

The Quantum Effects of Pore Structure on Hydrogen Adsorption

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Project ID #
ST107

Overview

Timeline

- Start: Nov 2011
- End: Oct 2013
- 75% complete

Budget

- Total project funding
 - DOE share: \$ 170 K
- Funding received in FY12:
 - \$85 K
- Funding for FY13:
 - \$ 71 K

Barriers

- A. System Volume
 - (2017 system goal 40 g/L)
- P. Lack of Understanding of Hydrogen Physisorption

Partners

- ALL-CRAFT group – University of Missouri Columbia
- Oak Ridge National Laboratory
 - Carbon Materials Technology Group
 - Neutron Sciences Division
 - Center for Nanophase Materials Sciences
 - Scanning Transmission Electron Microscopy Group
- University of Buffalo, SUNY

Relevance

- Relevance

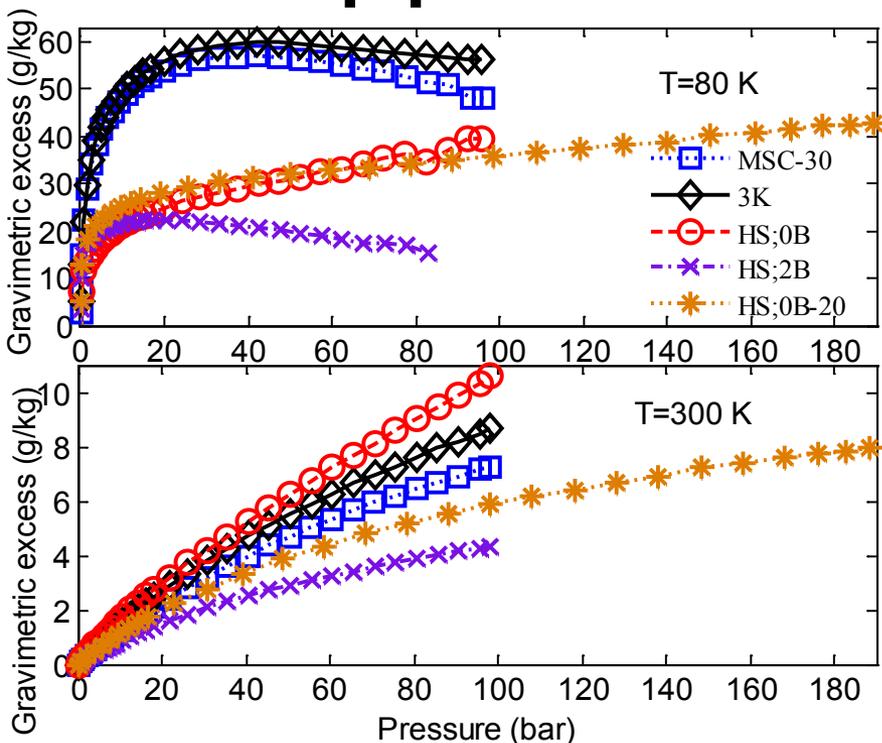
- Storage via physisorption preferred for quick refueling, feasible thermal management
- Carbon adsorbents particularly desirable for low cost and chemical stability
- Adsorbent systems do not meet volumetric targets, particularly at ambient temperature
- Chemical systems (eg. chemical hydrides) can meet volumetric targets, but not gravimetric targets

- Objectives

- To understand a carbon adsorbent (HS;0B) with volumetric storage 40-75% larger than similar carbons, despite having $\frac{1}{4}$ of the surface area (700 m²/g)

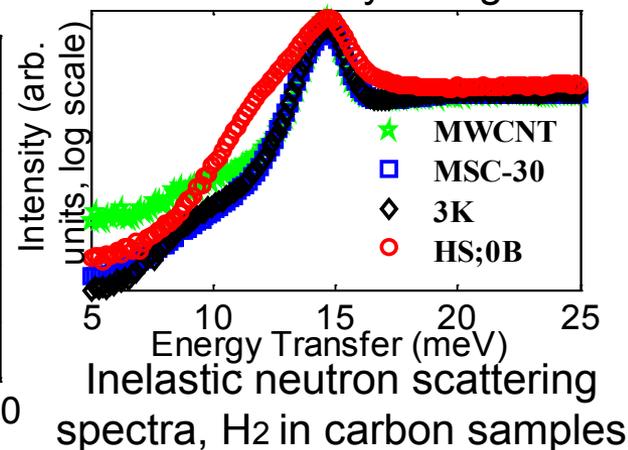
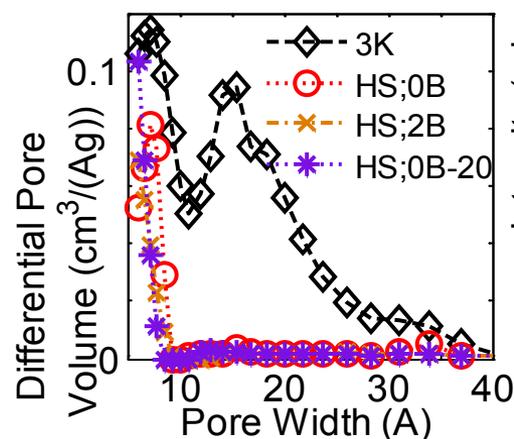
Characteristic	Units	2017 Target (System)	2017 Target (Material)	Temperature /Pressure	MSC-30 (AX-21)	HS;0B	Hypothetical HS;0B
Volumetric Storage	g H ₂ / L system	40	~80	300 K 90 bar	8.5	14.7	26.1
				80 K 90 bar	41.6	58.4	103
Gravimetric Storage	wt % (g total H ₂ / g system *100)	5.5	~11	300 K 90 bar	2.21	1.22	4.39
				80 K 90 bar	9.9	4.68	15.4

Approach-Preliminary Data



- H₂ isotherms, Hiden HTP1 volumetric analyzer
 - Verified by NREL (P. Pfeifer, 2010 AMR)
- Measurements repeated multiple times
- Kinetics show no evidence of a leak
- HS;0B and HS;2B (difference in boron content) synthesized and measured Jan. 2010
- HS;0B-20 synthesized & measured >1 year later, July 2011
- Calorimetry: isosteric heat 19% larger for HS;0B, consistent with smaller carbon pores
- Bulk density of HS;0B show no evidence of significant pore volume missed by nitrogen

sample	Surface area (m ² /g)	Pore volume (cm ³ /g)
MSC-30	2600	1.9
3K	2500	1.7
HS;0B	700	0.34
HS;2B	600	0.32
HS;0B-20	900	0.43

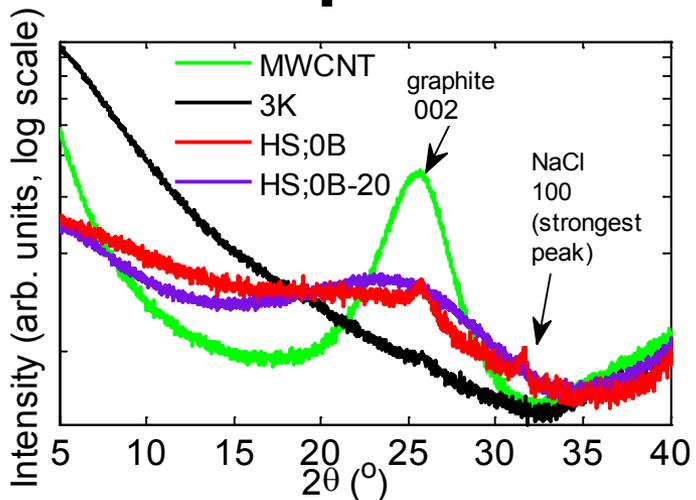


R. J. Olsen, PhD Thesis, University of Missouri (2011). Data & samples courtesy of ALL-CRAFT

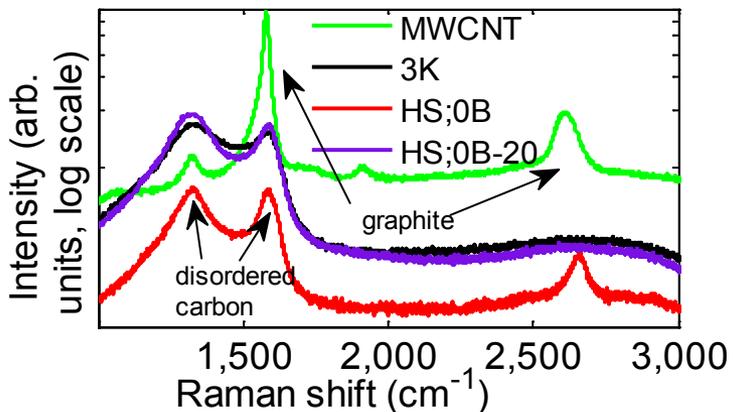
Approach

- Hypotheses:
 - Unusual properties of HS;0B (high H₂ adsorption, structure, and measurable differences in quantum states) are linked.
 - There exists significant quantum effect(s) which are highly dependent on the pore structure and increase adsorption
- Experimental approach
 - Characterization of the structure and composition of the sample
 - Microscopy, XRD, CO₂ adsorption, and Raman
 - Measure quantum states with inelastic neutron scattering
 - Detailed measurement of quantum states in a typical sample
 - Spectra of variants of the sample of interest
- Theoretical approach
 - Calculate quantum states
 - Explain theoretical origin of quantum states observed experimentally
 - Develop theory for mechanism of action

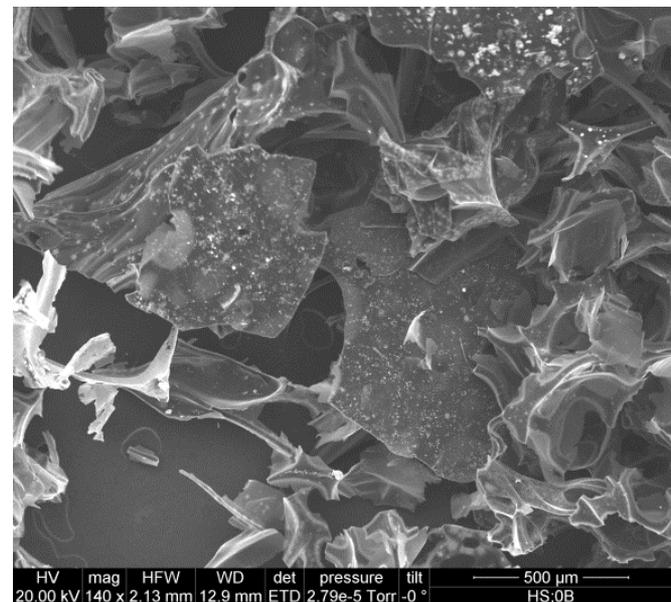
Sample Structure & Composition



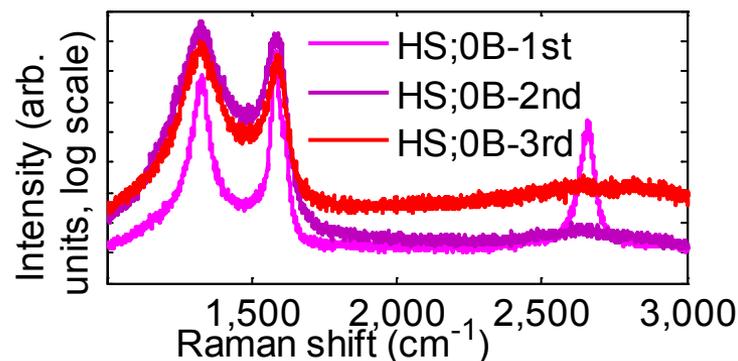
- XRD Spectra for several carbons



- SEM image of HS;0B showing white spots on carbon flakes, (courtesy ALL-CRAFT.)
- Previous chemical analysis also showed significant Na & Cl content

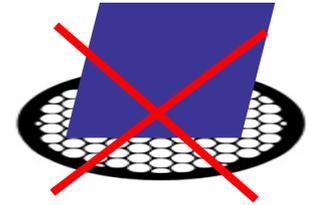
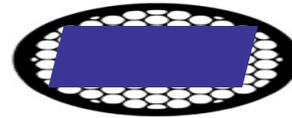
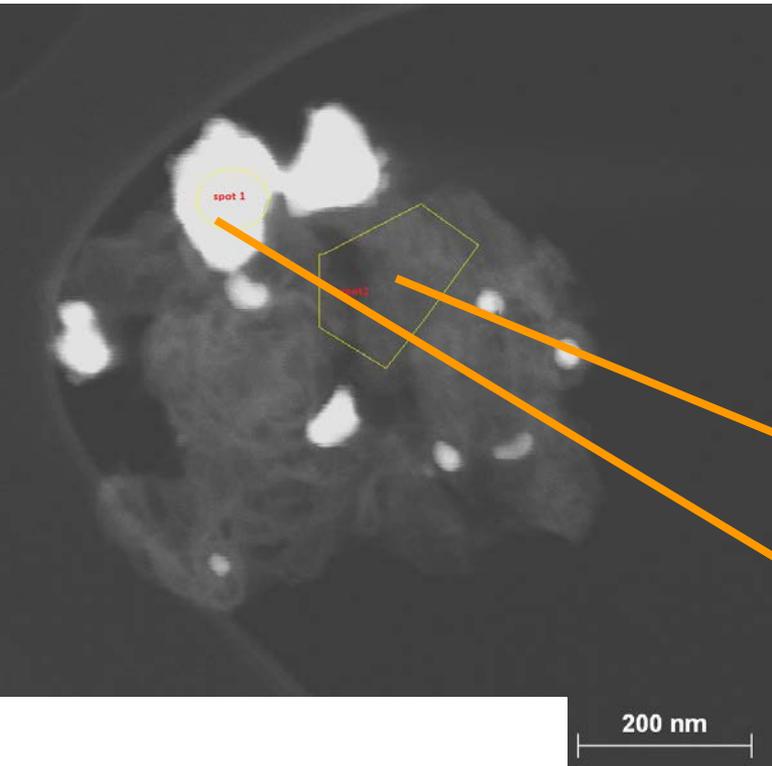


- Raman only characterizes a small area at once.
- Multiple spectra from HS;0B show significant heterogeneity



- X-Ray Diffraction shows strong but broad graphite peak
- Also evidence of rock salt (NaCl)
- Raman also shows evidence of graphite, distributed heterogeneously

Sample Composition

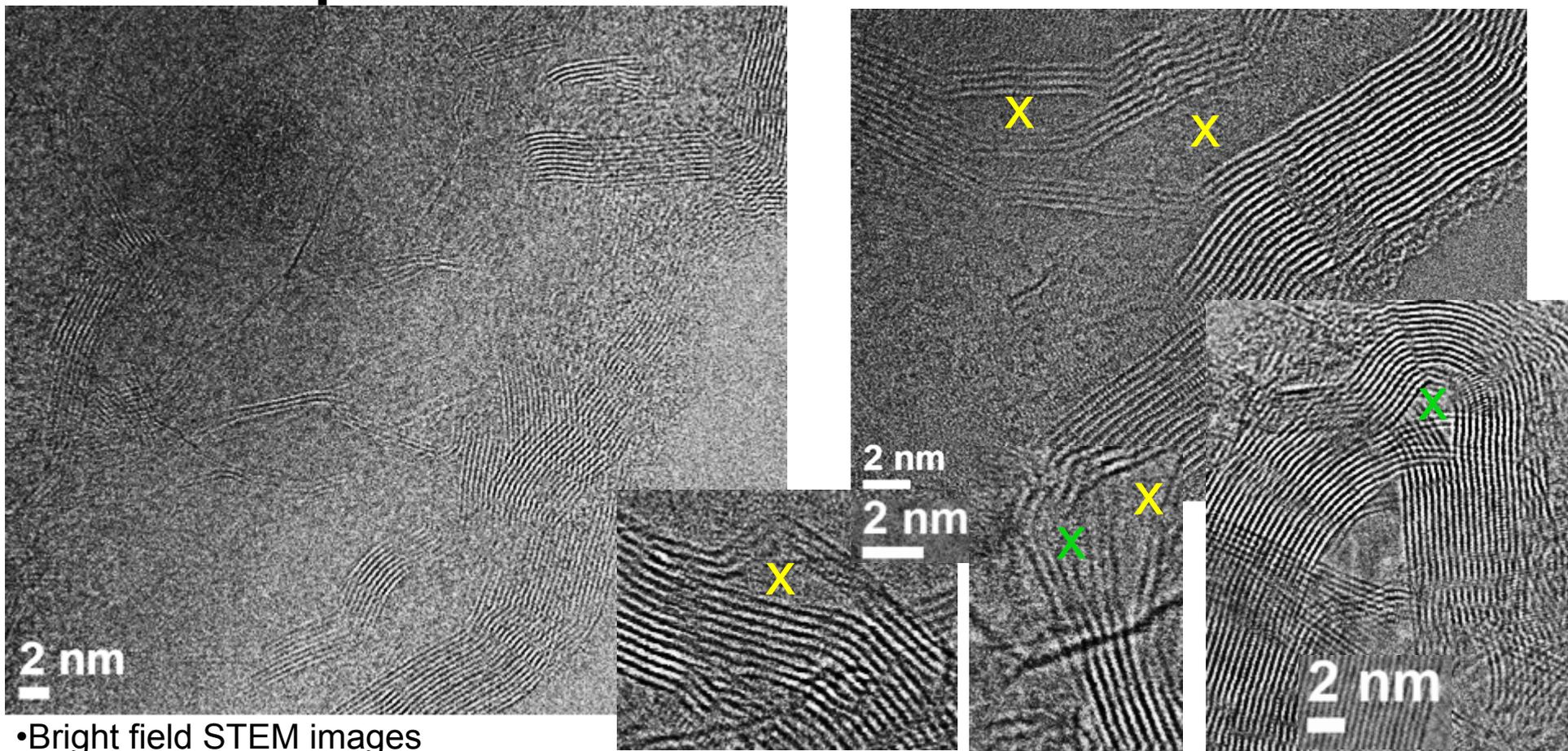


- Flakes lay flat on the copper TEM grid
- Energy dispersive X-ray spectra (EDS) show:
 - “dark” areas:
 - Primarily carbon,
 - Trace chlorine, oxygen, iron
 - “bright” areas:
 - Primarily iron and chromium
 - Trace carbon, oxygen
- Even though EDS shows trace iron spread over the surface, individual iron atoms could not be imaged
 - Indicative that the iron is in an oxide form

- Dark field STEM image of HS;0B.
- Sample was compressed before being placed on grid
- Nevertheless, sample is still flaky

- Sample contains chunks of stainless steel, which likely originate from vessel using manufacturing
- Rust is also dispersed over the surface

Sample Structure, >1 nm Pores



•Bright field STEM images

- Sample is highly graphitic, forming “ribbons” of 1-20 layers of graphene
- Ribbons visible are highly curved, creating variation in c-plane spacing
- Pores form where graphene layers split apart
- Most pores visible have widths >1 nm

Sample Structure, <1 nm pores

•TEM can only see graphite c-planes perpendicular to the field of view



View from the top:

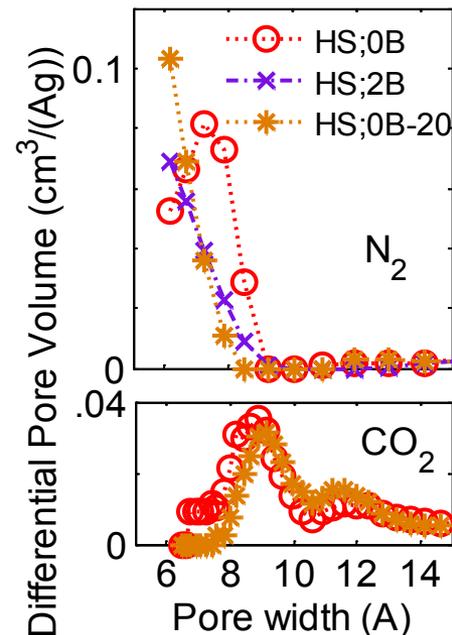


View from the side:



•Amount of curvature depends on how c-planes are oriented relative to the flake

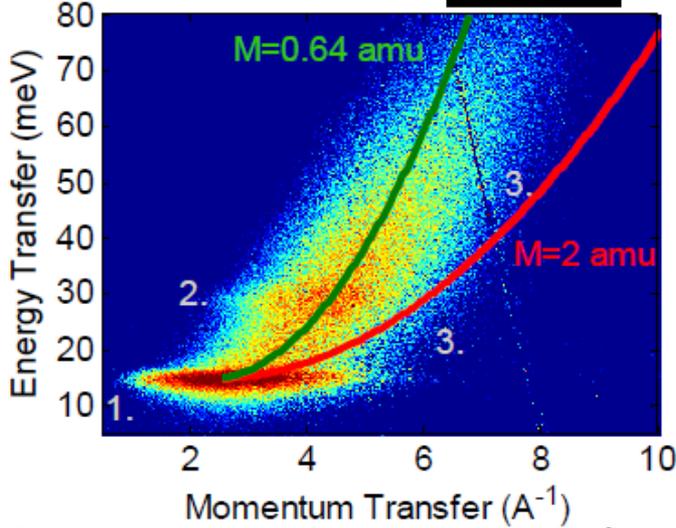
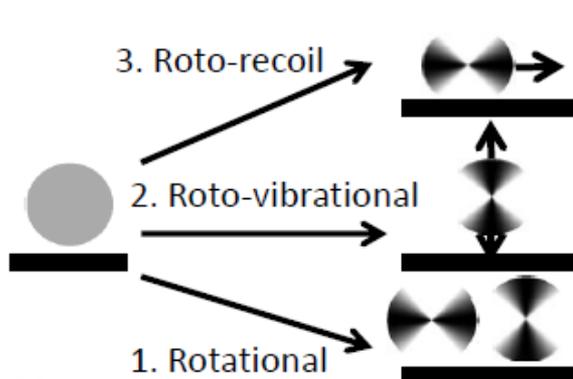
•Pores formed from a “bubble” in graphite have different structure depending on their orientation



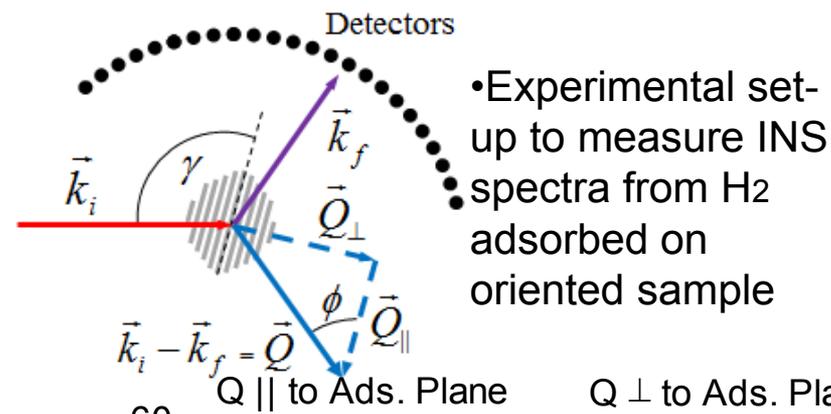
•CO₂ adsorption better at characterizing small pores
•Peak at ~9 Å

- Hypothesis: undifferentiated areas are also at least partially graphitic, but some c-planes lie parallel to the flakes
- Hypothesis: pores still form from “bubbles” where graphene layers split
- Flatness of the flakes would should result in narrow flat pores

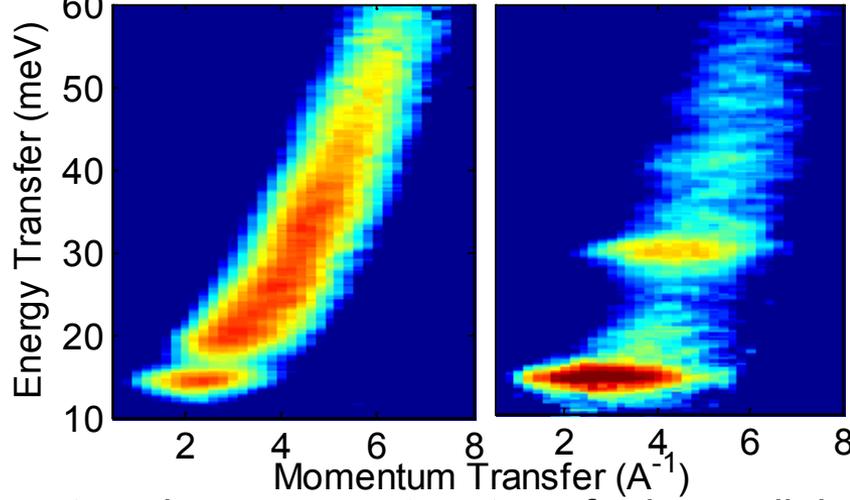
Measure Quantum States



• Oriented sample constructed from Grafoil



• Experimental set-up to measure INS spectra from H₂ adsorbed on oriented sample



• Inelastic neutron scattering (INS) spectrum, measures transitions between quantum states
R. J. Olsen et al., Carbon DOI 10.1016/j.carbon.2013.02.026 (2013)

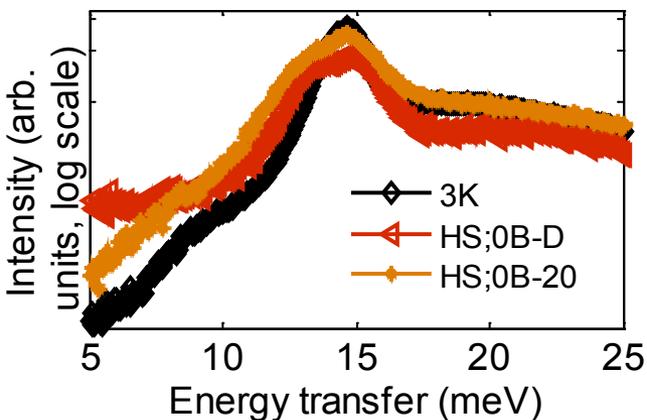
• INS spectra where momentum transfer is parallel (left) or perpendicular (right) to the adsorption plane
R. J. Olsen & M. B. Stone, Physical Review B under review(2013)

• Measured quantum states of adsorbed hydrogen adsorbed in powdered carbon samples, and an oriented Grafoil sample.

Measure Quantum States

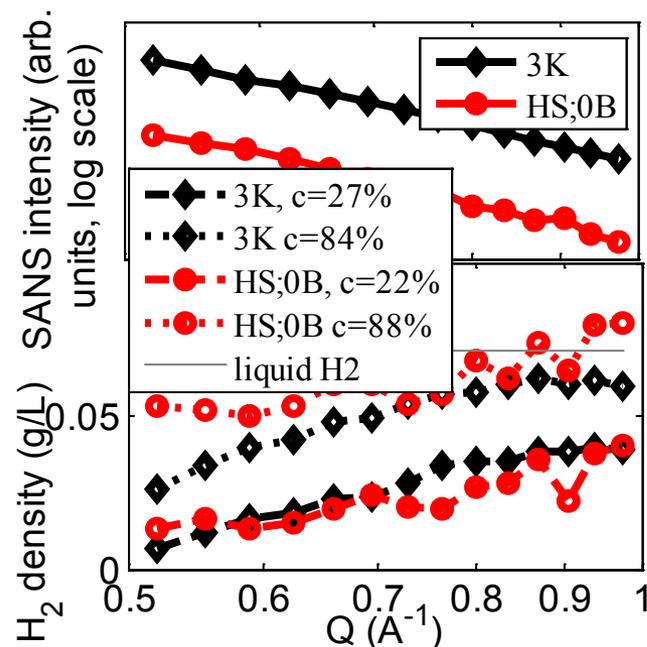


•Variation in the equilibrium orientation and perpendicular position as a function of lateral position, causes coupling between recoil and rotational motion, as well as between recoil and vibration.



•Both HS;0B's show same asymmetrical broadening as original
•The two HS;0B's are also different from one another

•INS spectra collected for 3K and two variants of HS;0B as a function of temperature



•Small angle scattering sensitive to surfaces
•Preliminary SANS spectra collected during INS
•Addition of H₂ increases surface contrast, can be used to estimate H₂ density

- Found coupling between different degrees of freedom
- Coupling needs to be incorporated into theory to analyze powder data
- Small-angle scattering consistent with BET surface area

Theoretical Adsorption Mechanism

Non-interacting particles

Interacting particles

Classical statistics: density of available quantum states (DOS) \gg density of particles

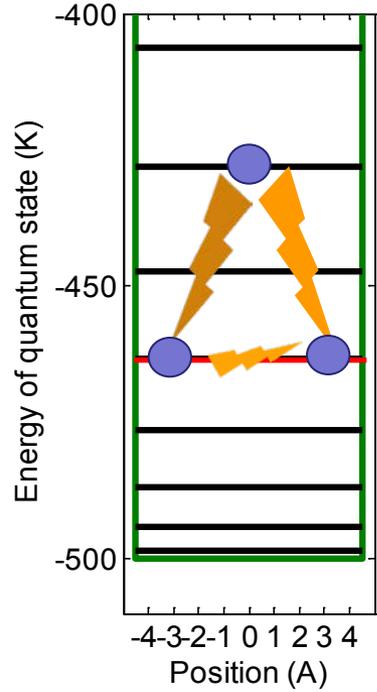
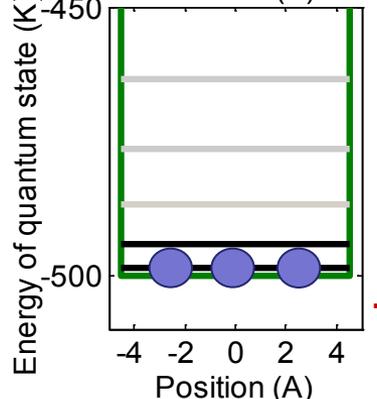
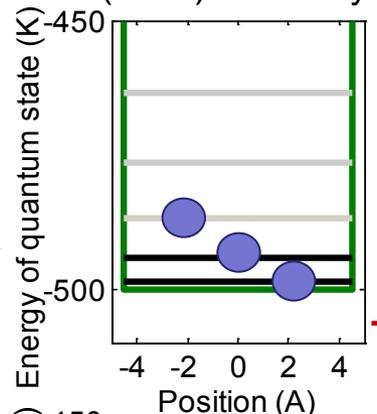
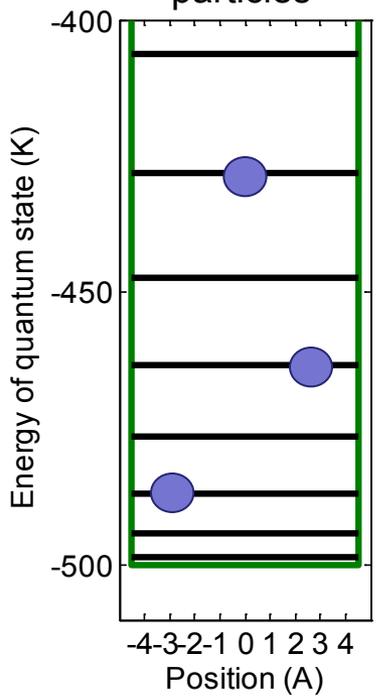
Fermions: only one particle allowed per state

Bosons: Multiple occupation of a state is preferred

H₂ is a boson!

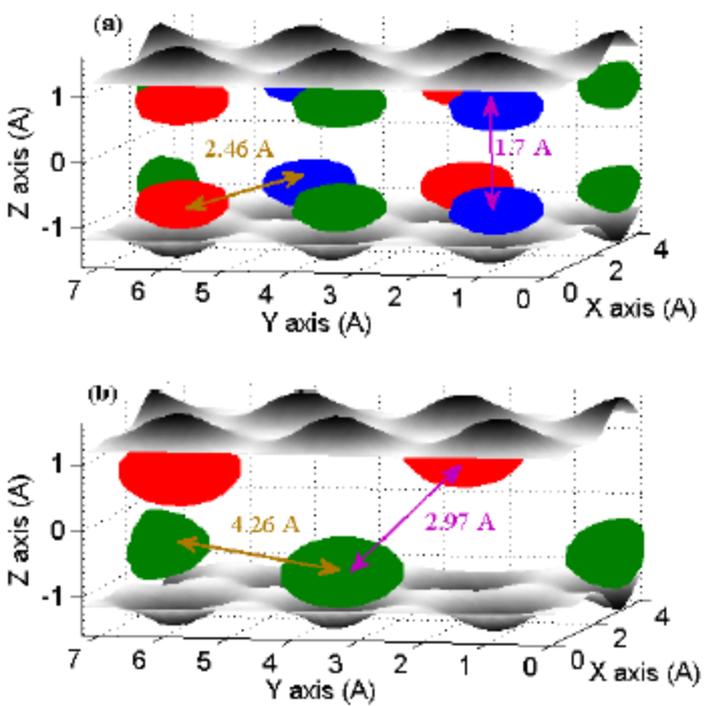
Quantum statistics (DOS) \sim density

New high temperature Bose system: there is a preferred quantum state which minimized the repulsive interaction energy



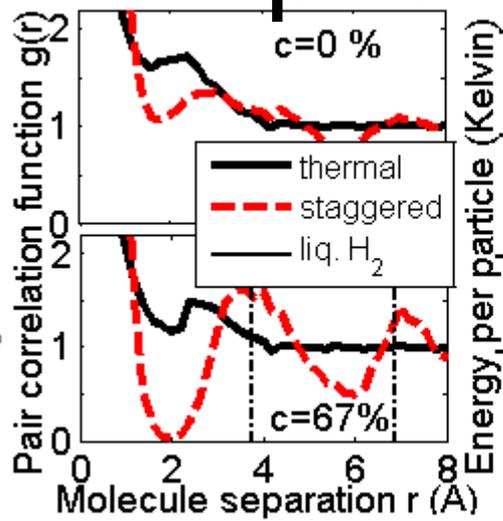
- Proposed how quantum effects normally observed at temperatures < 2.2 K may persist to higher temperatures
- There must exist a quantum state which minimizes the interaction energy

Theoretical Adsorption Mechanism

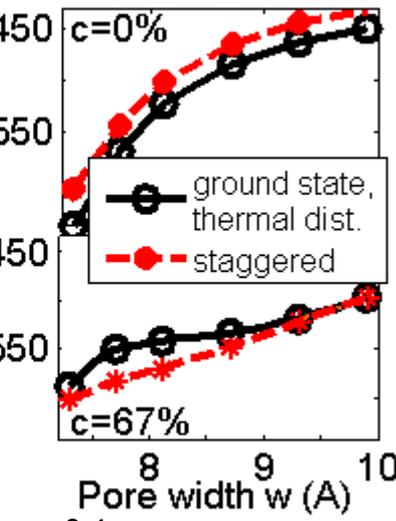


• In narrow graphene pores, there exists a “staggered” quantum state (bottom) which minimizes the interaction energy relative to a thermal distribution of states (top)

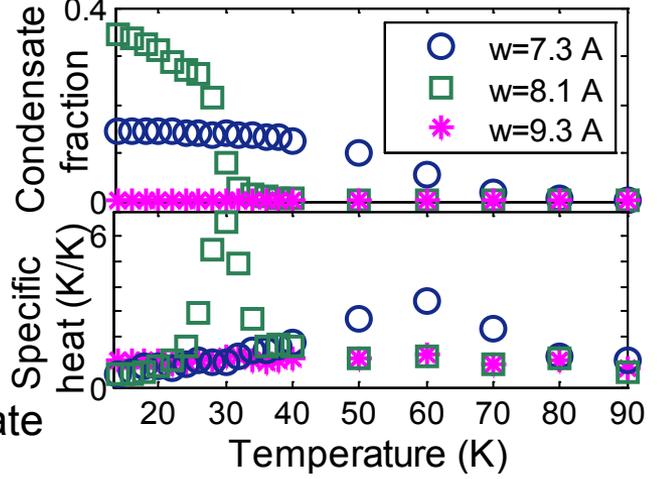
R. J. Olsen, under review



• At $c=67\%$, condensation at temperatures as high as 70 K
 • Specific heat has same cusp as typical Bose-Einstein condensate



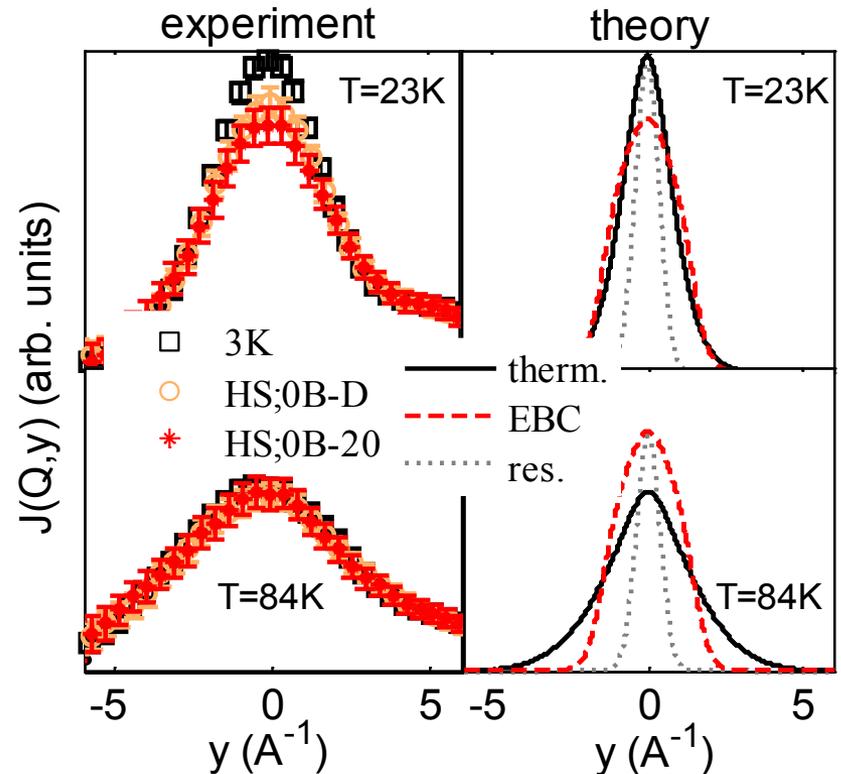
• The staggered state is an excited state, but becomes the many-body ground state at high coverage



• Showed that a quantum state which minimizes the interaction energy exists in narrow graphene slit pores near the single/bi-layer transition
 • Significant Bose condensation at temperatures up to 70 K

Experimental Evidence

- Deep inelastic neutron scattering (DINS) measures momentum distribution of the H₂ molecules.
- For a typical Bose-Einstein condensate,
 - Many molecules in the ground state with a momentum of 0
 - Results in a more peaked profile
- For the new Bose condensate
 - Many molecules in the staggered state, with non-zero momentum
 - Results in a broader scattering profile
- To confirm results, we need to repeat with wider range of temperature and coverage, and a smaller instrument resolution



- Preliminary DINS spectra at $c=25\%$ consistent with new excited Bose condensate in HS;0B variants at 23 K, but not 84 K

• Preliminary deep inelastic neutron scattering spectra are consistent with the proposed quantum effect in HS;0B

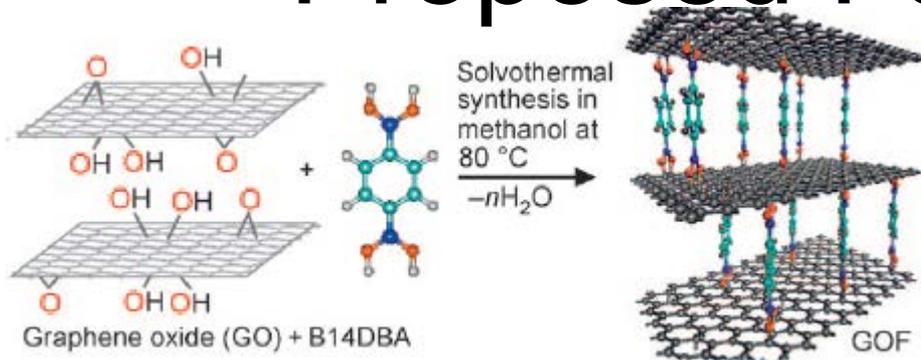
Conclusions

- Sample is graphitic
 - Hypothesized that narrow pores are graphene slit-pores
- Showed theory predicting a new type of Bose condensate which forms in graphene slit-pores
- Preliminary experimental evidence consistent with this phenomena in HS;0B
- Full connection with adsorption still needed
 - Particularly need to increase temperature/density range of the increased adsorption

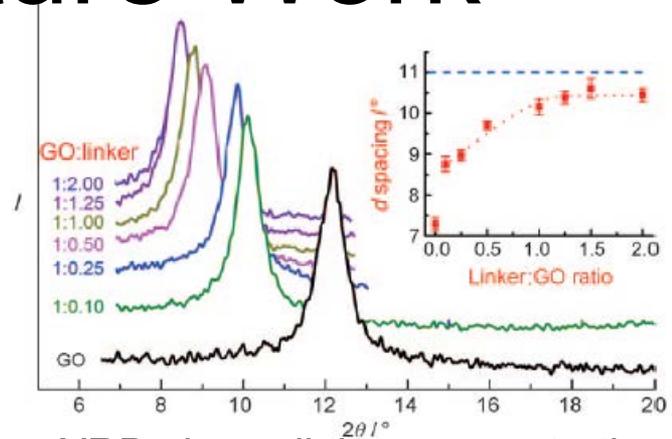
Collaborations

- **(ALL-CRAFT) – University of Missouri Columbia**
 - Peter Pfeifer (group leader), Carlos Wexler (PhD adviser, theory discussions), Mark Lee (sample manufacturing)
 - Matt Beckner (H₂ adsorption, INS), Tyler Rash (sample manufacturing & characterization, INS), Dave Stalla (SEM, sample manufacturing, INS, SANS), Matt Connolly (theory discussions, expansion calculations, GOF manufacturing)
- **Oak Ridge National Laboratory (ORNL) – host site**
 - Carbon Materials Technology Group
 - Jamie Morris (mentor, theory discussions), Nidia Gallego (H₂ adsorption, SANS), Cristian Contescu (CO₂ adsorption, QENS), Valentino Cooper (theory discussions, DFT calculations)
 - Neutron Sciences Division
 - Matt Stone (INS measurements), Souleymane Diallo (plans for QENS), Yuri Melnichenko (plans for SANS)
 - Center for Nanophase Materials Sciences
 - Alex Puretzky (Raman), Adam Rondinone (XRD)
 - Scanning Transmission Electron Microscopy Group
 - David Cullen (TEM)
- **University of Buffalo, SUNY**
 - Eckhard Krotscheck (software for quantum calculations)

Proposed Future Work



- Linkers added to graphene oxide
- Burress et al., *Angew. Chem. Int. Ed.*, **49**, p. 8902 (2010)



- XRD shows linker concentration controls pore size

• Experimental

- ✗ – SANS under H₂ pressure to verify high H₂ densities calculated from isotherms
- DINS to verify predicted quantum effect, and study larger temp/density range
- QENS to measure diffusion in the new EBC
- Similar measurements with high surface area graphene oxide-frameworks (GOFs)
 - Being manufactured by Matt Connolly & Jacob Burress, ALL-CRAFT group
 - Tunable graphene slit pore, but oxides must be removed to increase SA, while linkers remain

• Theoretical

- Increase temperature/density range of results by incorporating rotational degrees of freedom, exchange (quantum interference term)
- ✗ – Further calculation of full quantum states to understand IINS results
- Simulation of formation and stability of pore formed from “bubbles” in graphite

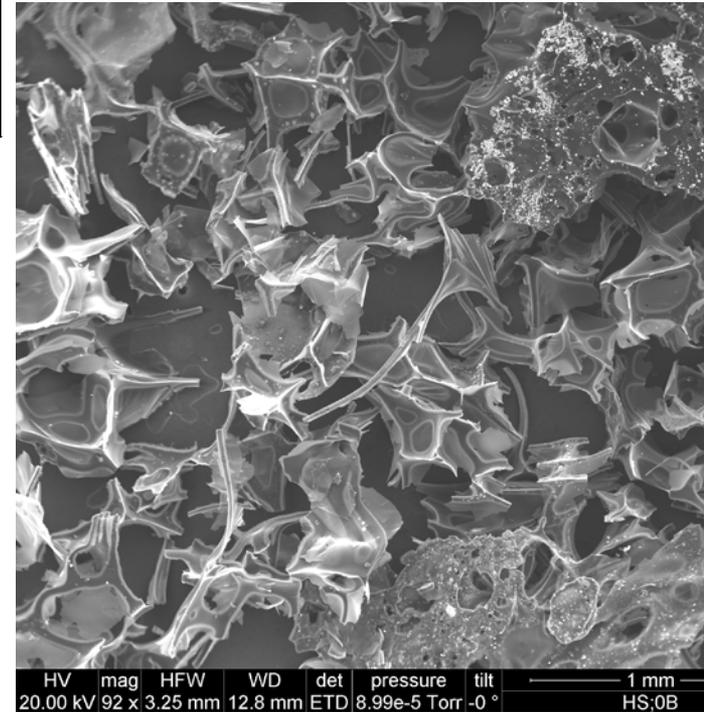
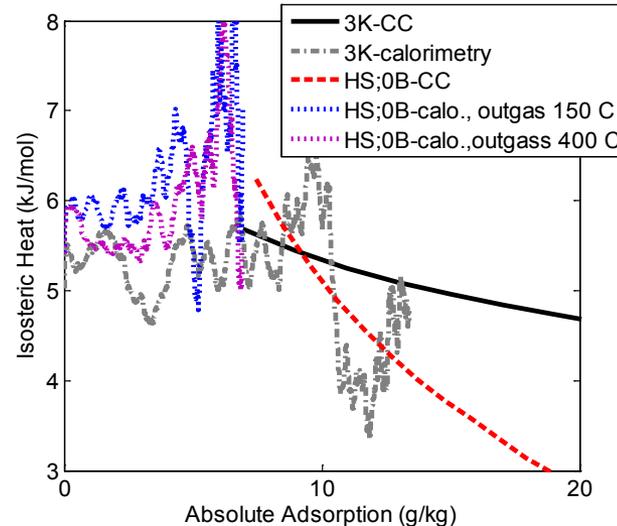
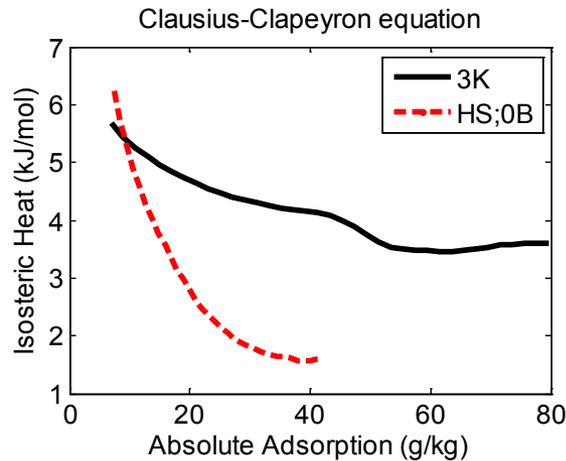
Summary

- **Relevance**
 - Increase understanding of hydrogen adsorption, volumetric & gravimetric storage
- **Approach**
 - Experimental study of carbon with high volumetric storage
 - Neutron measurements of quantum states of adsorbed hydrogen
 - Theoretical calculations of quantum states, quantum adsorption effects
- **Accomplishments**
 - Evidence of narrow graphitic pores with salt & rust contaminants
 - Neutron scattering has increased understanding of quantum states
 - Proposed new theory of significant quantum effect in narrow graphene slit-pores
 - Preliminary experimental data consistent with new effect at work in the sample
- **Collaborations**
 - University of Missouri: ALL-CRAFT Group
 - Oak Ridge National Laboratory: Carbon Materials Group, Neutron Sciences Division, CNMS, STEM Group
- **Future Work**
 - Refine theory to extend the temperature/density range
 - Neutron scattering to verify calculated hydrogen densities & verify and understand Bose condensation in HS;0B
 - Collaborate to manufacture and measure new samples (GOFs)

Technical Back-Up Slides

More Preliminary Data

R. J. Olsen, PhD Thesis, University of Missouri (2011).



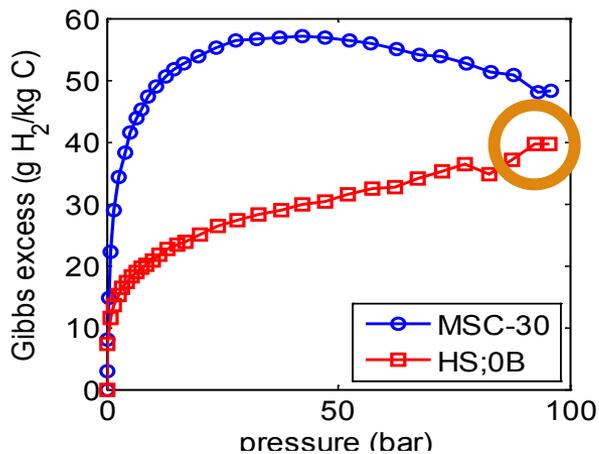
- (Left) Isosteric heats of adsorption calculated from gravimetric isotherms at 80 and 90 K corrected to absolute, using the Clausius-Clapeyron equations
- (Right) Isosteric heat of adsorption measured by calorimetry at 77 K

•Another SEM image

sample	Σ (m ² /g)	V_p (cm ³ /g)	ρ_a (g/cm ³)	ρ_b (g/cm ³)	ρ_c (g/cm ³)
3K	2,700	1.68	0.46	0.14	0.34
HS;0B	700	0.34	1.19	0.15	0.95

- Comparison of theoretical density, bulk “tap” density, and bulk density after compression

Other Examples from Literature



BET SA=700 m²/g
 Maximum excess 3.9 wt% @ 95 bar
5.57 wt% per 1000 m²
 R. J. Olsen, PhD Thesis, University of Missouri (2011).

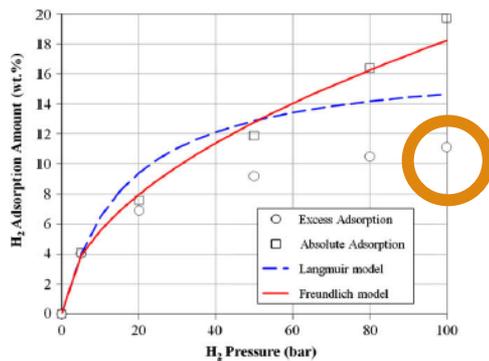


Fig. 6 - High pressure hydrogen adsorption isotherms in MOF-177 at 77 K.
 BET SA=3275 m²/g
 Maximum excess 11 wt% @ 100 bar
3.35 wt% per 1000 m²
 D. Saha et al., *Int. J. Hyd. Energy* **33** p 7479 (2008)

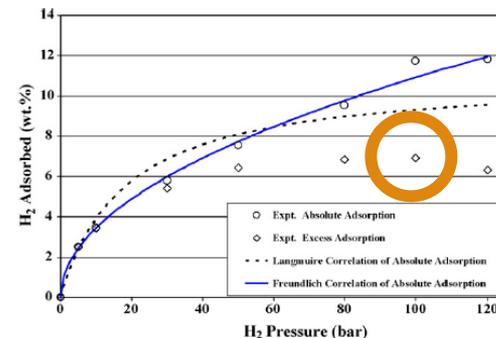
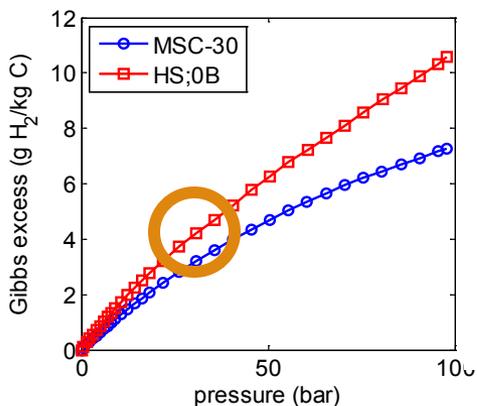
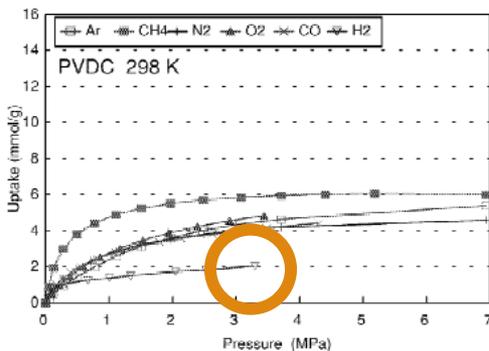


Fig. 6. Hydrogen adsorption isotherms at 77 K and pressure up to 120 bar.
 BET SA=2450 m²/g
 Maximum excess 7 wt% @ 100 bar
2.85 wt% per 1000 m²
 D. Saha et al., *Separation & Purification Tech.* **64** p 280 (2009)



BET SA=700 m²/g
Excess 0.44 wt% @ 33 bar, 303 K



BET SA=1000 m²/g
Excess 0.4 wt% @ 33 bar, 303 K
 D. F. Quinn, *Carbon* **40** p 2767 (2002)

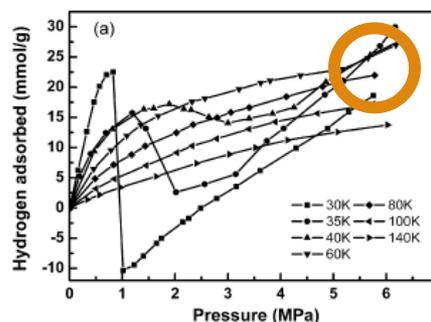


Fig. 4. Hydrogen adsorption isotherms on activated carbon
 BET SA=920 m²/g, Maximum excess 4 wt% @ 60 bar
4.34 wt% per 1000 m²

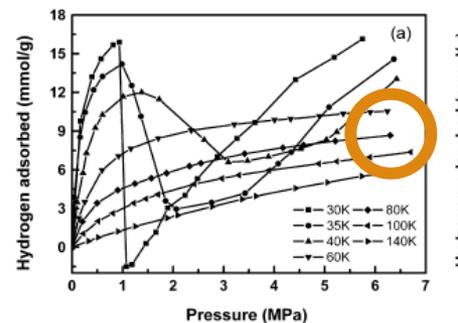


Fig. 5. Hydrogen adsorption isotherms on zeolite NaX
 BET SA=580 m²/g, Maximum excess 1.4 wt% @ 60 bar
2.92 wt% per 1000 m²

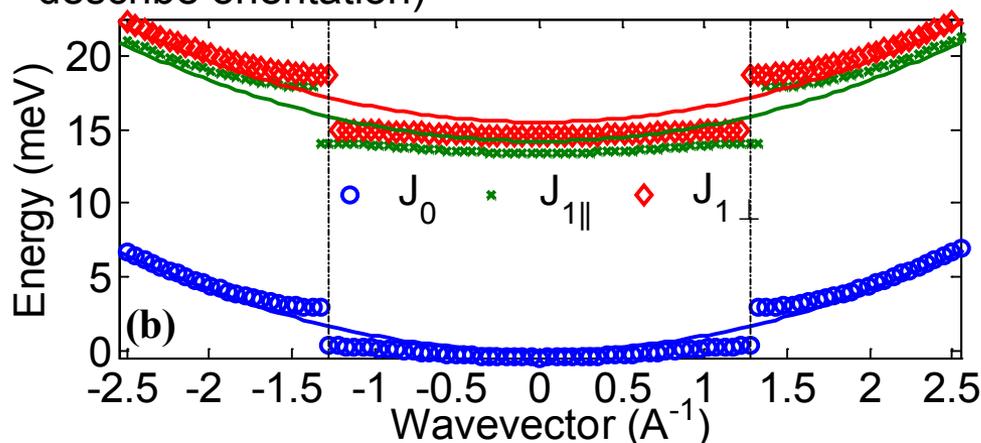
J. Li et al., *J. Supercritical Fluids* **49** p 196 (2009)

Mixing of Degrees of Freedom



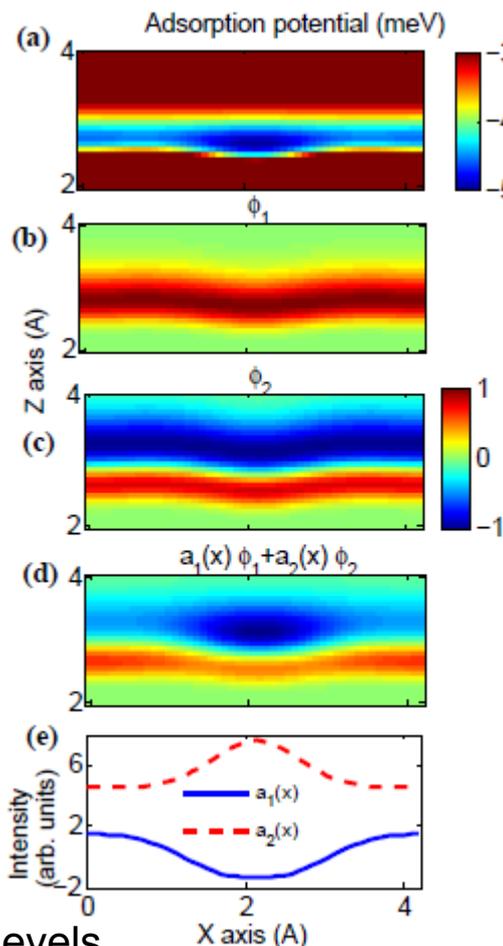
$$V(x, \theta, \phi) = A + B \cos(bx) + C \cos(2\theta) + D \sin(2\theta) \cos(\phi) \sin(bx),$$

• Analytical 3D potential (x , and θ , ϕ which describe orientation)



• Resultant band structure of $J=0,1$ rotational energy levels
 • Roto-recoil coupling lowers net energy of $0 \rightarrow 1$ rotational transition. This effect has been long observed but unexplained until now.

R. J. Olsen & M. B. Stone, Physical Review B under review(2013)



• The 3D (x, y, z) potential also mixes the motion parallel to the plane with the highly quantized motion perpendicular to the plane (vibration).
 • Panels (b) and (c) show the 1st and 2nd vibrational solutions of the Schrodinger equation solved independently at each X position

• The solution of the full 3D Schrodinger equation (d) mixes the 1st and 2nd solutions in proportions which vary as a function of X (e)

Calculation Methods

$$\rho_t = \frac{1}{\sum \exp(-\beta E_{\vec{k},m,n})} \sum \exp(-\beta E_{\vec{k},m,n}) |\psi_{\vec{k},m,n}|^2,$$

$$\rho_a = \left| \frac{1}{2}(\psi_{K,1,0} + \psi_{K',1,0}) + \frac{1}{\sqrt{2}}\psi_{0,1,0} \right|^2,$$

$$\rho_s = \left| \frac{1}{2i}(\psi_{K,1,0} - \psi_{K',1,0}) + \frac{1}{\sqrt{2}}\psi_{0,1,1} \right|^2,$$

- Forms of thermal, aligned, and staggered commensurate quantum states used in calculation

$$\rho^{N,N_a,N_s}(\vec{x}) = N_t \rho_t(\vec{x}) + N_a \rho_a(\vec{x}) + N_s \rho_s(\vec{x})$$

$$V_{dir}^{N,N_a,N_s}(\vec{x}) = \int u[\vec{x}, \vec{x}', \rho^{N,N_a,N_s}(\vec{x}')] d\vec{x}',$$

$$\hat{H}^{N,N_a,N_s} = \frac{\hbar^2}{2m} \nabla^2 + V_{ext}(\vec{x}) + V_{dir}^{N,N_a,N_s}(\vec{x}),$$

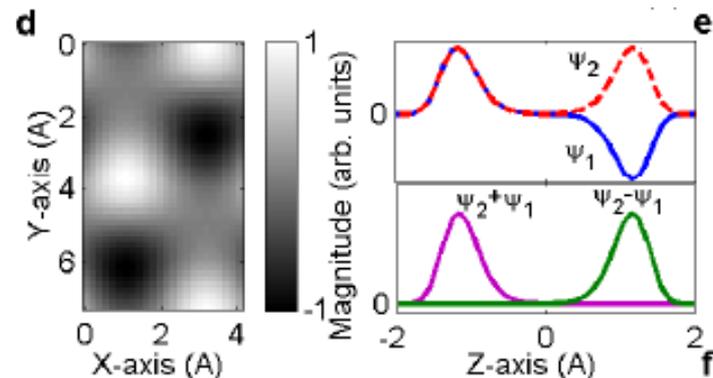
$$E_{\vec{k},m,n}^{N,N_a,N_s} \psi_{\vec{k},m,n}(\vec{x}) = \hat{H}^{N,N_a,N_s} \psi_{\vec{k},m,n}(\vec{x}),$$

$$V_{int}^{N,N_a,N_s} = \int V_{dir}^{N,N_a,N_s}(\vec{x}) \rho^{N,N_a,N_s}(\vec{x}) d\vec{x},$$

$$E(N, N_a, N_s) = N_t E_{0,1,0}^{N,N_a,N_s} + N_a E_a^{N,N_a,N_s} + N_s E_s^{N,N_a,N_s} - \frac{1}{2} V_{int}^{N,N_a,N_s}.$$

- This set of equations is solved iteratively until self-consistent solutions are found to find the energies of the states

R. J. Olsen, under review



$$u[\vec{x}, \vec{x}', \rho(\vec{x}')] =$$

$$\rho(\vec{x}') \times \begin{cases} \Phi_{LJ}(|\vec{x} - \vec{x}'|), & |\vec{x} - \vec{x}'| \geq h \\ \Phi_{LJ}(h), & |\vec{x} - \vec{x}'| < h \end{cases}$$

$$+ c\delta(\vec{x}' - \vec{x}) \left[\frac{3}{4\pi h^3} \int_{|\vec{x} - \vec{r}| \leq h} \rho(\vec{x} + \vec{r}) d\vec{r} \right]^\gamma,$$

$$\Phi_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right],$$

- This is the form and parameters for the H2-H2 interaction functional

parameter	h	ϵ	σ	c	γ
units	Å	K	Å	$\text{K}/\text{Å}^{3(1+\gamma)}$	-
value	2.93	34.2	2.96	2.19×10^{10}	4.25