



# Characterization of Hydrogen Adsorption by NMR



DOE “Hydrogen Sorption Center of Excellence”

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Project ST25

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# Overview

## Timeline

- Project start date  
2/1/2005
- Project end date  
1/31/2010
- Percent complete  
60%

## Budget

- Total project funding
  - DOE share: \$646,178
  - Contractor share: \$161,542
- Funding received in FY07  
\$170,000
- Funding for FY08  
\$190,000

## 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 (Heben)
  - Penn State (Chung, Foley)
  - ORNL (Geohegan)
  - LLNL (Baumann, Herberg)
  - Duke (Liu)



# Objectives

## 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.

## 2008

*Pore structures* are crucial for H<sub>2</sub> storage of sorbent materials. Most adsorbent materials have extremely complicated pore structures. Establishing clear correlations between synthesis, processing, pore structures, and H<sub>2</sub> storage is essential for optimizing the H<sub>2</sub> storage capacity of sorbent materials.

Our objective is to use *NMR porosymetry* analysis to obtain detailed information on the micropore structures. This approach is based on the information of local magnetic field inside micro- and meso-pores probed directly by H<sub>2</sub>. N<sub>2</sub> adsorption-based micropore analysis has certain ambiguities such as the accessibility of micropores by H<sub>2</sub> is not necessarily the same as that of N<sub>2</sub>.

Such NMR study offers a comprehensive picture and correlations between microstructures, binding energy, storage capacity, and kinetics of adsorbent materials.



# Approach



NMR is a sensitive detector for hydrogen. It determines quantitatively the number of hydrogen present in a material, provides information on the local environment at which adsorption takes place, and monitors molecular dynamics at different local environments under various conditions. Equipped with high pressure and variable temperature capabilities, all these important aspects of hydrogen storage can be studied as functions of temperature and pressure.

Specifically, NMR obtains information on the wt% of hydrogen storage, just as gravimetric and volumetric techniques provide. In addition, NMR reveals how much of the stored hydrogen are in micropores and how much are in mesopores. It also reveals how accessible micropores are for H<sub>2</sub> at various temperatures or after sample processing treatments of sorbent materials.

We developed an NMR porosymetry approach based on quantitative analysis of NMR parameters. Good correlations are established between the NMR porosymetry analysis and the storage capacity and synthesis and processing conditions of various sorbent materials provided by team members.



# Technical Accomplishments

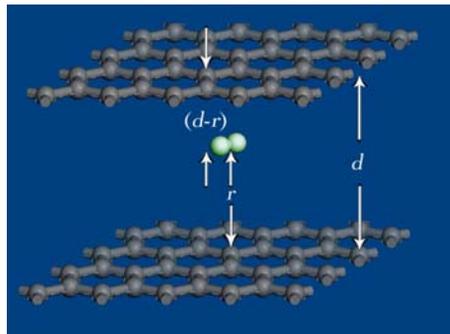


DOE Hydrogen Program

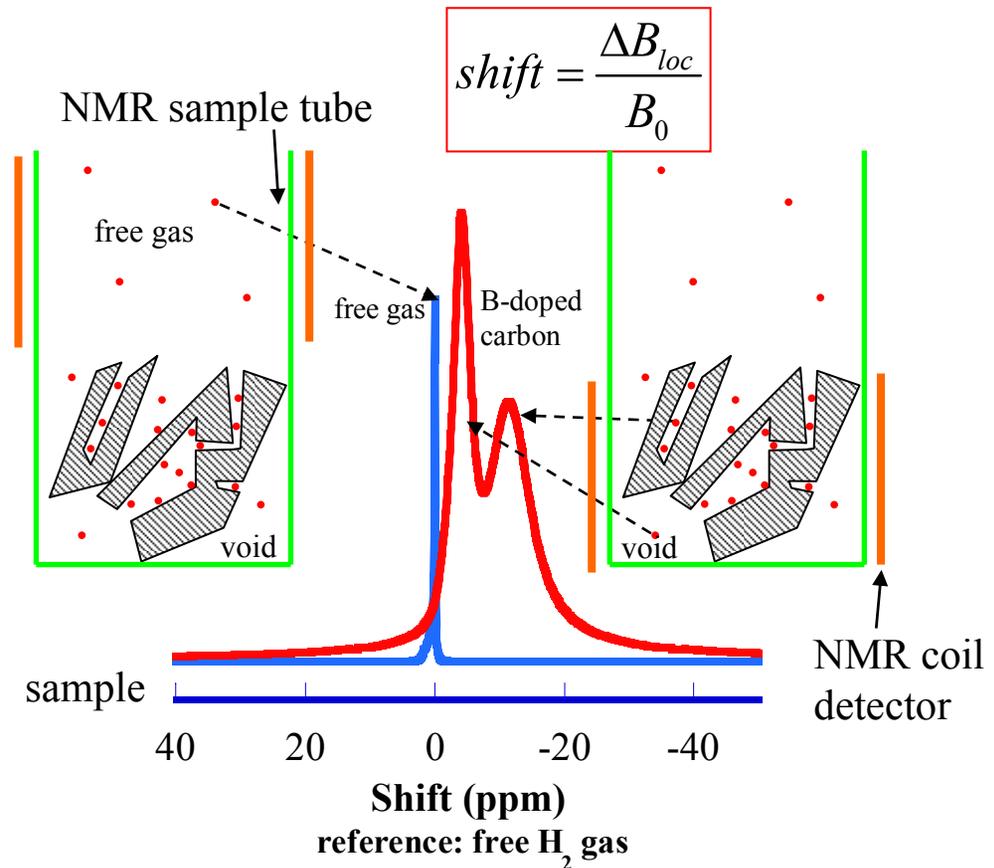
**NMR Porosymetry:** Established the link between the NMR spectral shift, its pressure dependence, and pore-size. Although the observed species is H<sub>2</sub> in all these samples, why is there such a large variation in shift?

Magnetic susceptibility  $\chi$  induces a local magnetic field  $B_{loc}$  in pores, depending on the distance between H<sub>2</sub> and the surface, and gives rise to a shift.

$$\Delta B_{loc} \propto \chi \left[ \frac{1}{r^3} + \frac{1}{(d-r)^3} \right]$$



Slit pore



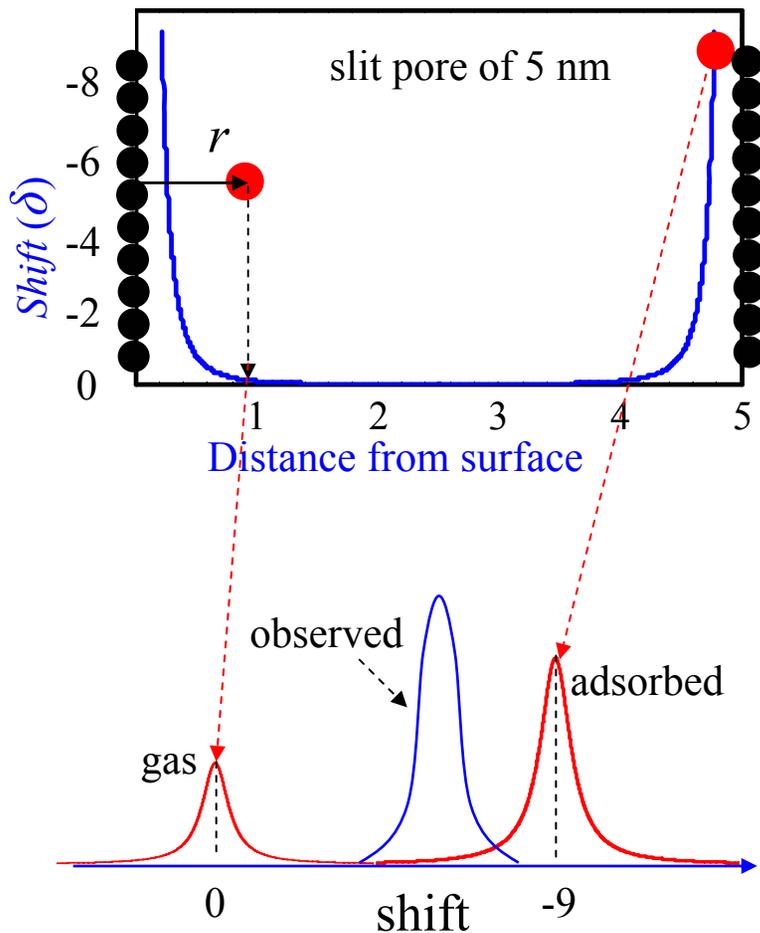


# Technical Accomplishments



DOE Hydrogen Program

$$\text{shift: } \delta \propto \chi \left[ \frac{1}{r^3} + \frac{1}{(d-r)^3} \right]$$



## NMR Porosymetry

The NMR spectral shift depends strongly on the distance  $r$  between  $\text{H}_2$  and the surface. There are basically two different values of shift,  $\delta_{\text{ads}}$  for adsorbed  $\text{H}_2$  and  $\delta_{\text{gas}}$  for not adsorbed  $\text{H}_2$ . Because of rapid adsorption and desorption on the NMR timescale, the observed one is the average given by

$$\delta_{\text{obs}}(P) = \frac{\delta_{\text{gas}} n_{\text{gas}}(P) + \delta_{\text{ads}} n_{\text{ads}}(P)}{n_{\text{gas}}(P) + n_{\text{ads}}(P)}$$

Since the amounts of adsorbed ( $n_{\text{ads}}$ ) and not adsorbed ( $n_{\text{gas}}$ ) hydrogen depend on pressure  $P$  differently,  $\delta_{\text{obs}}$  would depend on  $P$  unless one or the other dominates.



# Technical Accomplishments



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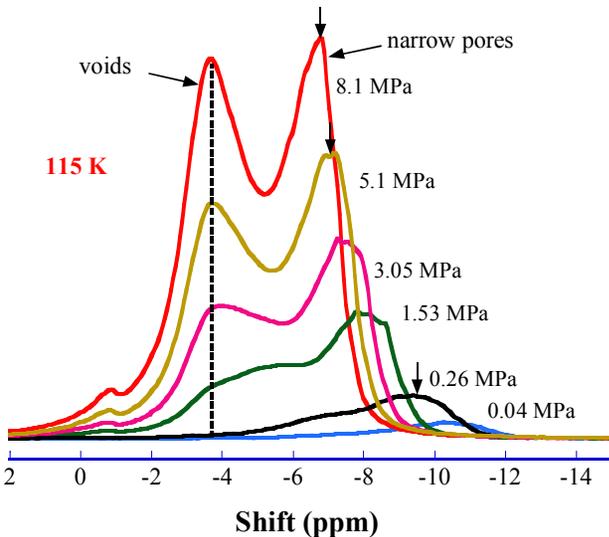
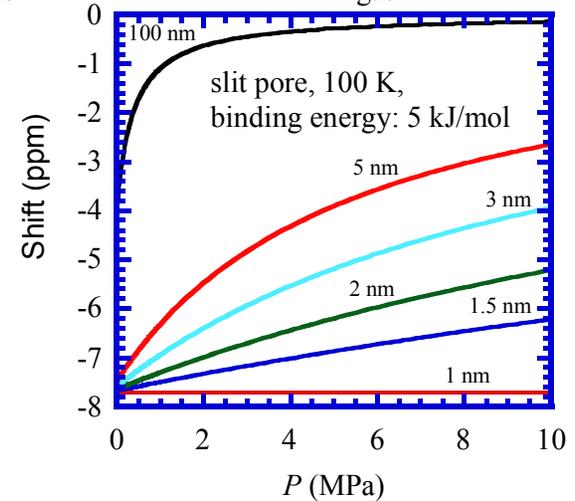
## Modeling

$$\delta_{obs}(P) = \frac{\delta_{gas} n_{gas}(P) + \delta_{ads} n_{ads}(P)}{n_{gas}(P) + n_{ads}(P)}$$

Since  $n_{ads}$  scales very differently with the pore size  $d$  than  $n_{gas}$  (2d v.s. 3d),  $n_{ads}$  dominates below 1 nm whereas  $n_{gas}$  dominates above 100 nm. Also, because of the differences in isotherms,  $\delta_{obs}$  depends also on  $P$  when the  $P$  dependence of  $n_{ads}$  becomes nonlinear.

### Model for a slit pore

$n_{ads}(P)$ : Langmuir;  $n_{gas}(P)$ : ideal gas law

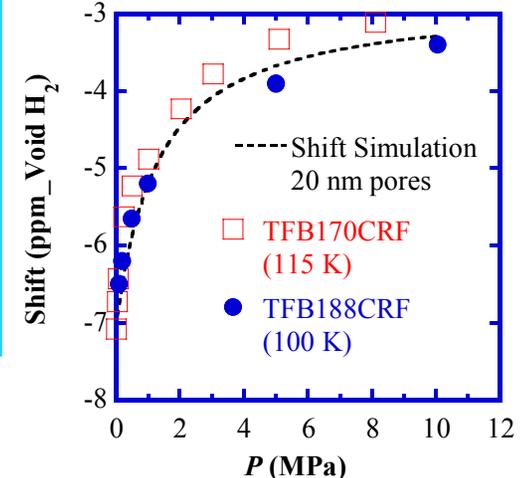


## Aerogel

TFB170CRF-Ted Baumann, Livermore  
2000 m<sup>2</sup>/g, 4.2 wt% at 77 K (volumetric)

$n_{ads}(P)$  and  $n_{gas}(P)$  can both be measured by NMR. 3.1 wt% at 115 K (NMR)

Average pore size: 20 nm





# Technical Accomplishments



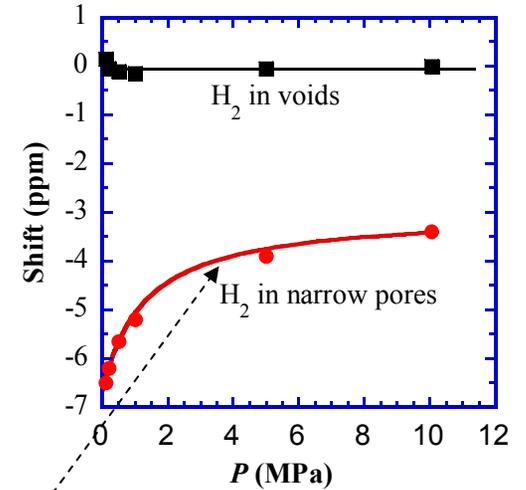
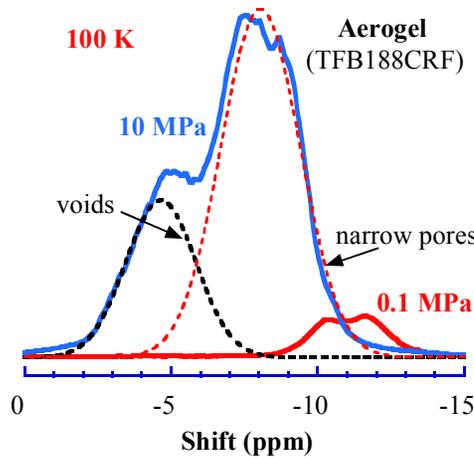
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## Aerogel

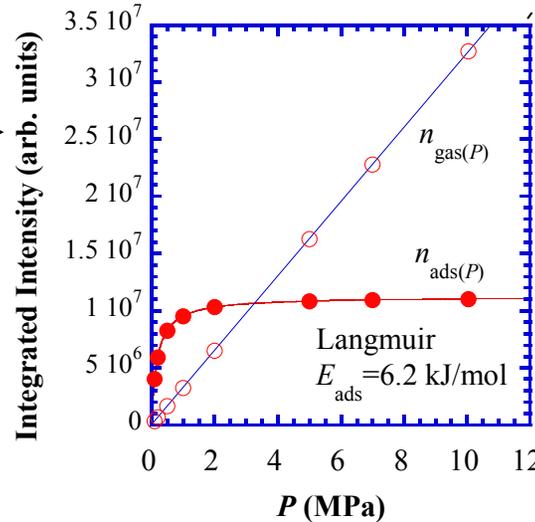
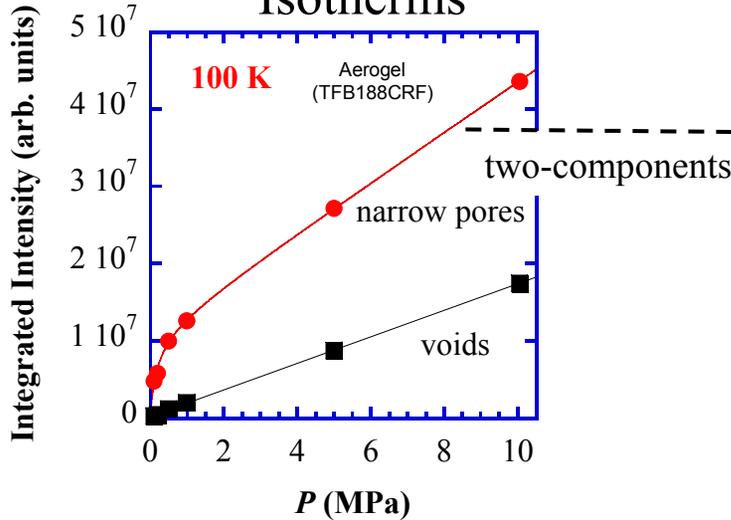
TFB188CRF-Ted Baumann, Livermore  
3200 m<sup>2</sup>/g, 5.2 wt% at 77 K (volumetric)

$n_{ads}(P)$  and  $n_{gas}(P)$  can both be measured by NMR. 5.4 wt% at 100 K (NMR)

Average pore size: 20 nm;  $E_{ads}=6.2$  kJ/mol



## Isotherms



$$\delta_{obs}(P) = \frac{\delta_{gas} n_{gas}(P) + \delta_{ads} n_{ads}(P)}{n_{gas}(P) + n_{ads}(P)}$$

## Langmuir Isotherm

$$n(P, T) = n_{\infty} \frac{bP}{1 + bP};$$

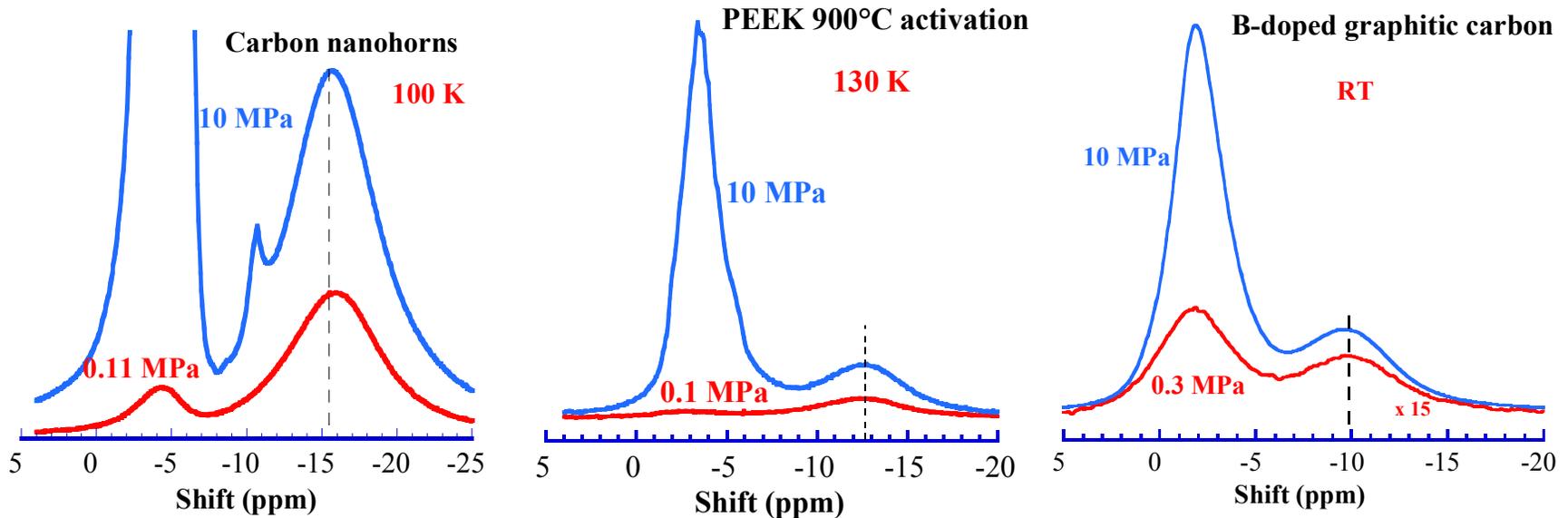
$$b = \frac{\sigma}{v_0 \sqrt{2\pi m k_B T}} \exp(E_{ads} / k_B T)$$

Using these measured  $n_{ads}(P)$  and  $n_{gas}(P)$  to fit the  $P$  dependence of the shift shown on the upper right corner. From that, an average pore size of 20 nm is obtained for Aerogel TFB188CRF, comparable to the pore size of Aerogel TFB170CRF discussed in the previous slide, but with much larger surface area.



# Technical Accomplishments

## Systems with predominant micropores



In contrast to aerogels, all three samples show a distinct upfield peak that does not shift with increasing pressure. This indicates that all three materials possess micropores of 1 nm in size rather than mesopores. However, the isotherms of carbon nanohorns and activated PEEK do not deviate significantly from linear behavior at room temperature unlike that of B-doped graphitic carbon. Thus, the binding energy of the latter is enhanced as reported earlier.

Carbon nanohorns: David Geohegan (Oakridge)

Activated carbon (PEEK): Jie Liu (Duke)

B-doped graphitic carbon: Mike Chung (Penn State)



# Technical Accomplishments



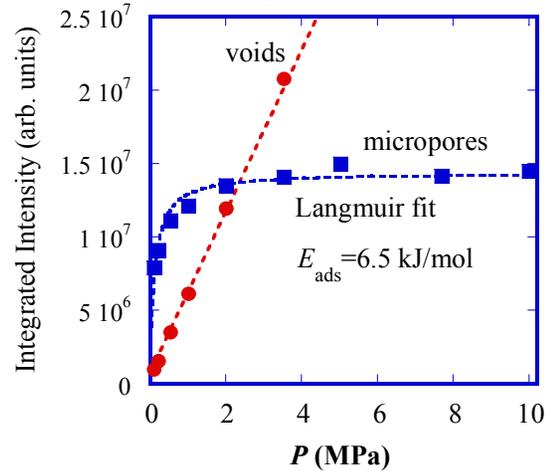
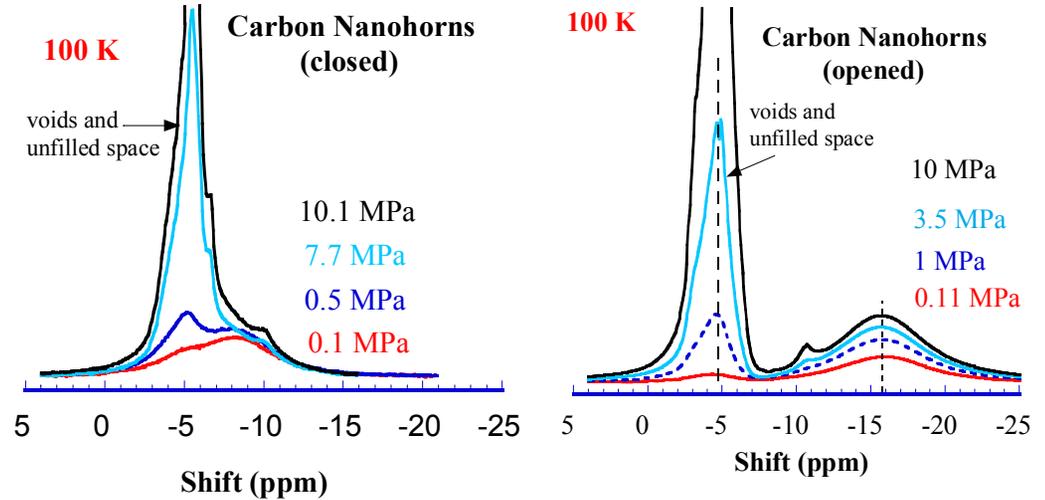
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## Carbon Nanohorns

David Geohegan, Oakridge

Average pore size: 1 nm;  $E_{ads} = 6.5$  kJ/mol

The Oakridge group has recently gained control in their production method over the tube diameter and produced nanohorns with small (~1 nm) diameters. Here we show our NMR study of such small diameter nanohorns. One sample is unopened and the other is opened small diameter nanohorns.



## Langmuir Isotherm

$$n(P, T) = n_{\infty} \frac{bP}{1 + bP};$$

$$b = \frac{\sigma}{v_0 \sqrt{2\pi m k_B T}} \exp(E_{ads} / k_B T)$$

The unopened sample shows a small amount of adsorption, which is apparent at low pressure (0.1 MPa). The opened nanohorns (oxidation in air) show clearly a peak associated with micropores. Since its shift does not depend on pressure, the pore size is estimated to be about 1 nm. The associated binding energy is 6.5 kJ/mol.



# Technical Accomplishments



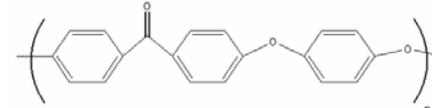
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## Activated Carbon (PEEK)

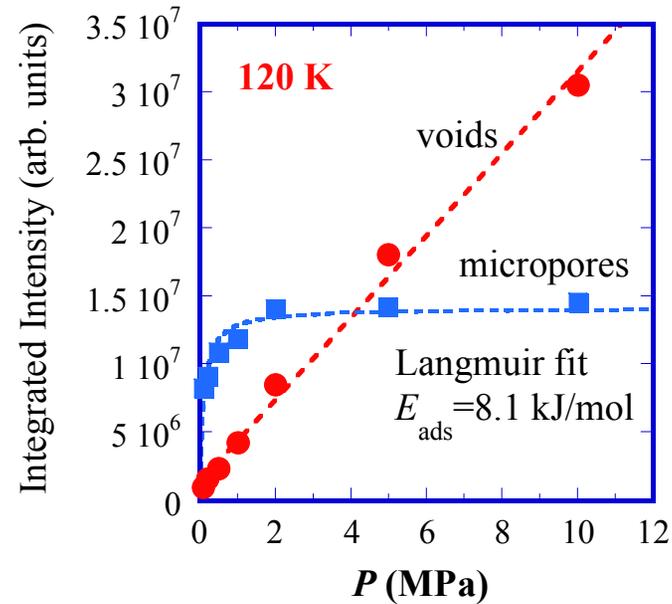
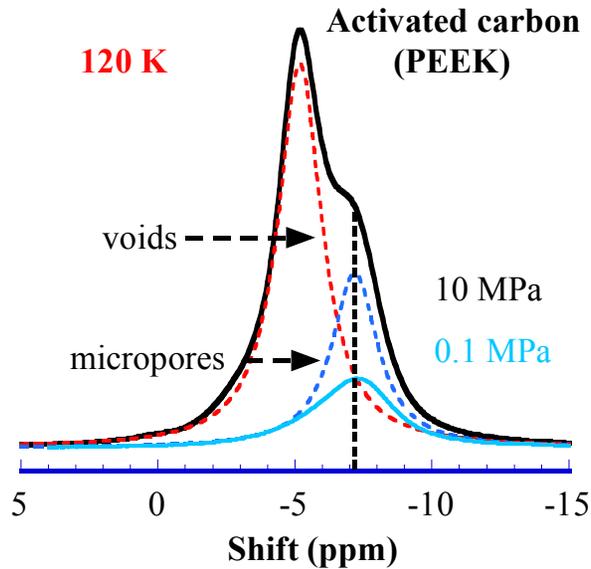
Jie Liu, Duke University

About 2 wt% at 77 K (volumetric)

Average pore size: 1 nm;  $E_{\text{ads}}=8.1$  kJ/mol (NMR)



PEEK is being graphitized through activation in  $\text{CO}_2$  at  $900^\circ\text{C}$  for certain time period of hours. Some of the samples were found to adsorb more  $\text{H}_2$  at 77 K than predicted by the Chahine rule, i.e. 1 wt% for  $500 \text{ m}^2/\text{g}$  (see Jie Liu's presentation). A possible reason could be that  $\text{N}_2$  cannot access all of the pore regions available to  $\text{H}_2$  thus underestimating the surface area.



This sample was PEEK activated in  $\text{CO}_2$  at  $900^\circ\text{C}$  for 2 hours producing 5 % weight loss followed by 2 more hours of activation with 82 % weight loss due to leak in the system.

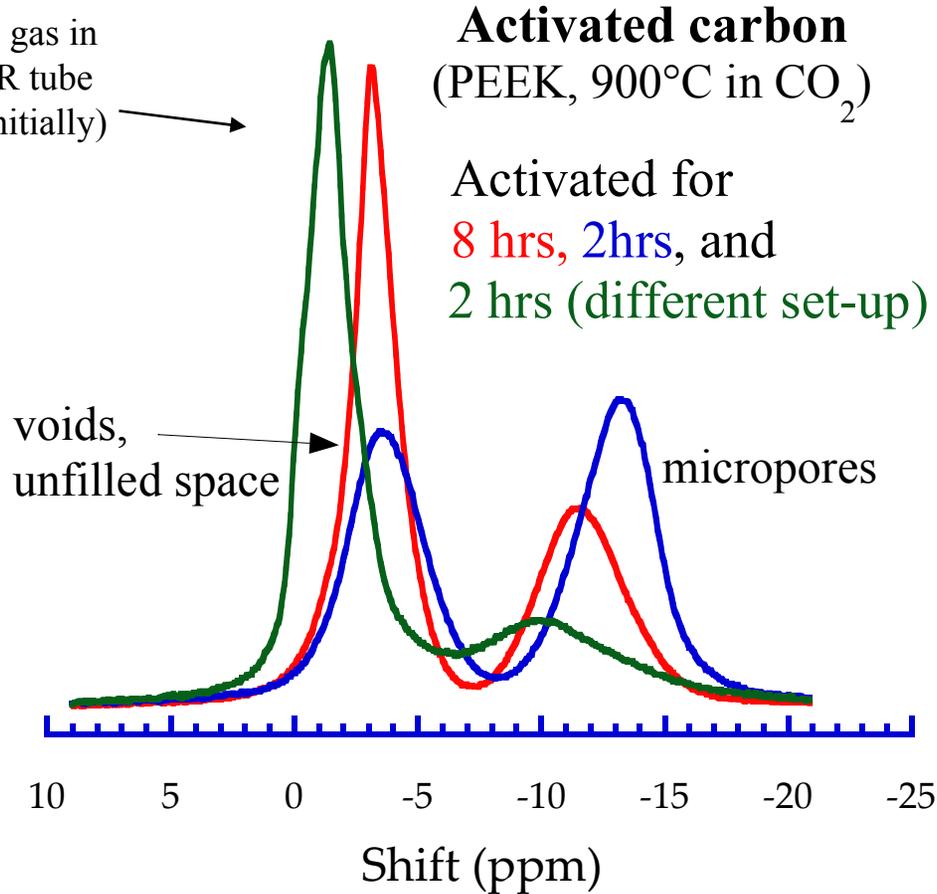


# Technical Accomplishments



DOE Hydrogen Program

Shifted due to free H<sub>2</sub> gas in partially unfilled NMR tube (not enough sample initially)



This shows that micropores change significantly with the activation process and can be probed sensitively by NMR. The peaks associated with micropores in all these samples show linear pressure dependence at RT unlike in B-doped graphitic carbons. Improvement of binding energy, perhaps by B-doping, is needed for RT H<sub>2</sub> storage.



# Technical Accomplishments



DOE Hydrogen Program

## B-doped graphitic carbon

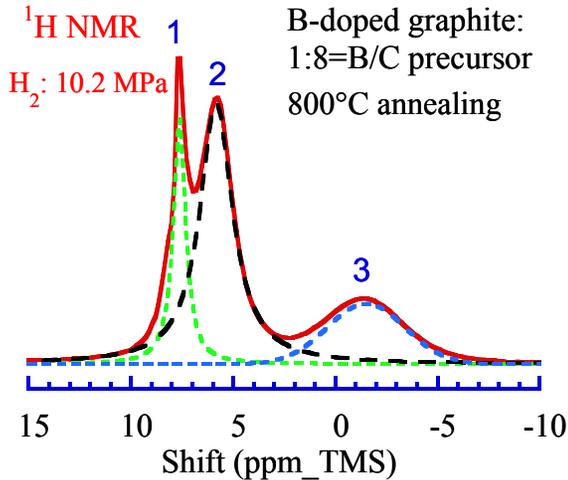
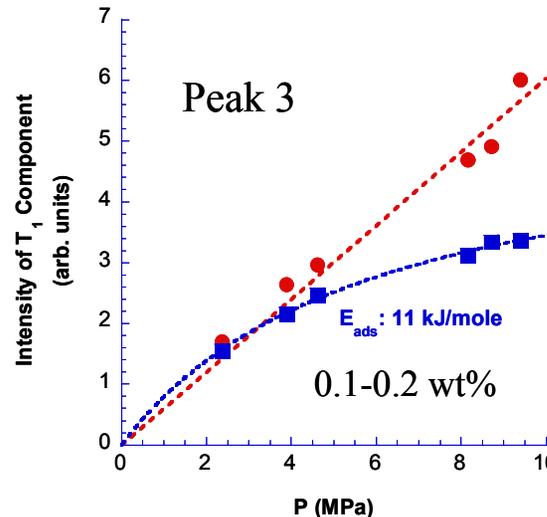
Mike Chung, Penn State University

Average pore size: 1 nm;  $E_{ads}=11$  kJ/mol (NMR)

Sample is produced with B-containing precursor, polymerized, and graphitized by annealing at certain temperature, in this case, 800°C (see Mike Chung's presentation).

## Langmuir adsorption

$$n(P,T) = n_{\infty} \frac{bP}{1+bP}, \quad b = \frac{\sigma}{v_0 \sqrt{2\pi m k_B T}} \exp(E_{ads} / k_B T)$$



Peak 1 is due to free gas in a capillary as an intensity gauge, peak 2 is due to gas in voids, and peak 3 corresponds to H<sub>2</sub> in micropores.

It becomes increasingly clear that all carbon-based systems we have looked so far, B-doped graphitic carbon is the only one with a binding energy larger than 11 kJ/mol. The issue is how to increase the number of such adsorption sites with large binding energy.



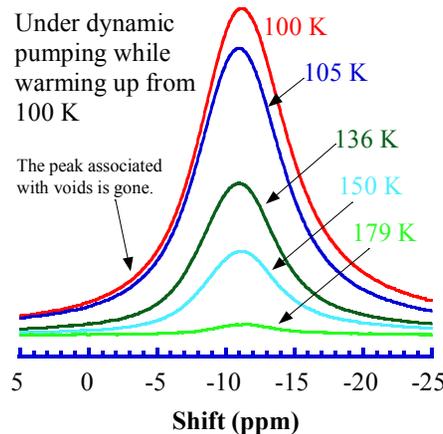
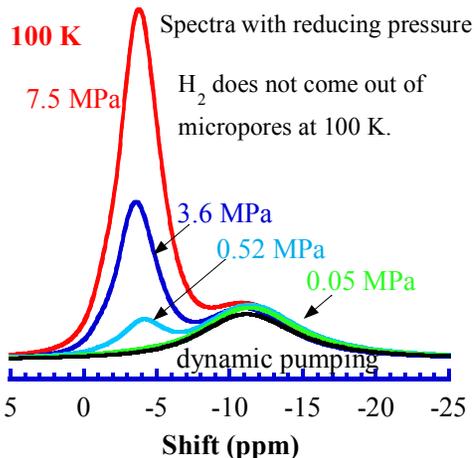
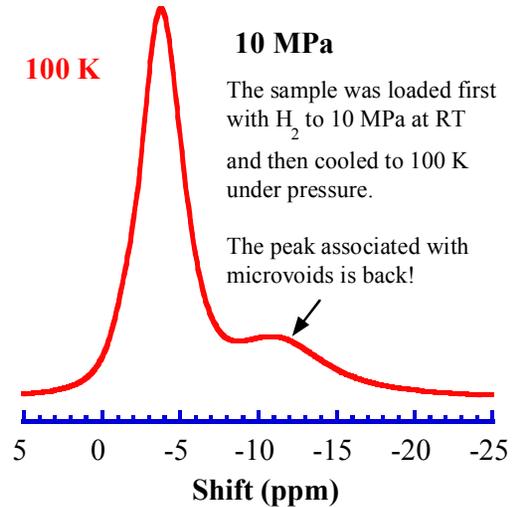
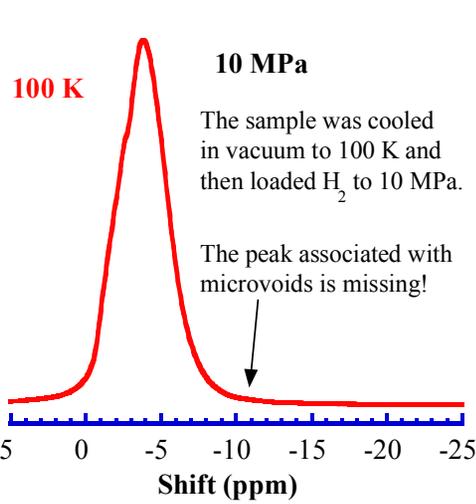
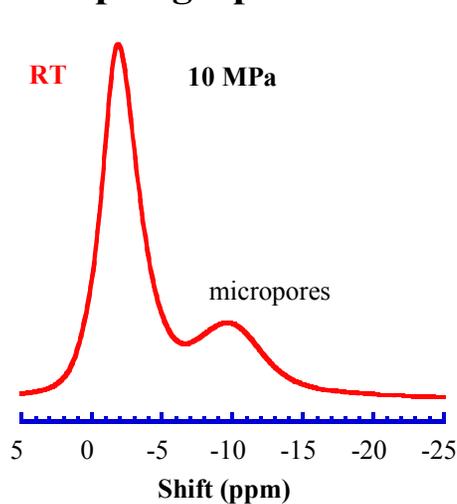
# Technical Accomplishments



DOE Hydrogen Program

Another important issue is the accessibility of micropores by  $H_2$ . Here we demonstrate that this is particularly an important issue at lower temperature.

## B-doped graphitic carbon



At 100 K,  $H_2$  could not access the micropores and could not come out if it is already inside. Warming up to 150 K speeds up the process significantly. The timescale at 100 K is much longer than 10 hours as we tested. Thermally activated diffusion process could play a crucial role in accessing narrow pores.



# Technical Accomplishments



DOE Hydrogen Program

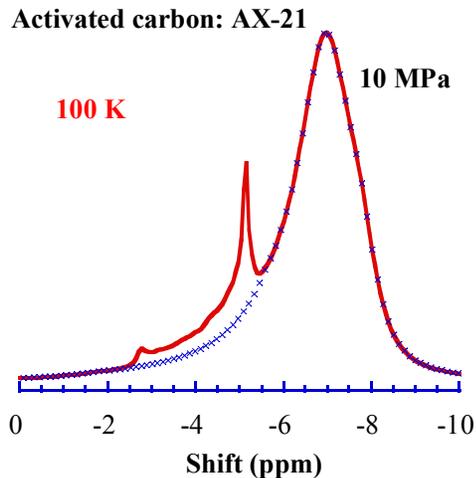
## Mass Calibration of NMR Spectra and Isotherms

The  $^1\text{H}$  line intensity is directly proportional to the number of hydrogen in the sample and thus provides the basis for measuring the absolute number of  $\text{H}_2$  present. Spectra with well defined lines associated with  $\text{H}_2$  in micropores can be separated into a free gas and an adsorbed component.

To measure the absolute intensity the observed line intensity has to be compared to a calibration sample. It is best to use the standard internally during a measurement, i.e. the standard and the sample are placed together inside the NMR coil.

Two methods are employed:

- 1) Insert a capillary in the sample tube surrounded by the sample and measure isotherm simultaneously.
- 2) Use PDMS (Polydimethylsiloxane) as a standard.



### Capillary Method

The capillary contribution to the spectrum (red-blue), a characteristic powder pattern, is compared to the spectrum of the sample (blue). The number of  $\text{H}_2$  in the capillary can be computed based on the known behavior of  $\text{H}_2$  gas.

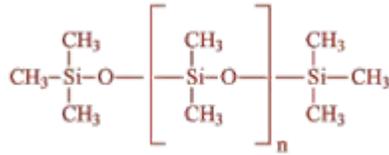
The capillary method was used to study adsorption in AX-21, yielding a value of 6.2 wt % at 10 MPa and 100 K. That compares well with the literature value of 5.5 wt % at 77 K.



# Technical Accomplishments

## Mass Calibration of NMR Spectra and Isotherms

### PDMS Method



The methyl groups of PDMS (Polydimethylsiloxane) gives rise to a sharp  $^1\text{H}$  NMR line which can be used conveniently as a intensity reference. About 6 mg of PDMS is added to the sample without great loss of sample space. The spin-lattice relaxation time  $T_1$  of PDMS (5 s) is 100 times longer than  $T_1$  of  $\text{H}_2$  (<50 ms) and thus the effect of PDMS on the spectra of the sample can be eliminated by fast acquisition when not needed. The PDMS spectrum is measured under dynamic vacuum conditions, integrated and based on its proton content ( $4.9 \cdot 10^{22}$  H/g) is used to calibrate the recorded spectra.

Results are summarized in the table. NMR results refer to measurements at 100 K and 10 (MPa), literature values are for 77 K.

Sample	wt % (NMR)	wt %_(volumetric) 77 K
AX-21	6.2 (capillary) 100 K	5.5
TFB170CRF	3.1 (PDMS) 115 K	4.2
TFB188CRF	5.4 (PDMS) 100 K	5.2



# Future Work

## Fiscal Year 2008

- Refine models that quantitatively correlate the experimentally determined NMR parameters with pore sizes (on-going).
- Molecular dynamics simulations on H<sub>2</sub> in pores of various sizes and as function of  $T$  and  $P$  (on-going).
- Complete measurements and quantitative analysis of carbon nanohorns and B-doped graphitic carbons.
- Continue measurements of activated PEEK and MOF.

## Fiscal Year 2009

- Continue NMR measurements and analysis of systems developed by team members (see collaborations below).

In addition to measurements we employed so far, we plan to carry out lower temperature measurements in order to:

- Differentiate between H<sub>2</sub> in pores of different sizes by using lower temperature ( $< 77$  K) to slow down the exchange rate between pores.
- Determine H-H distance in adsorbed H<sub>2</sub> in boron doped graphite ( $30$  K  $> T > 4.2$  K).

## Collaborations:

- Oakridge nanohorn samples: explore synthesis and processing parameters on promising scaffold (on-going)
- Activated PEEK: fine tune processing parameters (on-going)
- Polymer samples from Argonne (on-going)
- B-doped activated carbon with small pore size from Penn State (Chung, Foley)
- Spillover samples from Michigan and Livermore; emphasis on nature of adsorbed hydrogen: atomic or molecular
- MOF samples (on-going)



# 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:

- Developed an NMR porosymetry approach connecting NMR parameters to pore sizes and hydrogen storage capacity.
- Estimated pore size, binding energy and weight percentage of various samples provided by team partners.
- Categorization of samples according to pore size and interconnectivity of their pores and measured binding energies.
- Small nanohorn samples and activated PEEK were found to be composed of a network of narrow pores.
- Boron doped graphitic carbon shows enhanced binding energy but with slow kinetics at low temperature.



# Project Summary

Sample	Average Pore Size	Binding Energy (kJ/mole)	Wt %	
			NMR	Volumetric
B-doped graphitic carbon M. Chung, Penn State	~ 1 nm (very slow kinetics)	11	0.2	?
Nanohorns D. Geohegan, Oakridge	~ 1 nm	6.5		
Activated PEEK J. Liu, Duke	~ 1 nm (slow kinetics)	8.1		
Aerogels T. Baumann, Livermore	~ 20 nm (connected pores)	6.2	3.1 (TFB170) 5.4 (TFB188CRF)	4.2 5.2
AX-21	connected pores	5.6	6.2	5.5