Characterization of Hydrogen Adsorption by NMR (Project ST079)
DOE "Hydrogen Sorption Center of Excellence"

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Overview

Timeline

- Project start date
  2/1/2005
- Project end date
  1/31/2010
- Percent complete
  100%

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_2 accessible micropores and H_2 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

Overall

Nuclear Magnetic Resonance (NMR) measurements contribute spectroscopic information as well as quantitative analysis of adsorption processes in support of HSCoE partners. ^{1}H NMR provides microscopic information on di-hydrogen adsorption, on molecular dynamics of hydrogen in micro pores, on diffusion of hydrogen between macro and micro pores and on the pore size for pores of width between 1.2 and 2.4 nm.

2010

• Continue to develop NMR as a technique that determines pore size using H_2 as the probe molecule (porosymetry).

       - Determine the limits of the technique and the benefits to the HSCoE program.

       - Use activated PEEK as a benchmark for the NMR method.

• Explore graphene – a model system for H_2 adsorption.

Approach

NMR experiments are based on a specialized setup that allows in situ measurements as a function of H_2 pressure between 0.13 Pa and 10 MPa and temperature between 77 K and 300 K.

NMR spectral intensity is directly proportional to the number of H_2 contributing to the spectrum. Using an internal standard H_2 capacity is measured.

Materials based on graphitic carbon produce spectra where the H_2 confined in micropores produce spectral lines that are distinct from NMR lines associated with H_2 in macropores and gaseous H_2.

Thus confined H_2 provide direct access to probing the pore structure. NMR lines associated with confined H_2 show a chemical shift that depends on H_2 pressure. The chemical shift and its pressure dependent variation is the key to determining the pore structure.

Use relaxation measurements to probe the molecular dynamics of the adsorption process and use spectral analysis and 2d exchange to probe the kinetics.

Technical Accomplishments

Continued development of NMR porosymetry based on H$_2$ as the probe molecule:
Test Material: Activated PEEK (Duke University; J. Liu)

Samples: PEEK carbonized at 900 C in flowing Ar for 30 minutes (51 % weight losss)
Activated at 900°C in flowing steam or CO_2 for varying times; measured weight loss after carbonization is defined as burn-off (BO). **Activation produces predominantly micropores.**
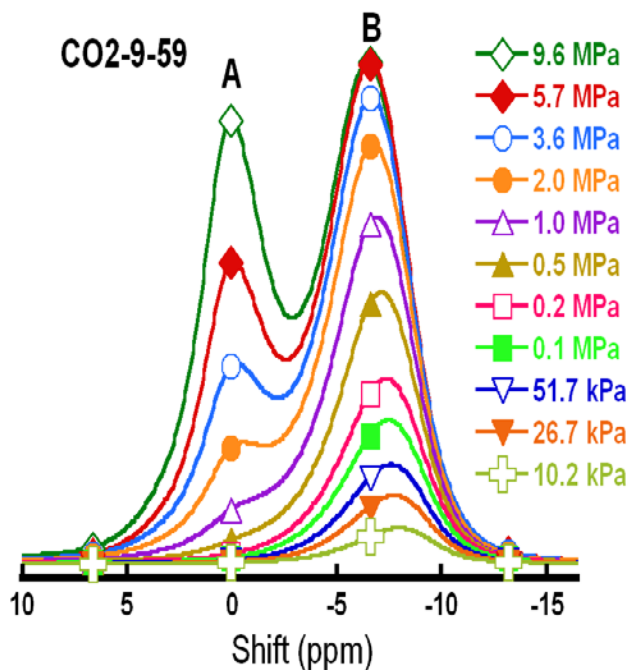

CO2-9-59:
CO_2 activated @ 900°C with BO of 59 %).

Pressure Dependence of ^{1}H NMR spectra at 100 K

- A: Hydrogen in intergranular pores; gas like: peak intensity ~ P; linewidth decreases with P; chemical shift (CS) similar to that of H$_2$ gas.
- B: Hydrogen in intragranular pores; confined H$_2$: Peak intensity saturates with P; linewidth independent of P; large CS difference with respect to H$_2$ gas.
- Significance of 2 observed peaks: H$_2$ does not exchange on the NMR timescale (100 µs).
- Used 2d exchange to extend time scale: H$_2$ does not exchange between the two populations over 10 ms.

Change in Chemical Shift as function of H_2 Pressure
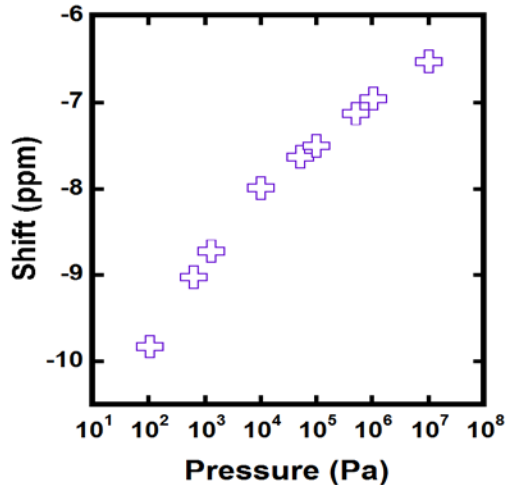
Chemical Shift of peak B changes as a function of pressure:
Peak B moves towards peak A as pressure is increased.
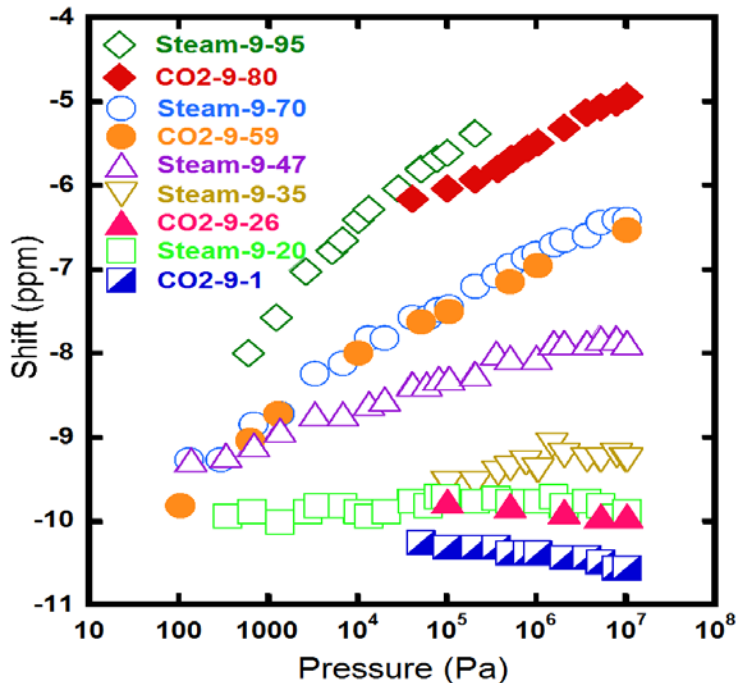
Observed CS variation as function of applied H_2 pressure for activate PEEK with varying BO.

- 3 samples with small BO $\leq$ 35 % show little variation in CS.
- With increasing BO the slope of CS change with P increases.
- When extrapolated to zero pressure a common CS value of -10 ppm is observed.

NMR Porosymetry: Chemical shift tells the story.

The large upfield CS difference between H_2 gas and H_2 in peak B and the downfield change of peak B as a function of pressure is the basis of NMR porosymetry.

The large upfield (-10 ppm) shift observed for peak B with respect to H_2 gas (0 ppm) arises from local magnetic fields due to ring currents induced in the graphitic plane. The dipolar moment associated with those local ring current gives rise to a magnetic field $\sim \mu/z^3$; where z is the vertical distance between the hydrogen and the graphene plane. H_2 adsorbed on the graphene plane will show the effect of the induced field through the large observed CS of -10 ppm. Because of the strong z dependence H_2 removed from the surface, in the center of a pore of 5 nm, however, will be exposed to a much lower field and have a CS of $\sim$ 0 ppm (see pictorial description below).
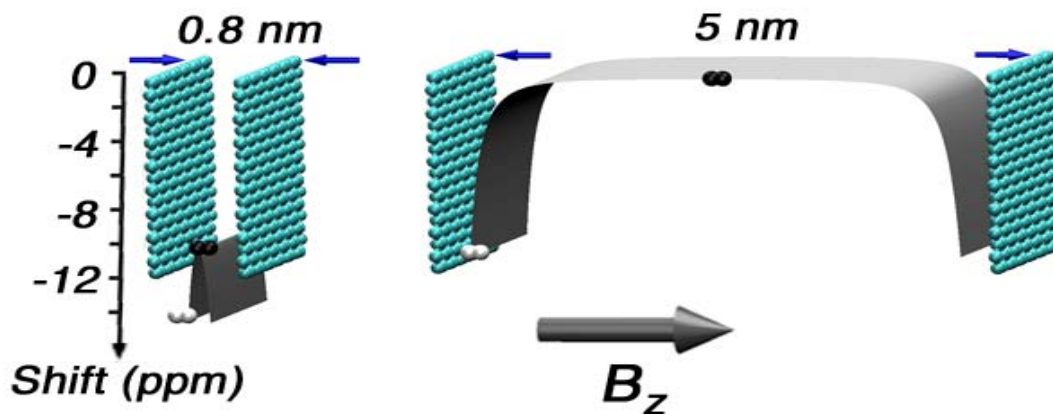
The two Population Model

Even at 100 K H_2 will adsorb and desorb at a rate much faster than the inverse NMR timescale. Thus two hydrogen populations with CS of -10 ppm (adsorbed) and 0 ppm (nearly free gas in center of pore) will exchange rapidly and only one exchange narrowed line will be observed. The observed CS will be an average weighted by the populations of two H_2 populations, with occupancy n_{ad} (adsorbed) and n_{fg} (free gas):

$$\delta_{ob}(P) = \frac{\delta_{ad} n_{ad}(P) + \delta_{fg} n_{fg}(P)}{n_{ad}(P) + n_{fg}(P)}$$

δ: chemical shift; n: # of H_2
ob: observed; ad: adsorbed; fg: free gas.

While n_{fg} increases linearly with P (gas), n_{ad} shows a Langmuir pressure dependence.

Estimated limits:

1. Narrow slit pore: diameter $d < 1.2$ nm; enough space to adsorb a H_2 on each wall; no gas contribution: $\delta_{ob}(P) \sim \delta_{ad} \, n_{ad}(P)$. No change of line position will be observed with P.

2. Large pore: $n_{fg}(P) >> n_{ad}(P)$; $\delta_{ob}(P) \sim \delta_{fg} \, n_{fg}(P)$. Large pores where the number of gas molecules exceed by far the number of adsorbed molecules also show no pressure dependence but the NMR line will be at $\delta_{fg} \sim 0$ ppm.

3. For pores with $n_{ad} \sim n_{fg}$: δ_{ob} will be a function of P.

Pores in activated PEEK:

- BO < 35 %: no observed change in CS: pores are ~ 1.2 nm or smaller (Limit 1).
- Peak A: no observed shift with P; $\delta_{ob}(P) \sim 0$; very large pore (Limit 2)
- BO > 35 %; intermediate pore (Limit 3).

Estimate of upper limit for pore diameters resolvable by NMR porosymetry

Micropores can be distinguished from macropores as long as peak A and peak B can be differentiated. Peak A and B have to be separated by more than the observed half width at half maximum (HWHM) which is 1.75 ppm for peak A.

Based on the geometry of a slit pore, a diameter dependent expression for the CS of adsorbed and free H_2 can be derived:

$$\delta_{ad} = -\lambda \left(\frac{1}{z^3} + \frac{1}{(d-z)^3} \right) \qquad\qquad \delta_{fg} = -\lambda \frac{d}{w^2 (d-w)^2}$$

Here: $z \sim 0.32$ nm; $w \sim 0.6$ nm; λ: phenomenological constant related to ring current induced local field $\sim$ susceptibility of graphite.

When combined, an upper limit for discernable pore sizes can be estimated:

$$| \delta_{fg}(d_{max}) | = | \delta_{ad} | \frac{z \cdot d_{max}}{(d_{max} - z)^2} \geq (\Delta_A \sim 1.75 nm)$$

$$| \delta_{fg}(d_{max}) | \sim 2.4 nm$$

NMR distinguishes pores with diameters between 1.2 nm and 2.4 nm and is sensitive to the pore size that is desired for H_2 storage materials.
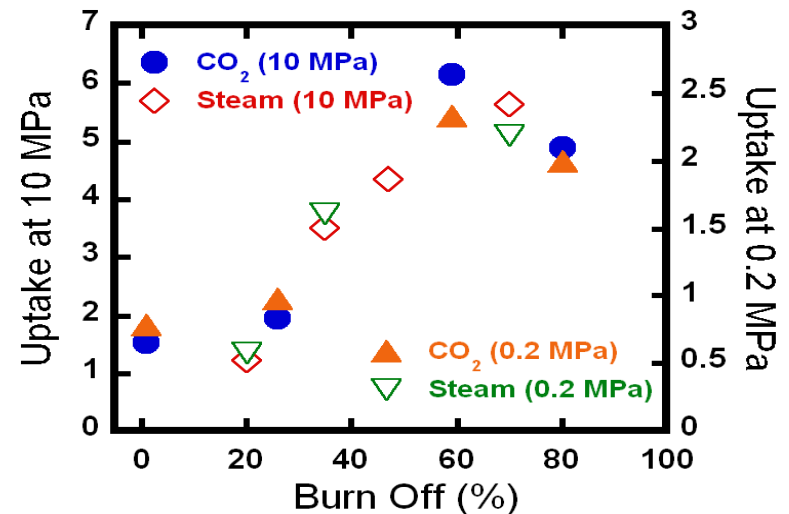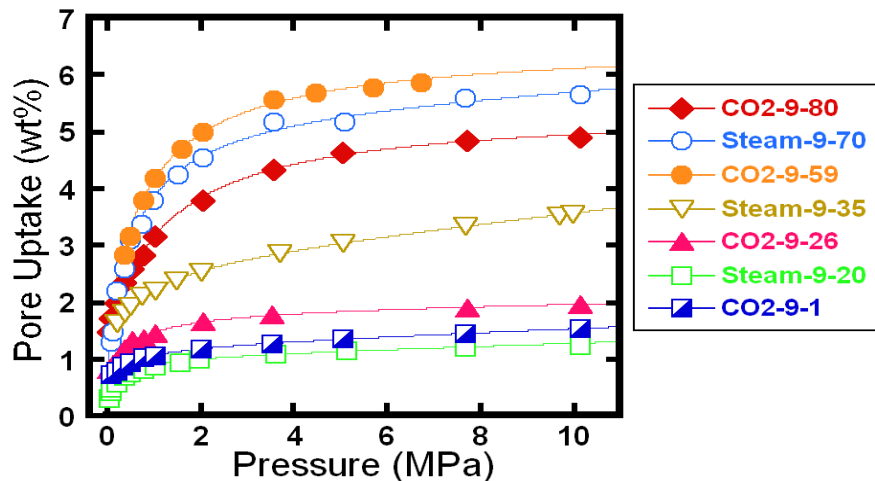(LN$_2$ BET measurements are reliable above 1.5 to 2 nm pore size and RT CO_2 determine pore size below 2 nm.)
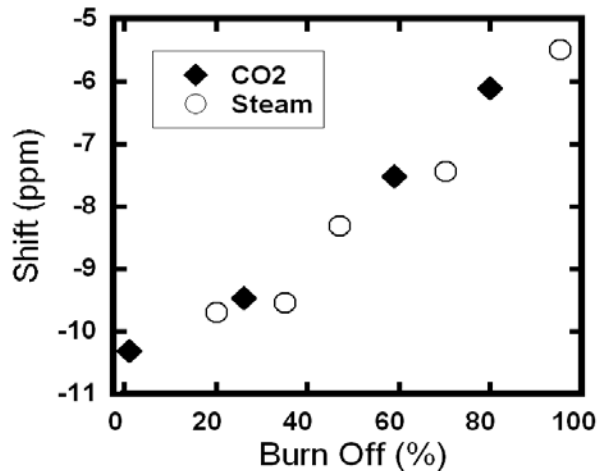
Measured CS of peak B (H_2 in micropores) at 100 K and 10^5 Pa (1 atm) as function of BO.

The CS for peak B increases linearly from -10 ppm at 1 % BO to -5.3 ppm at 95 % BO. The specific surface area (SSA) also increases nearly linearly with BO (ST-081-Liu). Because $n_{ad} \sim$ SSA and $n_{fg} \sim$ d*SSA at a given P the observed change in CS with BO reflects that the average pore diameters are increasing with BO.

NMR determined capacity of micropores at 100 K

The intensity of peak B, when properly calibrated, provides the number of H_2 molecules confined in micropores. The capacity in wt % as function of pressure is plotted for samples characterized by BO producing the Langmuir isotherms shown on the upper left. Surprisingly the samples with higher BO (70 & 80 %) and also higher SSA show a lower capacity than the sample with 59 % BO which is shown more clearly when the uptake at 0.2 MPa and 10 MPa is plotted against BO (upper right). The observed decline with BO occurs although the SSA is still increasing up to 80 % BO.

The NMR capacity reflects the confinement in micropores with graphene-like adsorbing surfaces. With increasing BO SSA beyond 2660 m²/g, the SSA for a graphene sheet, can only be reached by compromising the integrity of graphene surface by introducing holes and edge sites. H_2 on edge sites may contribute to peak A. In addition, H_2 in large pores that exchange with H_2 in intergranular pores will also be lost to the intensity of peak B.

**NMR pinpoints the samples which on average are characterized by the desired micropore distribution.**
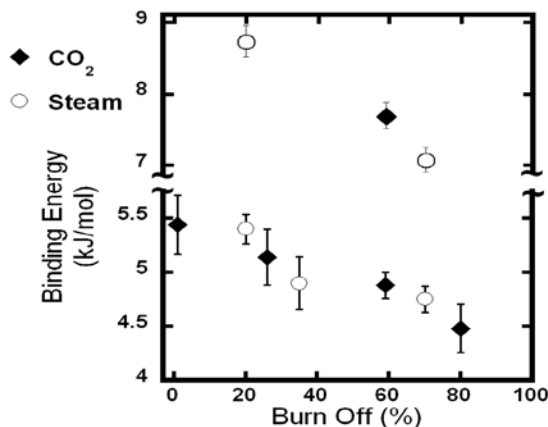
The isotherms at 100 K are fitted to a Langmuir expression to extract the binding energy. Full isotherms measured from 20 Pa to 10^7 Pa revealed two sites with a binding energy ratio of ~ 1.6.

For both sites the binding energy decreases with BO.

$$n_{ad}(P,T) = n_\infty \frac{bP}{1+bP} \qquad b = \frac{\sigma}{v_0\sqrt{2\pi m_{H_2} k_B T}} \exp(\frac{E_b}{k_B T})$$

Evidence of exchange between pore A and B at high BO
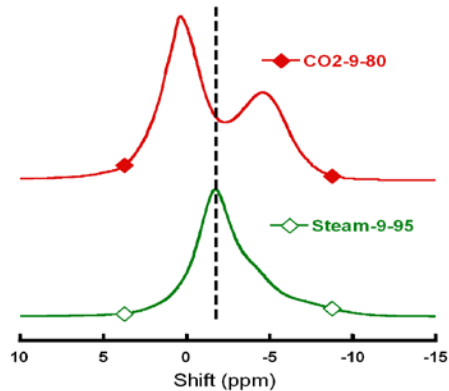
The steam activated sample with 95 % BO serves as an example where H_2 exchanging between the two reservoirs, inter- and intra-granular, is clearly observed. As a result of the exchange only one dominant peak is observed at high pressure with a position near the midpoint between Peaks A and B of CO2-9-80, an indication of significant exchange present only in samples with very high BO.
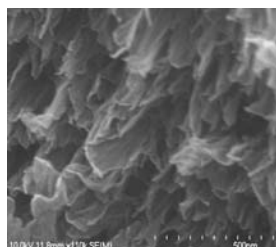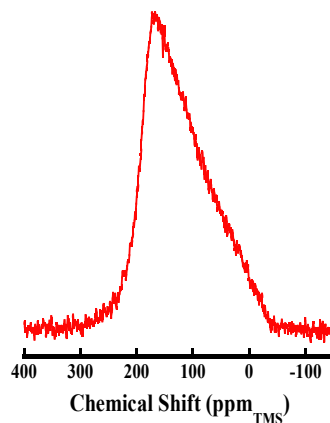
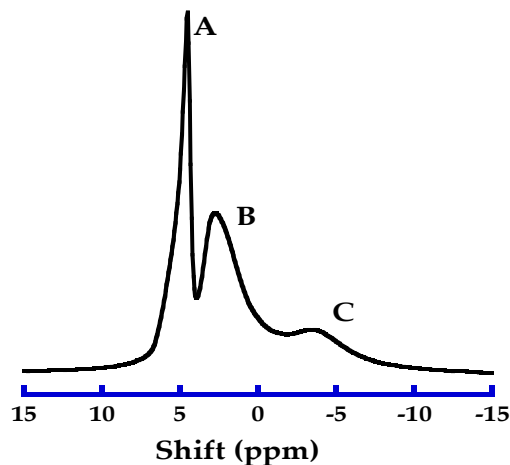Graphene - a model system for H$_2$ adsorption on ideal planes.
Each "block" of graphene sheets contains a small number of sheets with enlarged planar separation.

Graphene flakes:
BET specific surface
area: 513 m^2/g

^{13}C NMR spectrum
shows characteristic
powder pattern
for planar sp^2 bonded
carbon.

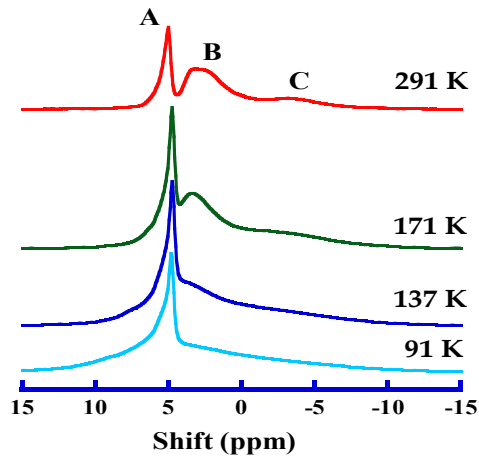Chemical Shift (ppm$_{TMS}$)

^{1}H NMR spectrum at 10 MPa and RT:
A: H$_2$ gas above sample (provides calibration);
B: H$_2$ in inter-flake space;
C: H$_2$ in intra-flake, between graphene sheets.
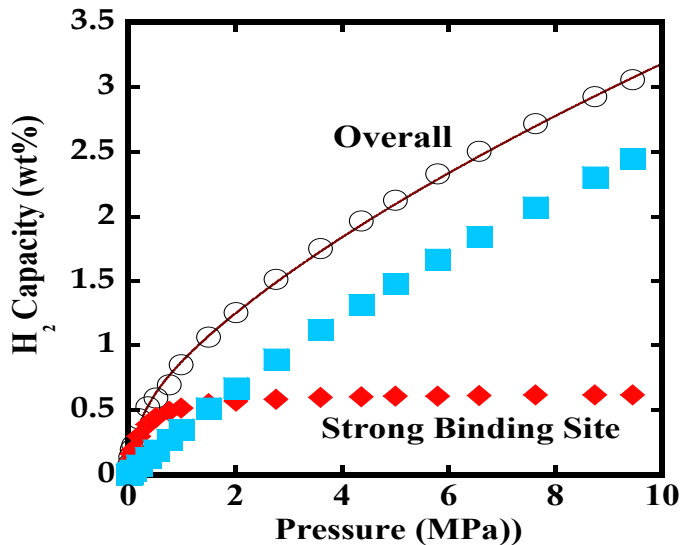
Shift (ppm)

Graphene (continued)

Temperature Dependence of Spectra:
Below 137 K distinction between NMR lines B and C is lost. Lines broaden indicating that H_2 motion is slowing down.
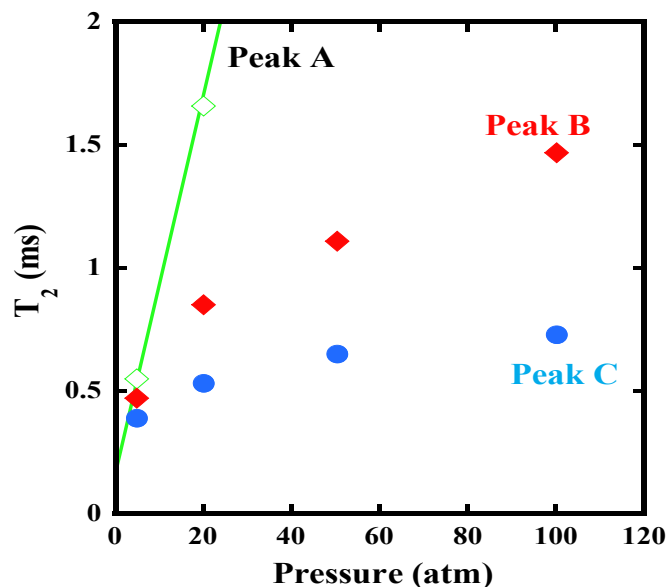

H_2 Capacity (at 100 K) (preliminary):
Relevant strong binding site (red data points): 0.3 to 0.5 wt%
Binding energy: 6.6 kJ/mol

Spin-spin relaxation measurements (T_2) at RT show that interaction with surface changes H_2 relaxation behavior dramatically:

- T_2 in Peak A $\sim T_1 \sim P$; $\rightarrow$ gas like; long (8 ms at 100 atm).
- T_2 in Peaks B, C affected by interaction with surface: T_2 is much shorter than for gaseous H_2; at 100 atm: $T_2(A)/T_2(C)$: ~11.
- Pressure dependence of T_2 not linear for B and C.

  $\rightarrow$ **H_2 relaxation profoundly affected by confinement.**

Conclusion:

• Graphene is a model system for H_2 adsorption and provides defined surfaces and relatively well defined geometrical pore spaces.

• Distinct spectral lines for inter- and intra-flake pores $\rightarrow$ selective adsorption measurement.

• Interesting and unexpected relaxation behavior.

• H_2 motion slows down below 130 K indicating that kinetics are affected at 100 K.

• Oxidized graphene with flexible pore space may be more suitable for H_2 storage.

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 NMR technique to determine pore sizes covering the range from 1.2 to 2.4 nm.
- Applied the the technique to activated PEEK.
- Suggested that 59 % BO provides the optimum activation for uniform production of micropores.
- Explored graphene as a model system for H_2 adsorption.