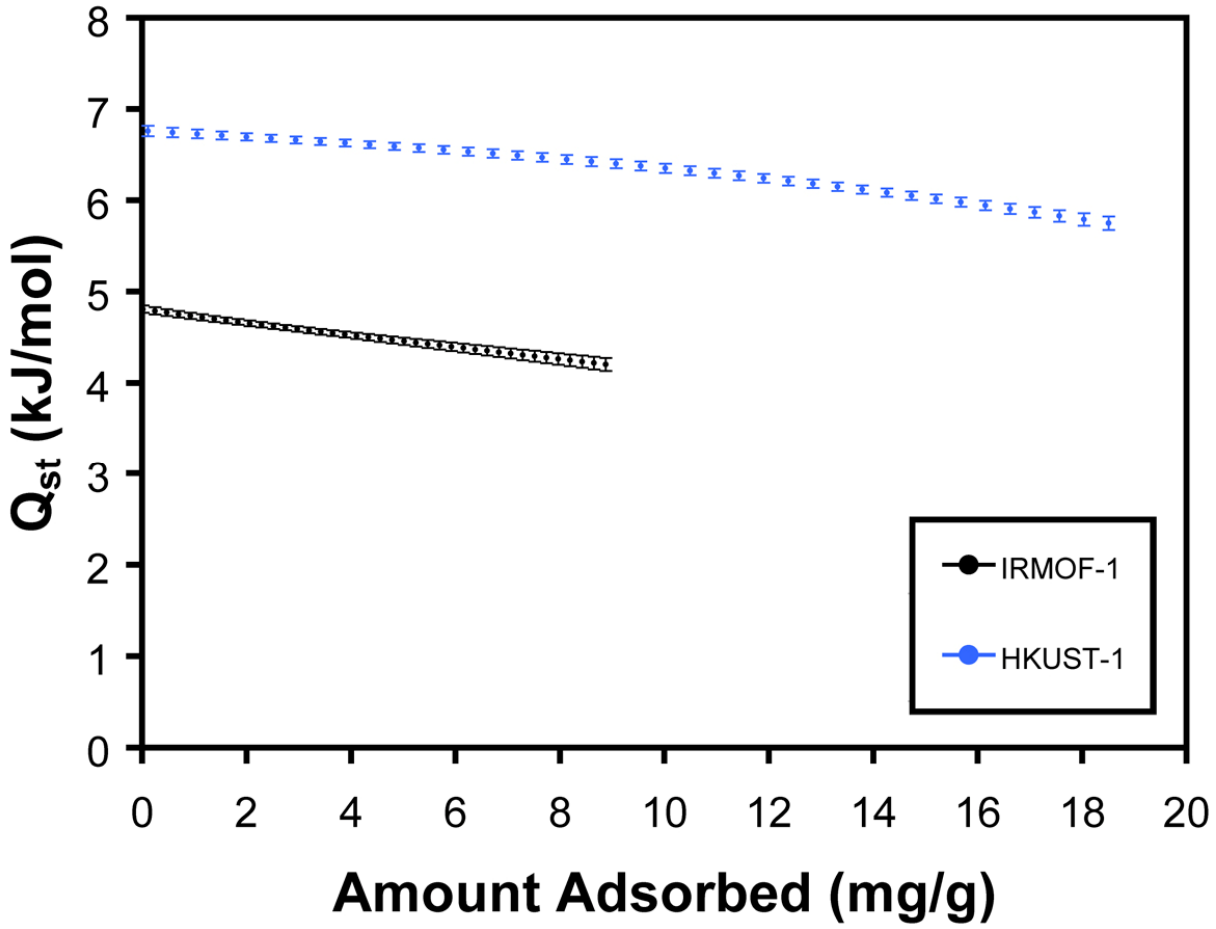


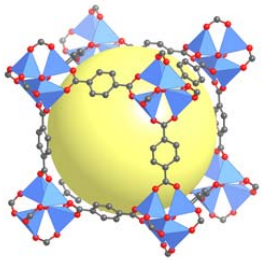
HKUST-1

J. L. C. Rowsell and O.M. Yaghi, *JACS,* **2006,** *128*, 1304.

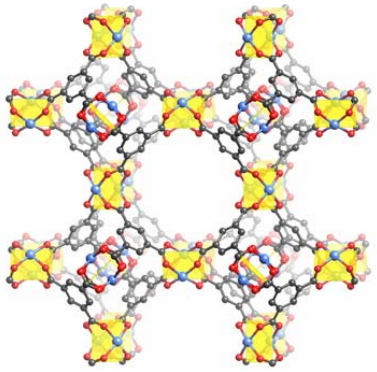
Isosteric Heats of Adsorption

- Continuous curve indicates continuous filling of various sites



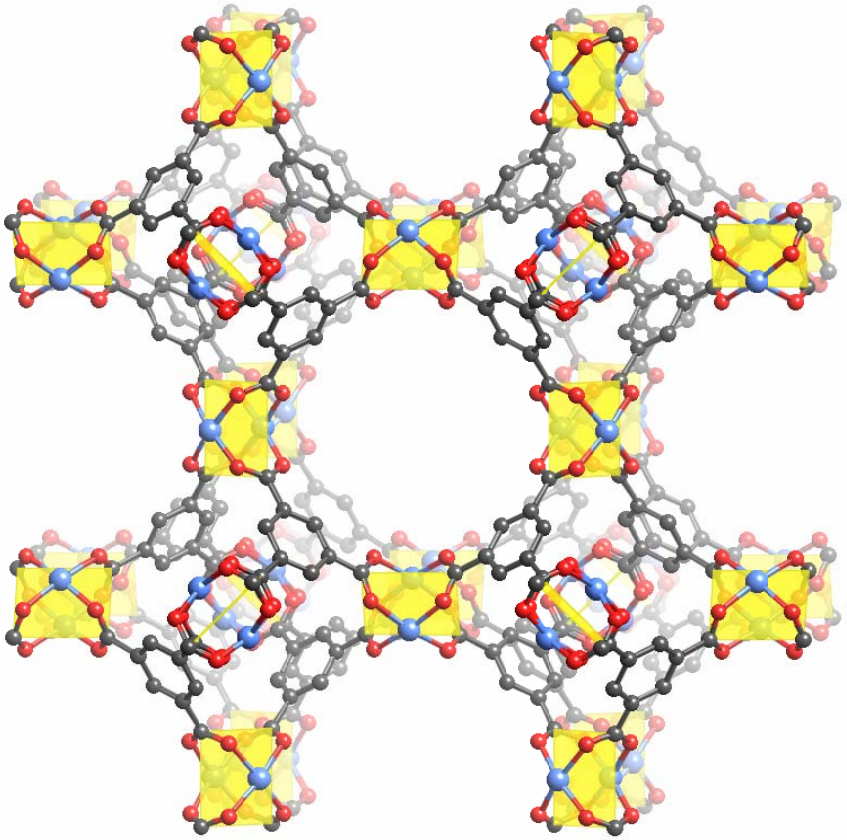


IRMOF-1



HKUST-1

Details of HKUST-1 Structure



- $Cu_2(C_9H_3O_6)_{4/3}$
- Cubic, Fm-3m, a=26.343 Å
- 6 atoms in asymmetric unit
- Square $Cu_2(O_2C\text{-})_4$ “paddlewheels” linked by trigonal mesitylene
- Pores 6.9 Å, 11.1 Å and 13.2 Å in diameter
- Calculated free volume: 62-72 %
- Surface areas and pore volume determined by N_2 adsorption at 77 K:

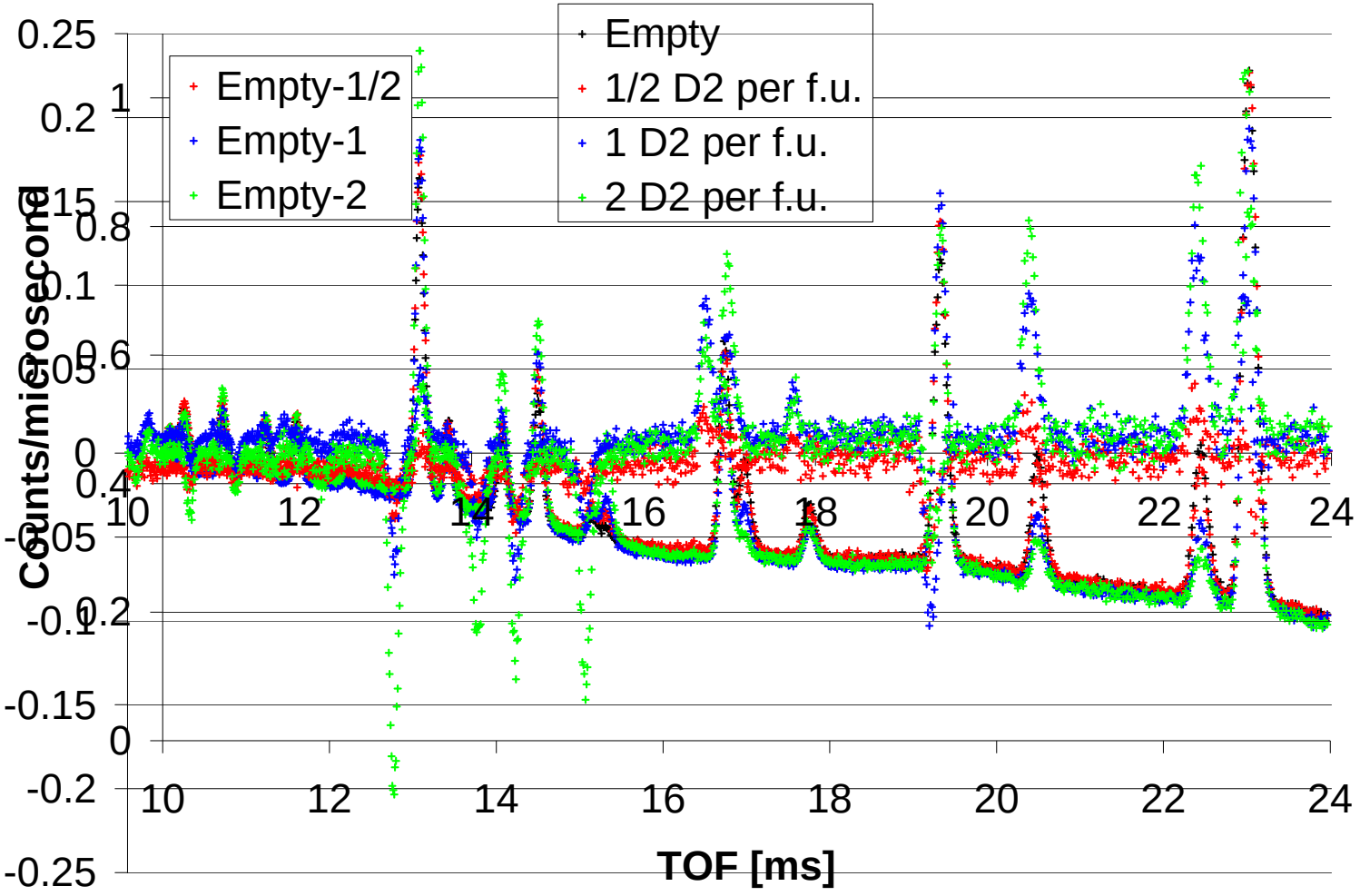
A_{Lang}	2175 m^2/g
A_{BET}	1507 m^2/g
V_P	66%

- H_2 adsorption sites unknown!

Experimental setup

- 1.18 g of Cu-BTC loaded in V-can under He
- Texture free powder
- V-can attached to displex in evacuated top-hat
- Measurement at 25 K (to localize H_2 molecules)
- Heated to 100K followed by equilibration for loading
- Controlled addition of D_2 at 100K using gas manifold
- Cooling at ~2 K/min back to 25 K,
  equilibration for 30 minutes and ND measurement

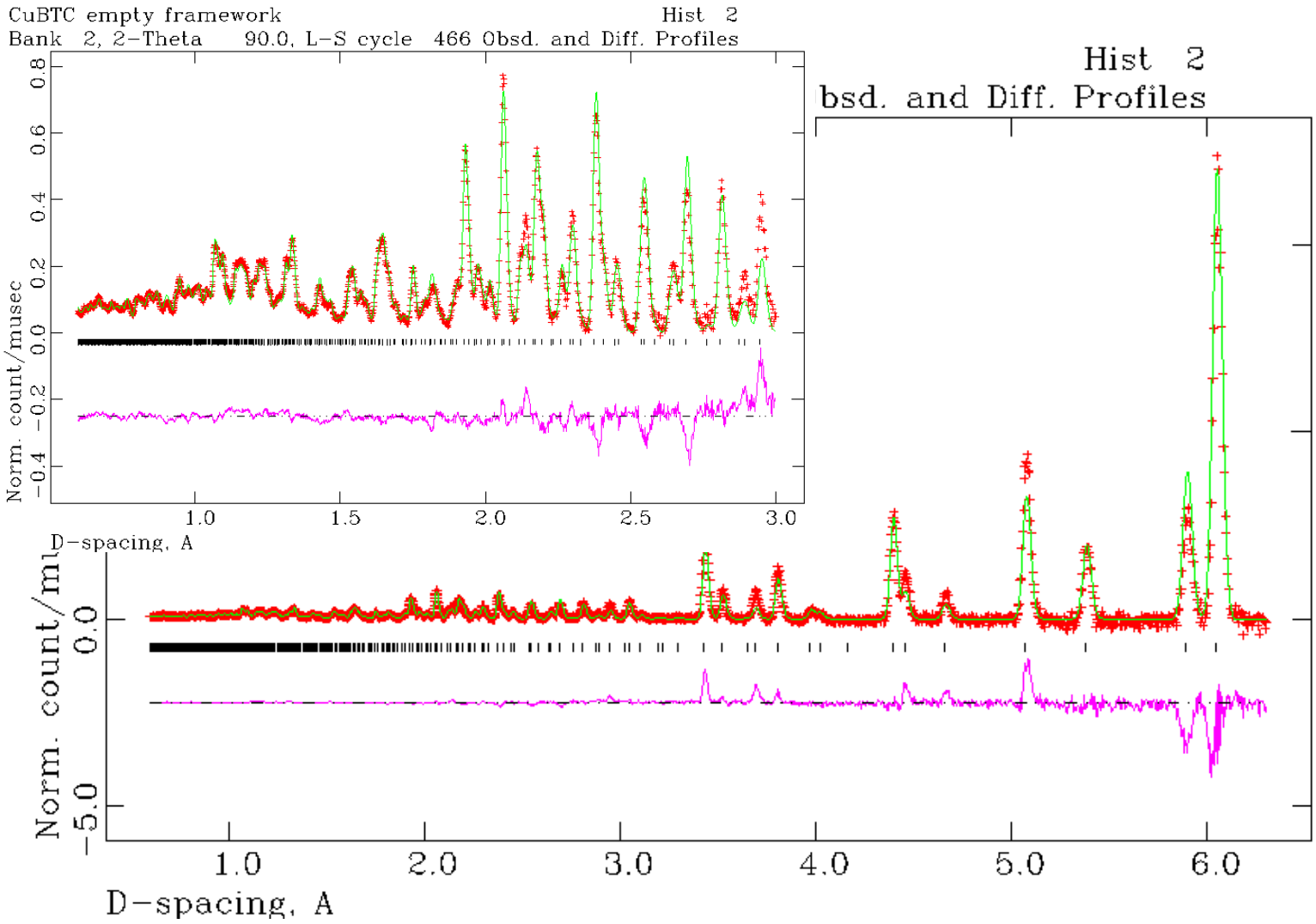
Results


Empty-1/2
Empty-1
Empty-2
Empty
1/2 D2 per f.u.
1 D2 per f.u.
2 D2 per f.u.
Counts/microsecond
TOF [ms]
0.25
0.2
0.15
0.1
0.05
0
-0.05
-0.1
-0.15
-0.2
-0.25
1
0.8
0.6
0.4
0.2
0
10
12
14
16
18
20
22
24

Refinement of empty structure

- Initial structure from Chui et al.
- 6 atoms in asymmetric unit (Cu, O, 3 C, 1 D/H), D/H constrained together
- Set SOF of D/H to 0.97/0.03 (as provided by vendor)
- Refined against integrated histograms for HIPPO's 140º, 90º, and 40º detectors (multi-pattern Rietveld)
- Rietveld refinement using GSAS
- 6 background coefficients, one scale factor, peak width per histogram
- Incident intensity from measured Vanadium spectrum
- Refined diffractometer constants DIFC and DIFA for each histogram (Absolute lattice parameter impossible with TOF without a standard)
- Refined U_{Iso} for each atom and position of H/D, all other structural parameters fixed
- Small negative absorption correction, likely to compensate for unaccounted air scatter in incident intensity (~30 cm flight-path were in air)
- Total of 42 variables, reduced χ^2=8.21

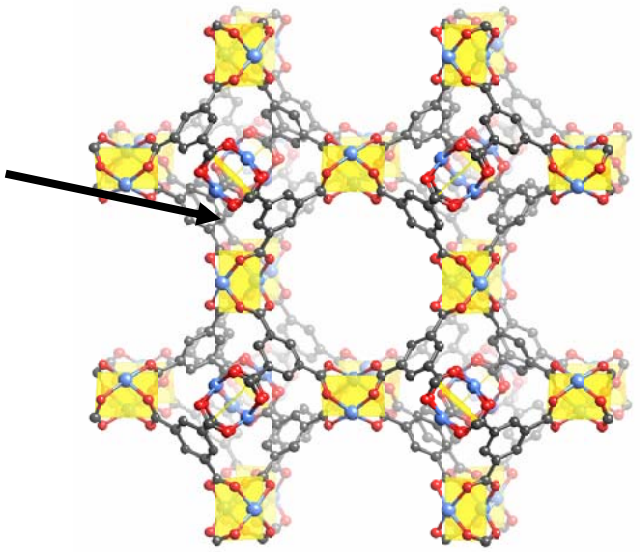
Refinement of empty structure



Refinement of empty structure

- 5 most intense peaks in difference Fourier map are

	Rho	X	Y	Z	
1	-0.078	0.1563	0.1563	0.1563	(center of window to small pore)
2	-0.069	0.2208	0.2208	0.1521	(inside small pore)
3	0.068	0.2175	0.2175	0.0000	(Cu site! Artifact? Cu position?)
4	0.053	0.1781	0.1781	0.0000	(expected site for O of H_2O)
5	0.052	0.1999	0.1999	0.1999	



- Negative intensities possibly from residual H (b_{coh}= -3.739 fm, all other possible elements have positive scattering length) from solvents
- 1-4, 2-4 distance are too far for H_2O molecule
- Removing H/D atom: Reduced χ^2 = 35.25 (was 8.21)
- 5 most intense peaks in difference Fourier map are

	Rho	X	Y	Z	
1	0.146	0.2500	0.1364	0.1364	(0.8 A away from original position!)
2	-0.113	0.2308	0.2308	0.1640	(close to #1 above)
3	-0.111	0.1558	0.1558	0.1558	(close to #2 above)
4	-0.096	0.2157	0.2157	0.1064	(inside small pore)
5	0.083	0.0693	0.0000	0.0000	(close to center of big pore, artifact)

- Negative intensities increase on previous most negative positions
- Difference Fourier seems to have error bar of 0.8 Å for H/D position(?)

Refinement of loaded structures

1. Refinement starting from empty structure, vary only lattice parameter
2. Difference Fourier Peak search
   e.g. $2D_2$ per f.u.:

	Rho	X	Y	Z
1	0.161	0.1551	0.1551	0.0000
2	0.156	0.2006	0.2006	0.2006
3	0.112	0.1826	0.1826	0.1826
4	0.111	0.2361	0.2361	0.2361
5	0.097	0.1300	0.1300	0.1300

3. Insert D atom at two maxima positions
   (referred to as Q1 and Q2, respectively)
4. Refine positions and site occupation of Q1/Q2
5. Refine U_{iso} for Q1/Q2

Refinement of loaded structures

	ε	χ^2(empty)	χ^2(full)
Empty		8.21	8.21
1/3 D2 per f.u.	0.0148%	10.3	6.06
1 D2 per f.u.	0.0292%	23.6	7.18
2 D2 per f.u.	0.0262%	34.3	5.50

	Frac Q1	Frac Q2	Sum [per f.u.]
Empty			
1/3 D_2 per f.u.	0.13(1)	0.71(1)	0.84 [0.42]
1 D_2 per f.u.	0.49(2)	1.15(2)	1.64 [0.82]
2 D_2 per f.u.	1.58(2)	1.70(2)	3.28 [1.64]

Future Work & Summary

- Found two positions in difference Fourier map that increase in nuclear density with loading
- Refinement of occupancies yields reasonable numbers
- Q1 (0.200 0.200 0.200) position has reasonable distance from framework atoms (~3.6 Å to C, r_C=1.7 Å, r_{D2}=1.45 Å)
- Q2 (0.155 0.155 0.000) position is too close to framework for van der Waals interaction (~2.2 Å to Cu, r_{Cu}=~1.4 Å)

- Future work:
  - How good is initial structure from X-Ray diffraction?
  - Can we refine H_2O in “empty” structure?

Synthesis of Deuterated HKUST-1