IV.C.9 The Quantum Effects of Pore Structure on Hydrogen Adsorption

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Fiscal Year (FY) 2012 Objectives

- Neutron characterization of variants of sample of interest
- Measurement of quantum states in idealized oriented carbon adsorbent
- Demonstrate theoretical origin of measured quantum states

Technical Barriers

This project addresses the following technical barrier from the Hydrogen Storage section (3.3) of the Fuel Cell Technologies Program Multi-Year Research, Development, and Demonstration Plan:

(A) System Weight and Volume

Technical Targets

In this project, a carbon adsorbent with unusually high volumetric storage (Table 1) compared to similar samples

is studied. This sample has already been synthesized by the ALL-CRAFT group at the University of Missouri [1]. The purpose of this project is to investigate the mechanism(s) at work in this sample, with the ultimate goal of identifying novel techniques to increase volumetric and gravimetric storage in inexpensive carbon materials.

FY 2012 Accomplishments

- Measured inelastic neutron scattering spectra from variants of the sample of interest, demonstrating significant differences between quantum states measured in different carbon samples.
- Measured inelastic neutron scattering spectra from an oriented graphite sample, identifying important aspects missing from current theory and developing use of inelastic scattering as a sample characterization technique.
- Completed numerical solutions of the three-dimensional Schrodinger equation for pores composed of expanded graphite, revealing the physical origin of several features of measured quantum states.

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Introduction

It seems unlikely that modest improvements in current hydrogen storage systems using well-understood techniques, such as increasing the surface area or binding energy of adsorbants, will be able to reach the ultimate DOE goals for gravimetric and volumetric storage. Instead, a major technological breakthrough is needed. The ALL-CRAFT group at the University of Missouri has produced a carbon adsorbent, HS;0B, with several unusual and desirable characteristics [1,2]. In particular, its volumetric storage is 40-75% higher than similar carbon adsorbents. While its gravimetric performance is 40-55% smaller than similar carbons, it is notable that these values are achieved with a sample surface area of only 700 m^2/g, which is nearly a quarter of comparable nanoporous materials. The most unusual feature of the cryogenic excess isotherm is the lack

TABLE 1. Volumetric and gravimetric performance of sample of interest (HS;0B) compared with an industry standard activated carbon (MSC-30)

Characteristic	Units	2017 Target (System)	HS;0B		MSC-30	
			300 K 90 bar	80 K 90 bar	300 K 90 bar	80 K 90 bar
Volumetric Storage	g H_2/L sample	40	14.7	58.4	8.5	41.6
Gravimetric Storage	wt% (g H_2/g sample *100)	5.5	1.24	4.90	2.26	11.1

of a peak, indicating the film can still easily accommodate more molecules, despite the large amount adsorbed for the surface area [1,2]. If the same performance could be attained in a similar material with maximal surface area, the 2017 targets could be easily achieved at cryogenic temperatures, even when the mass and volume of the system is included, and the system would be close to meeting targets at room temperature. Several samples with similarly unusual properties have been reported in the literature [3-6], indicating the presence of adsorption mechanism(s) which are not currently understood. Thus it is also possible that a robust understanding of these samples could lead to more impressive gains, bringing ultimate targets into reach.

Because the performance of HS;0B cannot be explained with classical adsorption theory and because the measured quantum states of hydrogen molecules adsorbed in the sample are significantly different than in comparable carbon samples, a logical hypothesis is that there is a quantum effect at work in the sample. Work accomplished as part of this project uses both experimental and theoretical techniques to investigate this hypothesis.

Approach

This project seeks answers to several major questions about the system under study. Preliminary work has shown HS;0B has a unique structure, and structure can have a significant effect on quantum states. Thus a number of experimental techniques are used to study the structure of variants of HS;0B in order to learn how they are different from other carbon samples and from one another. If a quantum mechanism is at work, it is essential that the quantum states of hydrogen molecules adsorbed both in the sample of interest and in similar carbon samples be understood. Inelastic neutron scattering (INS) is an invaluable tool for study of this problem [7]. Incident neutrons lose energy while exciting transitions in the quantum states of adsorbed molecules. INS has been used in this work both to study variants of HS;0B, as well as an idealized carbon sample with large, clean, flat surfaces whose orientation relative to incident neutrons can be controlled. In addition, the theoretical origins of the measured quantum states of both HS;0B and other carbon samples have been studied with both analytical and numerical techniques. This work enables use of INS data collected as an additional method of pore characterization, and advances understanding of the mechanism(s) of action in HS;0B.

Results

Currently, INS spectra have been collected during two experiments from six powdered carbon adsorbents, including three variants of HS;0B and three other carbons used for comparison purposes. Figure 1 shows a spectrum around the first rotational peak at an energy transfer of 14.7 meV, which
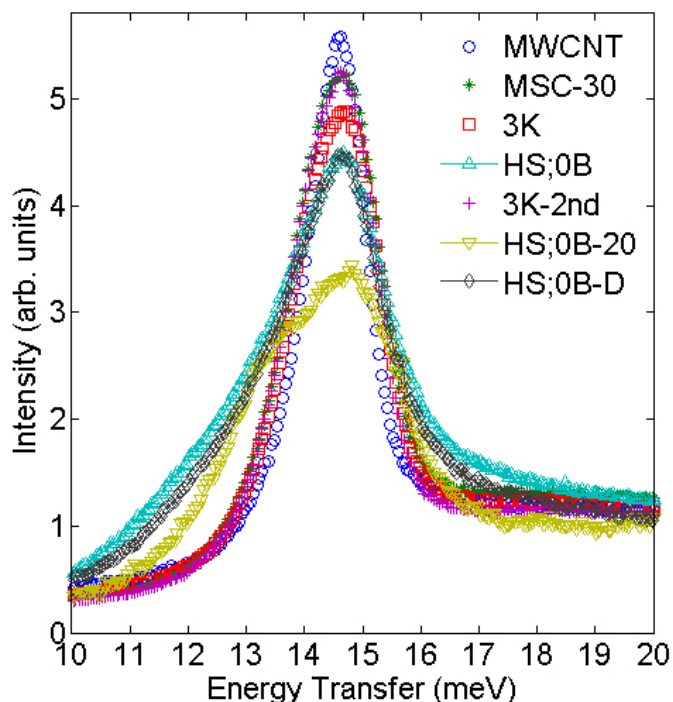

FIGURE 1. INS spectra collected from three HS;0B variants and several comparable carbon samples, including a sample of multi-walled carbon nanotubes (MWCNTs) and two activated carbons (MSC-30 and 3K, with the later measured twice). Temperature is 15 K, and each sample contains hydrogen at ~85% coverage. All spectra have been normalized by the amount of hydrogen.

represents a transition in the highly quantized rotational motion of the two hydrogen atoms about their mutual center of mass. All samples also have a tail (called the roto-recoil tail [8]) extending from the rotational peak on the high energy side, which represents a continuous spectrum of transitions in the translational motion of the hydrogen molecules along the adsorption plane. The three carbons used for comparison purposes all have spectra quite similar to one another, with minor differences which we have related to surface heterogeneity [8]. The spectra of the three HS;0B variants are significantly different from the other carbons. All show asymmetric broadening on the low energy side, but there are also significant differences between the three samples, both in the broadening and in the amount of recoil on the high energy side.

INS spectra have also been collected from an idealized carbon substrate with pores of infinite width, where the alignment of the adsorption surfaces with respect to the scattering neutrons can be controlled. Figure 2 shows this sample, which was constructed from 29 parallel sheets of an exfoliated graphite foil. The purpose of this experiment was to refine physical understanding of the motion of the adsorbed hydrogen molecules. Figure 3 shows the experimental geometry for the experiment and several key results. There are stark differences in the spectra based on the

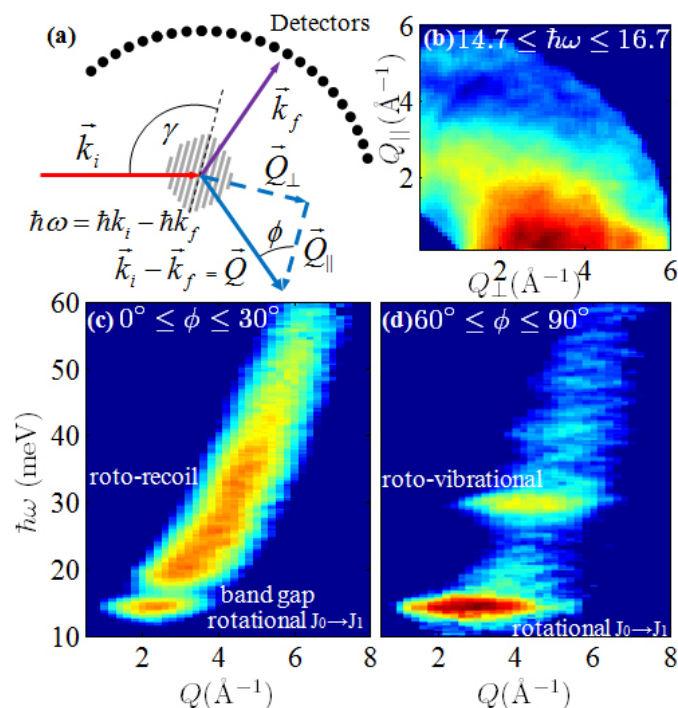**FIGURE 2.** Sample with oriented adsorption planes used for INS experiment.

FIGURE 3. (a) Experimental geometry for IINS measurements of an oriented carbon sample, with energy transfer (ħω) and momentum transfer relative to the adsorption plane (Q) defined. (b) Spectrum of the main rotational peak as a function of Q∥ and Q⊥. (c) Spectrum with the momentum transfer tending to be parallel or (d) perpendicular to the adsorption plane. Intensity is plotted on a log scale, temperature is 15 K, and the sample contains hydrogen at 25% coverage.

direction of momentum transfer (Q) relative to the adsorption plane. When Q tends to be parallel to the plane (Figure 3c), a continuous spectrum of transitions in the translational motion along the plane, the roto-recoil tail, extends from the main rotational peak at 14.7 meV. In contrast, when Q tends to be perpendicular to the plane (Figure 3d), roto-vibrational transitions are observed instead, where vibration refers to the bound motion of the molecule in the adsorption potential. The intensity, Q-dependence, and energy of the main rotational peak also varies significantly with the direction of momentum transfer (Figure 3b). While some of these results were expected, others were not.

To understand these experimental results, numerical solutions of the Schrodinger equation [9] have been performed for various two- and three-dimensional adsorption potentials. Figure 4 shows a representative quantum state for a hydrogen molecule adsorbed on a graphene plane. Previous work in the field has treated motion parallel to the plane and motion perpendicular to the plane separately. However, current results show an important relationship between these two types of motion, with highly coupled states where the vibrational wavefunction changes with the position of the molecule along the plane. This effect is caused by the corrugation of adsorption plane, which causes the distance of the potential minimum from the plane to vary with position. This coupling also results in non-zero angular momentum of the hydrogen center of mass, making it likely that this translational motion also couples to the rotational motion of the hydrogen atoms about their mutual center of mass. Indeed, a preliminary four-dimensional solution (with two translational and two rotational degrees of freedom) does show roto-translational coupling. Previous work in the field has also ignored this aspect of the problem in developing analysis techniques to use INS as a characterization method. So far, these theoretical results are consistent with the unexpected features observed in INS spectra.

To understand how this coupling is dependent on features of the potential, extensive solutions of an idealized two-dimensional adsorption potential have also been performed. The degree of coupling increases with both the degree of corrugation and the width of the potential. It is difficult to see how the amount of corrugation may be increased significantly in a carbon material by varying pore structure. However, calculations [7] have shown that for slit-shaped pores composed of two parallel sheets of graphene, the width of the potential is significantly larger with pore sizes between 7.5 and 9 Å. (Above 9 Å, the two walls are essentially independent adsorption potentials, whereas below 7.5 Å the adsorption potential is narrower because the two walls are quite close.) Pore size distributions of HS;0B generally show a peak around 8-9 Å. Pores of this size are also just large enough to allow bi-layer adsorption [10], and interaction between two nearby layers may be another significant source of quantum adsorption effects
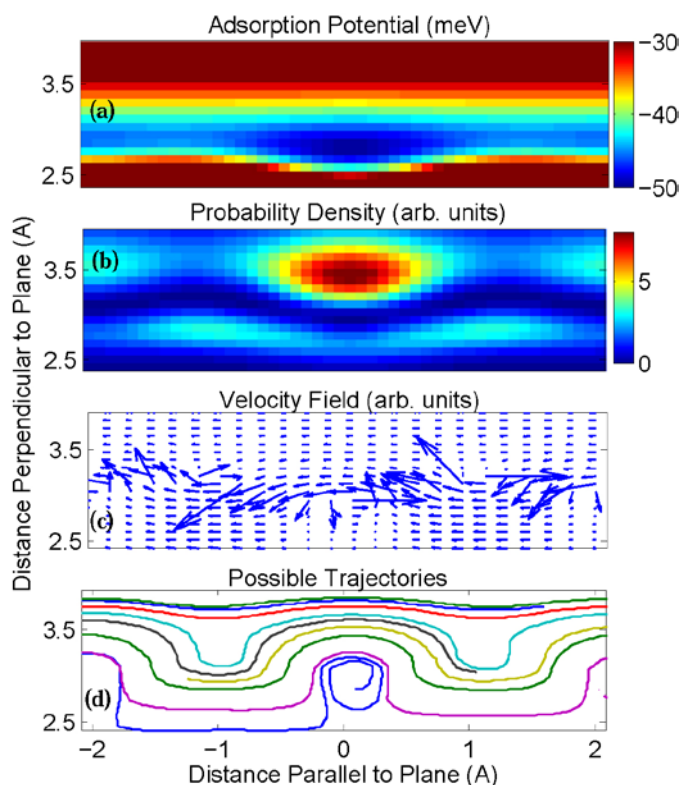
FIGURE 4. (a) Adsorption potential above the center of a hexagonal graphene unit cell, showing corrugation. (b) Probability density of a state which shows strong coupling between motion parallel and perpendicular to the plane. (c) Velocity field calculated from the wavefunction, which shows the magnitude and direction of the velocity at each point. The molecule has a met motion to the left, but the coupling creates areas where the velocity reverses direction, resulting in non-zero angular momentum of the molecular center of mass which varies with position. (d) Several representative classical trajectories calculated using the velocity field and an arbitrary initial position, which show rotational motion. All plots show a two-dimensional cut of a three-dimensional function.

Conclusions and Future Directions

- Based on work done so far, it seems likely that at least some of the unique characteristics of HS;0B are due to its average pore width of approximately 8-9 Å. Additional methods of pore characterization, including Raman scattering, X-ray diffraction, transmission electron microscopy, and pore size distributions measured with CO_2 will be used to verify these results and explore any other structural features which may affect the storage capabilities of this sample.

- Experimental INS work done with an oriented carbon sample shows that certain assumptions made during analysis of INS spectra from carbon samples in previous work need to be refined. These results will be used to develop INS as a more sensitive pore characterization technique, and applied to INS spectra which have also been collected from variants of HS;0B.

- Numerical solutions of the three-dimensional Schrodinger equation for an adsorbed hydrogen molecule show that coupling between the motion parallel and the motion perpendicular to the plane has a significant effect on the quantum states, and varies as a function of pore width. These solutions also show the coupling creates curved paths, making it likely that translational motion will also couple to rotational motion. Solutions of the five-dimensional Schrodinger equation will be done to explore this effect, and its relationship to the INS spectra measured for HS;0B and other carbon samples.

FY 2012 Publications/Presentations

1. Raina Olsen, "The Quantum Effects of Pore Structure on Hydrogen Adsorption" 2012 Annual Merit Review, Washington, D.C., May 16, 2012.

2. Raina Olsen, "Recoiling and Bound Quantum Excitation Spectrum of Adsorbed Hydrogen as an Assessment of Planarity" 6th Workshop on Characterization of Porous Materials, Delray Beach, FL, April 30, 2012.

3. Raina Olsen, "Quantum Excitations of Adsorbed Hydrogen Studied by Inelastic Neutron Scattering" Carbons for Energy Applications, Atlanta, GA, March 30, 2012.

4. Raina Olsen, "The Stationary States of Adsorbed Hydrogen" 2012 March Meeting of the American Physical Society, Boston, MA, March 1, 2012.

References

1. P. Pfeifer. et al., 2010 DOE Hydrogen Program Review, "Multiply Surface-Functionalized Nanoporous Carbon for Vehicular Hydrogen Storage," (http://www.hydrogen.energy.gov/pdfs/review10/st019_pfeifer_2010_o_web.pdf).

2. R.J. Olsen, *Investigations of Novel Hydrogen Adsorption Phenomena* (PhD thesis), University of Missouri Columbia (2011).

3. D.F. Quinn, "Supercritical adsorption of 'permanent' gases under corresponding states on various carbons," *Carbon* **40**, 2767-2773 (2002).

4. J. Li et al., "Adsorption of hydrogen on porous materials of activated carbon and zeolite NaX crossover critical temperature," *Journal of Supercritical Fluids* **49**, 196-202 (2009).

5. D. Saha et al., "Hydrogen adsorption equilibrium and kinetics in metaliorganic framework (MOF-5) synthesized with DEF approach," *Separation and Purification Technology* **64**, 280-287 (2009).

6. D. Saha et al., "Equilibrium, kinetics, and enthalpy of hydrogen adsorption in MOF-177," *International Journal of Hydrogen Energy* **33**, 7479-7488 (2008).

7. R.J. Olsen et al., "Sub-nanometer characterization of activated carbon by inelastic neutron scattering," *Carbon* **49**, 1663-1671 (2011).

8. R.J. Olsen et al., "Recoiling and bound quantum excitations of adsorbed hydrogen observed by inelastic neutron scattering," *Physical Review B*, under review.

9. S.A. Chin et al., "An arbitrary order diffusion algorithm for solving Schrodinger equations," *Computer Physics Communication* **180**, 1700-1708 (2009).

10. B. Kuchta et al., "Numerical estimation of hydrogen storage limits in carbon based nanospaces," *Carbon* **48**, 223-231 (2010).