



DOE Hydrogen Program

**NIST**

# Neutron Characterization in support of the DOE Hydrogen Storage Program

Craig M. Brown  
Dan A. Neumann  
Terrence J. Udovic

**NIST**

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

May 11, 2011

ST067

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

## Timeline

- Project start FY10
- Project end FY13
- 40% complete

## Budget

- FY10 \$534K
- FY11(planned) \$474K
- FY12(projected) \$493K
- FY13(projected) \$513K

NIST continues to provide access to neutron facilities and FTEs for the DOE Hydrogen Storage Projects.

### NIST Associates

Nina Verdal	Hui Wu
John J. Rush	Wei Zhou
Matt Hudson	Wendy Queen

## Barriers addressed

- A. System Weight and Volume
- P. Lack of Understanding of Hydrogen Physisorption and Chemisorption

## Partners

Caltech, Delaware GM, JPL, LLNL, Maryland, Michigan, Missouri-St. Louis, NREL, Ohio State, Penn, Penn State, Sandia, Stanford, UC Berkeley

**Overall:** Support the DOE-EERE-funded hydrogen-storage projects by providing timely, comprehensive characterization of materials and storage systems using state-of-the-art neutron methods.

- Characterize structures, compositions, hydrogen dynamics, and adsorption/absorption-site interaction potentials for candidate storage materials as well as their by-products and intermediates.

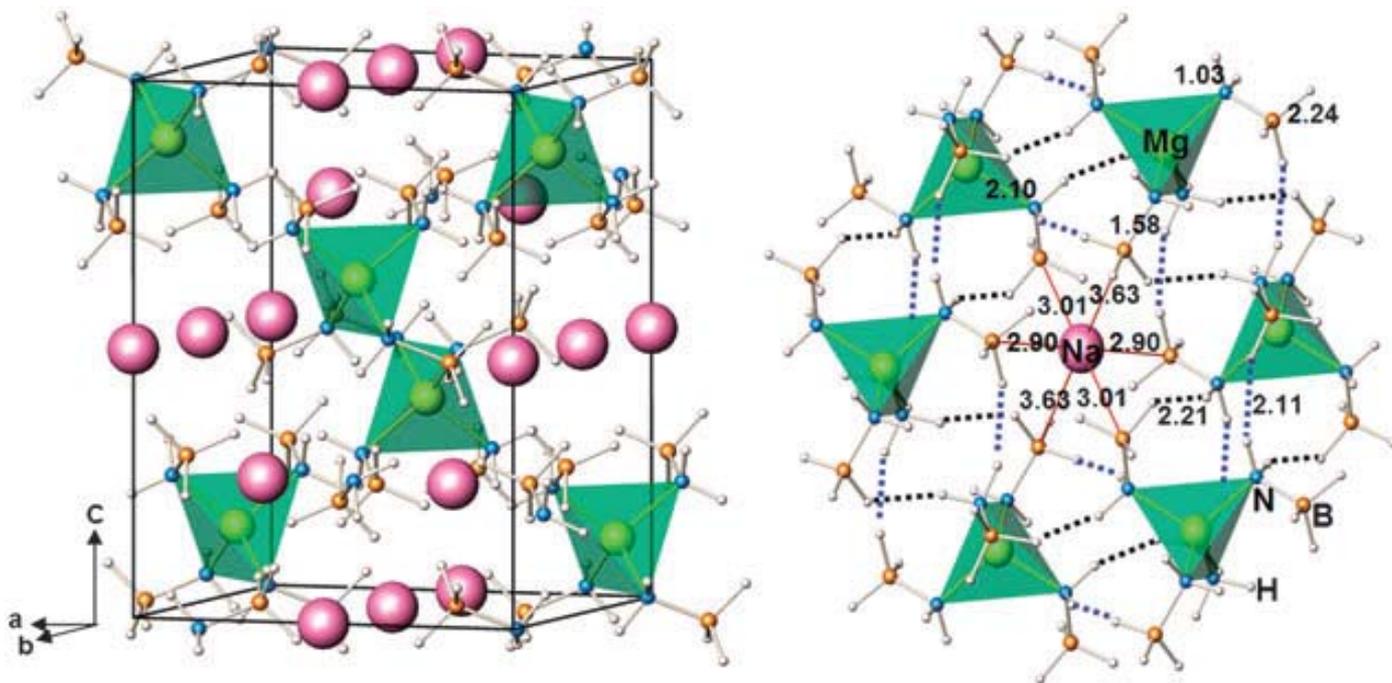
## Neutron methods

- determine elemental compositions of materials (prompt- $\gamma$  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)

Neutron methods, synthesis expertise, and DFT computations were used to further the goals of the DOE Hydrogen-Storage Program.

Motivation: to synthesize new compounds potentially promising for hydrogen storage

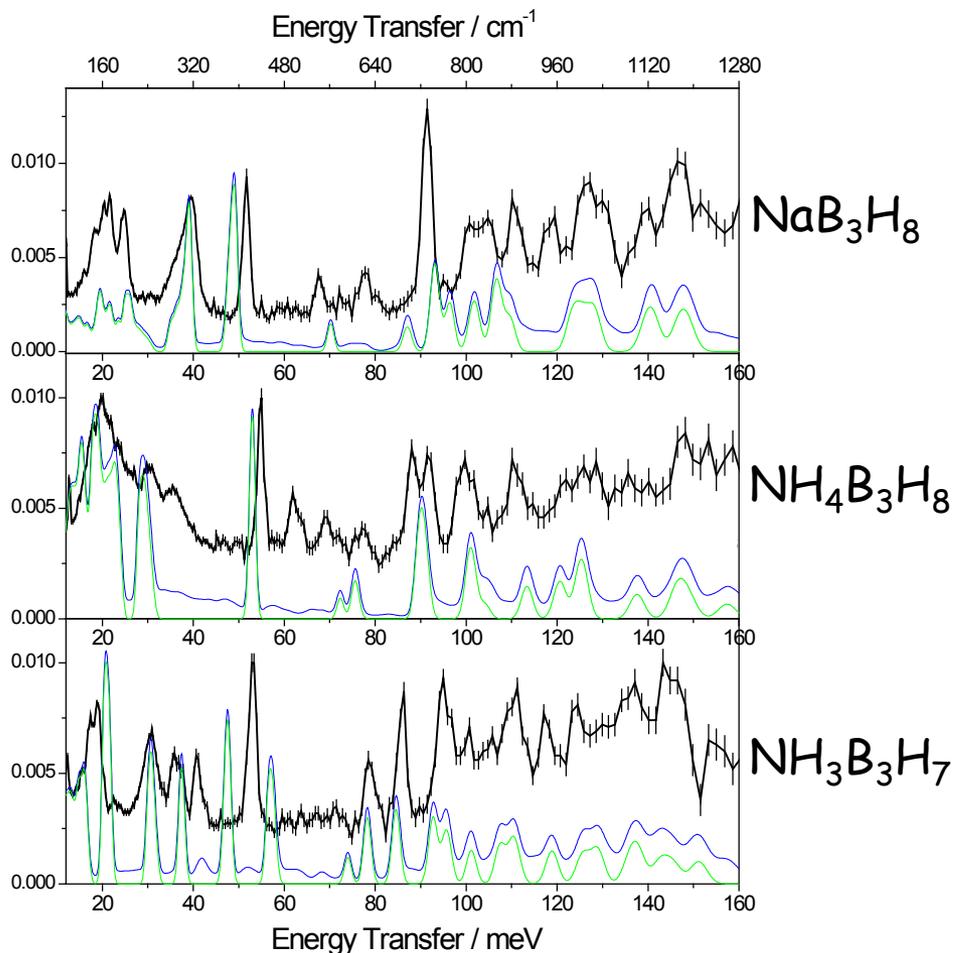
Sodium magnesium amidoborane: the first mixed-metal amidoborane



H. Wu *et al.*, *Chem. Commun.* **47**, 4102 (2011)

\* Compared to  $\text{NH}_3\text{BH}_3$  and monometallic amidoboranes,  $\text{Na}_2\text{Mg}(\text{NH}_2\text{BH}_3)_4$  can release 8.4 wt% pure hydrogen with significantly less toxic gases.

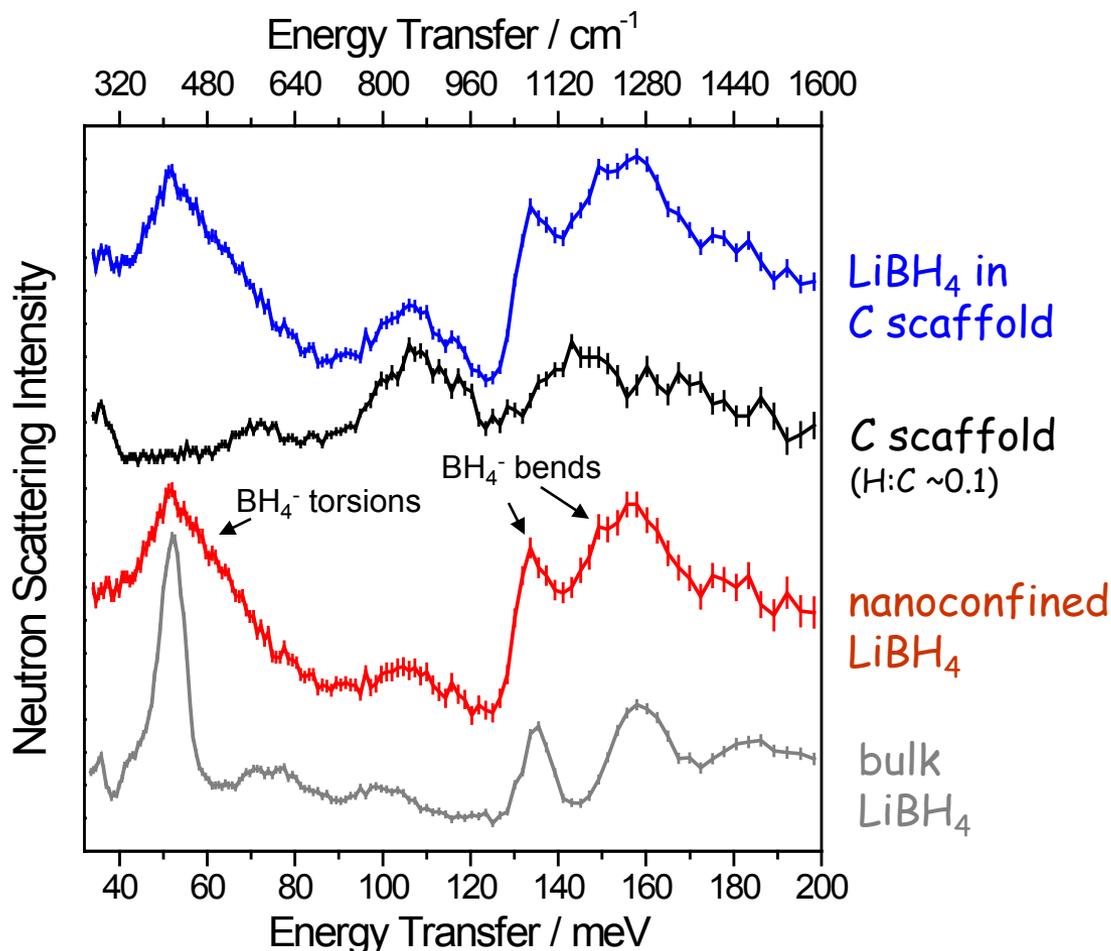
Motivation: to characterize novel lightweight borohydride materials



The neutron vibrational spectra (black) of  $\text{NaB}_3\text{H}_8$ ,  $\text{NH}_4\text{B}_3\text{H}_8$ , and  $\text{NH}_3\text{B}_3\text{H}_7$  and corresponding DFT phonon calculations (green: 1-phonon; blue: [1+2]-phonon) from the experimentally derived crystalline structures

\* The limited agreement between the neutron vibrational spectra and calculations suggests that the DFT descriptions of bonding interactions may be somewhat lacking.

Motivation: to characterize the properties of nanoconfined  $\text{LiBH}_4$



Shown are the observed neutron vibrational spectra of  $\text{LiBH}_4$  sequestered inside a carbon scaffold with 2 nm pores, the corresponding bare carbon scaffold, and bulk  $\text{LiBH}_4$ . The result of the carbon scaffold spectrum subtracted from the melt spectrum is also shown.

The nanosequestered  $\text{LiBH}_4$  exhibits a much broader torsion peak (at 52 meV or  $419 \text{ cm}^{-1}$ ) compared with bulk  $\text{LiBH}_4$ . This indicates a large inhomogeneity in the rotational potential experienced by the confined  $\text{LiBH}_4$ .

\* NVS data indicate disordered, non-bulk-like  $\text{LiBH}_4$  in the nanoporous carbon

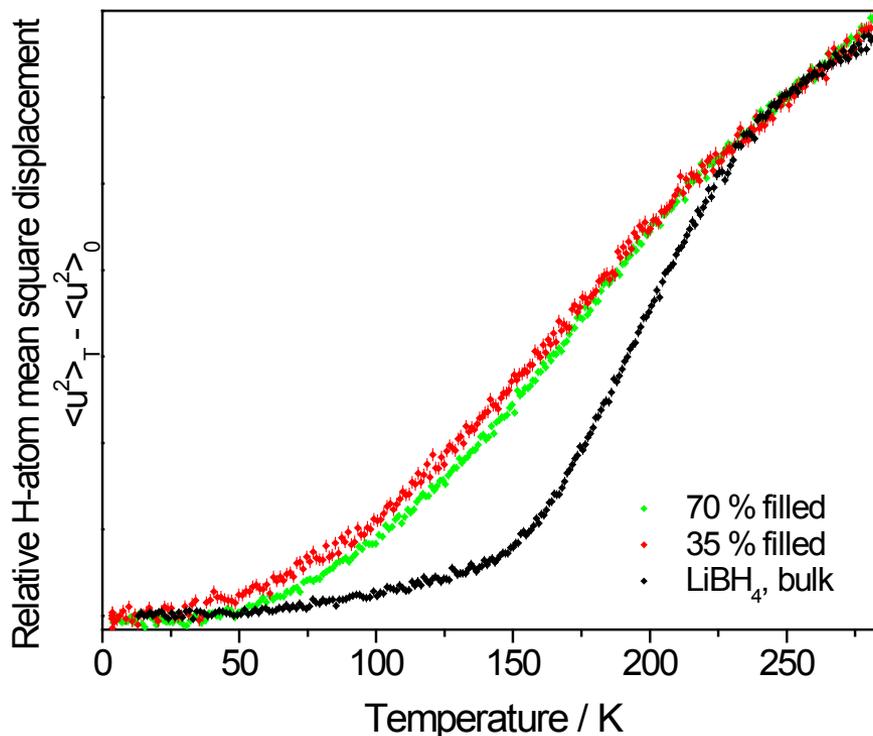
Motivation: to investigate borohydride dynamics perturbations in nanopores

Rotational dynamics for  $\text{LiBH}_4$  was characterized by quasielastic neutron scattering

$\text{LiBH}_4$  melt-infiltrated into  $\sim 2$  nm diameter hexagonal pores

A comparison was made between  $\text{LiBH}_4$  sequestered inside 2 nm ordered pores of a carbon scaffold and bulk  $\text{LiBH}_4$ .

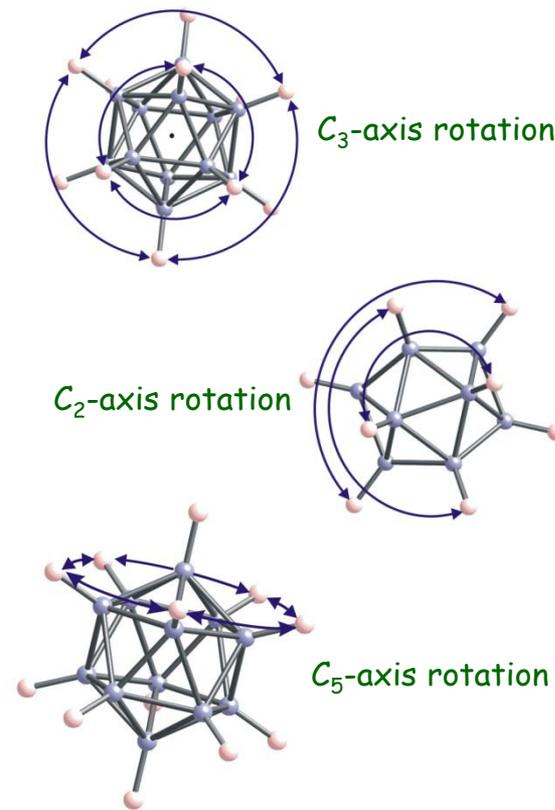
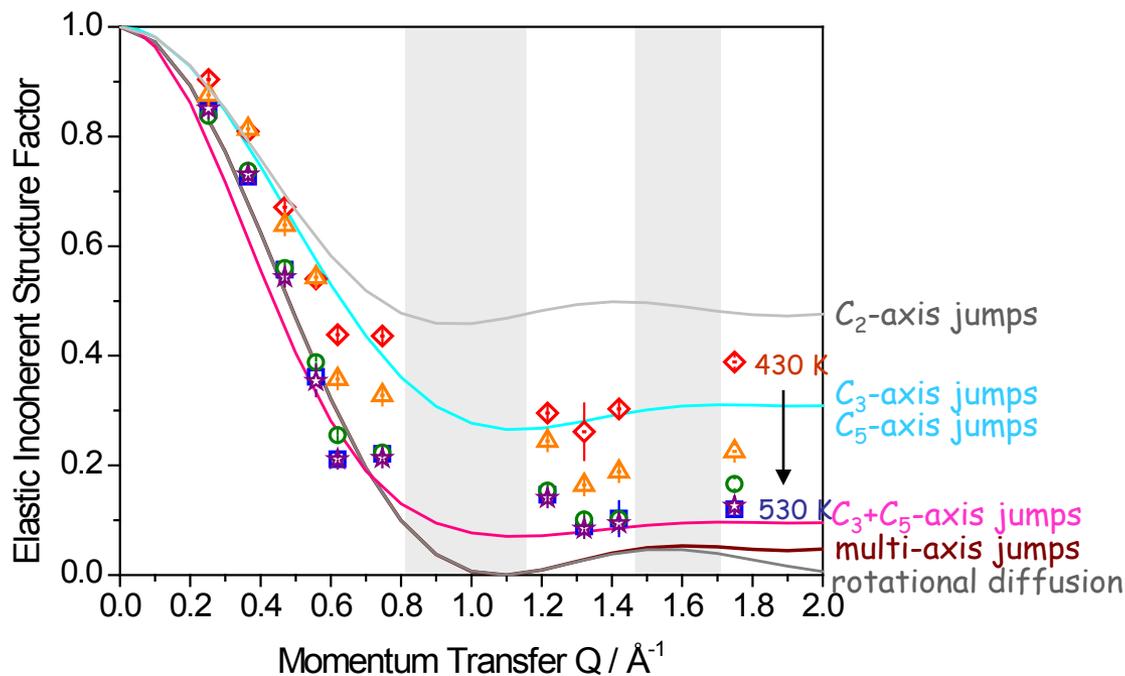
The relative mean square displacement of H atoms determined from a neutron fixed-window scan shows that the onset of  $\text{BH}_4^-$  rotational motion occurs  $\sim 100$  K lower for the confined material than for bulk  $\text{LiBH}_4$ .



\* Nanoconfinement appears to perturb the bulk thermodynamic properties of  $\text{LiBH}_4$

Motivation: to help characterize the dynamics of borohydride intermediates

Quasielastic neutron scattering (QENS) data for  $Cs_2(^{11}B)_{12}H_{12}$  was measured at 430-530 K.



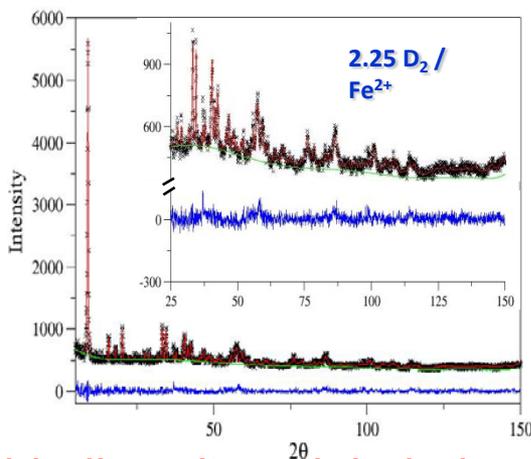
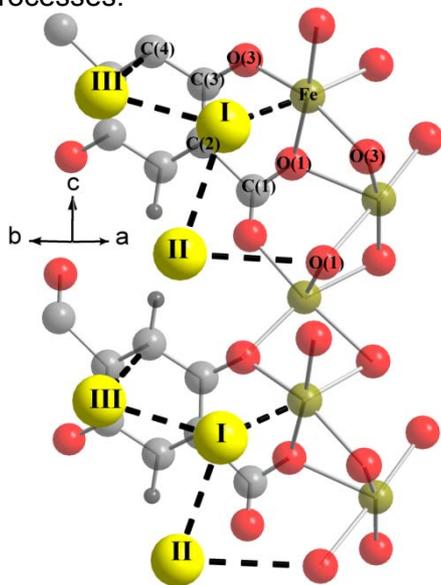
Comparison of QENS data for  $Cs_2B_{12}H_{12}$  to different rotational models

\* QENS data suggest that the  $[B_{12}H_{12}]^{2-}$  anion in  $Cs_2B_{12}H_{12}$  changes from uniaxial ( $C_3$  or  $C_5$ ) rotational jumps near 430 K to two-axis rotational jumps near 530 K.

## Motivation: understanding of new high surface area MOFs

• In MOFs unsaturated metal centers (UMCs) enhance binding energy and surface packing density of adsorbates.

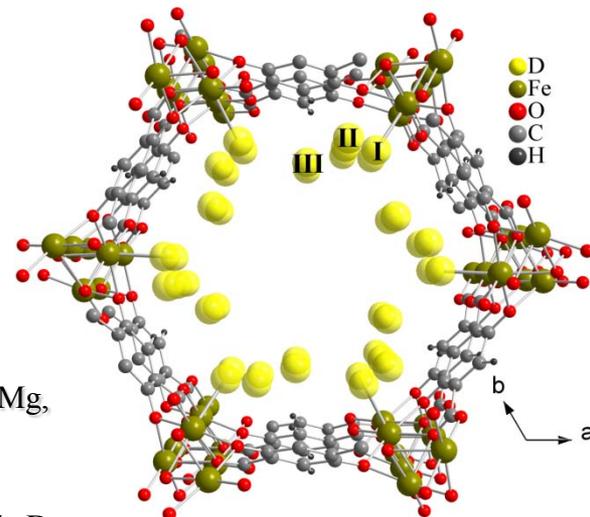
• Neutron powder diffraction (NPD) allows us to probe structural changes in the framework in sorption processes.



### 3 D<sub>2</sub> binding sites : labeled as I-III according to binding strength

- M-MOF 74, an extensive compound family, (M<sup>2+</sup> = Mg, Fe, Co, Ni, or Zn)
- BET surface area ≈ 1300 m<sup>2</sup>/g
- Has 5-coordinate M-ions that decorate the inside of 1-D hexagonal windows
- NPD on the framework loaded with 0.75 and 2.25 D<sub>2</sub>/Fe<sup>2+</sup> site reveals 3 D<sub>2</sub> binding sites.

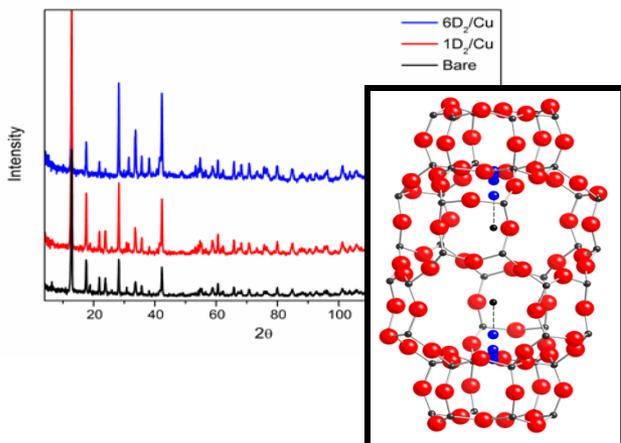
100% desolvation of UMCs



Coordination at UMC for D<sub>2</sub>  
 Fe-D<sub>2</sub>(I) ≈ 2.46 Å  
 D<sub>2</sub>-framework distances ≈ 3.22 – 3.24 Å  
 D<sub>2</sub>-D<sub>2</sub> distances ≈ 2.86 – 3.07 Å

New systems with magnetic ions allow us to probe the extent of this interaction on hydrogen storage strength.

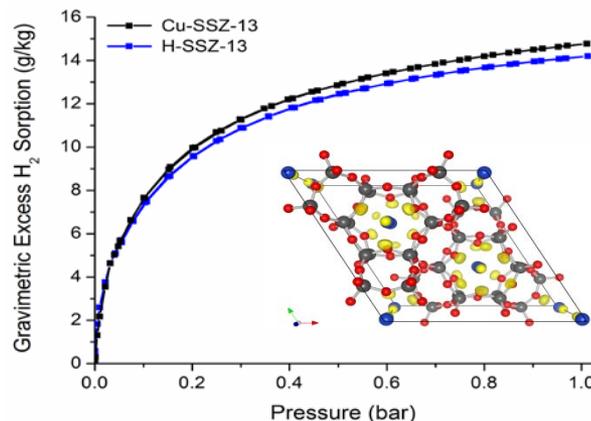
## Motivation: to characterize H<sub>2</sub> adsorption in exchanged zeolites



Powder ND was performed as a function of H<sub>2</sub> gas loaded and the location of the gas inside the host determined by Reitveld refinement

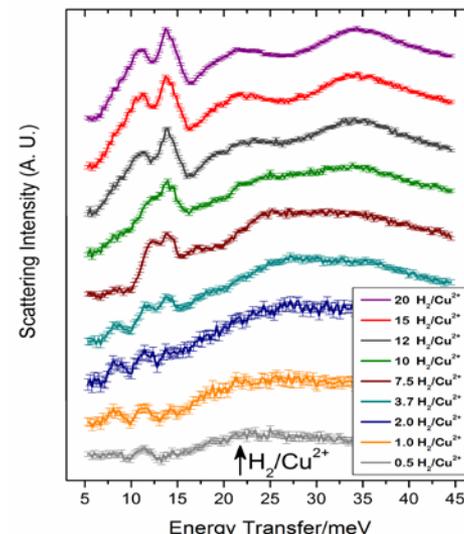
Two binding sites in Cu-SSZ-13 determined from ND: (1) at Cu(II) and (2) in the 8-member ring window

Cu(II) site is not occupied at low gas loadings but fully occupied at moderate pressures



The H<sub>2</sub> sorption for the cation-exchanged zeolite is enhanced over the H-SSZ-13 (inc. ≈ 4% at 1 bar) due to extra Cu(II) binding site

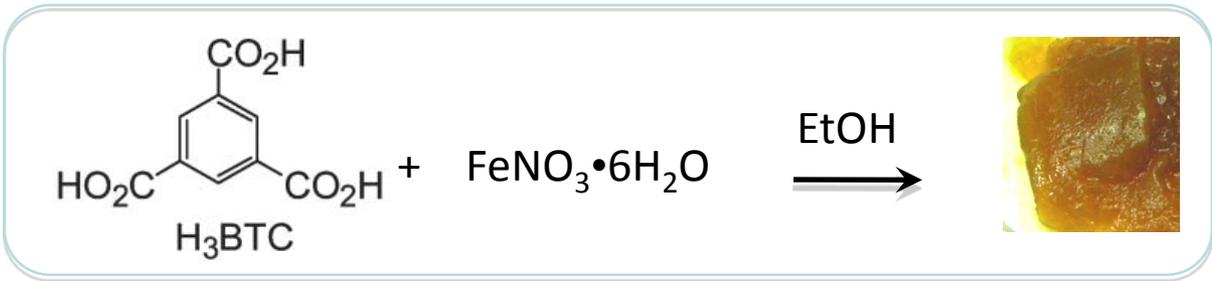
At 77 K and 1 bar, the adsorption for H-SSZ-13 and Cu-SSZ-13 is 1.38 g/kg (wt. %) and 1.48 g/kg, respectively



Inelastic neutron scattering (INS) spectroscopy was further used to probe the relative energies of the adsorption sites: (1) Cu(II), E = 8.3 meV and (2) (2) window site, E = 11.4 meV. A third peak at 14.7 meV is from bulk H<sub>2</sub> non-interacting with the host framework

We need to understand the relationship between accessible ions and hydrogen storage characteristics in porous storage materials.

Motivation: to generate high surface area amorphous MOF gel

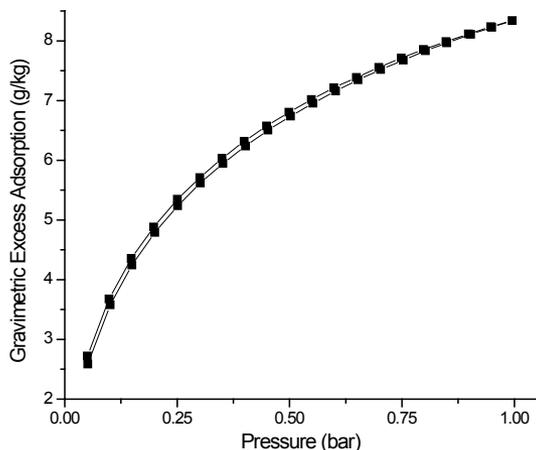


Multipoint BET Surface Area:

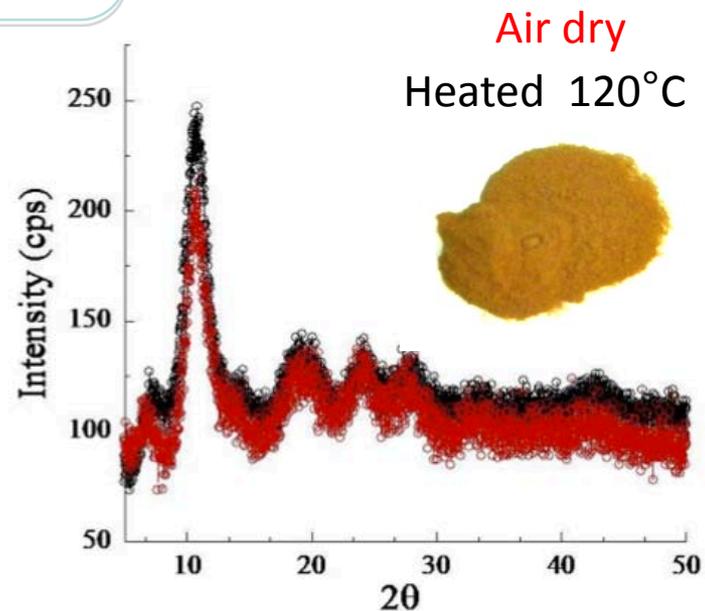
freeze dried – 279 m<sup>2</sup>/g,

Aerogel – 507 m<sup>2</sup>/g after drying 120°C

Aerogel - 1300 m<sup>2</sup>/g after drying with supercritical CO<sub>2</sub>



Compare to 2250-3200 m<sup>2</sup>/g in literature for crystalline versions



CO<sub>2</sub> extraction yields no improvement in low-pressure H<sub>2</sub> uptake despite surface area increase : just opens access for N<sub>2</sub> not H<sub>2</sub>

## Partners (Type of Institution): What we provide to them

**CalTech** (Univ./MHCoE): neutron measurements of various porous materials.

**Delaware** (Univ./Indep.): neutron measurements of various zeolites.

**GM** (Industry): neutron characterization of complex hydrides.

**JPL** (Fed./MHCoE): neutron and x-ray measurements and DFT calculations of various alanates, borohydrides, and related materials; neutron imaging of hydrogen-storage beds.

**LLNL** (Gov./HSCoE/MHCoE): Supercritical drying high surface area materials; neutron measurements of aerogels and nanoconfined storage materials.

**Maryland** (Univ.): neutron and x-ray measurements of alanates, borohydrides, and related materials.

**Michigan** (Univ.): neutron measurements of  $\text{BH}_4^-$  dynamics in neat and nanoconfined metal borohydrides.

**Missouri-St. Louis** (Univ./Indep.): neutron measurements of various alanates, borohydrides, and related materials.

**NREL** (Gov./HSCoE): neutron measurements / isotherm measurements of various spillover related materials.

**Ohio State** (Univ./Indep.): neutron and x-ray measurements of borated compounds.

**Penn** (Univ.): neutron measurements of amidoboranes and other storage-related materials.

**Penn State** (Univ./HSCoE): neutron measurements of various boron doped carbons.

**Sandia** (Fed./MHCoE): neutron measurements and DFT calculations of various alanates, borohydrides, and related materials.

**Stanford** (Univ./MHCoE): neutron reflectivity measurements of H profiles in H-cycled Mg thin films.

**U.C. Berkeley** (Univ./Indep.): neutron measurements of various metal-organic framework materials, alanates, borohydrides, and related materials.

## Remainder of FY2011:

- Continue to perform neutron-based structural and spectroscopic characterizations of new materials in conjunction with the needs of the DOE-funded projects, including nanoporous materials, borohydrides, and nanoscaffolding materials of interest.

## Neutron methods continue to provide crucial, non-destructive characterization tools for the DOE Hydrogen-Storage Program.

- The structure of the newly synthesized mixed-metal amidoborane  $\text{Na}_2\text{Mg}(\text{NH}_2\text{BH}_3)_4$  was solved by XRD and characterized by NVS. It can release 8.4 wt% pure hydrogen with significantly less toxic gases.
- NVS measurements of novel complex borohydrides  $\text{NaB}_3\text{H}_8$ ,  $\text{NH}_4\text{B}_3\text{H}_8$ , and  $\text{NH}_3\text{B}_3\text{H}_7$  indicated only limited agreement with DFT phonon calculations, suggesting that the DFT descriptions of the bonding interactions need to be improved.
- Quasielastic neutron scattering (QENS) measurements of  $\text{Cs}_2\text{B}_{12}\text{H}_{12}$  allowed us to characterize, in detail, the rotational dynamics of the  $\text{B}_{12}\text{H}_{12}^{2-}$  anions.
- QENS and NVS measurements of  $\text{LiBH}_4$  sequestered in 2-nm-pore carbon scaffolds indicated that the  $\text{LiBH}_4$  is disordered and exhibits significant non-bulk-like behavior with respect to  $\text{BH}_4^-$  rotational dynamics.
- Hydrogen uptake, neutron diffraction, and NVS characterization were performed on MOF-74 variants.
- NVS measurements of spillover hydrogen on activated carbons indicate excess-hydrogen modes at room temperature.
- Robust, but low uptake of hydrogen in model zeolite compounds were characterized and, for the first time, hydrogen adsorption sites were determined in a zeolite.
- Metal-organic gels were synthesized and characterized. Difficult-to-improve surface areas compared to crystalline parent materials.