

HyMARC Core Activity: Sorbent



Enabling twice the energy density for onboard H₂ storage

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COVID-19 Pandemic halted all work in February 2020. Milestones to be evaluated after re-opening.



This presentation does not contain any proprietary, confidential, or otherwise restricted information

Project ID #: ST202

Overview



Timeline*

Phase 1: 10/1/2015 to 9/30/2018

Phase 2: 10/1/2018 to 9/30/2022

Project continuation determined annually by DOE.

(*previously a component of NREL's materials development program and supported annually since 2006)

Budget

DOE Budget (Entire HyMARC Team)

Total FY19: \$4.3M

Total FY20 (Planned): \$6.25M

SNL: \$1.15M

NREL: \$1.5M (covers NIST and SLAC)

PNNL: \$1.1M

LLNL: \$0.9M

LBNL (Long): \$1.1M

LBNL (Prendergast) \$0.5M

Barriers addressed

General:

A. Cost, B. Weight and Volume, C. Efficiency, E. Refueling Time

Reversible Solid-State Material:

M. Hydrogen Capacity and Reversibility
N. Understanding of Hydrogen Physi- and Chemisorption
O. Test Protocols and Evaluation Facilities

Partners/Collaborators

NIST – Craig Brown, SLAC – Michael Toney

HyMARC – SNL, LLNL, LBNL, PNNL team members

H₂ST², USA – Hydrogen Storage Tech Team

Colorado School of Mines - Colin Wolden, Brian Trewyn,

Univ. Hawaii – Craig Jensen, Godwin Severa

Université de Genève – Hans-Rudolf Hagemann, Angelina Gigante

HyMARC Energy Materials Network: enhanced, highly coordinated capabilities to accelerate materials discovery

Enabling twice the energy density for hydrogen storage



- Foundational R&D
- Computational models
- Synthetic protocols
- Advanced characterization tools
- Validation of material performance
- Guidance to FOA projects
- Database development

Seedling Projects

- Applied material development
 - Novel material concepts
 - High-risk, high-reward
- Concept feasibility demonstration
- Advanced development of viable concepts

Approach

- 1.A Enthalpy/entropy under practical conditions (with NREL, PNNL)
- **1.B Optimization of sorbent binding energies**
 - 1.B.1 Electronic structure computations (LBNL, LLNL)
 - 1.B.2 Strong-binding sites (LBNL, NREL, NIST)
- 1.C Sorbent packing: MOF monolith synthesis (LBNL, SNL, NREL)
- 1.D Dynamic sorbent materials (LBNL, NREL)
- 1.E Multiple H₂ binding (LBNL, NIST)

Relevance

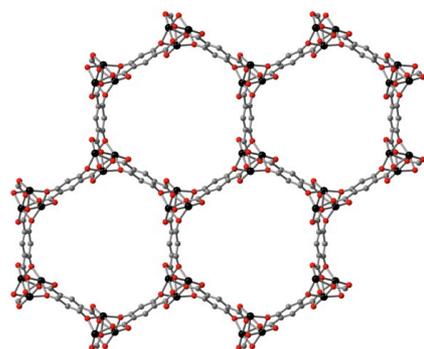
Research and development of metal–organic frameworks with high volumetric and gravimetric H₂ storage capacities (Barrier A – C, E).

- Adsorption enthalpy in the optimal range of –15 to –25 kJ/mol
- Open metal sites that adsorb more than two H₂ molecules

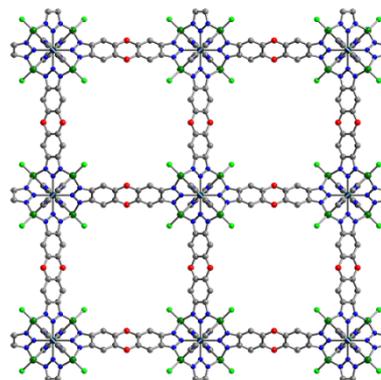
Approach 1.B.2: Sorbents with Optimal Binding Energies

Is it possible to create MOFs that adsorb H_2 with an enthalpy in the optimal range of **-15 to -25 kJ/mol**?

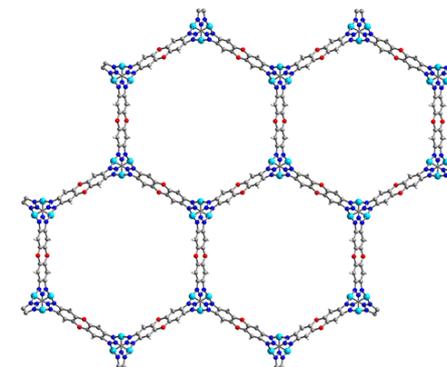
- Values are based upon assumptions about the correlation between adsorption enthalpy and entropy. However, these assumptions are not always valid.



$Ni_2(m\text{-dobdc})$



$Cu\text{-MFU-4l}$



$V_2Cl_{2.8}(btdd)$

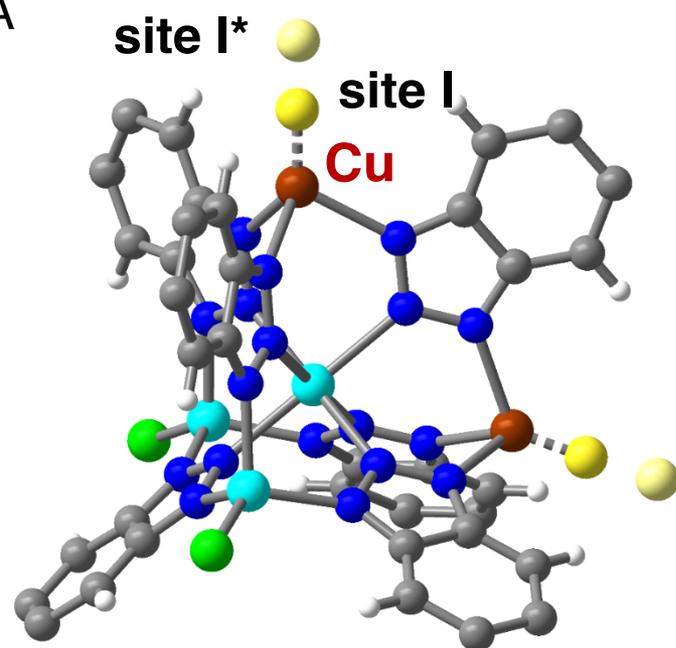
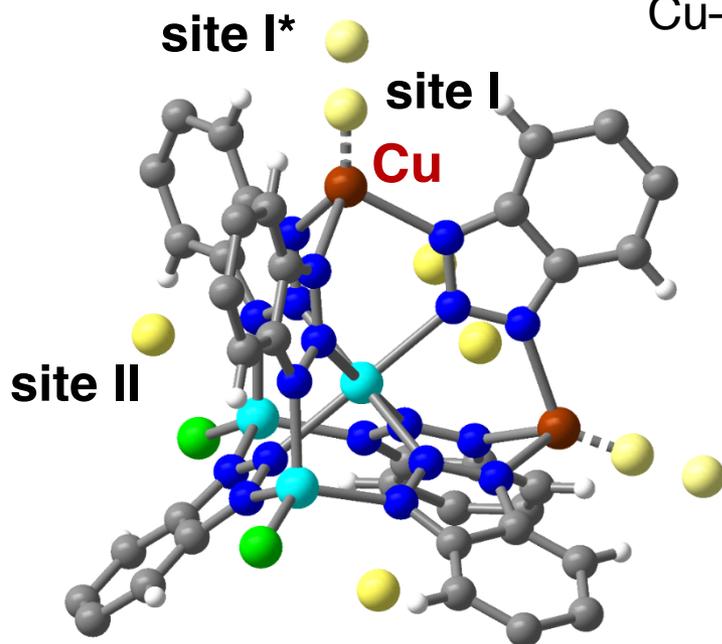
The Lewis-acidic open metal sites are capable of polarizing and accepting electron density from H_2 ; however, ΔH is lower than 15 kJ/mol.

π -Backdonation plays a primary role in strong H_2 binding: therefore, π -basic metals (Cu^I and V^{II}) will be incorporated into frameworks.

Accomplishment 1.B.2: *In situ* Powder Neutron Diffraction of Cu-MFU-4l

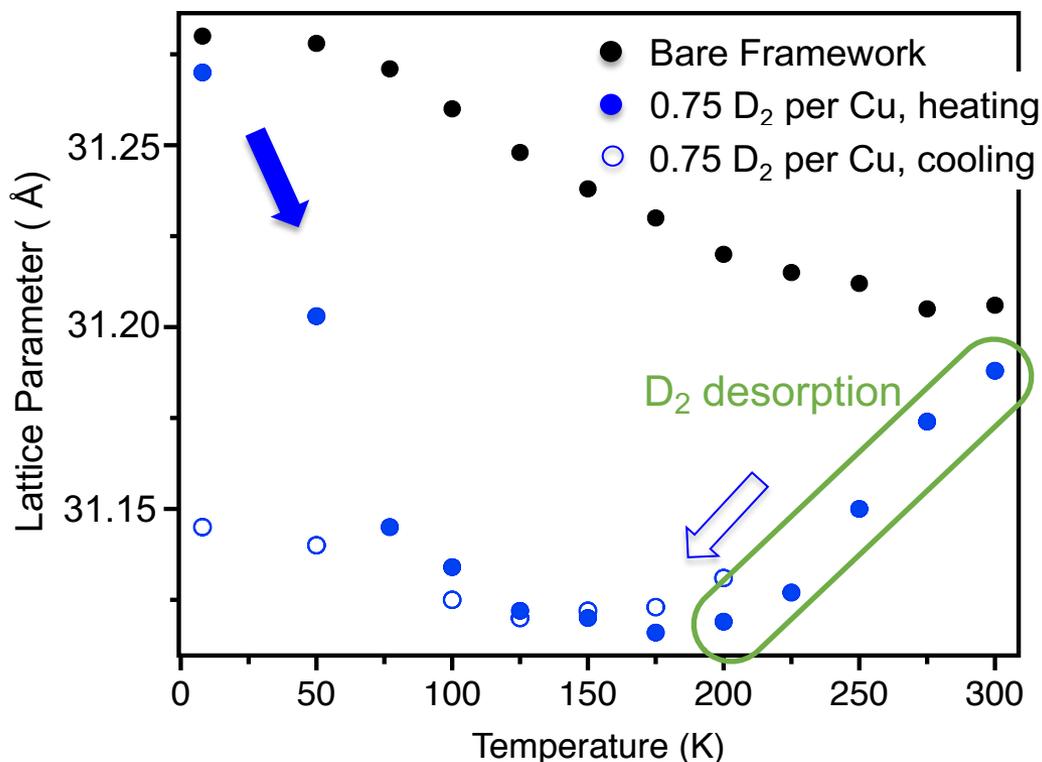
$\text{Cu-D}_2(\text{I}) \approx 1.6 \text{ \AA}$

$\text{Cu-D}_2(\text{I}^*) \approx 3 \text{ \AA}$



- Sample dosed with 0.75 D_2/Cu at 40 K and then cooled to 7 K
- Occupation of two distinct D_2 sites near Cu^+ is apparent
- Occupancy of site I increases upon dosing at successively higher T

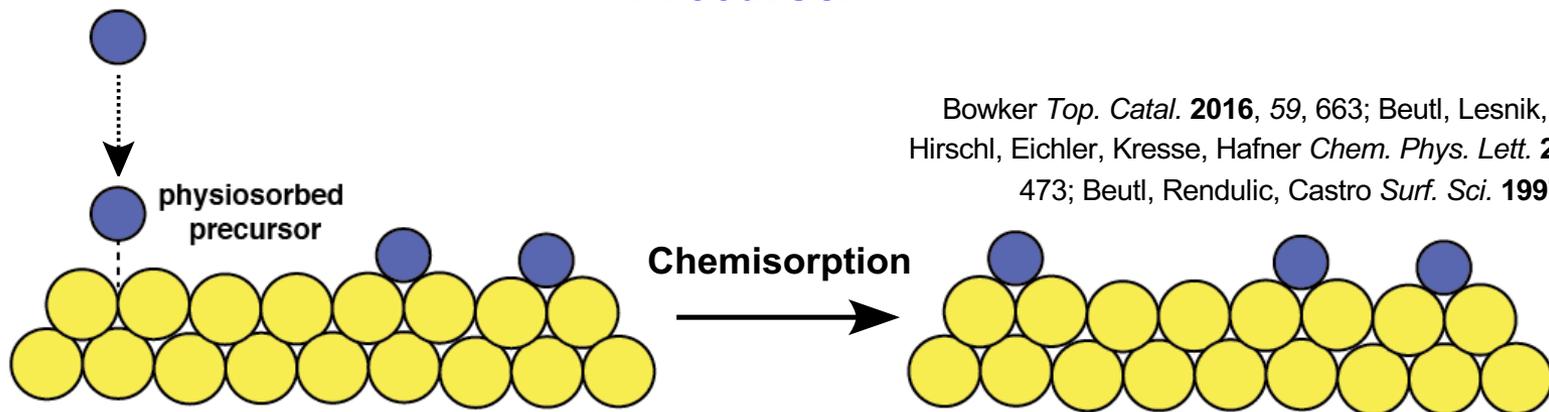
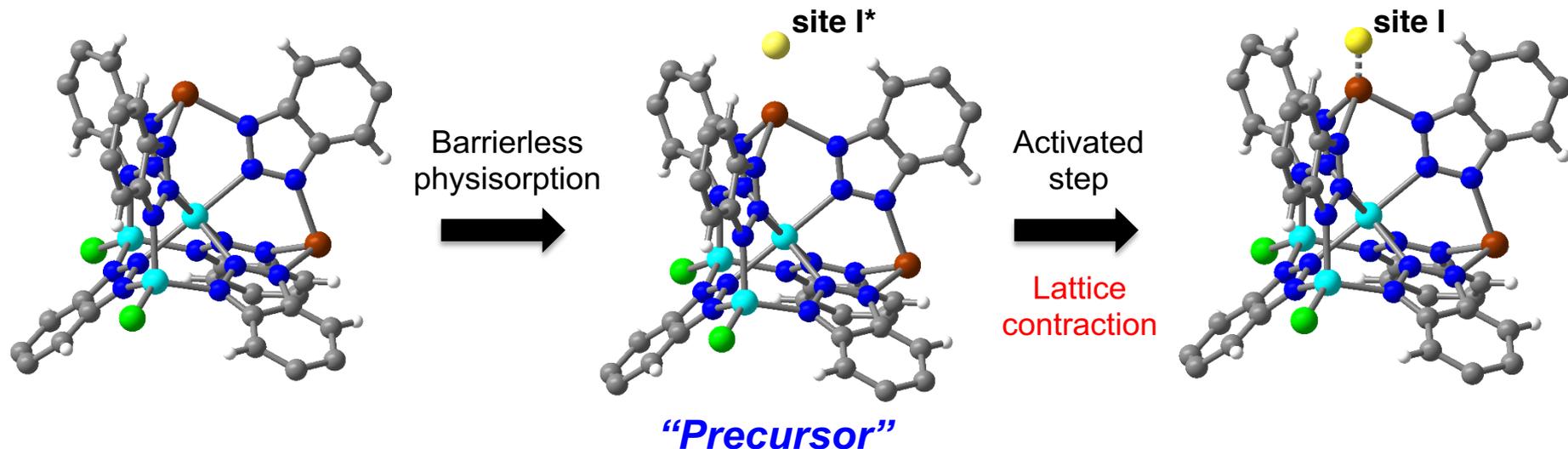
Activated D₂ Binding in Cu^I-MFU-4l



Dosing temp.	Site I occ. (D ₂ per Cu)	<i>a</i> (Å)
none (bare MOF)	—	31.2744(14)
40 K	0.10(2)	31.2174(10)
77 K	0.48(2)	31.1652(10)
300 K	0.602(14)	31.1505(6)

- Significant lattice contraction with strong D₂ binding
- Spontaneous desorption begins around 200 K
- Hysteresis observed on cooling below 100 K

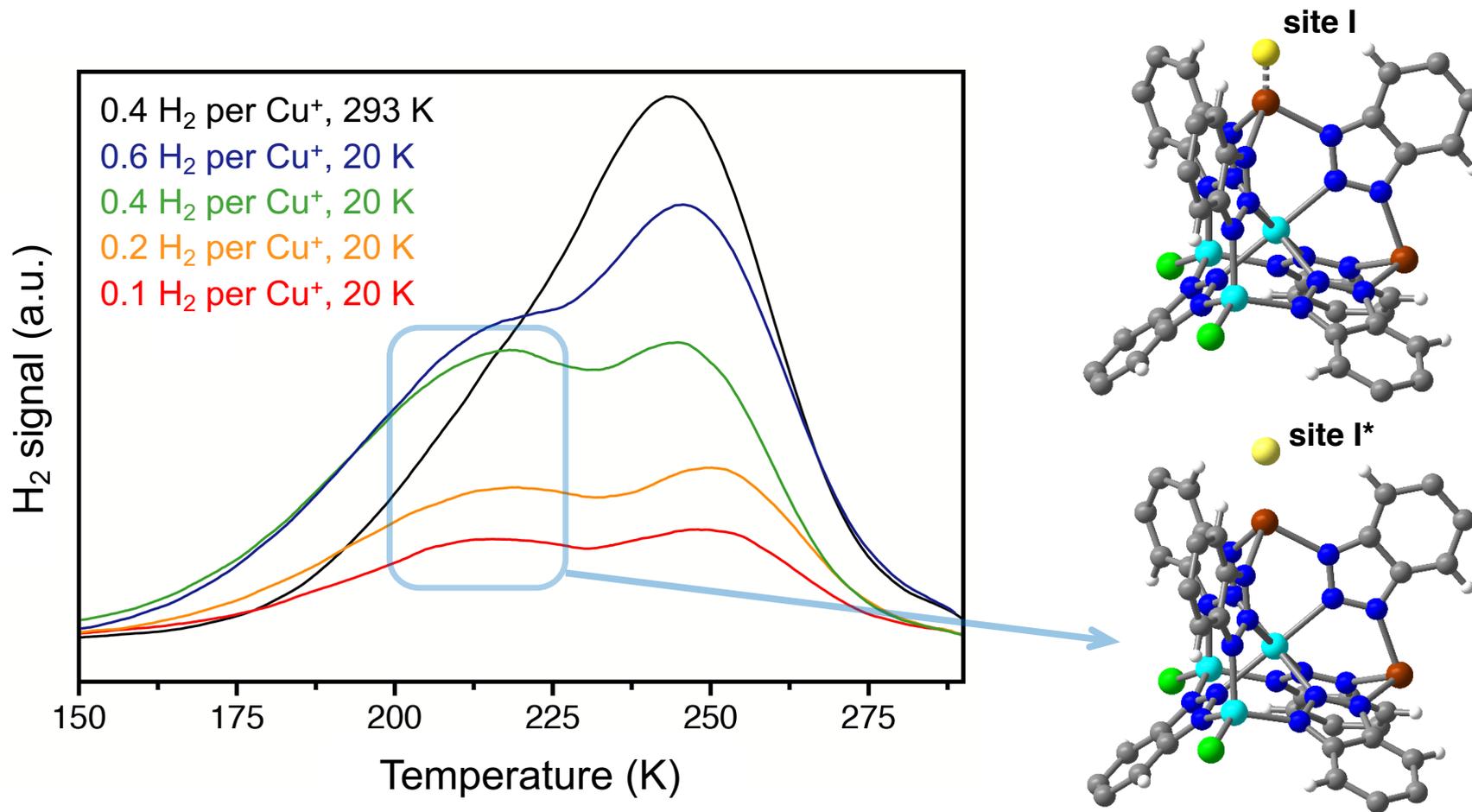
Elucidating the Mechanism of H₂ Chemisorption



Bowker *Top. Catal.* **2016**, 59, 663; Beutl, Lesnik, Rendulic, Hirschl, Eichler, Kresse, Hafner *Chem. Phys. Lett.* **2001**, 342, 473; Beutl, Rendulic, Castro *Surf. Sci.* **1997**, 385, 97

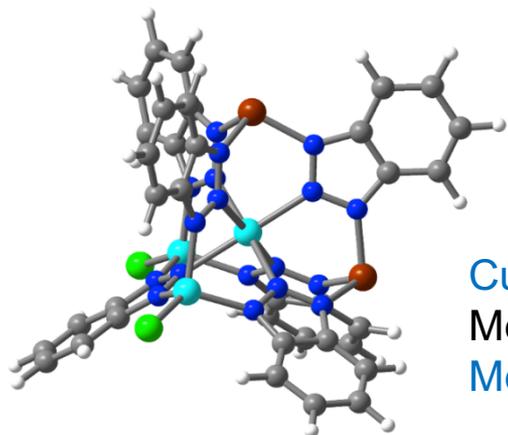
- Precursor state corresponds to local energy minimum en route to chemisorption
- Such states have been observed for dissociative and non-dissociative adsorption of various substrates (e.g., H₂, N₂, O₂, CO)

Direct Observation of Precursor Using TPD



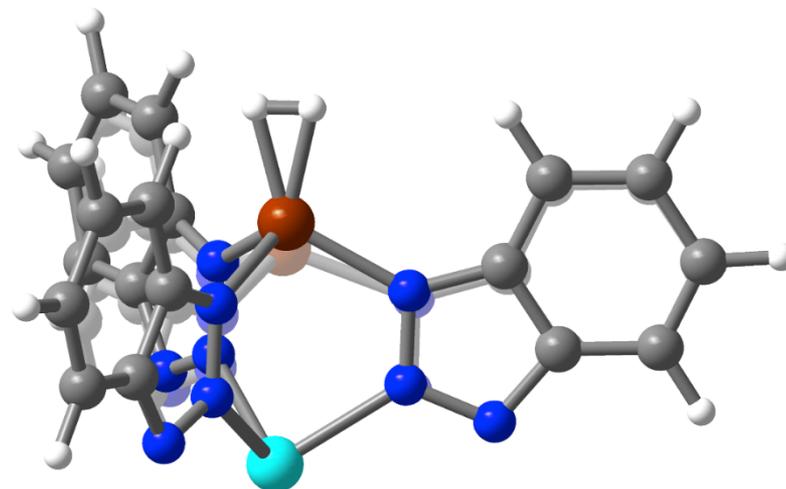
- New desorption peak around 200 K can be assigned to precursor state

Question: Why is there an activation barrier to adsorption at an open metal site?



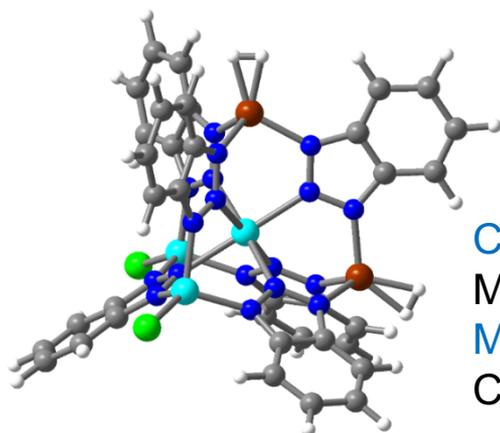
$\text{Cu-Zn}(O_h) = 3.27 \text{ \AA}$
Mean $\text{Cu-N} = 1.96 \text{ \AA}$
Mean $\text{N-Cu-N} = 108.6^\circ$

Bare cluster



Significant Structural Distortions upon H₂ Adsorption

- Cu moves away from center of cluster upon binding H₂
- Bonds between N and central Zn shorten by a mean value of 0.03 Å



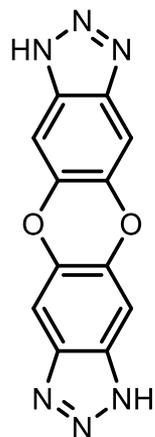
$\text{Cu-Zn}(O_h) = 3.49 \text{ \AA}$
Mean $\text{Cu-N} = 2.00 \text{ \AA}$
Mean $\text{N-Cu-N} = 101.2^\circ$
 $\text{Cu-H}_2 = 1.70 \text{ \AA}$

Cluster with adsorbed H₂

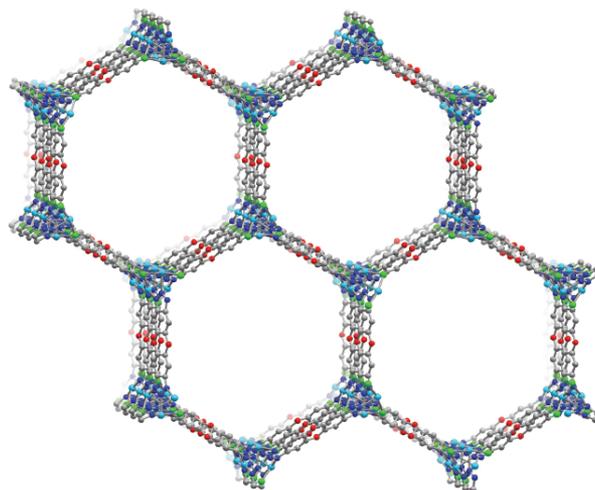
Previous Results: $V_2Cl_{2.8}(\text{btdd})$ Contains Open V^{2+} sites

Hypothesis: Increasing orbital interactions with H_2 will allow us to access this range

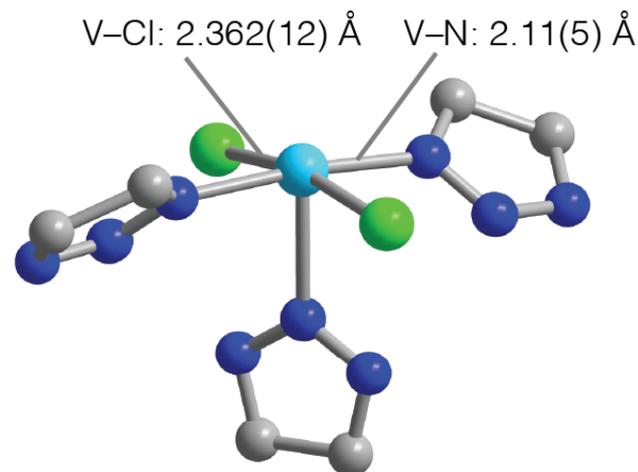
- Square pyramidal V^{2+} sites exhibit appropriate electronic structure



$H_2\text{btdd}$



$V_2Cl_{2.8}(\text{btdd})$

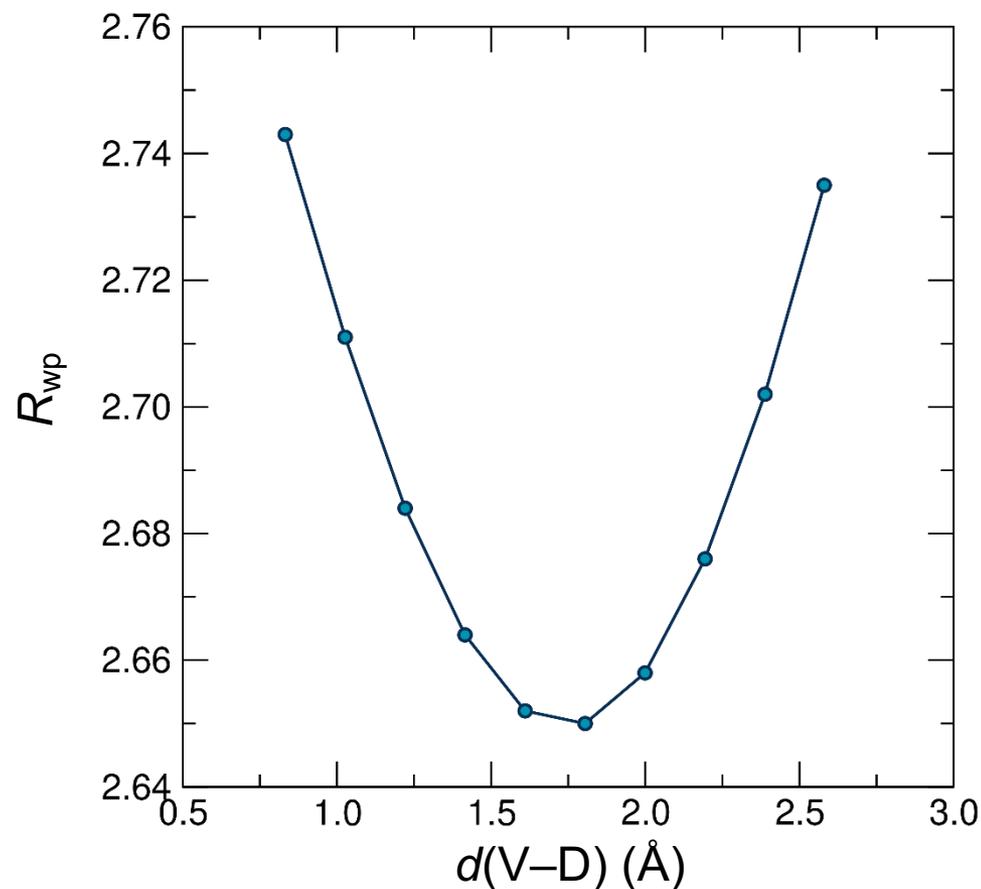
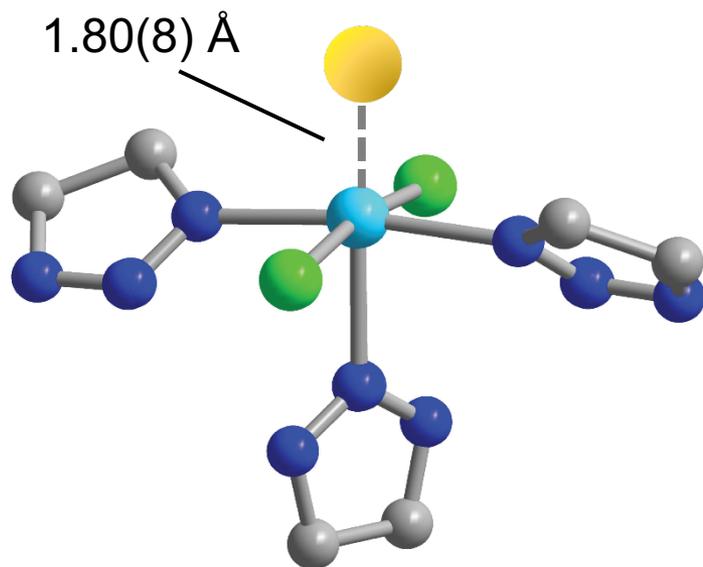


5-coordinate V^{II} site

- Triazolate linker stable to the highly reducing V^{2+} (unlike carboxylate linkers)
- $SA_{\text{Langmuir}} = 3290 \text{ m}^2/\text{g}$, $SA_{\text{BET}} = 1930 \text{ m}^2/\text{g}$

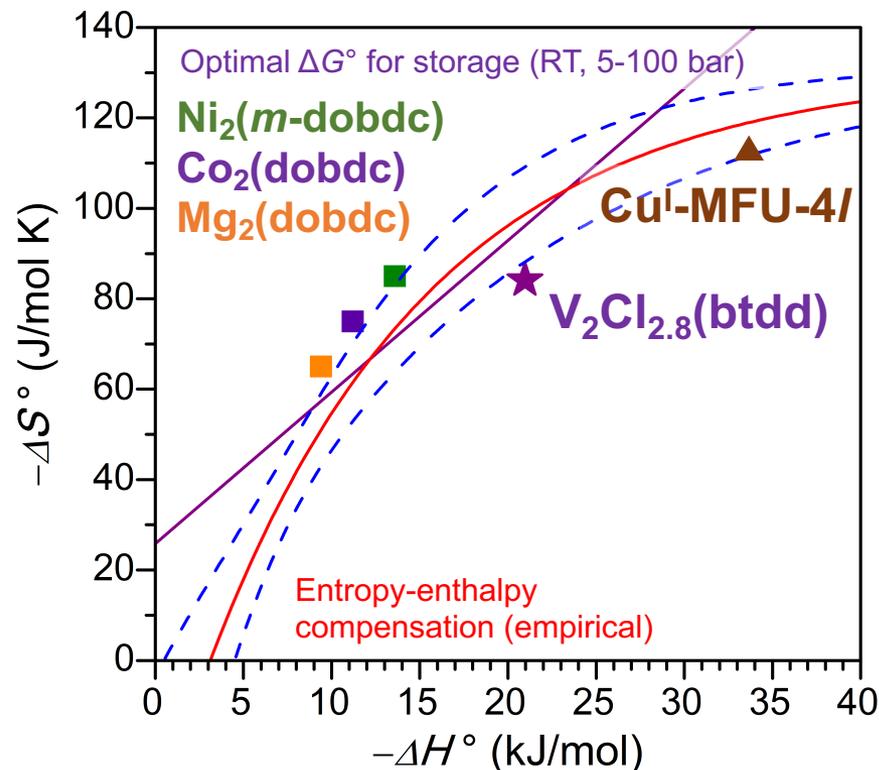
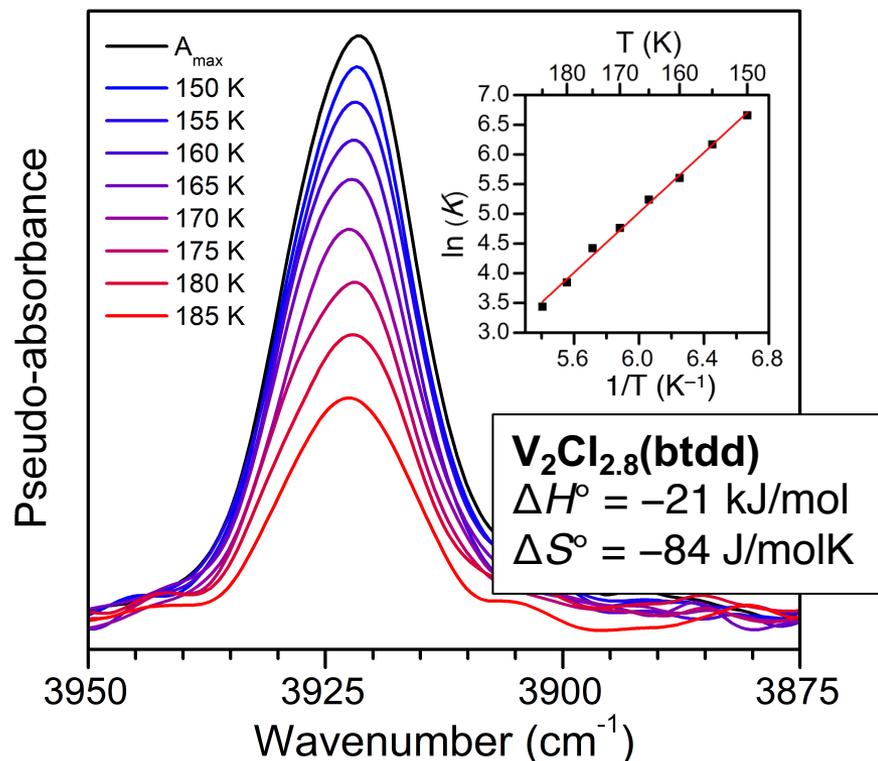
Accomplishment: Neutron Diffraction Characterization of V–D₂

V₂Cl_{2.8}(btdd) + 0.75 equiv. D₂



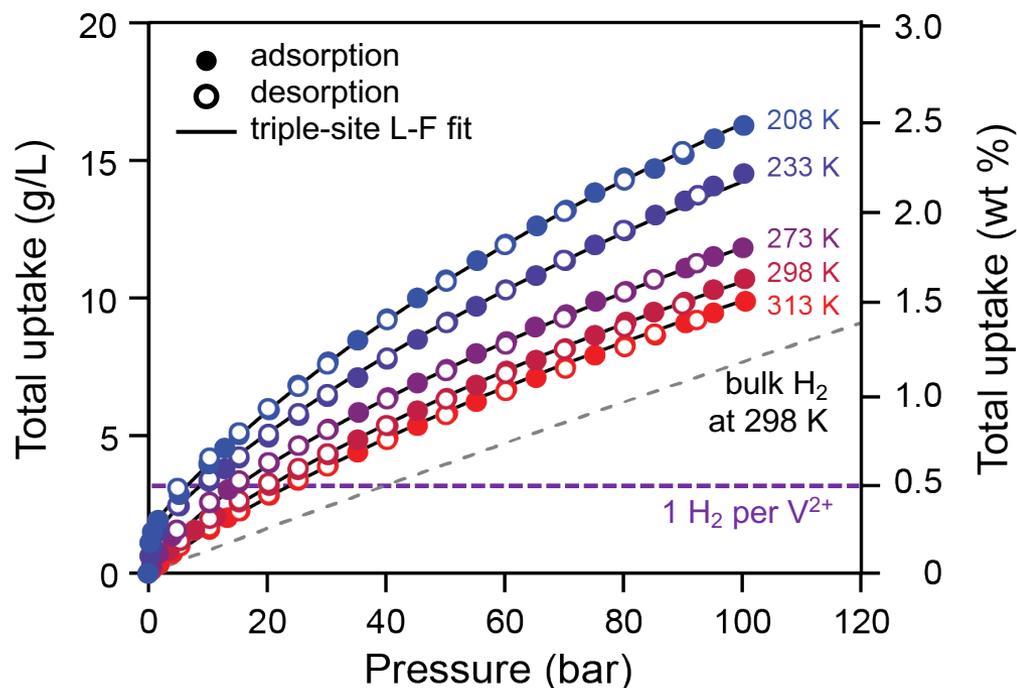
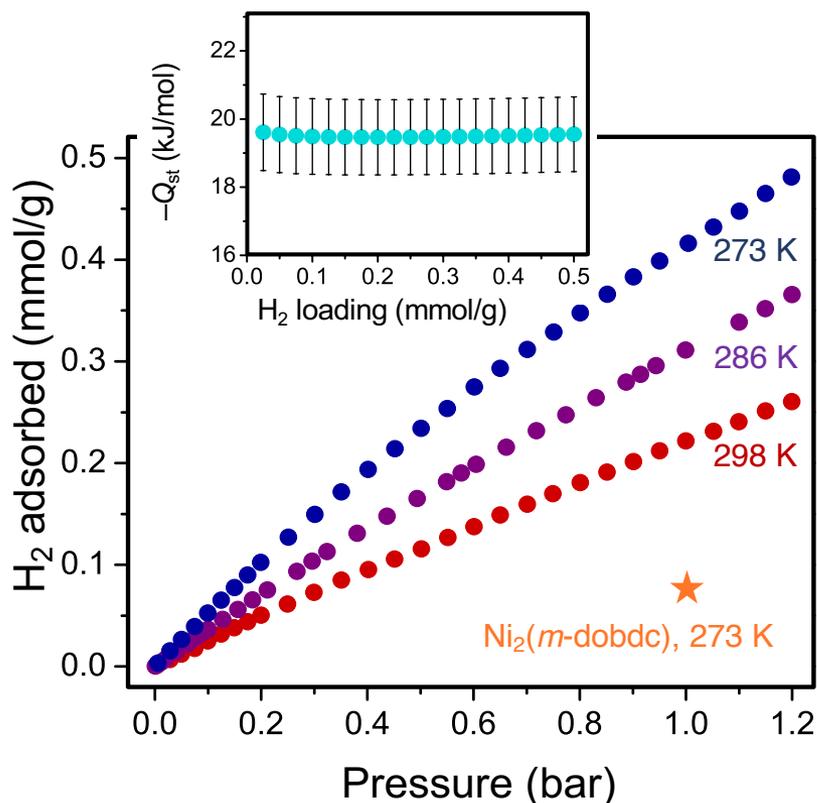
- V–D₂ can be resolved despite disorder with V^{III}–Cl sites
- $d(\text{Cu–D}_2) = 1.60(3) \text{ \AA}$ in Cu^I–MFU-4l; $d(\text{Ni–D}_2) = 2.18(4) \text{ \AA}$

Variable-Temperature IR Spectra of H₂



- First example of a MOF with ΔH in the optimal range between -15 and -25 kJ/mol
- Enthalpy-entropy relation distinct from $M_2(dobdc)$ family

Low- and High-Pressure Ambient H₂ Isotherms



- Gravimetric total uptake for V₂Cl_{2.8}(btdd) surpasses Ni₂(*m*-dobdc) at 298 K and 100 bar (1.64 vs. 0.98 wt %)
- Initial steep uptake can be observed below 233 K where V²⁺ sites do not contribute to usable capacity

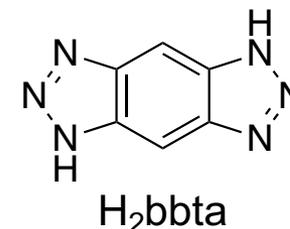
Future Plans (Task 1.B)

MOF	ΔH from DRIFTS ^a (kJ/mol)	Q_{st} from isotherms (kJ/mol)	Total H ₂ uptake at 298 K, 100 bar (g/L)	Usable capacity at 298 K, 5–100 bar (g/L)
Comp. H ₂	—	—	7.7	7.3
Ni ₂ (<i>m</i> -dobdc)	-13.7	-12.3	11.9 ^b	11.0 ^b
Cu ^I -MFU-4l	-33.6	-32.7	11.0 ^b	9.3 ^b
V ₂ Cl _{2.8} (btdd)	-21.0	-19.5	10.7 ^b	9.6 ^b
HKUST-1 ^c	n.d.	-6.9	9.8	9.0

^aDiffuse reflectance infrared Fourier transform spectroscopy, ^bApplied single crystal density,

^cHKUST-1 monolith prepared in Task 1.C.1

- Gain a complete understanding of H₂ adsorption in these V^{II} and Cu^I systems
- Post-synthetically reduce V₂Cl_{2.8}(btdd) to access an all vanadium(II) framework (vanadium density of 4.4 mmol/g)
- Synthesis of V₂Cl₂(bbta): greater gravimetric capacity (6 mmol/g) with likely binding enthalpy ~20 kJ/mol



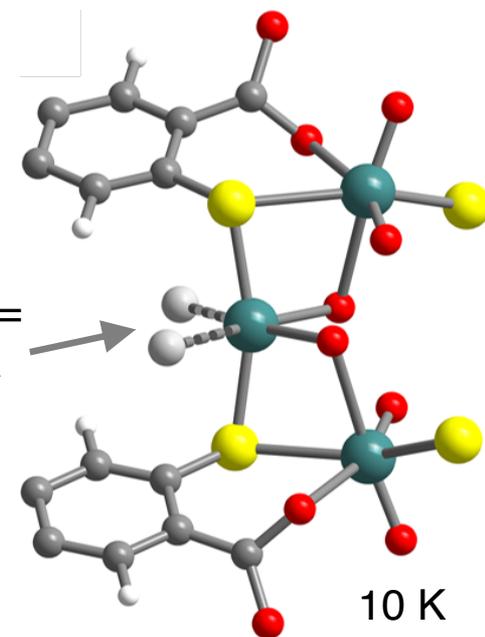
Any proposed future work is subject to change based on funding levels

Is it possible to create MOFs with open metal sites that adsorb more than two H₂ molecules?

- This is a long-standing “holy grail” in MOF chemistry
- Highly complex synthetic challenge

Mn₂(dsbdc) adsorbs two H₂ at a Mn²⁺ site: Runčevski, Kapelewski, Torres-Gavosto, Tarver, Brown, Long *Chem. Commun.* **2016**, 52, 8351.

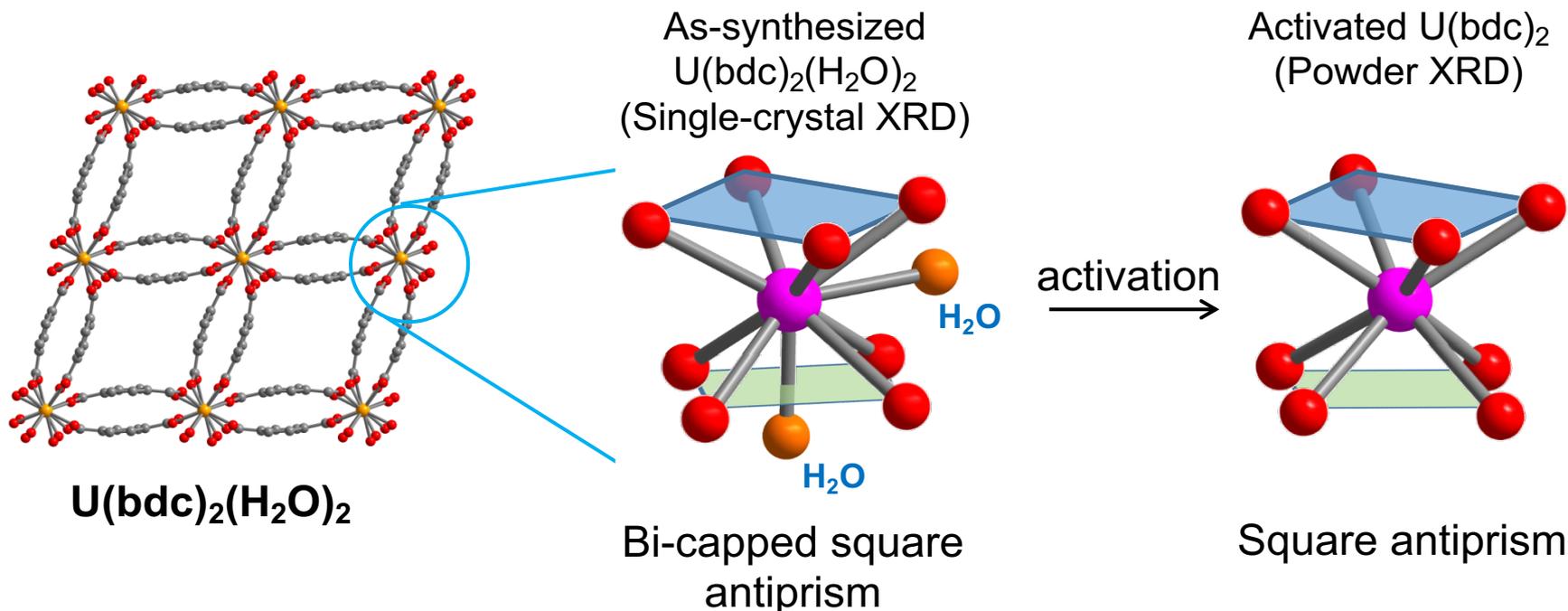
$d(\text{Mn}-\text{D}_2) = 3.07(3) \text{ \AA}$



Questions:

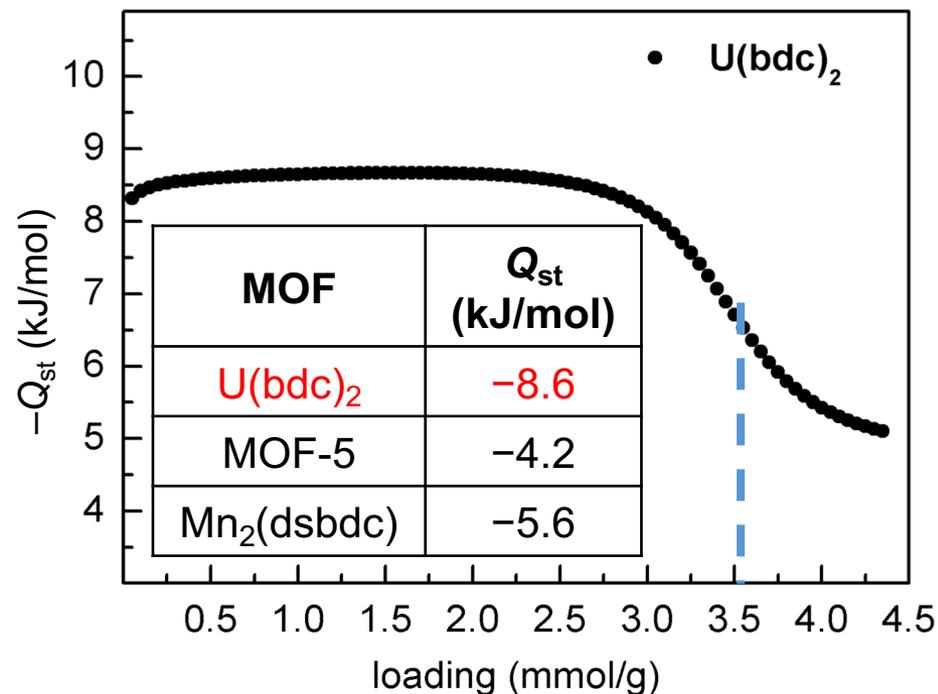
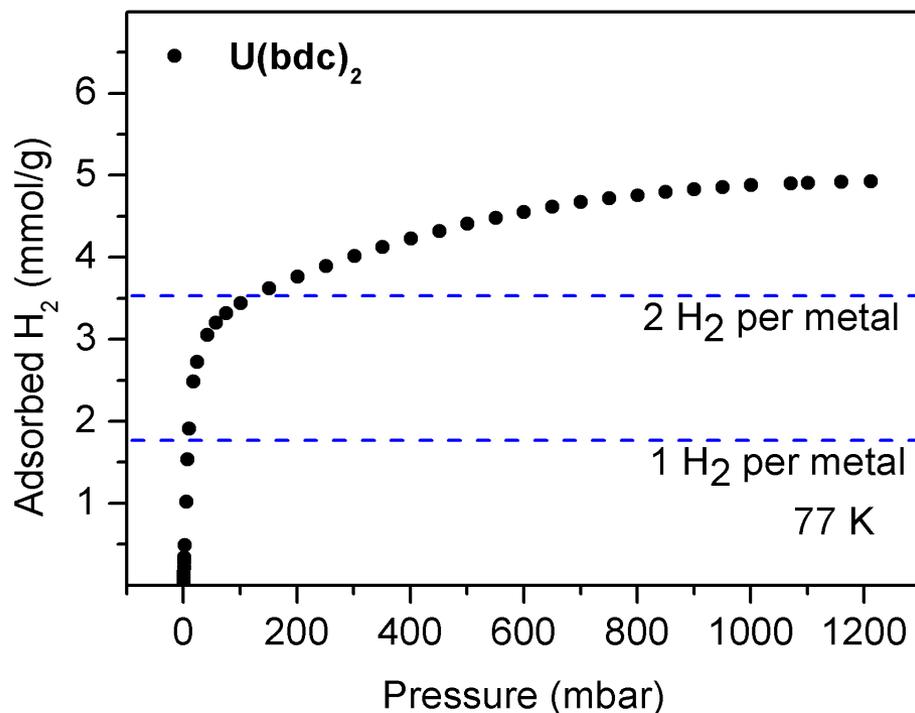
- Can we access multiple open sites per metal at secondary building units in MOFs?
- Can MOFs with the f-elements (coordination numbers up to 15) bind multiple H₂ per metal?

Accomplishment 1.E: A New 3-Dimensional Uranium MOF— $U(bdc)_2(H_2O)_2$

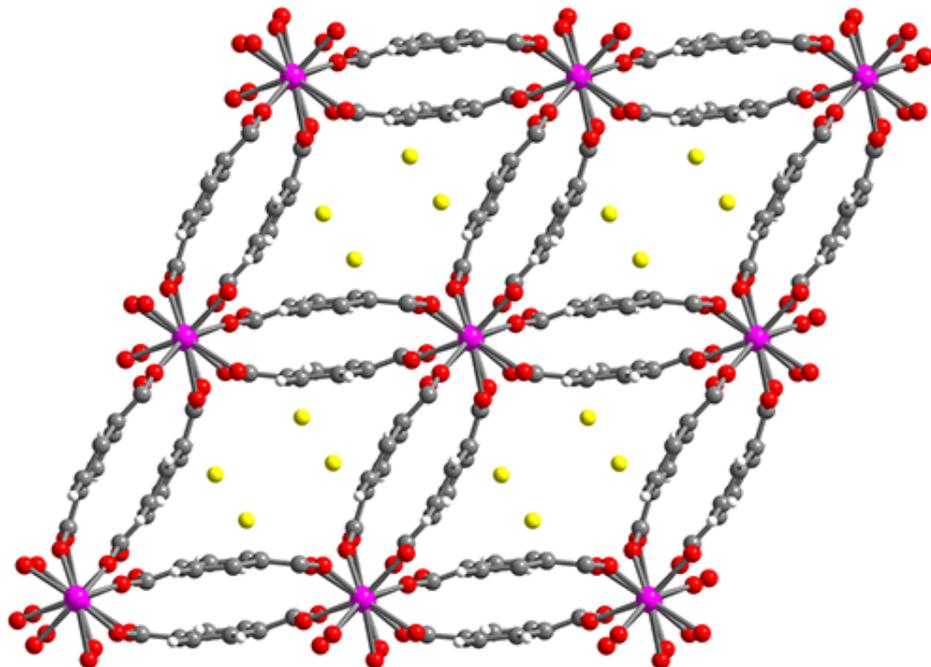


- Langmuir surface area = 570 m²/g
- Each uranium is coordinated by two H₂O (TGA shows desolvation step at 130 °C)
- Can we access two open metal sites for H₂ binding in activated $U(bdc)_2$?

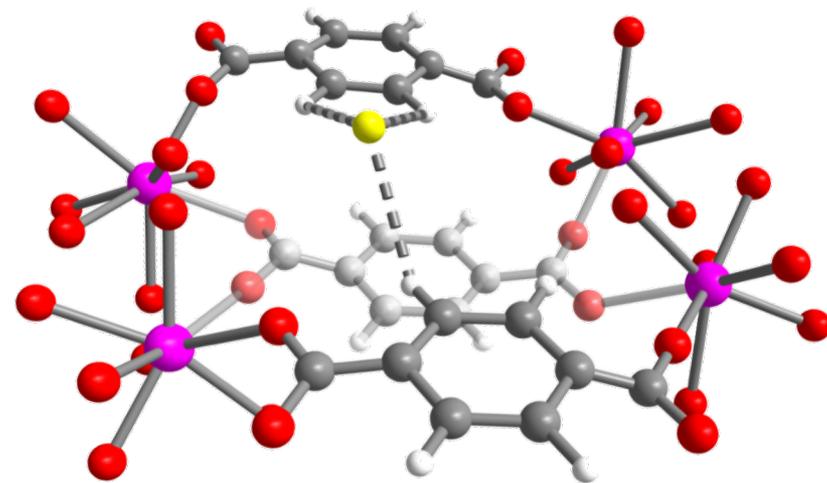
Low-Pressure H₂ Adsorption in U(bdc)₂



- Strong H₂ binding to theoretical capacity of 2 H₂ per metal
- Inflection point matches theoretical capacity of 2 H₂ per metal



4 D_2 per pore = 2 D_2 per U



Binding pocket: 3 C–H bonds

- Loading from neutron diffraction data is consistent with that observed in H_2 isotherms
- Unexpectedly there are no D_2 –U interactions

- **Mechanism of H₂ chemisorption in Cu^I-MFU-4l:** Used powder neutron diffraction and temperature-programmed desorption to characterize a metastable, adsorbed precursor intermediate in Cu^I-MFU-4l
- ***In situ* powder neutron diffraction:** Resolved V–D₂ bond distance in V₂Cl_{2.8}(btdd) despite disorder with V^{III}–Cl sites. Bond distance is compatible with strong binding
- **Multiple H₂ per metal:** Synthesized MOFs with multiple open sites per metal by harnessing larger ionic radii and high coordination numbers of the *f*-elements
- Obtained valuable insight into the mechanistic pathway of activated H₂ chemisorption in Cu^I-MFU-4l from DFT simulations of the Cu^I nodes
- Measured high-pressure H₂ adsorption isotherms for V₂Cl_{2.8}(btdd), which corroborated binding enthalpy within an optimal operation range
- Demonstrated N₂-induced flexibility at 77 K in two new Zn(bdp) derivatives
- Confirmed photochemical release of CO from Mn carbonyl complexes ligated by bipyridine (bpy) in the zirconium framework UiO-67-bpy
- Verified the synthesis of HKUST-1 monolith, which exhibits volumetric H₂ uptake 50% greater than the powder form

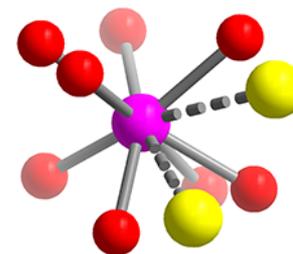
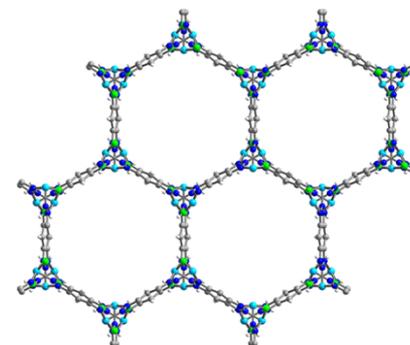
Summary (FY20 Internal Adsorbents Milestones)



Task	Milestone	Due	Status
1.B.1	Electronic structure computations: Develop a computational protocol to assess thermochemical effects (enthalpy and entropy) in hydrogen adsorption.	9/2020	30%
1.B.2	Optimal binding energies: Synthesize a derivative of Cu ^I -MFU-4l or V ₂ Cl ₂ (btd) with a modified ligand and measure H ₂ heat of adsorption.	9/2020	30%
1.C.1	MOF monoliths: Synthesize at least 2 monolith MOFs that outperform the volumetric storage capacity of monolith HKUST-1 at temperatures above 150 K and < 100 bar.	9/2020	30%
1.D.1	Flexible MOFs: Synthesize at least 2 different M(bdp) (M other than Co) frameworks and locate step pressures at 77 K.	9/2020	50%
1.E	Multiple H₂s per metal: Demonstrate either (a) binding of three H ₂ to a single metal center, or (b) binding of multiple H ₂ to a single metal center, with a maximum heat of adsorption of at least 8 kJ/mol.	9/2020	25%

Future Directions (Adsorbents)

- Use ^{65}Cu solid-state NMR to investigate whether thermodynamic or kinetic cooperativity between proximal Cu^I centers influences H_2 binding in Cu^I -MFU-4l
- Synthesize V-based MOFs with shorter linkers for greater volumetric H_2 storage capacities and a target binding enthalpy of ~ 20 kJ/mol
- Explore functionalized $\text{M}(\text{bdp})$ variants to tune the step pressure at ambient temperatures
- Explore new MOFs with f -elements featuring multiple accessible metal binding sites
- Optimize synthetic conditions of MOF-74-type monoliths to increase volumetric H_2 storage capacities
- Predict usable capacities from anharmonic free energy estimates in MOFs



Any proposed future work is subject to change based on funding levels

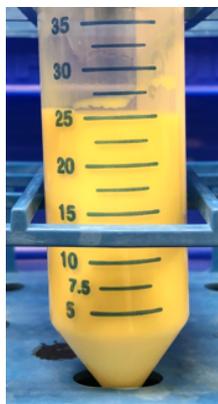
Additional slides

Task 1.C.1. COF Monolith Synthesis

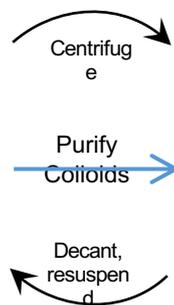
Relevant technical target improve volumetric capacity

Project success – Synthesis of first COF monolith

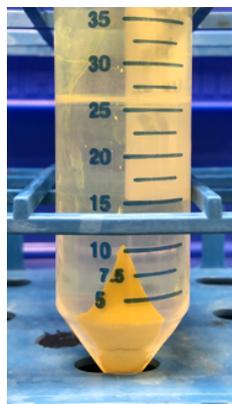
Colloidal Suspension



Colloidal Powder
500 m²/g
~0.1 g/cm³



Packed 'Gel'



'Regrowth'
(colloids fused)
Framework-Monomer
Equilibrium
Re-established

Wet Monolith



Soxhlet
Extraction
Slow
drying

Dried Monolith



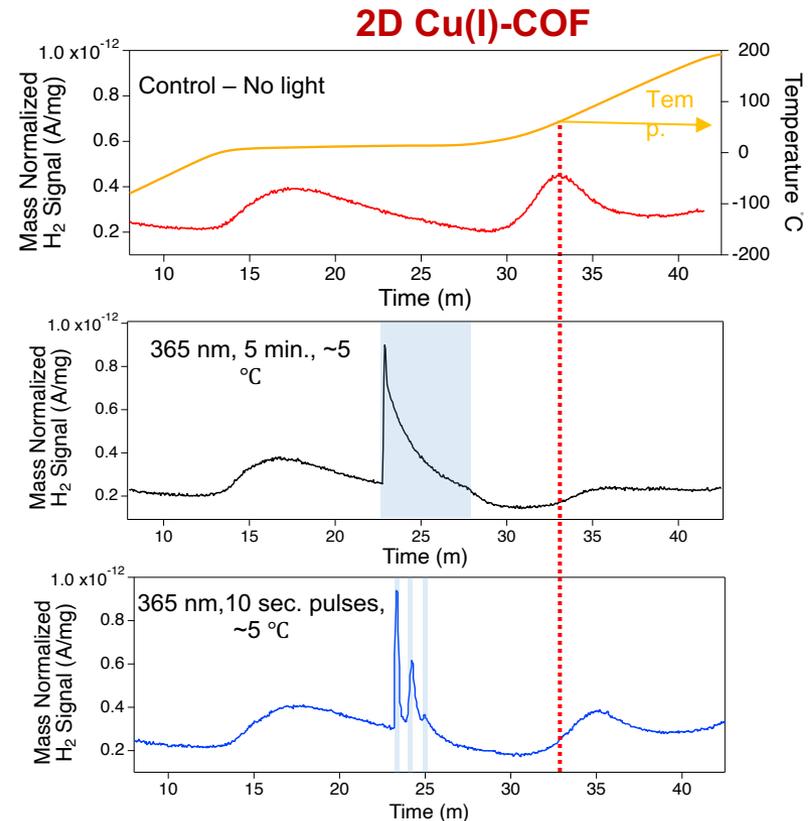
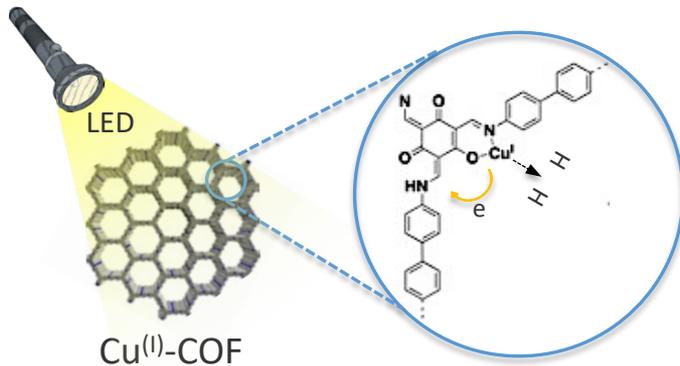
COF Monolith
400 m²/g
~0.5 g/cm³

Task 1.D.2. Thermal/photo-responsive sorbent matrices

Relevant technical target: ‘Tuning’ isosteric heats of H₂ adsorption

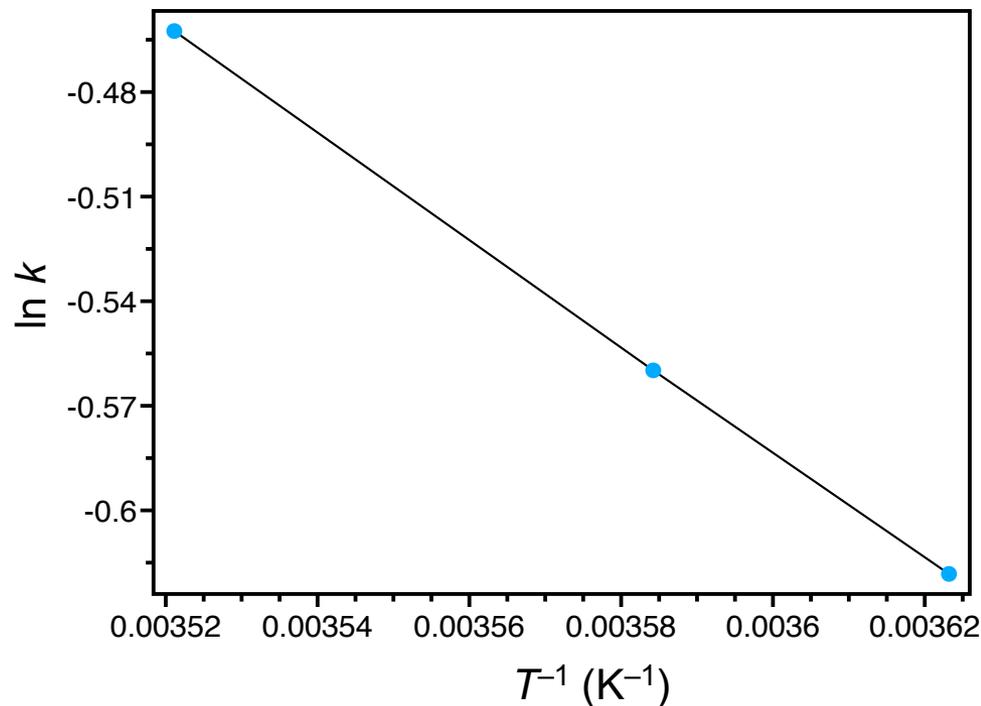
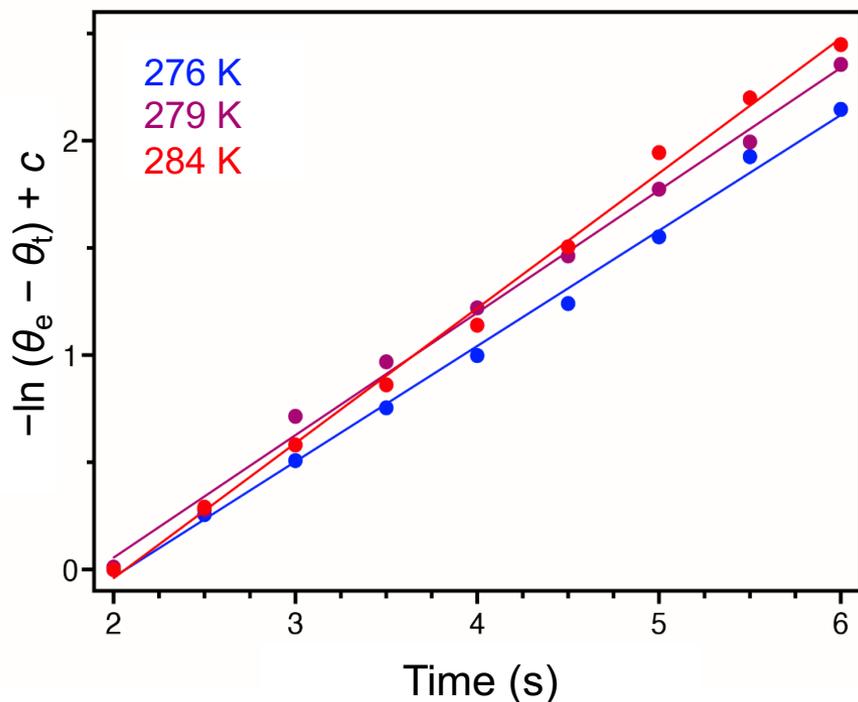
Approach:

- Cu loaded into a framework, heat treatment to generate open Cu^(I) binding site, enthalpy of H₂ desorption ~15 k/mol
- Photoinduced metal-ligand charge transfer from Cu^(I) to Framework generates ‘transient’ Cu^(II) with decreased π -backbonding
- H₂ evolves when exposed to light

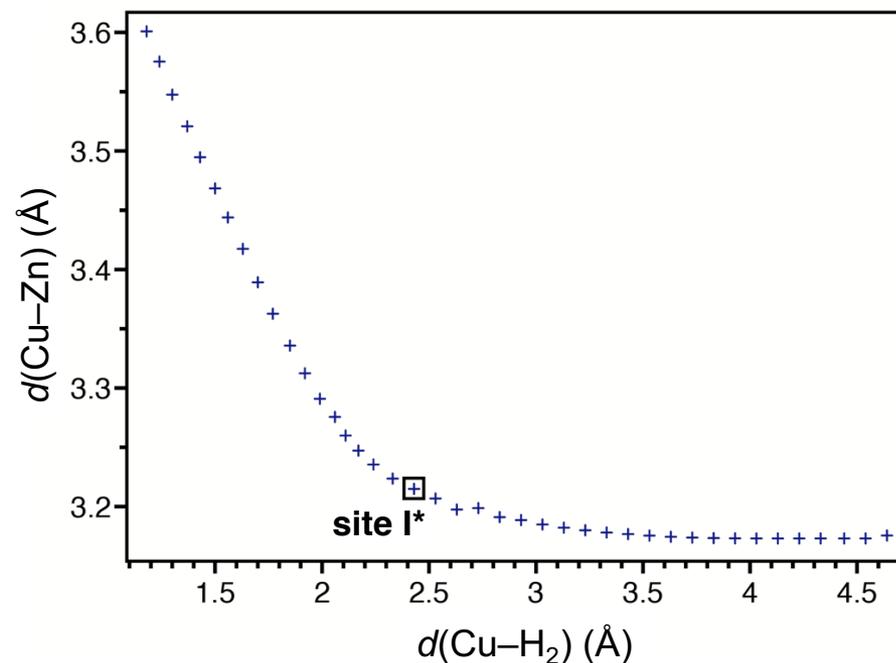
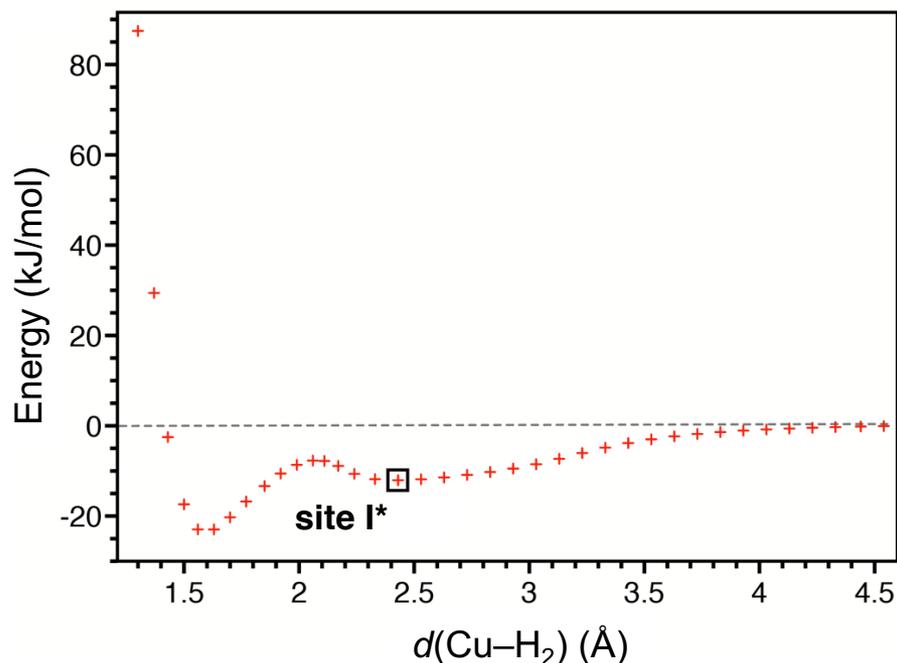


Accomplishment: Successfully demonstrated ‘on demand’ release of H₂ from sorbent

Project success → ‘On demand’ ambient temperature H₂ delivery



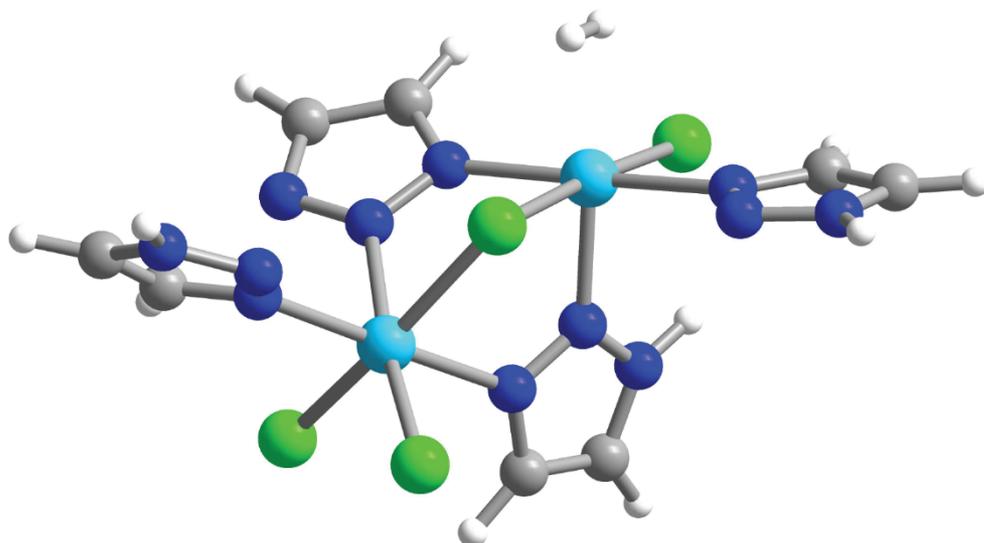
- Transient uptake measurements performed between 276–284 K
- Data were fit to first-order Langmuir-derived rate law
- Arrhenius equation gives an apparent activation barrier $E_a = 12.7 \text{ kJ/mol}$
- Value most reasonably represents lower bound of actual E_a



- Calculations are able to reproduce the presence of a local energy minimum
- Results are highly basis set dependent
- Activation barrier in these calculations is 4.4 kJ/mol

Calculations Show High Orbital Contribution

H₂ binding to V(II)V(III) model



V–H 2.118 Å $\Delta V_{\text{HH}} (\text{cm}^{-1}) = 240 \text{ cm}^{-1}$

Energy decomposition analysis

Component	Energy (kJ/mol)
Frozen	11.4
Polarization	–3.8
Charge transfer	–34.1
Total	–26.9

$\sigma \text{ H}_2 \rightarrow \text{V(II)}$	–22.7
$\pi \text{ V(II)} \rightarrow \text{H}_2$	–5.4

- 70% of total binding contributions come from CT

Romit Chakraborty, Martin Head-Gordon