



# Characterization of Hydrogen Adsorption by NMR



DOE “Hydrogen Sorption Center of Excellence”

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Project STP\_28\_Wu

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## Timeline

- Project start date  
2/1/2005
- Project end date  
1/31/2010
- Percent complete  
80%

## Budget

- Total project funding
  - DOE share: \$811,178
  - Contractor share: \$197,792
- Funding received in FY08  
\$250,000
- Funding for FY09  
\$161,178

## Barriers

- Barriers addressed
  - Lack of understanding of hydrogen physisorption and chemisorption
  - Insufficient information on H<sub>2</sub> accessible micropores and H<sub>2</sub> kinetics in micropores

## Partners

- Center partners
  - NREL (Dillon, Blackburn)
  - Penn State (Chung, Foley)
  - ORNL (Geohegan)
  - LLNL (Baumann)
  - Duke (J. Liu)
  - Argonne (D.J. Liu)
- Partners outside Center
  - UNC Chemistry (W. Lin)



# Objectives



DOE Hydrogen Program

## Overall

We provide nuclear magnetic resonance (NMR) support to DOE HS CoE team members in developing reversible adsorbent materials with the potential to meet DOE 2010 system-level targets.

## 2009

Evaluate materials synthesized by partners. Detailed work on MOF material, carbon nanohorns, activated PEEK, and porous polymers is based on:

- Isotherm measurements by NMR.
- NMR porosity analysis.
- Information on confinement and molecular dynamics.

H<sub>2</sub> in MOFs experience unexpectedly large crystal fields leading to strong binding and high H<sub>2</sub> capacity.

Opened large carbon nanohorns confine H<sub>2</sub> in an interconnected space composed of interstitial and endohedral sites.

Steam activation of PEEK leads to high microporosity and negligible mesoporosity, desired for high surface area substrates.



# Approach



DOE Hydrogen Program

$^1\text{H}$  NMR efficiently detects and measures the hydrogen content of a sample. NMR provides information on the microscopic environment and the molecular dynamics of the confined  $\text{H}_2$ . The average pore dimensions and the exchange of hydrogen between pores can be deduced.

The NMR technique is combined with a specialized setup that allows to perform in-situ measurements of hydrogen loading in pressures from 0.001 to 100 atm and temperatures between 77 K and room temperature.

NMR is especially useful when studying materials that show spectral distinction between free gas and hydrogen confined in micropores, as are found in MOFs, carbon nanohorns, and activated PEEK samples. Here, combining microscopic information with isotherm measurements (based on NMR line intensity measurements) proves to be a powerful approach to help team members in their material design.



## Hydrogen Adsorption in MOFs (Collaboration with Wenbin Lin, UNC-Chemistry)

### MOF:

- self assembly of organic linkers with inorganic metal-oxide clusters
- ultimate Lego<sup>®</sup> Set for design and synthesis of crystalline porous structures; infinite variations

#### Open Metal Sites



Stronger binding (up to 10 kJ/mol)  
but small number of sites

#### Organic linkers



Weak binding (4 to 7 kJ/mol)  
but large surface area

Unique MOF design - Interpenetrating network

Solvent/guest molecules maintain crystallinity and channel size.

After removal of guest molecules, channels become narrower, and long-range correlation is lost.

Upon H<sub>2</sub> absorption, with H<sub>2</sub> as new guest molecules, channel width adapts to H<sub>2</sub> size.

→ *Self adjusted H<sub>2</sub> trap*



## 2 MOFs with subtly different structure

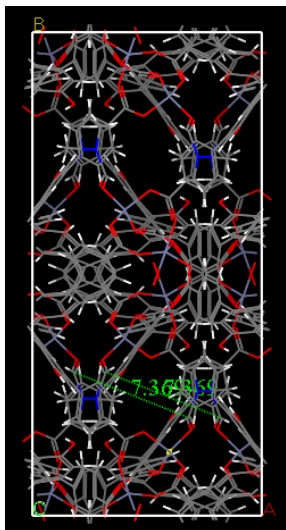
**2 fold interpenetration:** interpenetration occurs when a single framework has enough void space to accommodate a second (or third,..) identical frame work; → limit void space + H<sub>2</sub> in space between interpenetrating networks (ideally 4 Å wide)

2 MOFs are distinguished by the ligands that determine the space between networks:

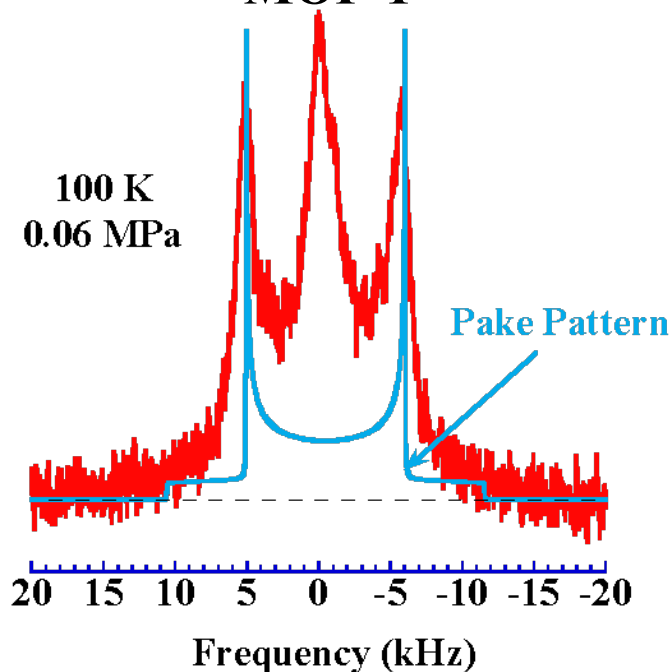
MOF-1: -OH

vs

MOF-2: -OCH<sub>2</sub>CH<sub>3</sub>



### MOF-1



### <sup>1</sup>H NMR evidence for new entrapping mechanism

The low temperature <sup>1</sup>H NMR spectrum is uniquely determined by the Pake pattern (blue line in figure) that is characteristic of H<sub>2</sub> molecules that do not rotate isotropically.

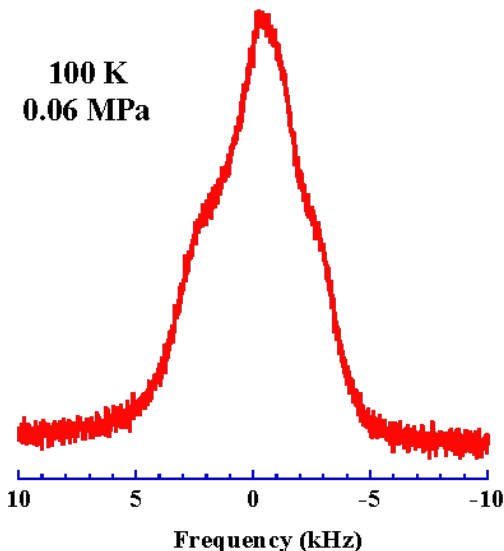
The hindered rotation of the H<sub>2</sub> is a result of **confinement** that exposes the H<sub>2</sub> to a strong crystal field also indicating strong binding.

(For comparison, the Pake doublet only appears in solid H<sub>2</sub> when cooled from 14 K to 1.7 K.)

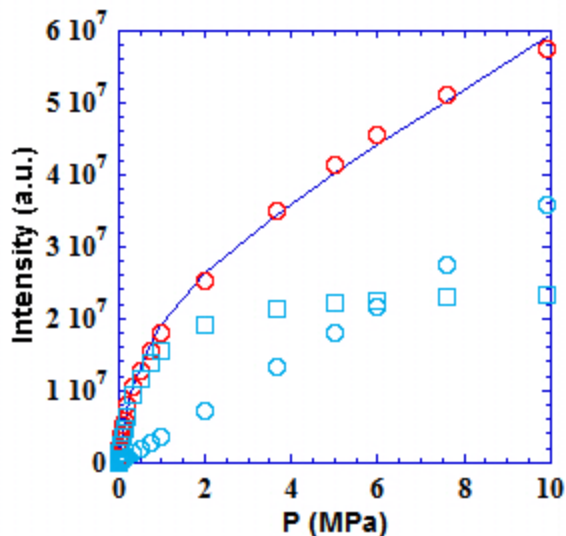


## MOF-2

## Confinement and crystal field depend on linker length.



The  $^1\text{H}$  spectrum for the MOF-2 under the same experimental conditions shows a much narrower Pake doublet (3.3 kHz vs. 11 kHz width). We associate the narrower width with a smaller crystal field between framework walls. This smaller crystal field correlates with longer ligands ( $-\text{OCH}_2\text{CH}_3$  vs  $-\text{OH}$ ) that keep the framework walls further apart after “guest molecules” have been removed.



## Storage Capacity and Binding Energy

Langmuir adsorption analysis yields an average binding energy of 5.7 kJ/mol.  
 $\text{H}_2$  capacities: 6 wt%.



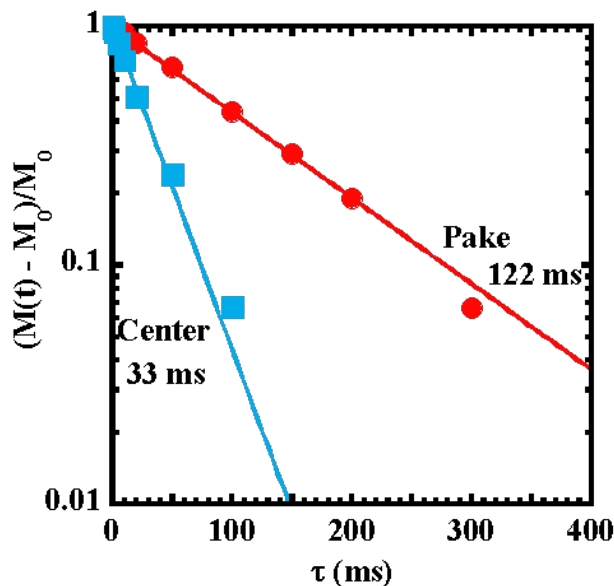
# Technical Accomplishments



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## Does confined and free H<sub>2</sub> exchange on the NMR time scale?

Measure spin lattice relaxation: if exchange occurs T<sub>1</sub> will be the same if not T<sub>1</sub>'s are different.



The relaxation times for the hydrogen producing the central peak and the Pake doublet are distinct. → **No exchange occurs between H<sub>2</sub> confined to narrow channels and “free” H<sub>2</sub> on at least a 30 ms timescale, again confirming the strong localization of H<sub>2</sub> molecules within the framework.**



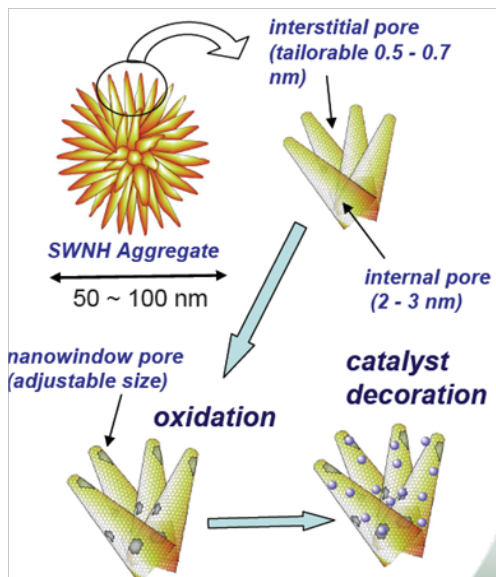


## Summary of MOF measurements

- The unusual Pake doublet  $^1\text{H}$  NMR spectra observed in the two MOFs reveal a strong confinement of  $\text{H}_2$  within the framework structure of the twice-interpenetrated network.
- The large observed crystal field leads to anisotropic rotation even at high temperatures.
- The hydrogen content correlates well with the large crystal field the hydrogen experiences.
- The correlation of the higher crystal field observed in the MOF with a shorter linker between the framework suggests that separation between frameworks after guest molecule removal and the flexibility of framework walls is a crucial element in designing new materials.

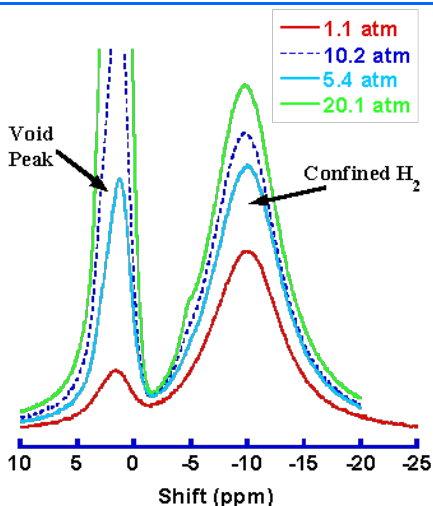


## Small versus Large Carbon Nanohorns (Collaboration: Oak Ridge NL; David Geohegan)



The Oak Ridge group has succeeded in synthesizing carbon nanohorns (CNH) with small or large diameters. Small CNHs will produce smaller interstitial pores, while large CNHs create larger interstitial spaces. When the CNHs are opened through oxidation two pore spaces are available for H<sub>2</sub> to adsorb: the endohedral space within the CNHs and the interstitial areas between nanohorns.

NMR will answer the question:  
Where do H<sub>2</sub> molecules reside in differently prepared samples?



### Small Carbon Nanohorns

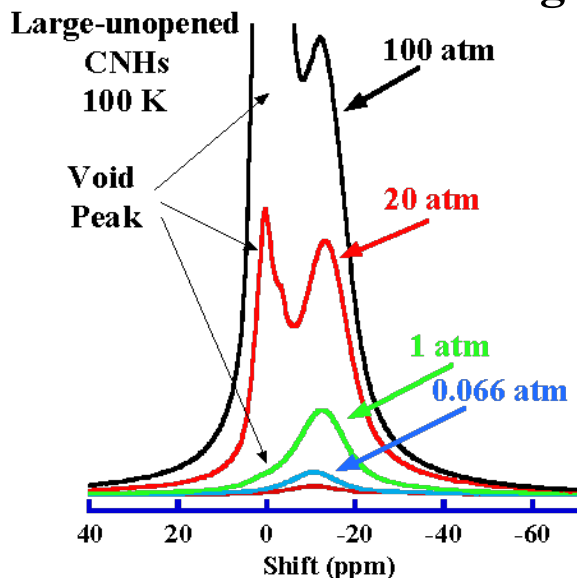
Previous measurements showed that small, unopened CNHs have no capacity for H<sub>2</sub> storage while opened CNHs show H<sub>2</sub> storage in narrow pores.

Conclusions:

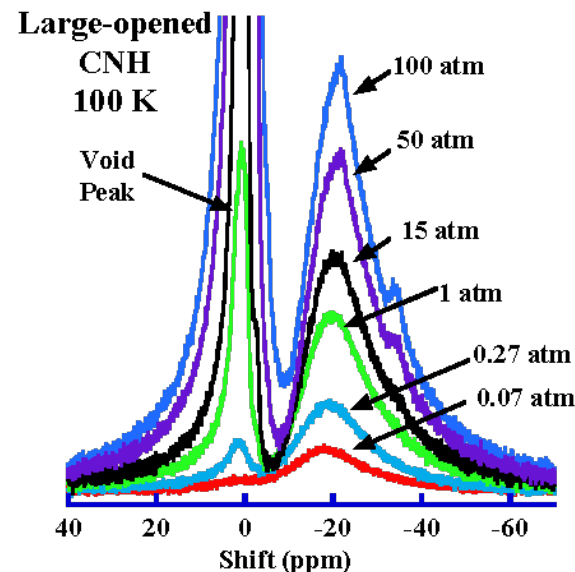
- 1) Interstitial sites in small, unopened CNHs are not accessible to H<sub>2</sub>.
- 2) Opening such nanohorns made the interior spaces accessible to H<sub>2</sub>.



## Large Carbon Nanohorns



**Unopened:**  $^1\text{H}$  spectra of large-unopened CNHs display an NMR line distinctly up-field shifted (to the right) associated with  $\text{H}_2$  confined in interstitials.



### Opened:

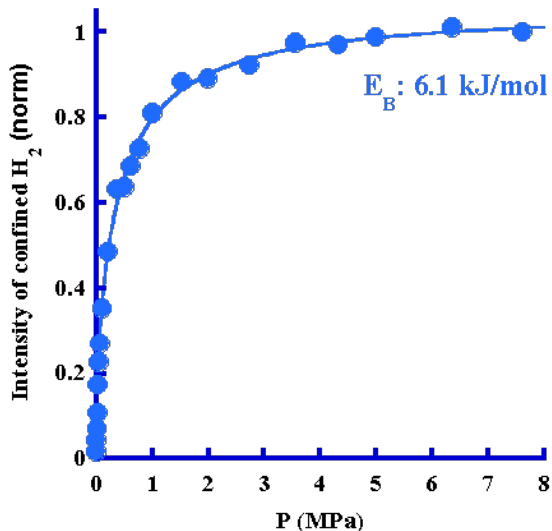
- NMR line broadens.
- Up-field shift increases.
- NMR line becomes more asymmetric with pressure.

→ Opening the nanohorns creates holes in the sidewalls connecting interstitial and endohedral spaces. Hydrogen adsorbing on interstitial walls can exchange with hydrogen endohedral to the CNHs.

(The line produced by exchange will shift upfield if  $\text{H}_2$  at the endohedral site experiences larger magnetic susceptibility, known to occur in carbon nanotubes.)



## Carbon Nanohorns



The large-unopened and large-opened CNHs have similar isotherms at 100 K in terms of binding energy, which is about 6.1 kJ/mol. Opening does lead to increase in the total amount of stored H<sub>2</sub> and is in the process to be quantified through careful intensity calibration.

## Carbon Nanohorns – Conclusion

The NMR work leads to the following morphology assessment:

- Small-unopened CNHs have neither interstitial nor endohedral pores available for H<sub>2</sub> storage.
- Small-opened CNHs provide narrow endohedral pores on the order of 1 nm.
- Large-unopened CNHs have interstitial sites with average diameter smaller than that of small nanohorns.
- Large-opened CNHs provide an interconnected space of interstitial and endohedral sites. The endohedral spaces are more graphitic with larger magnetic susceptibility.

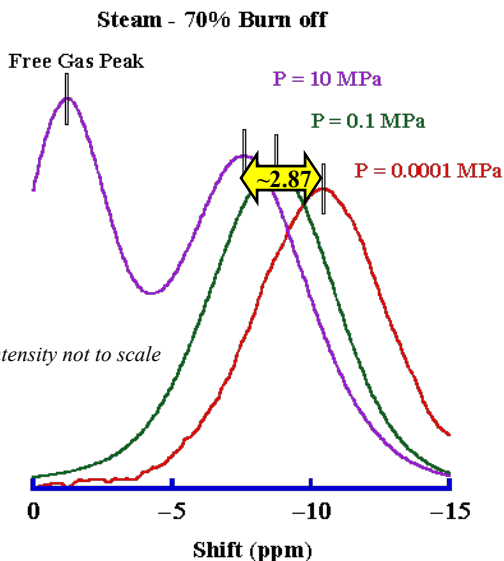


## Pore Evaluation in Activated PEEK (Collaboration: Duke University; Jie Liu)

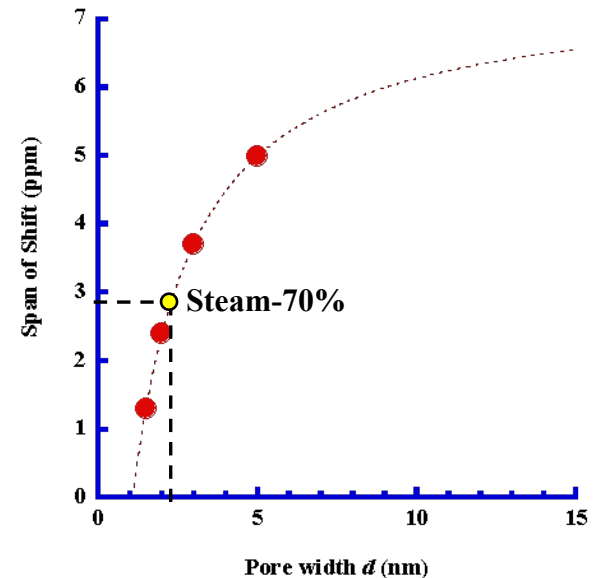
PEEK pellets are graphitized by activation at 900° C by two methods, CO<sub>2</sub> and steam. The morphology of the pores can be controlled by varying the activation time, with samples identified by mass percent of their burn off. Ideally, one of the methods coupled with the proper activation time will produce narrow pores (< 1 nm) while exhibiting high microporosity and negligible mesoporosity.

### NMR Porosymetry

The NMR line position of H<sub>2</sub> molecules confined in a pore is an averaged shift determined by the exchange of adsorbed H<sub>2</sub> (~ -12 ppm) with gas molecules in the pore interior (~ -1 ppm). The pressure dependence of gas and adsorbed H<sub>2</sub> is very different – linear vs. Langmuir. Thus the averaged line position as a function of pressure will change allowing us to estimate the pore diameter.



The span of this shift can be directly correlated to the average size of the pores. An approximate relationship has been established previously for a slit pore with binding energy of 5 kJ/mol at 100 K. Note that no shift is expected for  $d < 1$  nm.





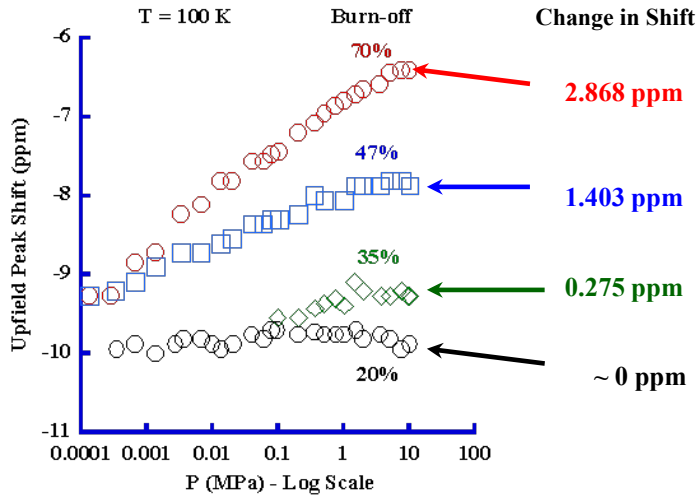
# Technical Accomplishments



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## PEEK Porosity: Steam vs. CO<sub>2</sub>

### Steam-Activated

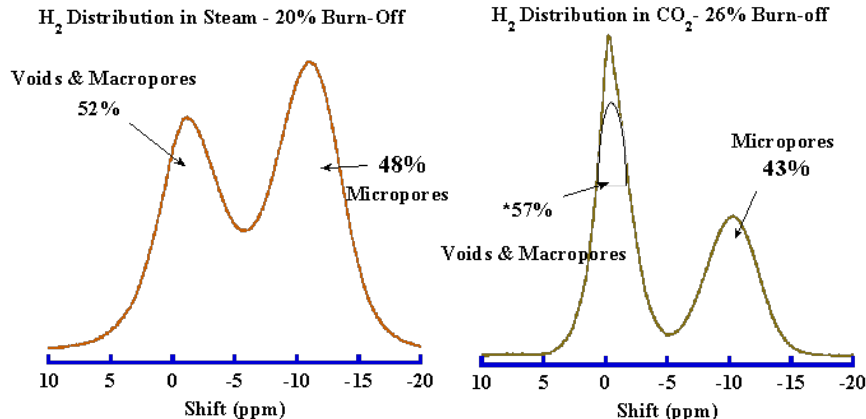


The shift data for the steam-activated samples clearly follows the general trend of increased pore size as a consequence of higher burn-off:

Sample	Total Shift	Est. <i>d</i> (nm)
Steam-70%	2.868	2.3
*CO <sub>2</sub> -80%	~2.5	2.0
Steam-47%	1.403	1.8
Steam-35%	0.275	1.1
Steam-20%	~0	< 1
*CO <sub>2</sub> -26%	~0	< 1
*CO <sub>2</sub> -1%	~0	< 1

*\*Not shown here*

This allows us to compare spectra (at 100 K and 10 MPa) of samples with similar pore sizes, and see which method is better suited to retain a larger total micropore volume. Steam appears to have an advantage over CO<sub>2</sub> with 48% of hydrogen residing in the pores at these conditions, compared to only 43% for the alternative method.

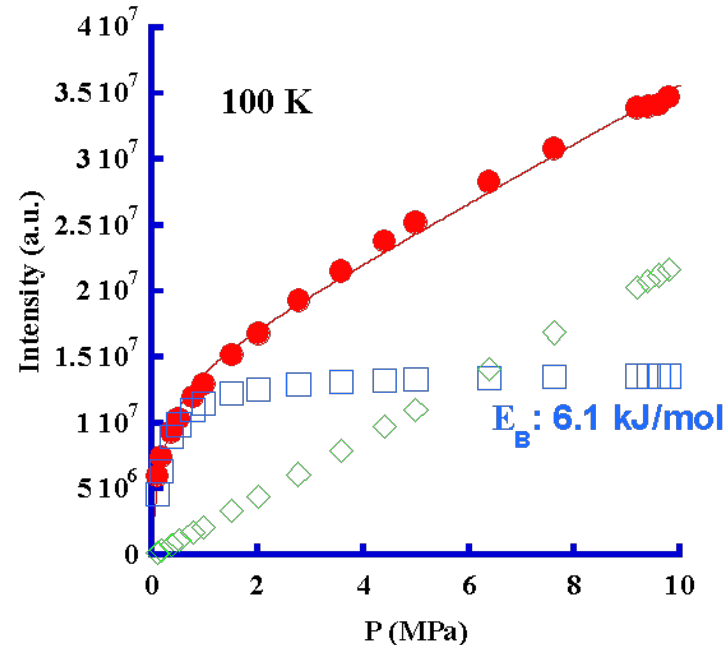
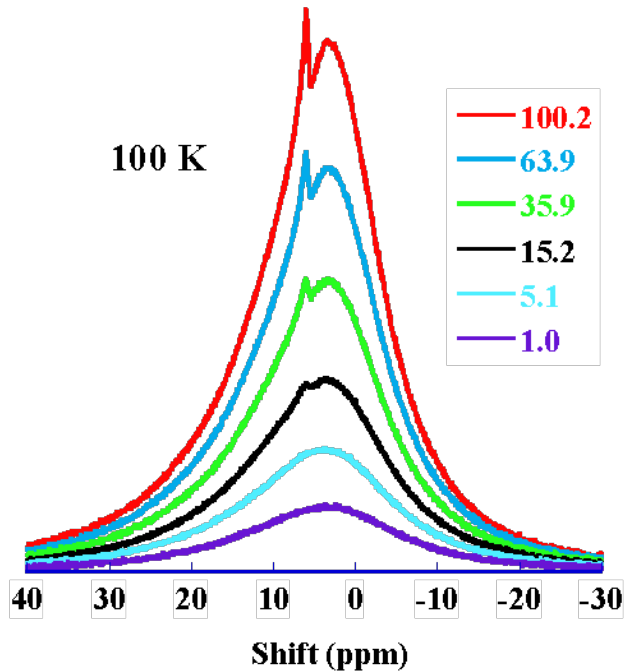


However, more samples of both types will be examined in future work to further test this conclusions. Furthermore, pressed pellets will be used to evaluate the packing density and its effect on H<sub>2</sub> storage.

*\*Volume of void space normalized by densities of samples.*



## Porous Polymers (D.J. Liu, Argonne National Lab)



- Porous polymer is an example of a material that does not provide clearly distinct spectral selection by NMR. However, confined and free H<sub>2</sub> can be separated by relaxation measurements.
- The binding energy of H<sub>2</sub> in this polymer is deduced from the isotherm measured by NMR and it is 6.1 kJ/mol.
- Intensity calibration is under way to determine the wt%.



# Future Work



DOE Hydrogen Program

## Fiscal Year 2009-10

- Continue measurements and quantitative analysis of carbon nanohorns (Oak Ridge)
- Continue measurements of activated PEEK (Duke).
- Continue measurements of interpenetrated MOF (UNC-Chemistry).
- Characterize porous polymer for H<sub>2</sub> storage (Argonne National Lab).
- Measure new B-doped graphitic carbons (Penn State).
- Measure B-doped carbon samples, with high boron content (Round Robin with NREL & NIST).
- Correlate NMR porosity measurements with CO<sub>2</sub> isotherm results. Measurements will be performed in collaboration with Oak Ridge.
- Continue NMR measurements and analysis of systems developed by team members (see collaborations below).
- Use pore size results obtained with Oak Ridge's collaboration to refine models that quantitatively correlate the experimentally determined NMR parameters with pore sizes.
- Molecular dynamics simulations on H<sub>2</sub> in pores of various sizes and as function of T and P (on-going).

## Collaborations:

- Oak Ridge nanohorn samples: explore synthesis and processing parameters on promising scaffold (on-going), D. Geohegan.
- Activated PEEK: fine tune processing parameters (on-going), J. Liu.
- Polymer samples from Argonne (on-going), D.J. Liu.
- B-doped activated carbon with small pore size from Penn State (Chung, Foley), M. Chung.
- Spillover samples from Michigan and Livermore; emphasis on nature of adsorbed hydrogen: atomic or molecular (on-going), R. Yang.
- MOF samples (on-going), W. Lin.





# Project Summary



**Relevance:** NMR provides a *microscopic picture* of adsorbed hydrogen that complements macroscopic techniques and offers immediate feedback for optimizing synthesis and processing conditions. Information about pore structures, including pore sizes and connectivity, can be extracted in addition to information about binding energy and the amount of adsorbed hydrogen.

## Technical Accomplishments:

- Discovered large crystal field in interpenetrated MOF structures after removal of guest molecules.
- Evaluated different processing methods for carbon nanohorns. Although counterintuitive large opened CNHs appear to be the promising material at low temperatures.
- Categorization of samples according to pore size and interconnectivity of their pores and measured binding energies.
- The pore structure in steam activated PEEK is dominated by micropores in comparison with CO<sub>2</sub> activated material.