NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Pacific Northwest
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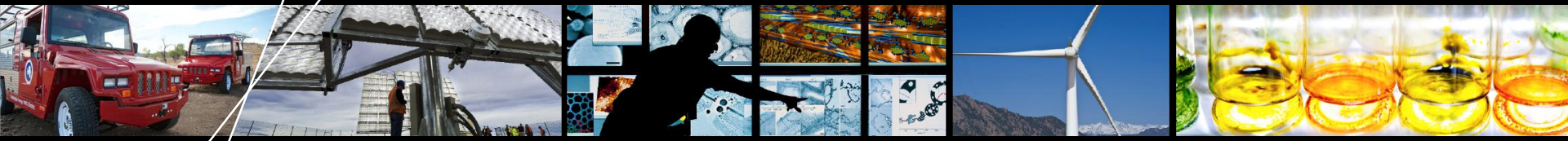
BERKELEY LAB

NIST



DOE-EERE FCTO – Hydrogen Storage: Core Characterization Capabilities and Materials Research Effort

FCTO Core Capability Advancement

A collaboration and synergistic research effort between:

PNNL, LBNL, NIST, NREL

To Develop and Enhance Hydrogen Storage Characterization Techniques

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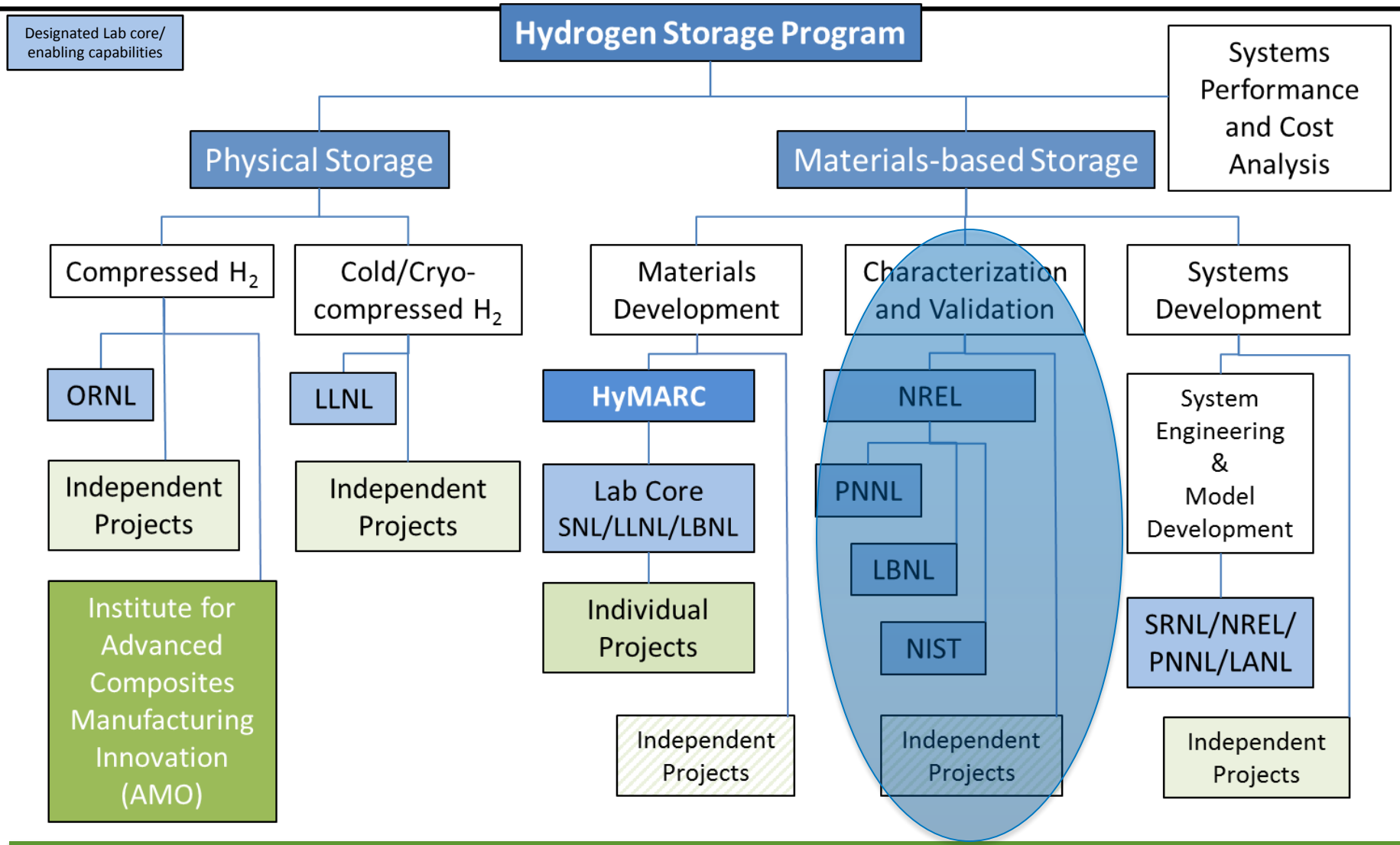
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Hydrogen Program Organization



Program organized to address near and long-term technology development

Current Team Structure

- **NREL: Gennett, Blackburn, Dameron, Hurst, Olsen, Parilla**
  - Characterization, Synthesis
- **LBNL: Long, Head-Gordon**
  - Characterization, Synthesis, Theory
- **PNNL: Autrey, Bowden, Karkamkar**
  - Characterization, Synthesis
- **NIST: Brown, Udovic**
  - Characterization (Neutron)

FY16 CORE CAPABILITY DEVELOPMENT

- **NREL**
  - Thermal Conductivity
  - Volumetric Measurements
  - TPD
- **PNNL**
  - NMR
  - Calorimetry
- **LBNL**
  - DRIFTS
- **NIST**
  - Advanced Neutron Scattering

CORE

- **Develop advanced characterization tools**
  - Determine specific sorbent-hydrogen and/or hydride-hydrogen interactions
  - Physiochemical intrinsic properties for sorption/desorption process.
    - NMR, DRIFTS, TC, PCT, Neutron, etc.
      - Design, synthesize and characterize materials to establish base behavior of possible gas-sorbent interations
        - e.g. Unsaturated metal centers
  - Validated Capacities

- **Rational design of materials and/or materials' matrix for advanced characterization tools**

  - **Go beyond the limitations of "Equilibrium" conditions**
    - Tailor element-specific "energies" of the system (*e.g.*, by modifying surface potentials, unsaturated metal centers, specific pore chemistries, modified hydrides.
    - We can reach these different phases by changing element-specific energies while remaining in "equilibrium" conditions, or by moving into a non-equilibrium (kinetically-limited) regime.
    - Facilitate technology transfer to enable faster scaling of new materials from lab to fab

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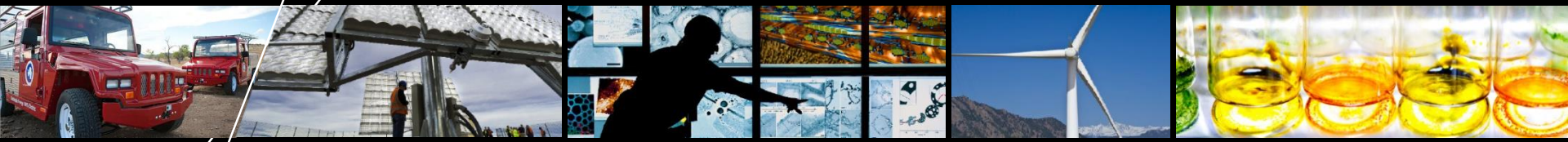

NREL Tasks

Initiate, with a minimum participation level of 5-laboratories, experimental determination of the gravimetric and volumetric capacities of an agreed upon standard sorbent material. Participant laboratories may include international collaborators.

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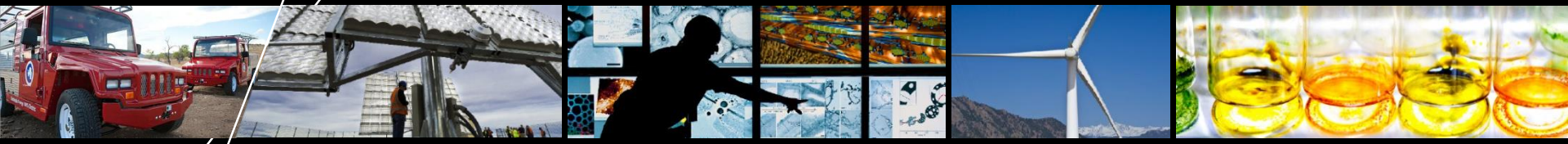


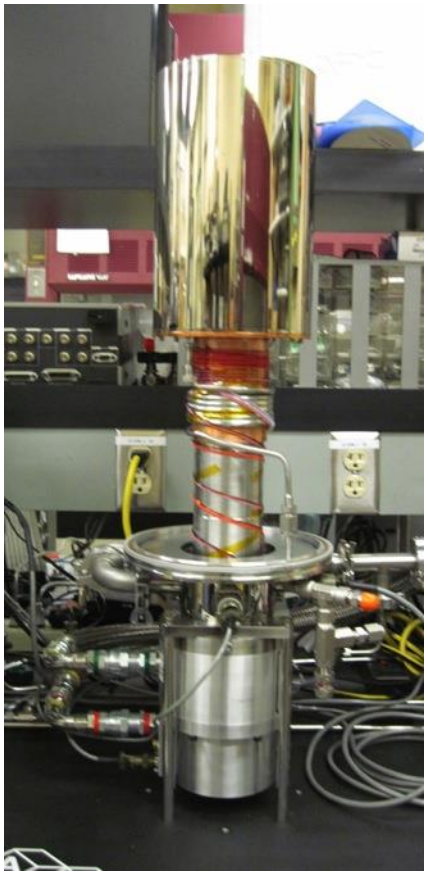
Thermal Conductivity Measurement Apparatus

Thermal Conductivity Apparatus: modular apparatus

- **Model transient temperature profile in single-sided measurement.**
  - No mathematical solutions for this configuration exist in the literature.
  - COMSOL modeling software allows numerical solutions and determination of the functional dependencies for the thermophysical properties of the modeled sample.
- **Design measurement modules.**
  - Designed plug-and-play sensor/sample holder units to allow for facile switching between measurement technique and sample form factor.
    - Capable of measuring pucks and powders and small-volume samples (down to ~ 0.5 cm^3)
    - System will accommodate expansion/sintering samples
- **Designed system to span temperature range (77K to 400K) and pressure range (0 to 150 bar).**
  - Customized a commercial ***cryostat*** to enable pressurized measurements.
  - Customized a commercial ***pressure vessel*** for electrical measurements.
- **Built and validated the apparatus in FY 15.**

Thermal Conductivity Apparatus Assembly

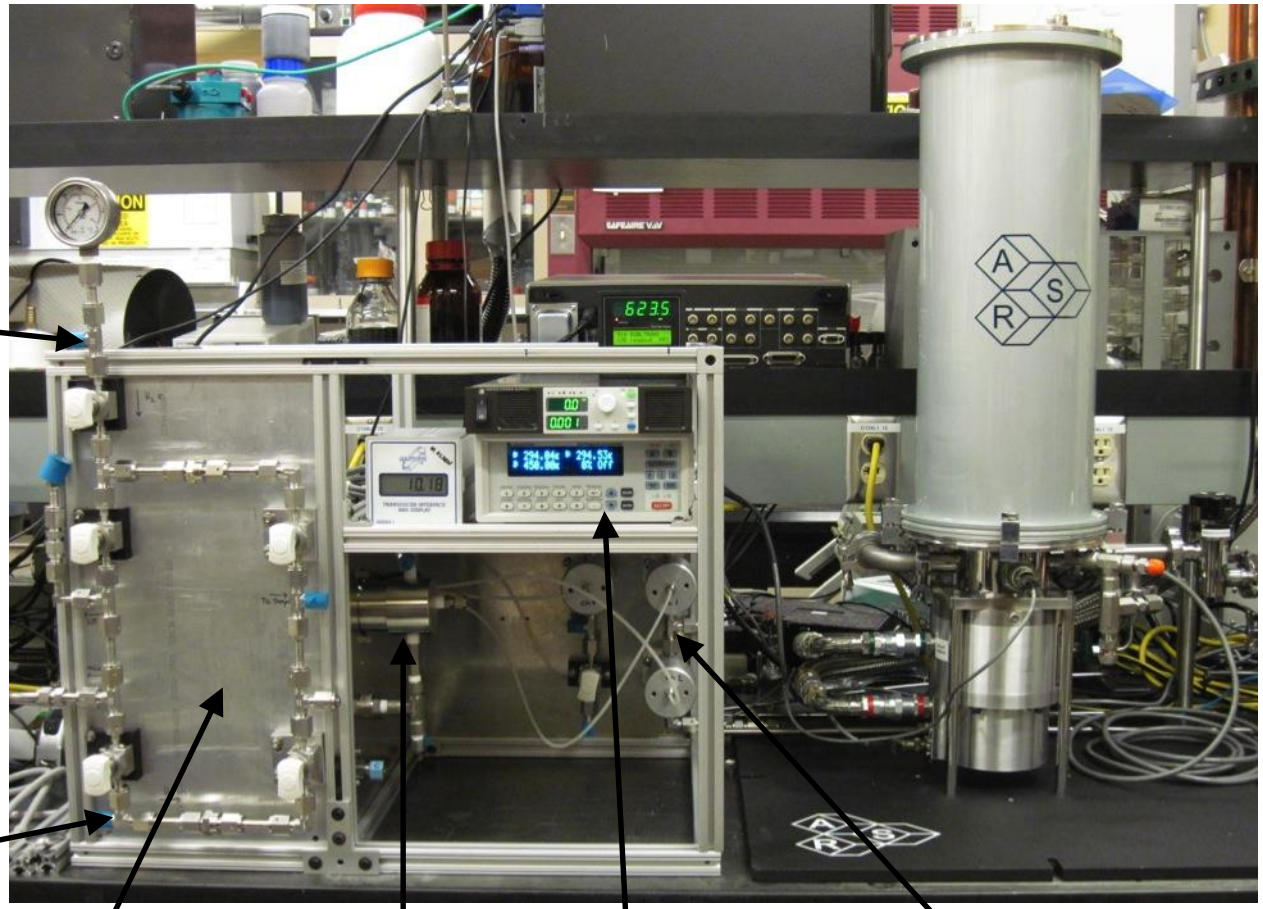
The pressure vessel mounts atop the cryo head.



The radiation shield surrounds the pressure vessel.

The entire system is enclosed in the vacuum shroud.

Cryostat and pressure-control system



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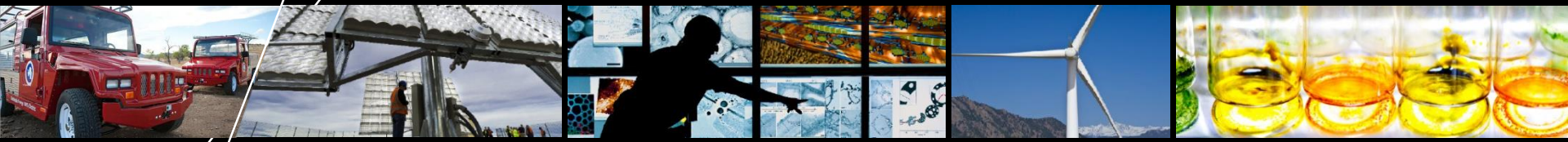


Variable Temperature PCT Measurements

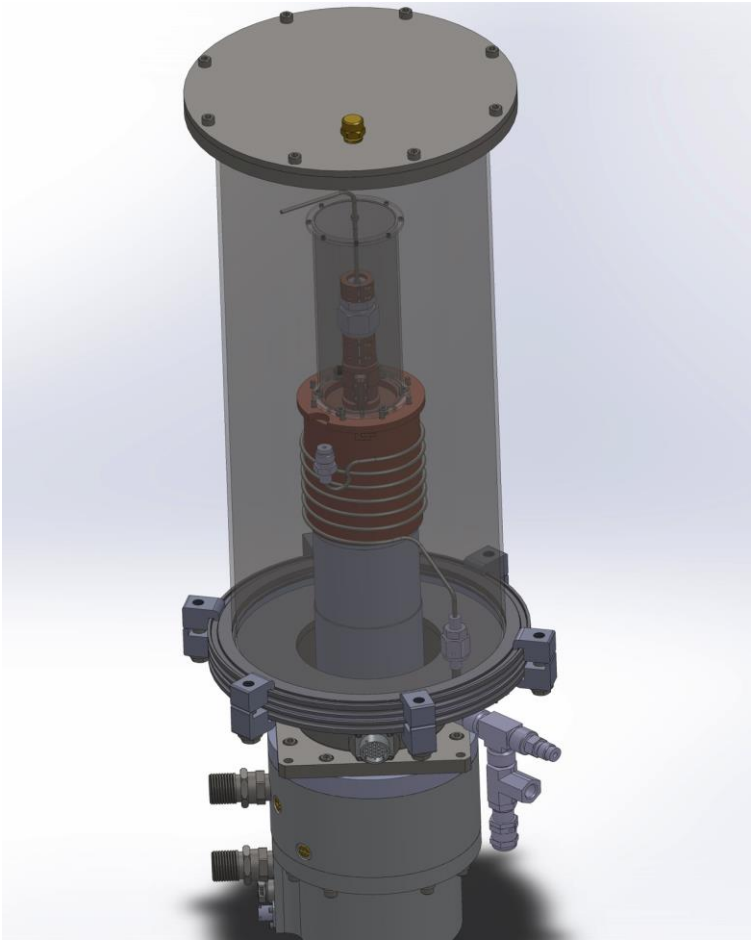
Variable Temperature PCT

- **Approved purchase request for the purchase of Model CS110AE-GME-19-NGA from Advanced Research Systems, Inc. Awaiting engineering designs**

- **Capabilities:**
- **Closed-cycle cryo-cooler (<25K – 450K)**
- **Helium compressor**
- **Custom design/construction of sample holder and copper jacketed components**

Variable Temperature PCT system

First Draft of Engineering Design



Other Capabilities

- **TPD-MS**

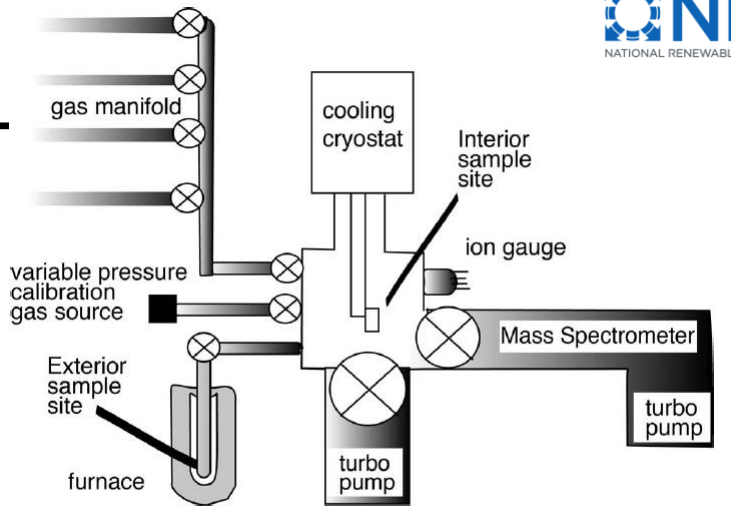


FIG. 1. Schematic of TPD apparatus.

- **BET Micromeritics ASAP 2020 BET instrument**
- **DRIFTS**
  - Thermo-Nicolet 6700 FTIR spectrometerfit with high pressure/high temperature DRIFTS cell. A Thermo Spectra Tech Collector II (P/N 700-0042) adapter was used to modify the spectrometer for reflection measurements, and the DRIFTS sample holder was a Thermo Spectra Tech High Temperature/Vacuum Chamber (P/N 0030-103) with ZnSe windows.
- **NEXAFS cell system up to 60 bar (Steve Christensen 10:15 am, Nov 5th.**

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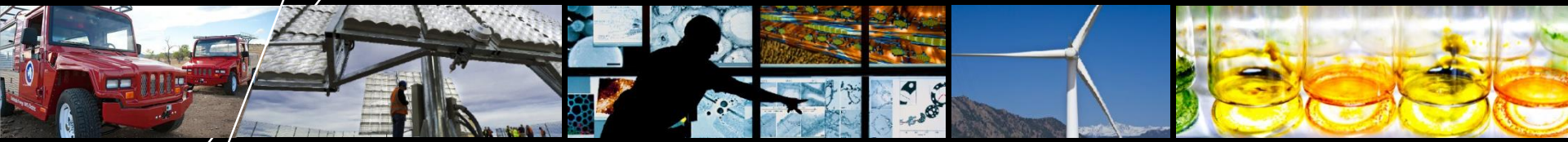


LBNL Advanced DRIFTS Characterization

Modified DRIFTS Spectrometer

- The resolution of the spectrometer will be 0.5 cm^{-1} or higher (0.1 cm^{-1}).
- The spectrometer will operate in the mid-infrared spectral region.
- Range of different gases (for example H_2, O_2, CO_2, N_2, CH_4) will be dosed
- The temperature of operation will be from 15 K (liquid helium cooling) to room temperature (with the possibility for spectra collection at elevated temperatures).
- The gas pressure will be from 0 to 30 bar. The gas will be dosed from an ASAP line (for low pressures) or from a custom-made setup (for high pressures).
- A separate sample holder will be designed to allow for higher gas pressures (up to 100 bar).

Modified DRIFTS Spectrometer

- Commercially available infrared spectrometer will accommodate DRIFTS setup (Figure 1). The DRIFTS setup will be paced into an evacuated chamber (Figure 2).
- The sample holder will be cooled *via* a copper slab attached to cold finger (liquid helium).
- The sample holder will be connected to an ASAP gas sorption analyzer for controlled dosing of gases at different pressures.

Figure 1. DRIFTS setup

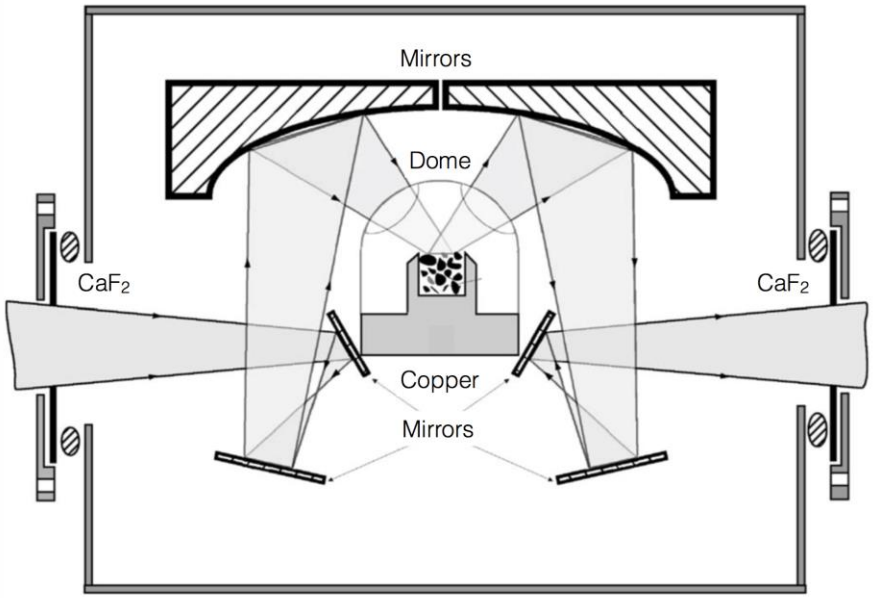
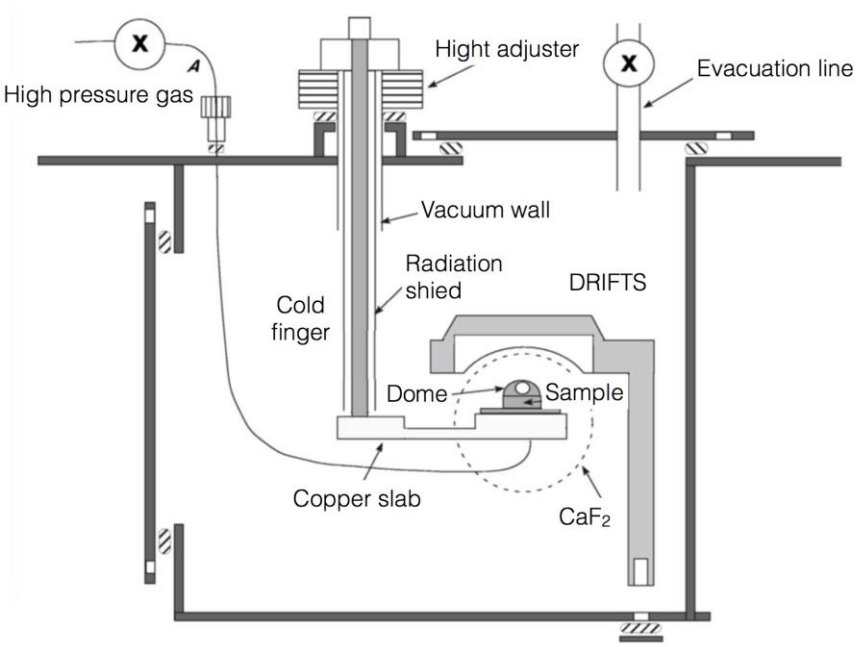
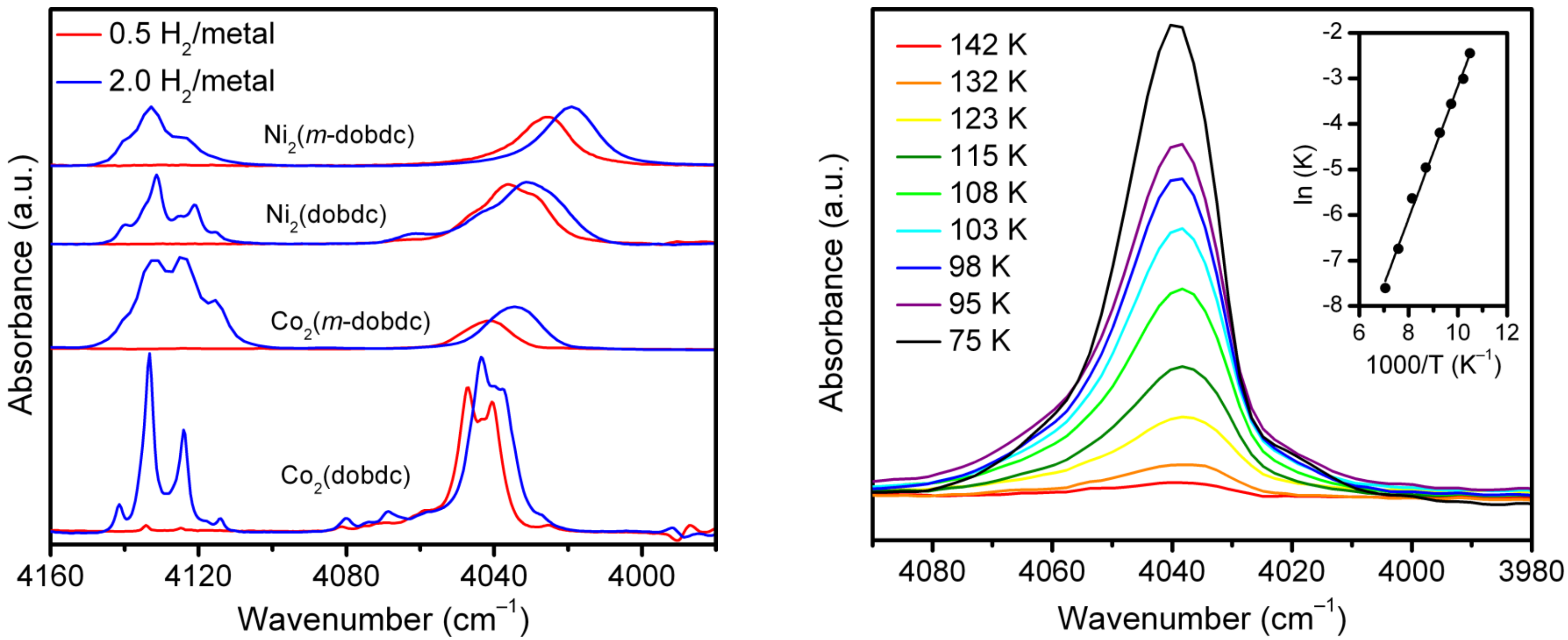


Figure 2. Evacuated chamber



S. A. FitzGerald et al. *Rev. Sci. Instr.* 77, 093110, 2006

In situ H_2-Dosed Infrared Spectroscopy



- We are designing and building a state-of-the-art infrared spectrometer with a controllable atmosphere and the capability of measuring spectra at low temperatures (15 K) and high pressures (100 bar)
- H_2 stretching can be studied upon adsorption in a metal-organic framework to determine binding strength
- Variable-temperature IR experiments are used to extract binding enthalpies and entropies

Kapelewski, Geier, Hudson, Stück, Mason, Nelson, Xiao, Hulvey, Gilmour, FitzGerald, Head-Gordon, Brown, Long *J. Am. Chem. Soc.* **2014**, 136, 12119

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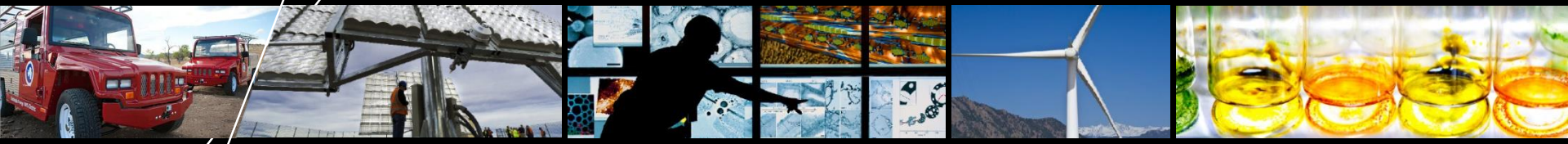


PNNL Characterization Techniques: NMR, TEM, Calorimetry

PNNL Characterization

Pacific Northwest NATIONAL LABORATORY

NMR spectroscopy.

PNNL has more than 15 multinuclear spectrometers suitable for both liquids and solids and ranging from 100 to 850 MHz. Many of these have wide-bore magnets accepting specialized sample probes for in-situ environments. The specialized facilities include:

High pressure solution NMR (to 500 MHz)

- **-Pressure to 70 bar**
- **-Temperatures -100 to +100 °C (+150 °C at lower pressure)**

High pressure MAS solid NMR (to 850 MHz)

- **-Pressure to 200 bar**
- **-Temperatures ambient to +100 °C**
- **-Pressurizing gases – include H_2, CO_2, CH_4, He and N_2**
- **-Uses standard commercial solid-state NMR probes in 5mm, 7.5 mm, and 6 mm OD rotors, using the full internal diameter for increased volume and sensitivity**

A new capability to probe H_2 gas adsorption by NMR as a function of temperature and pressure will be developed as part of the AOP project. This strategy will be used to measure *H_2-specific* pore size and adsorption energies by using H_2 gas as the probe.

PNNL Characterization Capabilities

Transmission Electron Microscopy.

Three aberration-corrected TEMs, including STEM, are available with optimum resolution ca. 0.7 Å. Key features of this capability include:

- **Heated sample stages with temperatures to 700 °C**
- **Environmental TEM with 10 mbar gas pressure (including H_2) at the sample**
- **Si_3N_4 window sample stage for 1.5 bar gas pressure and 500 °C with reduced resolution**
- **Elemental and chemical state information by EDS and EELS**

Reaction Calorimetry

Measure in-situ heats of reaction during a reaction in isothermal as well as temperature-ramp mode.

- **The C-80 calorimeter can be coupled to a GC to analyze evolved gases and the reversal mixing vessels allow for a range of reaction conditions.**
- **Liquid/liquid, solid/liquid and even gas phase reactions can be measured.**
- **Temperature range: ambient to +300 °C**
- **Pressure range: 1 to 100 bar**

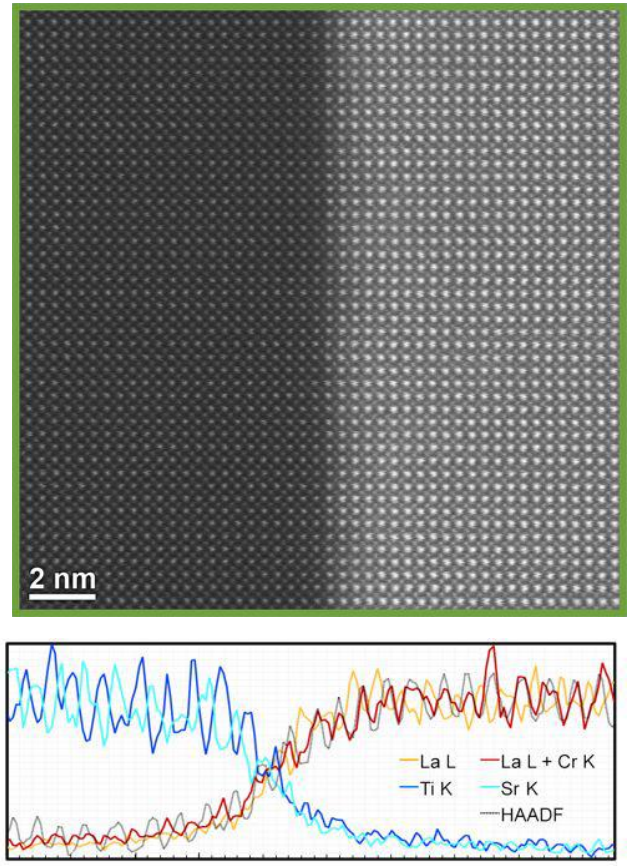
PEEK High-Pressure NMR Cell

- **Machined in-house from a large piece of PEEK rod**
- **Bottom is virgin PEEK, Top is carbon-filled PEEK (paramagnetic)**
- **Seal between the two is plastic-on-plastic cone-seal**
  - Finger tight, No O-rings, All other fittings are either plastic HPLC fittings from Upchurch, or HIP stainless steel

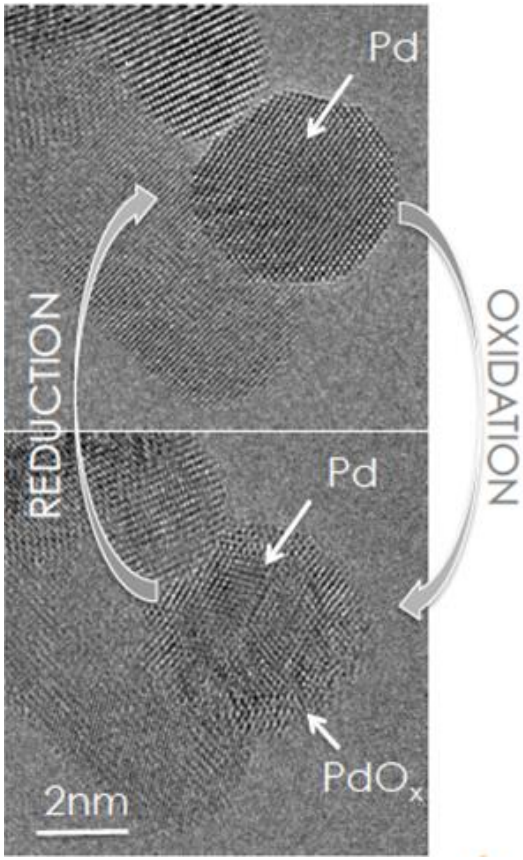
- A couple of cells from each machined batch are hydrostatically pressure tested to failure
  - 15,000 psi (1,000 atm) after 24 hours
- Reusable at 100 ^{o}C to -100 ^{o}C, (softens at 180 ^{o}C)
- 3 mm i.d. / 5 mm o.d. PEEK (plastic) NMR cells are **interchangeable** with standard glass NMR tubes
- No PEEK cell has failed during use (over 10 years)

J. Organomet. Chem. **2002**, *650*, 249-257; *Prog. Nucl. Magn. Reson. Spectrosc.* **2005**, *47*, 95-109

Transmission Electron Microscopy examples

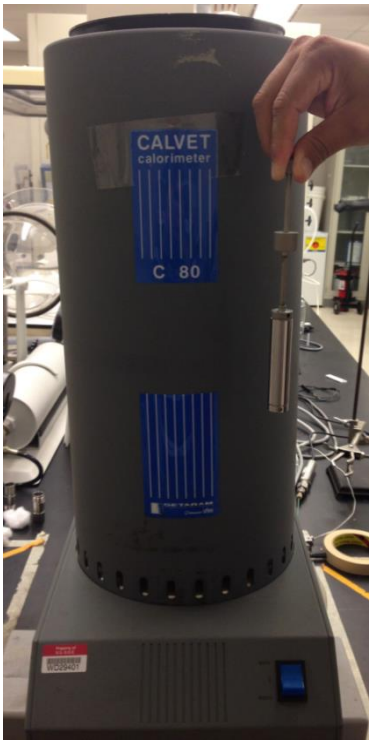


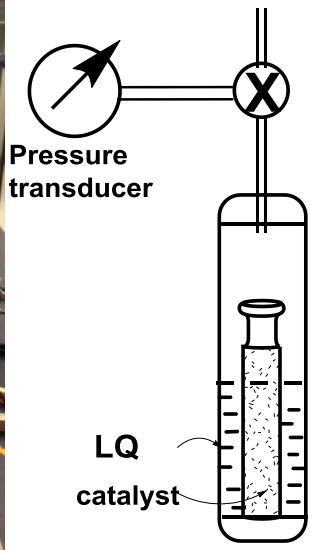
Atomic-resolution image of interface between $SrTiO_3$ and $LaCrO_3$ (top) with corresponding elemental profiles (bottom) showing interdiffusion

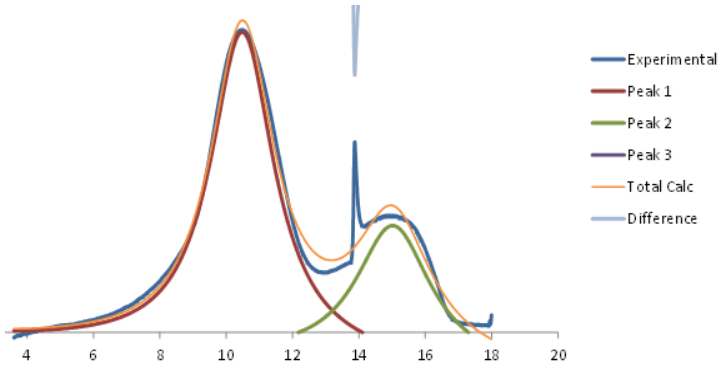


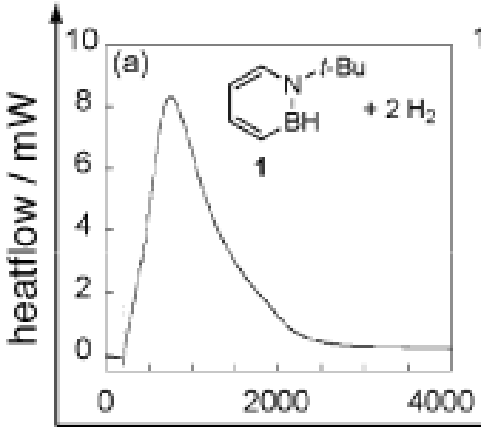
In-situ observation of oxidation and reduction of Pd nanoparticles, showing core-shell structure

Reaction Calorimetry Enthalpies (ΔH) of H_2 Uptake and Release



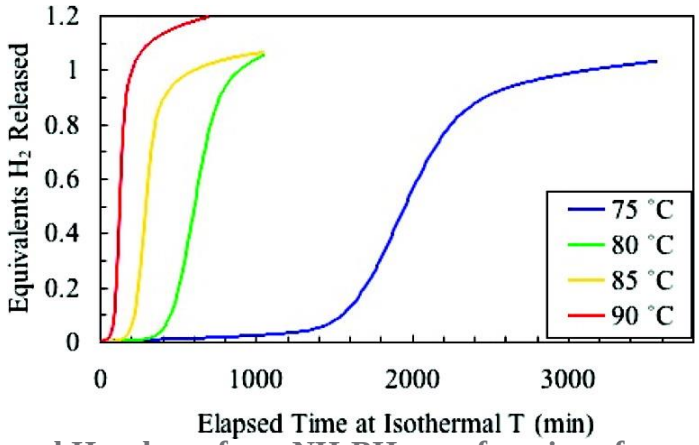






$CBN(H_2)_n \Leftrightarrow CBN + nH_2 + heat$ $LQ + H_2 \Leftrightarrow LQH_2 + heat$

Heat of reaction of dehydrogenation of $CBNH_2$ (comp. J) and hydrogenation of CBN



Isothermal H_2 release from NH_3BH_3 as a function of temperature illustrating the temperature-dependent induction period and yield of hydrogen release measured by gas burette.

Experimental ΔH critical parameter to benchmark theory. (compliment NMR T_{eq} experiments)

1. Carbazole
2. Triazine

Neutron Characterization in support of the DOE Hydrogen Storage Program

Terrence J. Udovic
Craig M. Brown

National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

NCNR Facts and Figures

- Partial user facility : 66% / 25% / 0%
- ≈ 240 operating days/year
- ≈ 99% reactor reliability
- 28 experimental beam instruments/experiments
- ≈ 2000 research participants/year
- ≈ 300 publications/year
  - ≈ 15% in very high impact journals

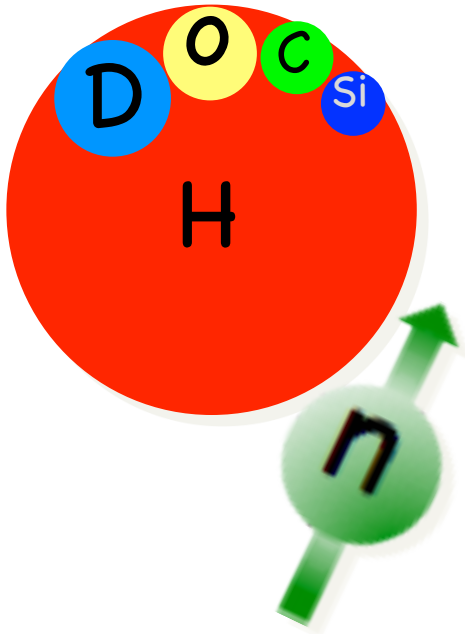
Neutron Properties

Isotopes have different scattering powers

H : 1 proton
1 electron

Incoherent scatterer
- Does not 'see' neighbor atoms

SPECTROSCOPY



D : 1 proton
1 neutron
1 electron

Coherent scatterer
- 'Sees' neighbor atoms

STRUCTURE

SPECTROSCOPY: "interesting" portions of the sample are hydrogenated and the "uninteresting" portions are deuterated.

Neutron magnetic moment interacts with spins

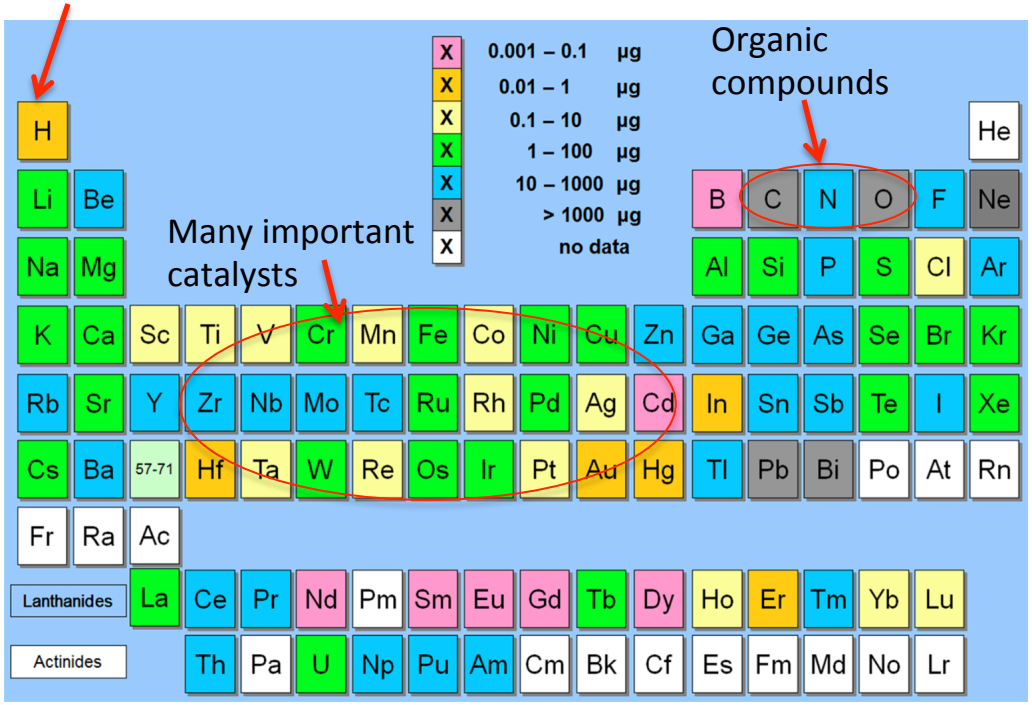
Neutron methods

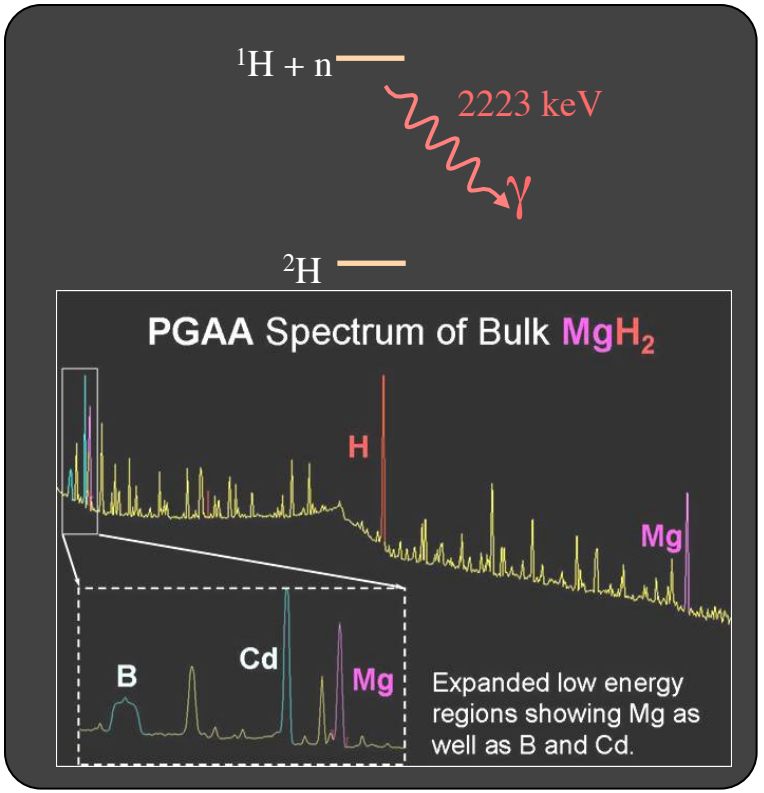
- determine elemental compositions of materials (prompt-γ activation analysis and neutron reflectometry of H stoichiometries and profiles)
- determine location of H and crystal structures of materials (neutron diffraction superior to XRD for "seeing" light H and D)
- determine bonding of absorbed H (unlike IR and Raman, neutron vibrational spectroscopy "sees" all H vibrations for straightforward comparison with first-principles calculations)
- elucidate H diffusion mechanisms (faster dynamics timescale of neutron quasielastic scattering complements NMR; transport mechanisms gleaned from momentum transfer dependence)

Absorption/Imaging

- Unambiguous, simultaneous multi-element measurement
- Bulk analyses (neutrons and gamma rays penetrate sample)
- Nondestructive and independent of chemical form

Best technique for
H measurement



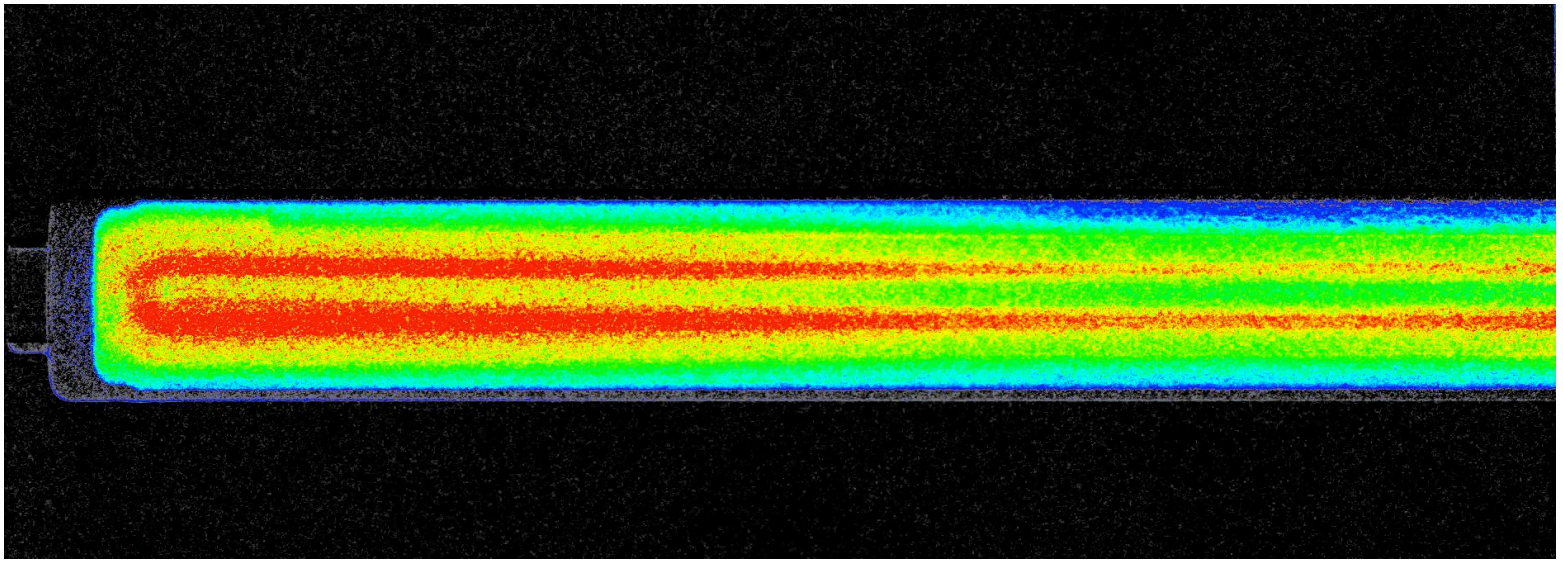


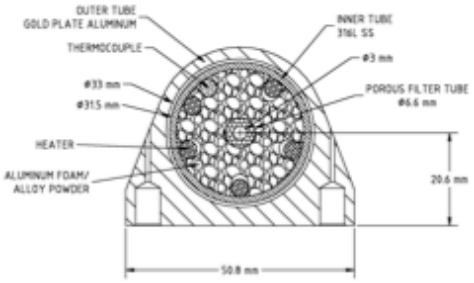
http://www.mlz-garching.de/pgaa

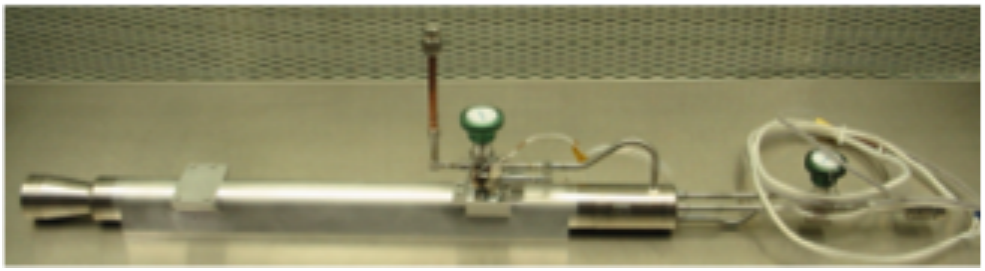
Absorption/Imaging

Collaboration with Bob Bowman

$LaNi_{4.78}Sn_{0.22}$ powder in 10% dense Al foam



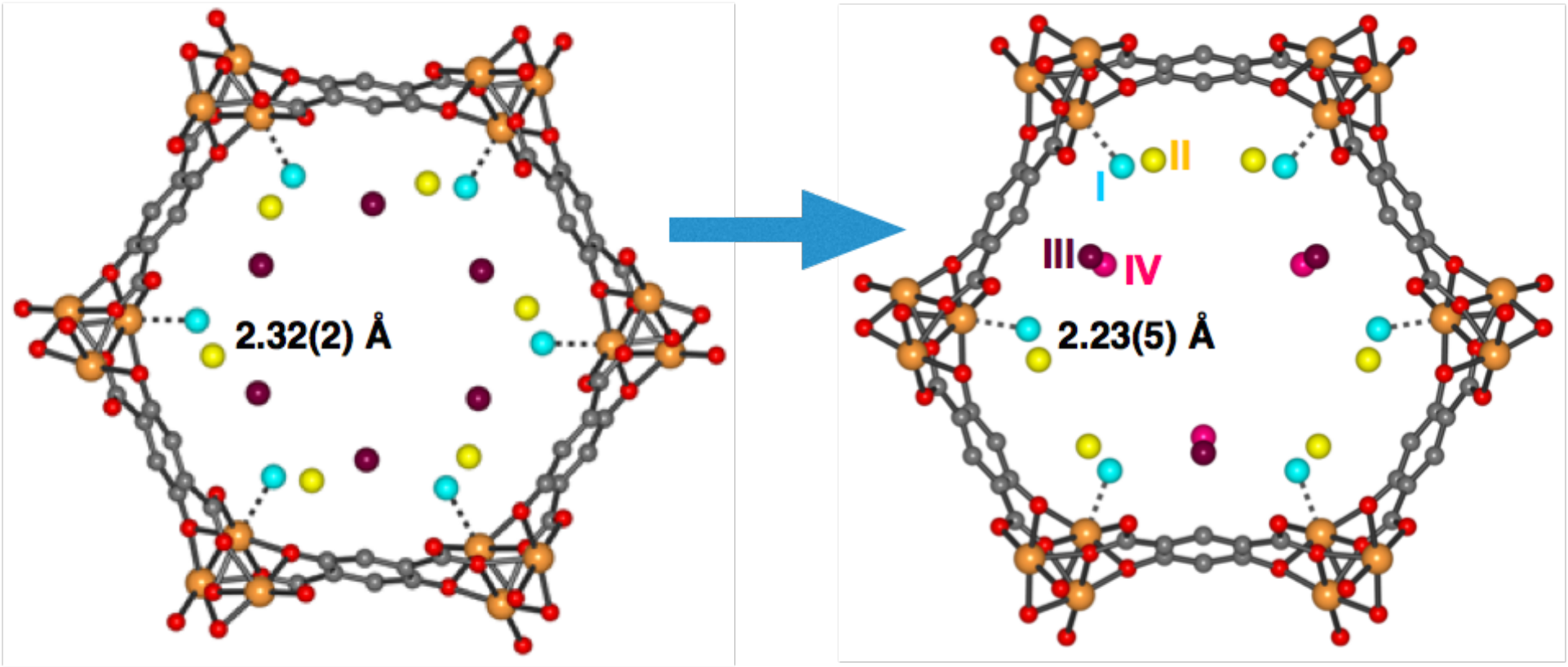




JPL Planck Sorption Cryocooler Compressor Element

M_2(m-dobdc)

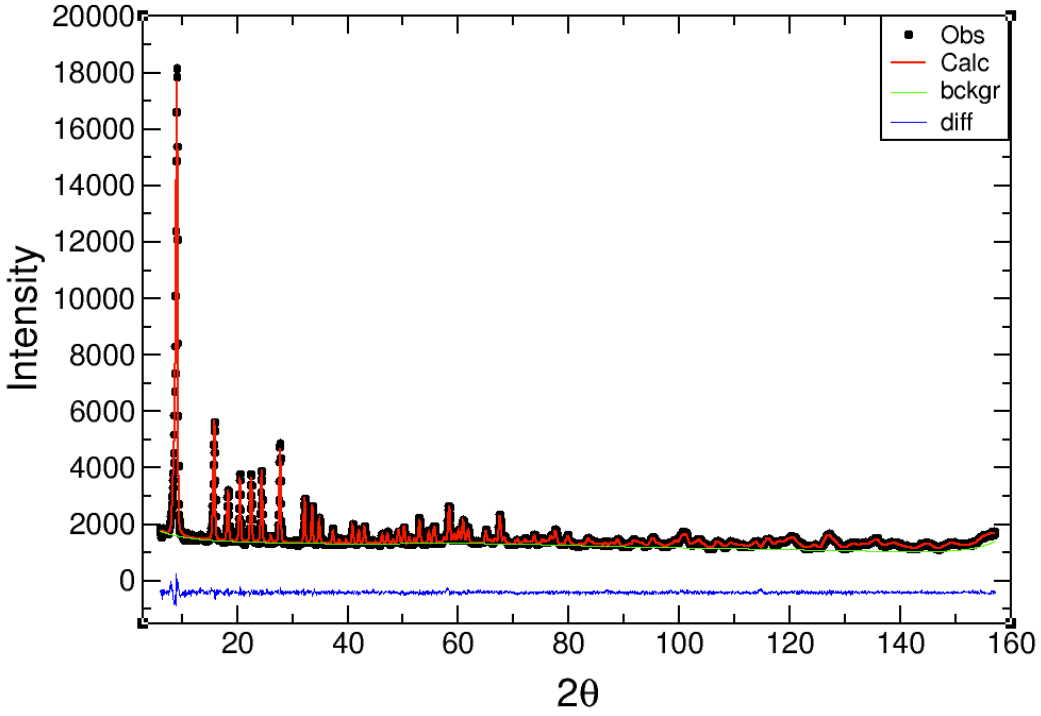
Collaboration with Jeff Long



M_2(m-dobdc)

Collaboration with Jeff Long

Can we use H_2 as the adsorbate with neutrons?



Low loading (0.5 per metal) binding sites are the same with slight distance difference

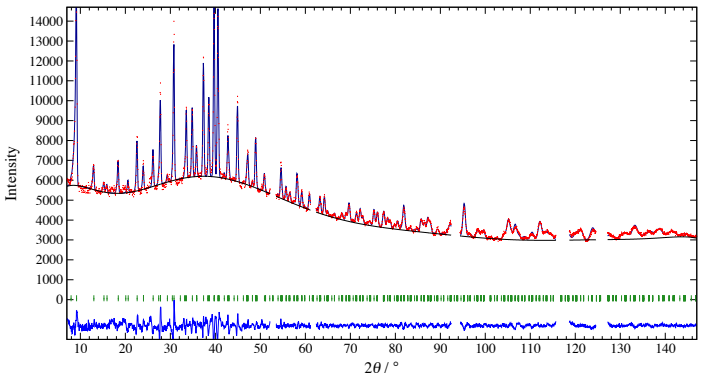
Co—D_2 = 2.23(5) Å
Co—H_2 = 2.27(3) Å

MOF-5

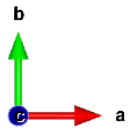
Collaboration with Mircea Dinca

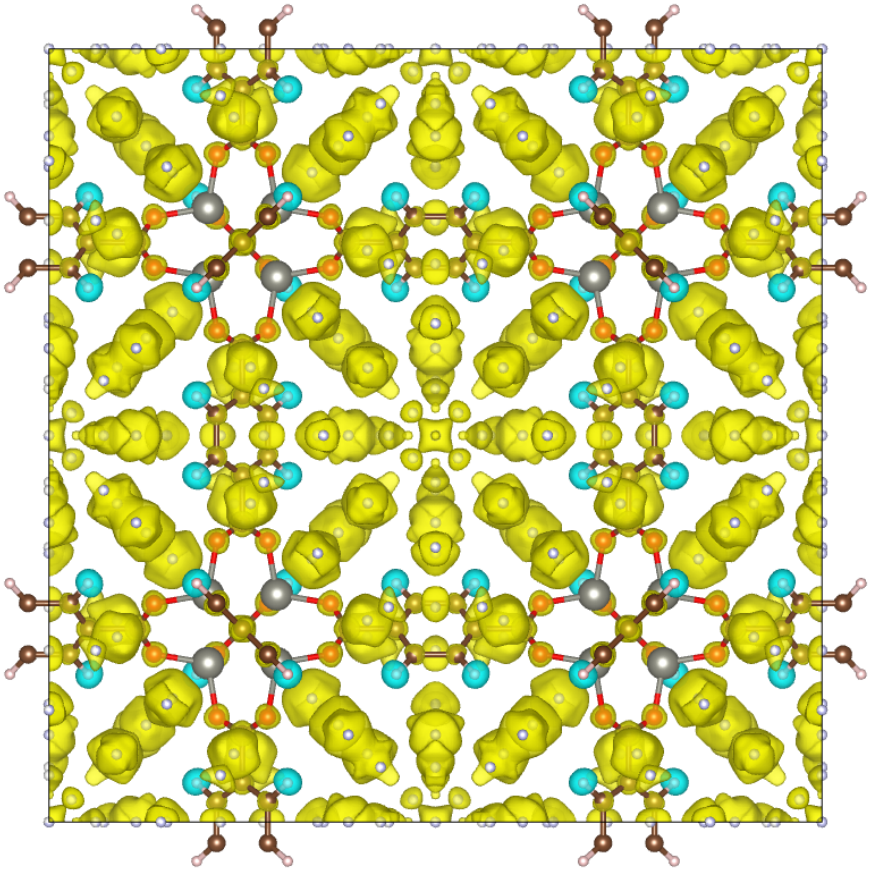
Neutron diffraction of MOF-5+ D_2 at 77 K and 100 bar

Le Bail extraction of intensities



NO
Atomic details



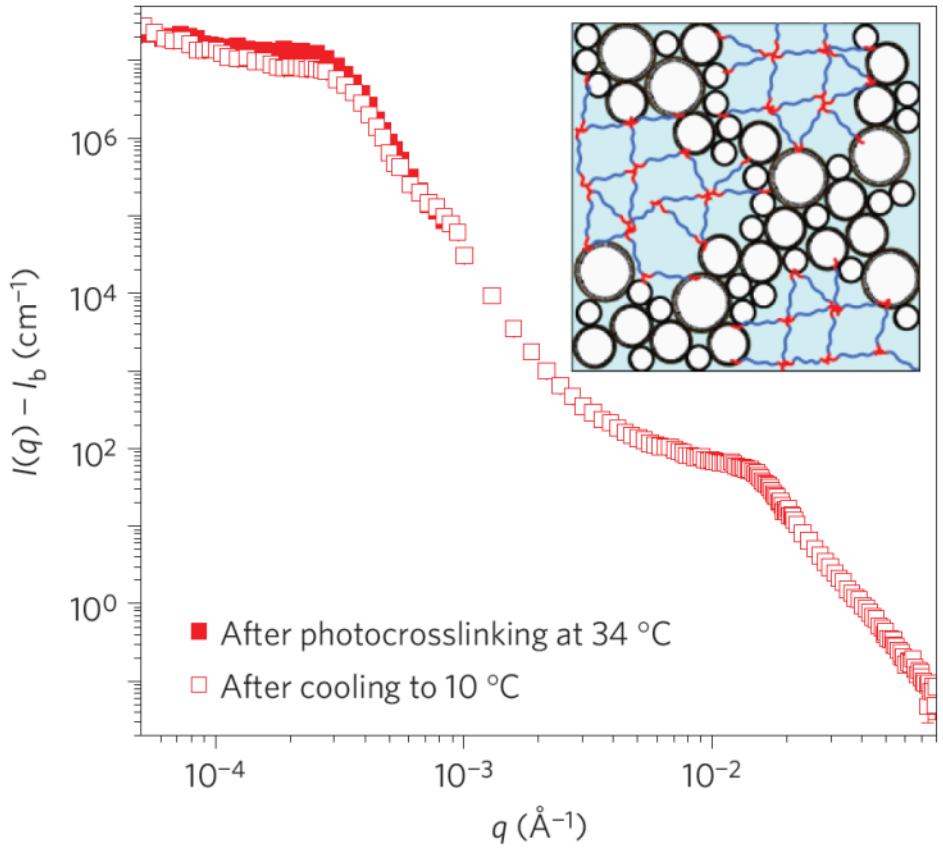


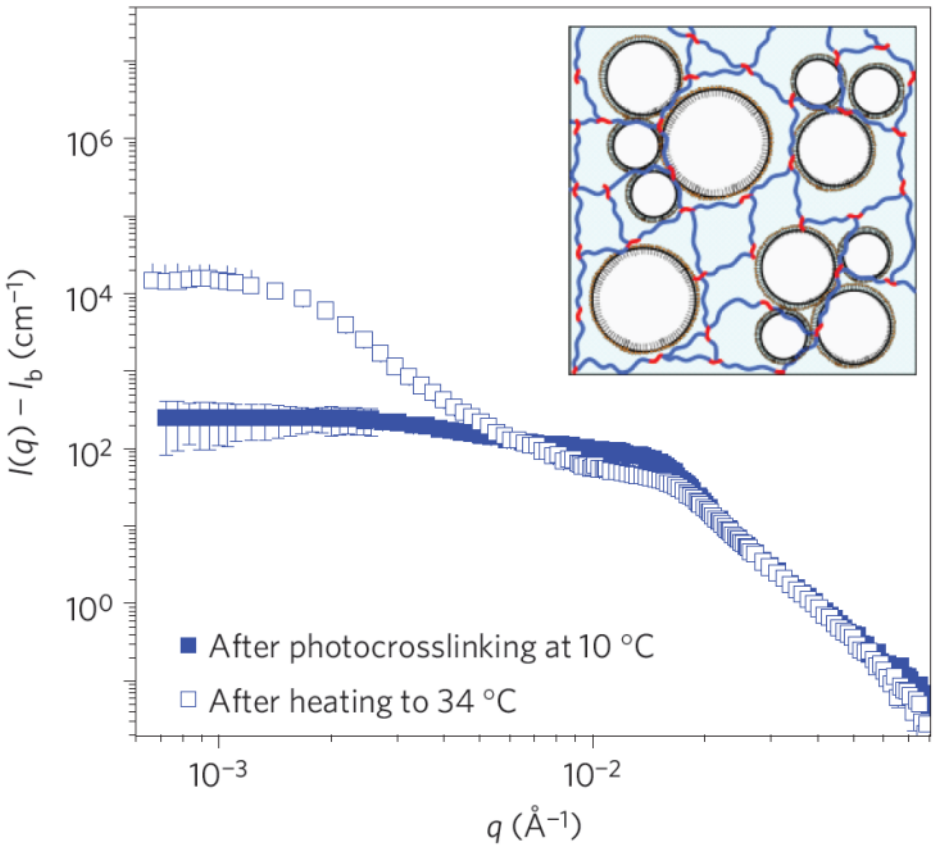
Maximum Entropy Map of unit cell contents →
7.28 wt% H_2 at 77 K 98 bar.

Z. Hulvey *et al.*, in prep

Small-Angle

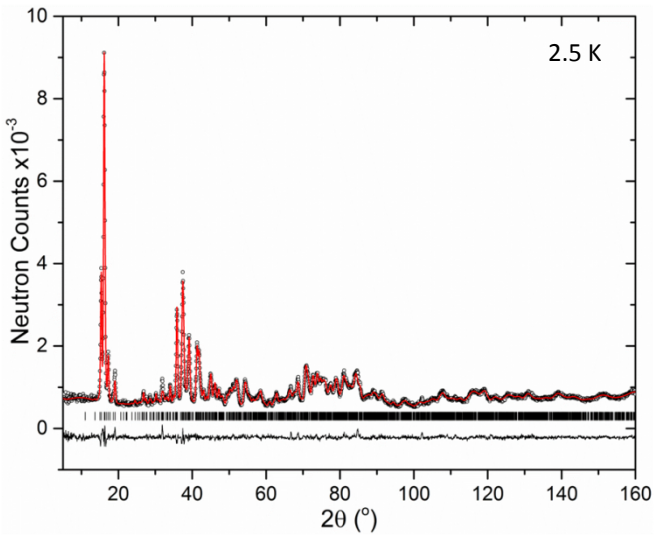
Mesoporous Organohydrogels
Pores sizes/geometries, particle sizes



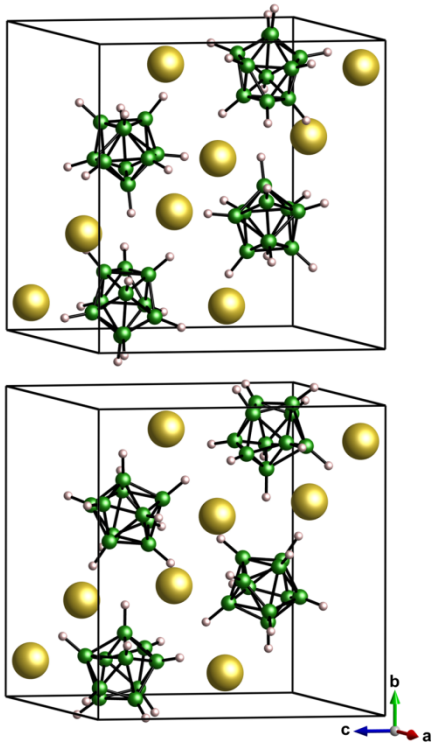


Characterization of $Na_2B_{10}H_{10}$

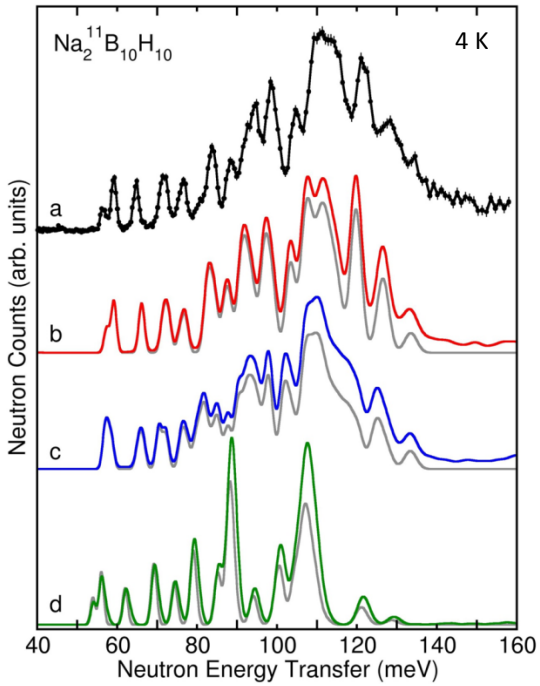
Collaboration with Maryland, Sandia National Laboratories



Neutron powder diffraction pattern and fit for $Na_2{}^{11}B_{10}D_{10}$ at 2.5 K.



The corrected monoclinic $Na_2B_{10}H_{10}$ crystal structure (top) compared to the published structure (bottom).



(a) Neutron vibrational spectrum of monoclinic $Na_2{}^{11}B_{10}H_{10}$ compared to DFT simulations for (b) the corrected structure, (c) the published structure, and (d) the isolated anion.

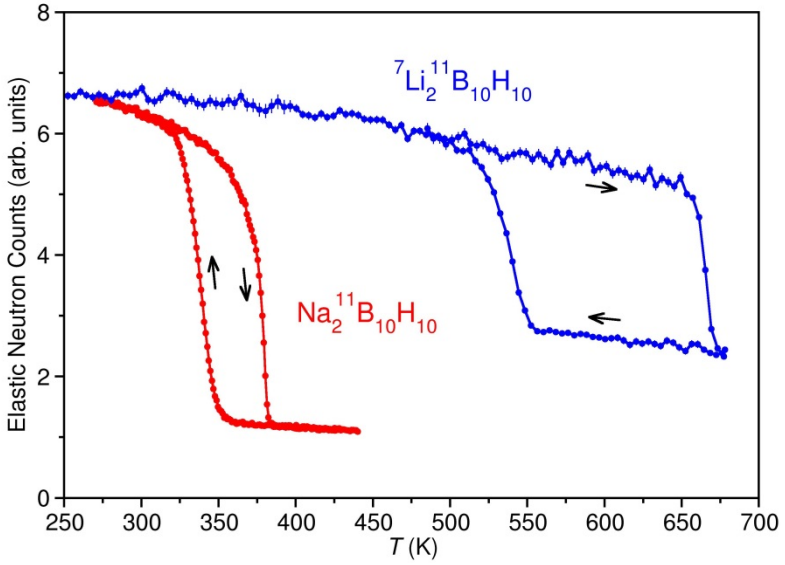
Using neutron scattering methods in conjunction with DFT, we have corrected structural errors in the previously published, monoclinic ordered $Na_2B_{10}H_{10}$ structure.

H. Wu *et al.*, CrystEngComm **17**, 3533 (2015).

Characterization of $Li_2B_{10}H_{10}$

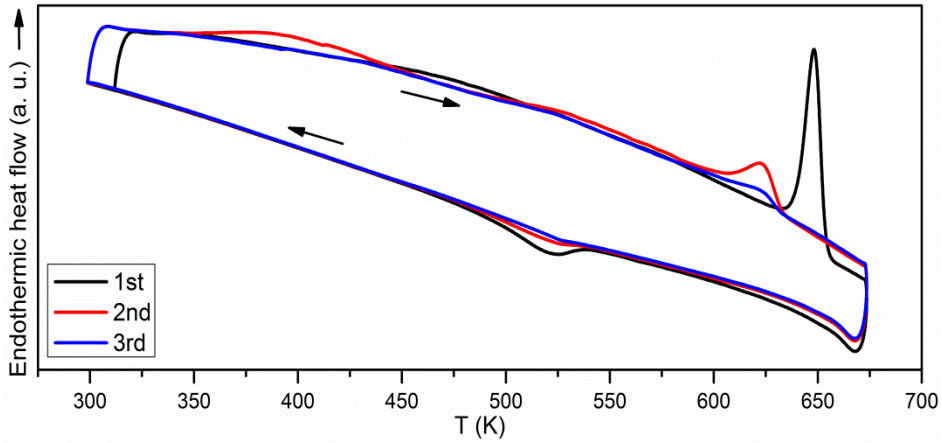
Collaboration with Maryland, Sandia National Laboratories

Neutron-Elastic-Scattering Fixed-Window Scans



Fixed-window scans of $^7Li_2{}^{11}B_{10}H_{10}$ indicate a transition to an unknown phase by 680 K with highly reorientationally mobile $B_{10}H_{10}^{2-}$ anions, possibly similar in character to $Na_2B_{10}H_{10}$.

Differential Scanning Calorimetry for $Li_2B_{10}H_{10}$



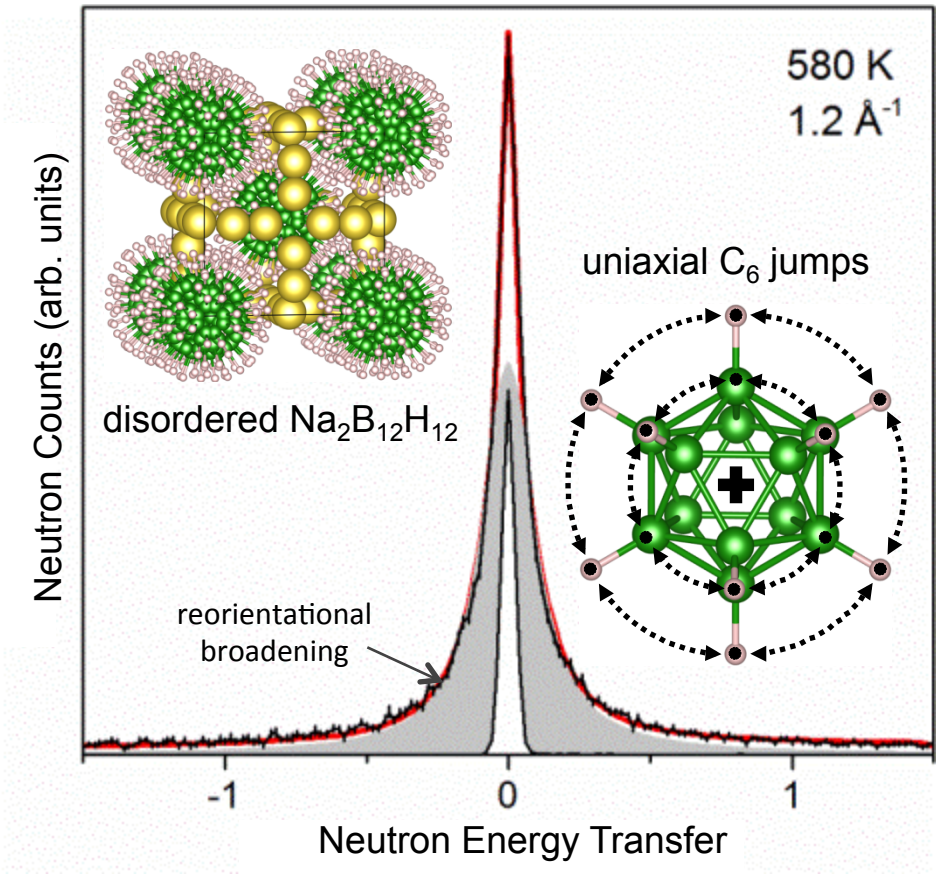
Multiple differential calorimetry scans for $Li_2B_{10}H_{10}$ suggest that this high-temperature phase is somewhat unstable.

$Li_2B_{10}H_{10}$, similar to its polyhedral cousin $Li_2B_{12}H_{12}$, completes an order–disorder phase transition by ~680 K. This information further elucidates the important Li-B-H phase diagram.

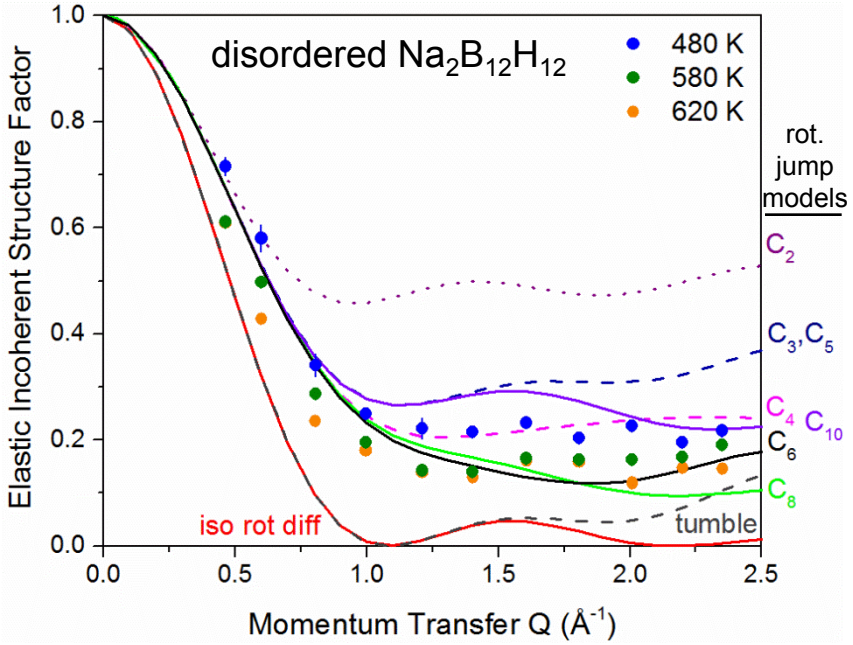
H. Wu *et al.*, J. Phys. Chem. C **119**, 6481 (2015).

Characterization of Anion Dynamics in $Na_2B_{12}H_{12}$

Collaboration with Maryland, Sandia National Laboratories, IMP Ekaterinburg



Elastic Incoherent Structure Factor (EISF) Models



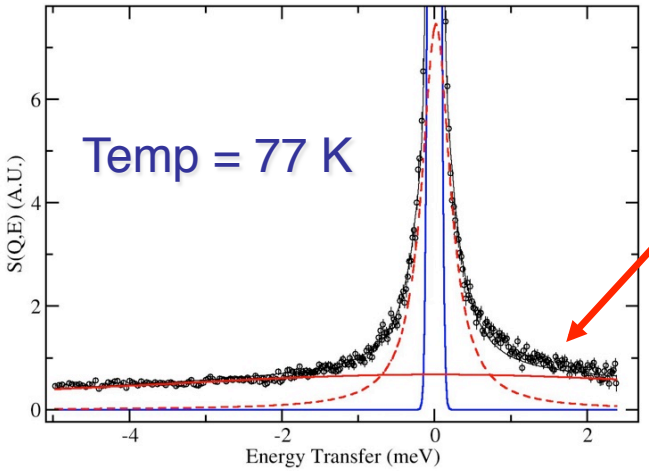
A comparison of the EISF data with different jump reorientation models suggests that $B_{12}H_{12}^{2-}$ anions undergo, on average, predominantly small-angle uniaxial jumps.

Quasielastic neutron scattering measurements of disordered $Na_2B_{12}H_{12}$ indicate rapid (>10^{11} jumps/s), mainly (small-angle) uniaxial, reorientational motions of the $B_{12}H_{12}^{2-}$ anions.

N. Verdal *et al.*, J. Phys. Chem. C **118**, 17483 (2014).

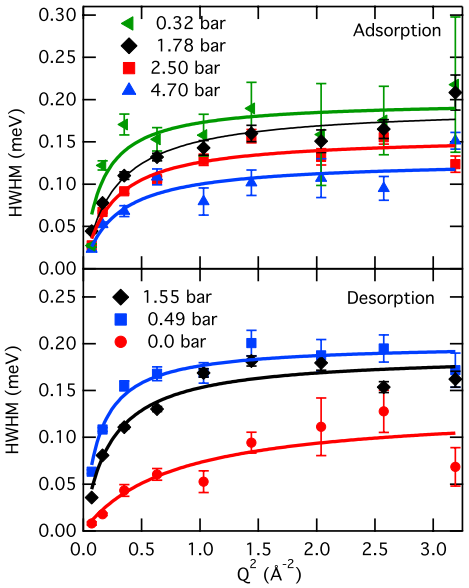
Mg-MOF74 H_2 dynamics

Collaboration with Jeff Long



Surface Diffusion 'liquid'
~0.2 ps between H_2 hops

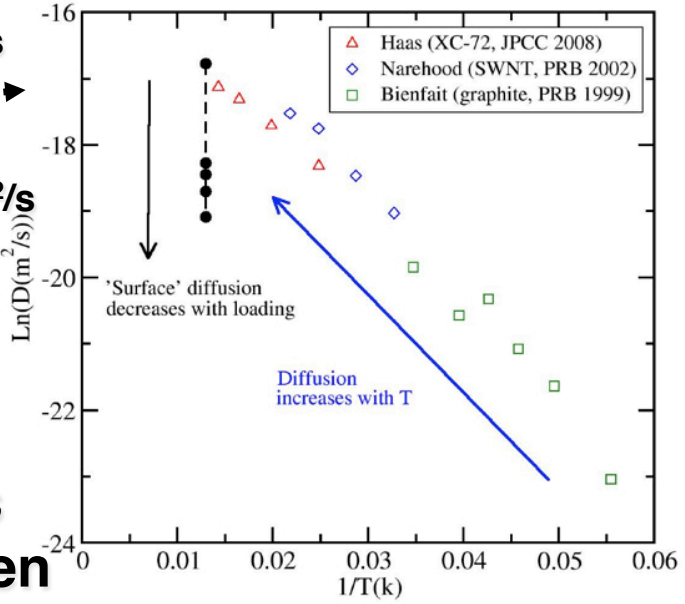
Fit widths



Extract Diffusion Models

D=1.2(1)x10^{-8} m^2/s
$l_0 \approx 3.5$ Å

D=5.1(2)x10^{-9} m^2/s
$l_0 \approx 2.2$ Å



~10 ps between H_2 hops