# Characterization of Hydrogen Adsorption by NMR

"DOE Center of Excellence on Carbon-based Hydrogen Storage Materials"

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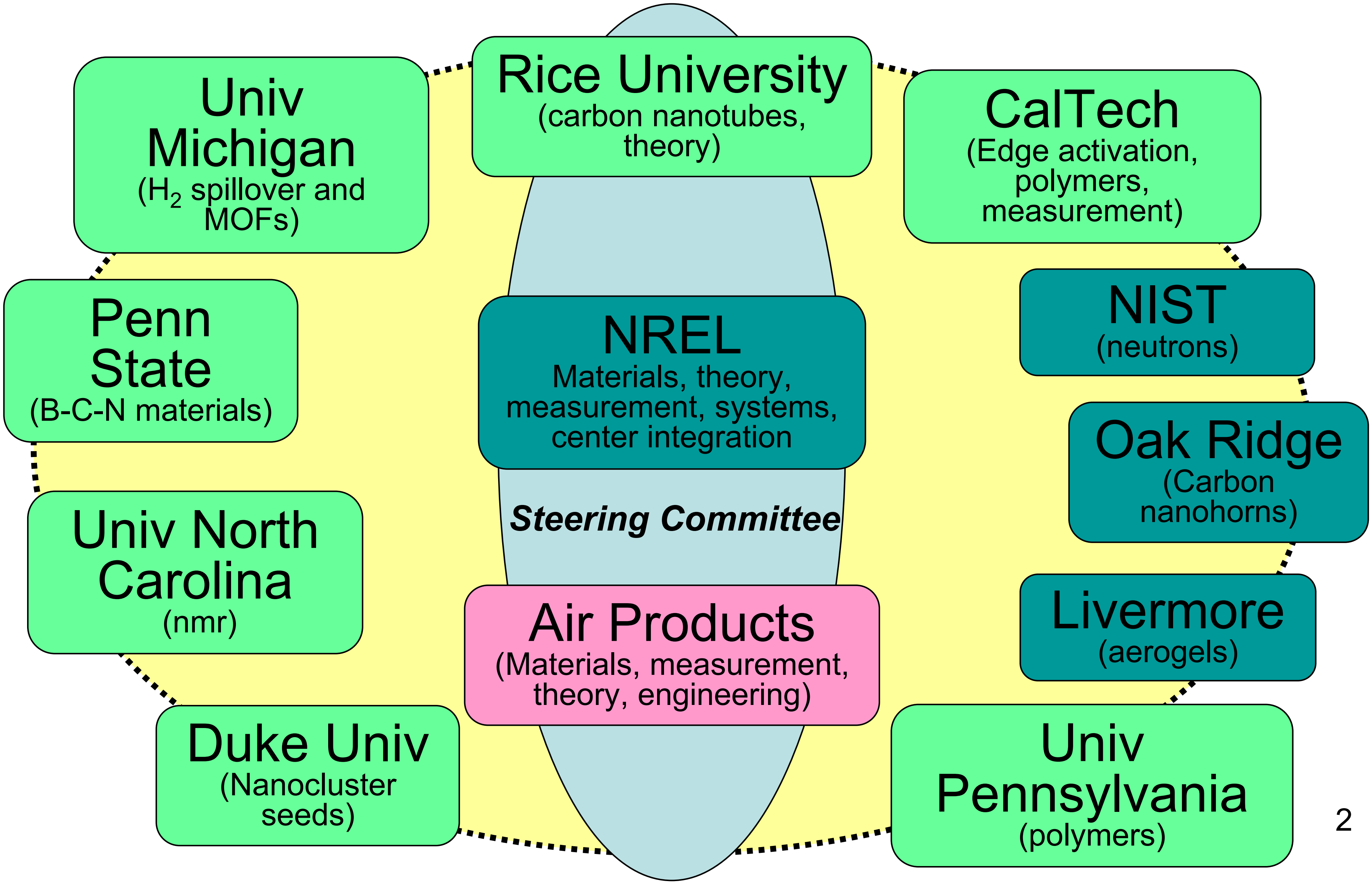
This presentation does not contain any proprietary or confidential information

**Project ID # STP41**

# CbHS Center of Excellence Partners

*9 university projects (at 7 universities), 4 government labs, 1 industrial partn*



# Overview

## Timeline

- Project start date
  2/1/2005
- Project end date
  1/31/2010
- Percent complete
  New project

## Budget

- Total project funding
  - DOE share: $626,177
  - Contractor share: $156,542
- Funding received in FY04
  $0.00
- Funding for FY05
  $65,000

## Barriers & Targets

•**General**

A. Cost

B. Weight and Volume

C. Efficiency

E. Refueling Time

•**Reversible Solid-State Material**

M. Hydrogen Capacity and Reversibility.

N. Lack of Understanding of H Physi- and Chemisorption.

O. Test Protocols and Evaluation Facilities.

•**Crosscutting Relevance**

Compressed Gas Systems Barrier H:

Sufficient Fuel Storage for Acceptable Vehicle Range.

Off-Board Hydrogen Storage Barriers S&T:

Cost and Efficiency

## Partners

NREL (Heben), Caltech (Ahn), LLNL (Baumann), Duke (Liu), Penn State (Eklund, Chung), U. Penn (A. MacDiarmid), Rice University (Smalley, Hauge), Michigan (Yahgi, Yang), Air Products,

# Objectives

- Using nuclear magnetic resonance (NMR) technique to support DOE CbHS CoE in developing reversible carbon-based hydrogen storage materials with 7 wt.% materials-based gravimetric capacity, with potential to meet DOE 2010 system-level targets.

–Establish molecular and atomic NMR signatures for adsorbed hydrogen in carbon-based and high surface area sorbent materials.

–Identify adsorption mechanisms based on molecular and atomic NMR signatures.

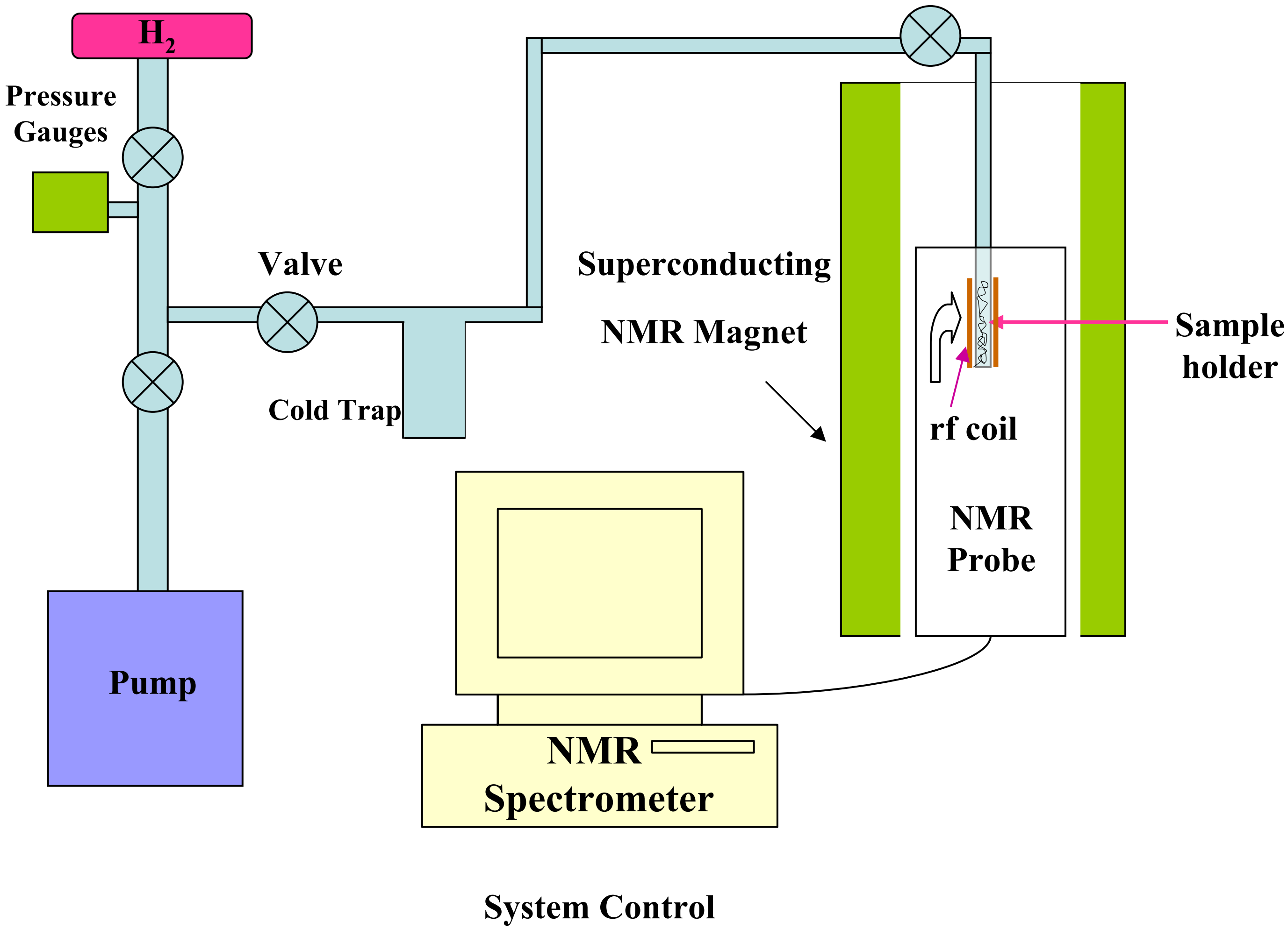
–Develop a quantitative and selective NMR method for measuring hydrogen adsorption capacity.

# Approach

- Just like atomic mass (the basis of gravimetric measurement of hydrogen adsorption), the $^1$H nuclear spin is another specific signature of hydrogen. The nuclear spin can be detected quantitatively and sensitively by NMR, similar to the detection of water in human body used by magnetic resonance imaging (MRI). Furthermore, the structure of carbon-based materials can also be investigated by $^{13}$C NMR. By carrying out NMR experiments under hydrogen pressure and temperature of practical interest, the amount of adsorbed hydrogen, molecular dynamics, and interactions with host lattice can be determined under relevant conditions. The NMR approach provides a complementary technique to volumetric and gravimetric measurements of hydrogen adsorption. It also provides detailed information of structure and dynamics on microscopic scale needed for the understanding of adsorption mechanisms.

# Technical Accomplishments/ Progress/Results

## NMR System with High-Pressure Capability



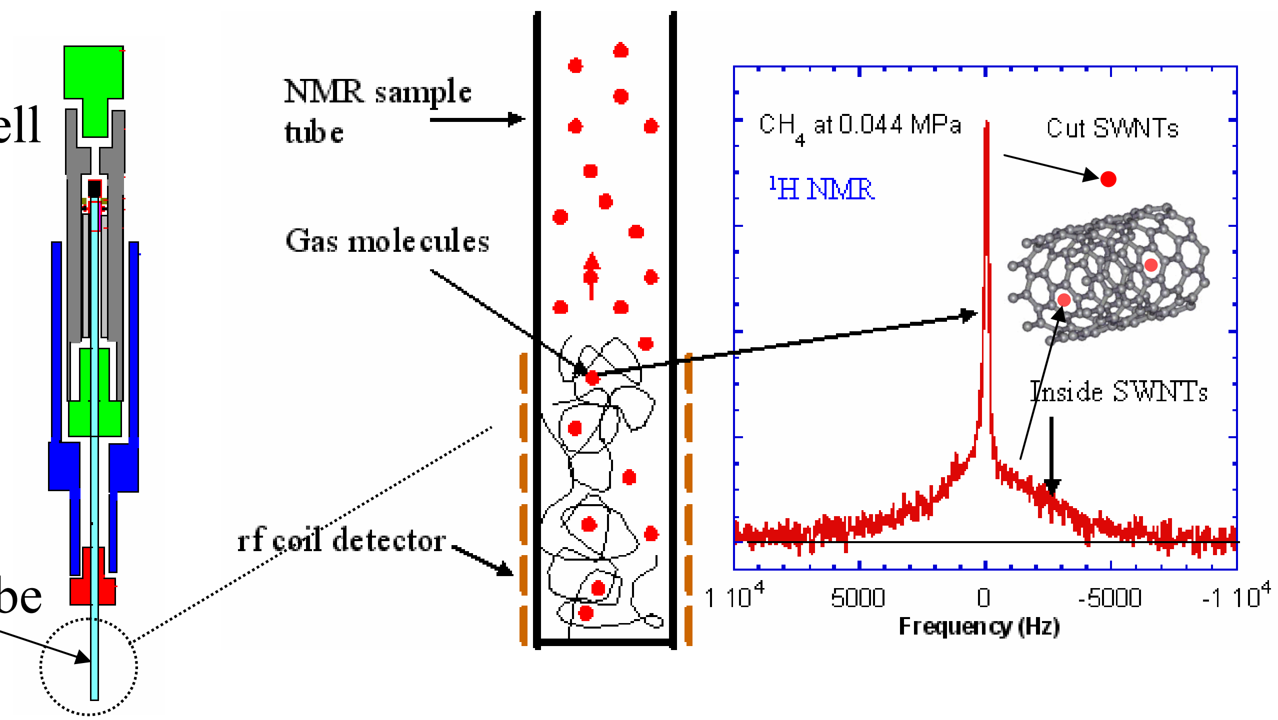
# Technical Accomplishments/ Progress/Results

## High-Pressure NMR Probe

$H_2$ pressure ranging from 1-100 atmospheres is required for evaluating hydrogen adsorption in carbon-based materials. Therefore, we need to carry out NMR measurements under $H_2$ pressure up to 100 atm.  A saphire-based high-pressure cell was built and tested successfully up to 100 atm. The high-pressure cell is incorporated in an NMR probe for high-pressure NMR measurements.

High-Pressure Cell

saphire sample tube

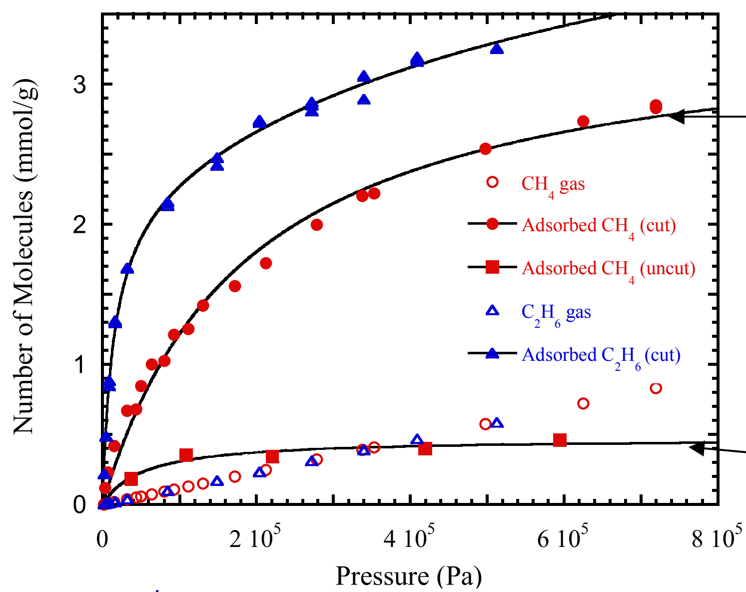


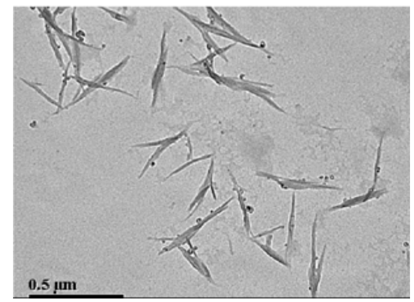

Proton NMR signal revealing both adsorbed (broad peak) and free gas (narrow peak) molecules in single-walled carbon nanotubes.

# Technical Accomplishments/ Progress/Results

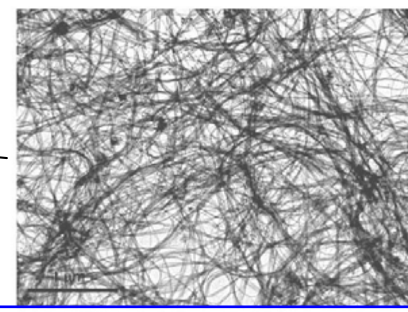
Gas adsorption isotherms measured by NMR showing the significant effect of cutting carbon nanotubes

NMR-detected adsorption isotherms

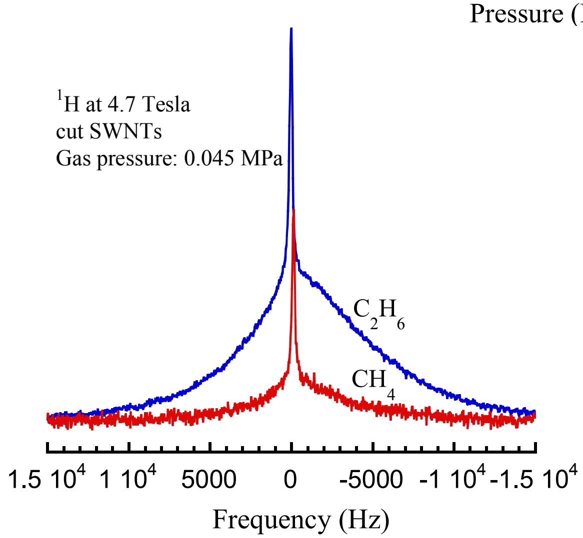



**Cut carbon nanotubes**



**Uncut carbon nanotubes**




$$n(P,T) = n_\infty \frac{bP}{1+bP}, \quad b = \frac{\sigma}{\nu_0\sqrt{2\pi\, mk_B T}} \exp(E_d / k_B T)$$

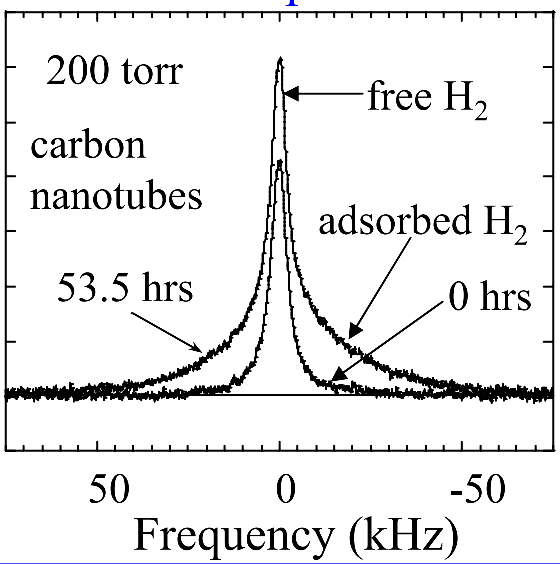
$E_d = 235\ \text{meV} = 22.7\ \text{kJ/mol}$ methane

$E_d = 303\ \text{meV} = 29.2\ \text{kJ/mol}$ ethane

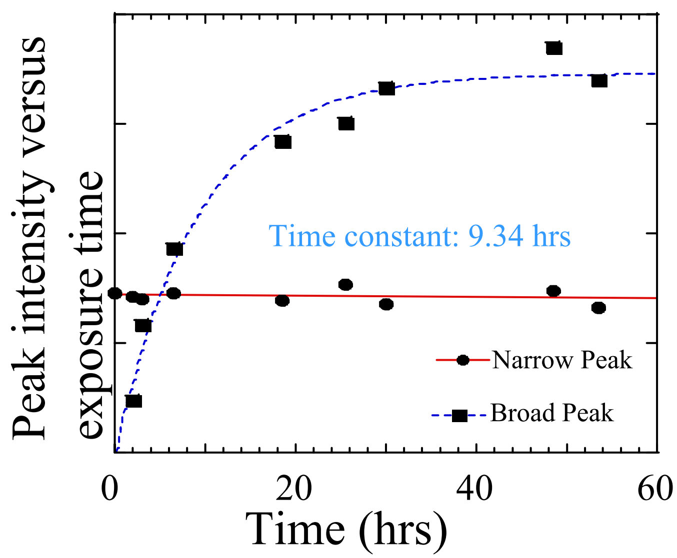
Determination of adsorption energy

# Technical Accomplishments/ Progress/Results

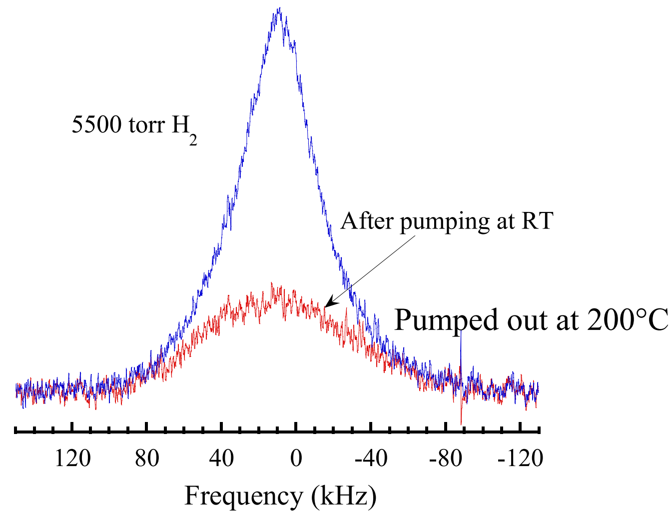
## Time Dependence

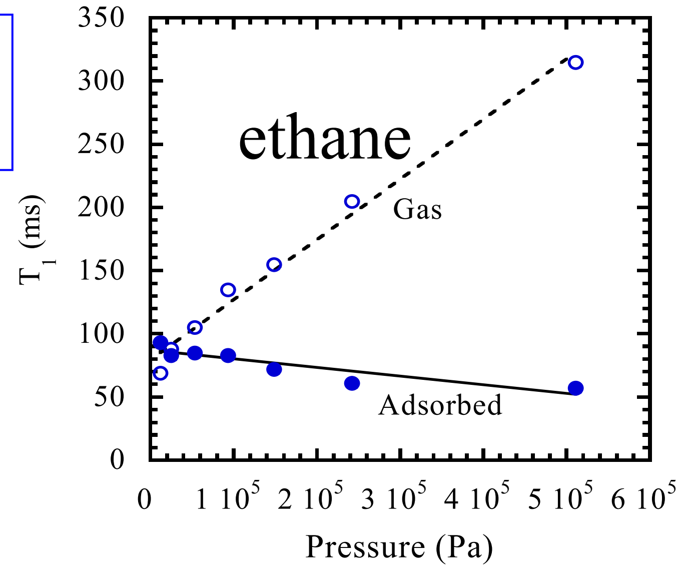



The broad adsorption peak appears very slowly indicating the adsorption mechanism is not simple physisorption, perhaps involving spill-over effect.



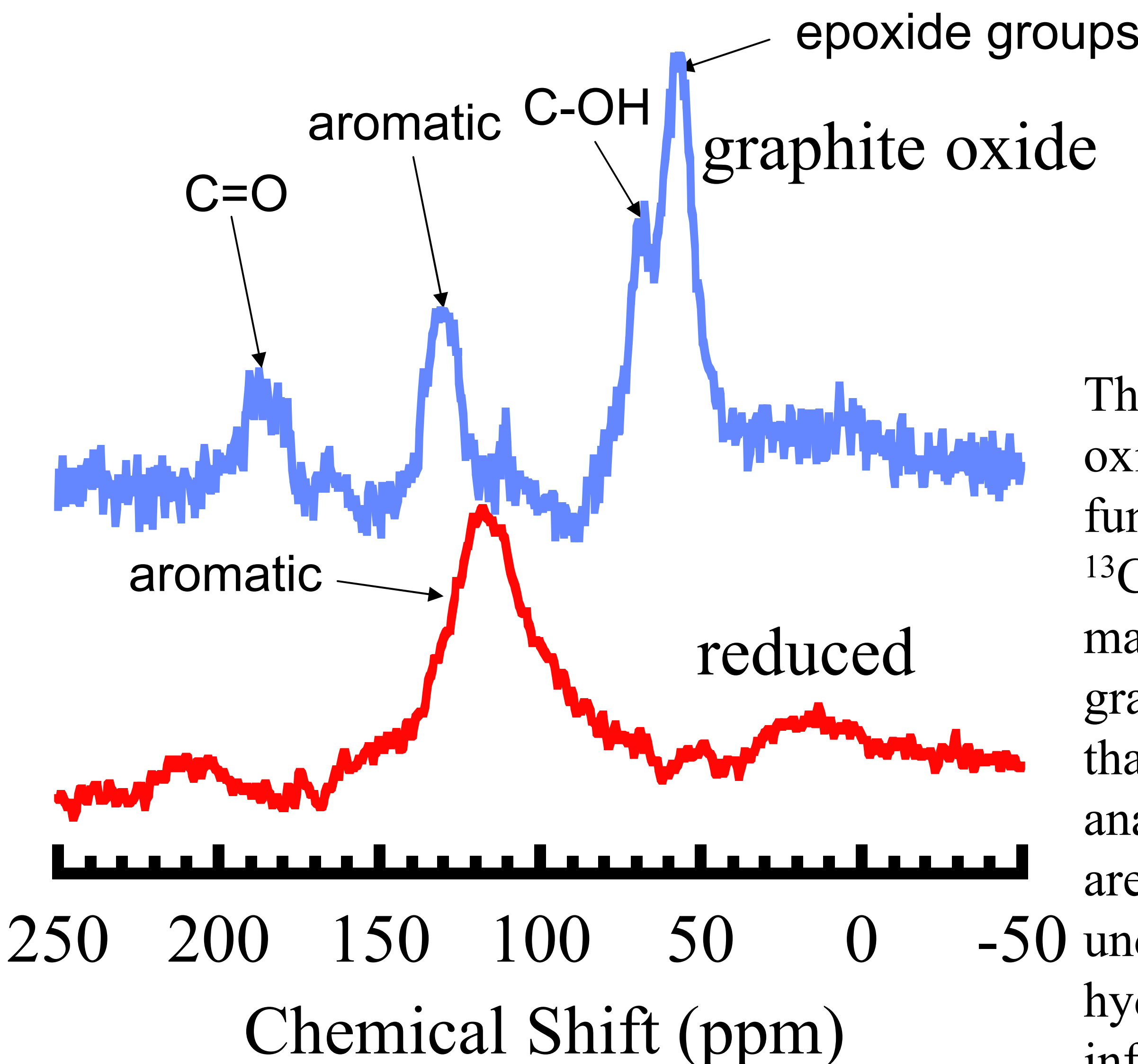

## NMR Detection of Partial Irreversibility

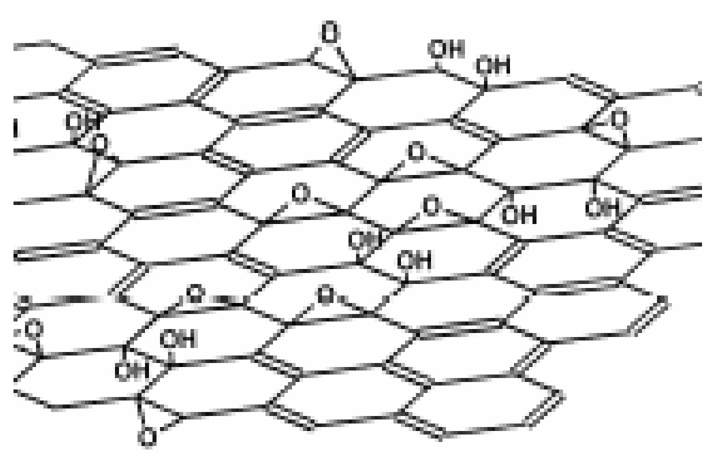



Adsorbed molecules show very different spin dynamics compared to free gas molecules as shown here by the different pressure dependence of spin-lattice relaxation.

# Technical Accomplishments/ Progress/Results



The $^{13}C$ NMR spectrum of graphite oxide reveals the details of the functional groups in this material. The $^{13}C$ NMR spectrum of the reduced material shows clearly the return to a graphitic structure. This demonstrates that $^{13}C$ NMR could be used to analyze the structure of high surface area carbon-based absorbents and understand the interactions with hydrogen. This could provide crucial information on hydrogen adsorption mechanisms.

# Future Work

•Remainder of FY 2005:

—Complete the testing of the sapphire tubing-based 100 atm high-pressure NMR probe.

—Obtain adsorption isotherms by NMR for two CbHS CoE carbon-based storage materials, carbon nanotubes and conducting polymers.

•FY 2006:

—Provide detailed NMR characterizations of the structures of CbHS CoE carbon-based storage materials.

—Identify adsorption sites, investigate their interactions with hydrogen, and understand the adsorption mechanisms.

—Obtain adsorption isotherms using NMR, evaluate adsorption capacity under practical conditions, and compare the results with volumetric measurements.

**Go/no go Decision Points:**

3Q Year 2: Importance of NMR technique to mission of the Center;

3Q Year 3: Promise of Center materials for meeting the FY10 system level targets with included system penalties.

# Hydrogen Safety

The most significant hydrogen hazard associated with this poject is: Failure of high-pressure cell and leak of hydrogen.

Our approaches to deal with this include:

—The area of experiment and the operator are shielded from parts of the equipment under high pressure avoiding immediate mechanical damage and injury.

—Install hydrogen detector to detect leak and accumulation of hydrogen gas in the lab. Provide sufficient air circulation in the lab.

—Follow careful operating procedures such as closing high-pressure gas cylinder valve immediately after gas loading.

Since this project is a new start, more details of safety plan are in the process of being developed.