



# The Quantum Effects of Pore Structure on Hydrogen Adsorption

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## Background and Introduction

Hydrogen is a desirable alternative fuel because it is clean burning and lightweight. However its density is quite low. Even liquid hydrogen requires significantly more volume to store than an equal amount of gasoline. At room temperature the situation is an order of magnitude worse, making practical use difficult, particularly for vehicles.

Various hydrogen storage systems have been proposed. In an effort to reduce the volume of the system, its weight is typically increased. Despite decades of research, current technologies are far from meeting DOE goals. Storage via adsorption to a high surface area material is a preferred method because its fast kinetics allow for quick and simple refueling, and carbon adsorbents are particularly desirable for their low cost and chemical stability. However, current carbon materials are able to meet targets for weight only at cryogenic temperatures, and are far from meeting volumetric targets at any temperature. Recent research has moved towards more complicated systems, but thus far these remain more costly and/or difficult to use without significant gains towards DOE goals.

Preliminary work done with the ALL-CRAFT group at the U. of Missouri has identified a carbon based sample (HS;0B) produced by the pyrolysis of the polymer poly(vinylidene chloride-co-vinyl chloride) (PVDC) with a number of highly unusual experimental characteristics, which include

- Room temperature excess adsorption by weight slightly larger than a high end activated carbon (3K) with over three times the surface area (Fig. 1a)
- Cryogenic excess adsorption which is similarly large for its surface area. This isotherm also lacks a peak, indicating the film is not yet near saturation (Fig. 1b)
- A smaller bulk density and nanopore volume than 3K. As a result,
  - The calculated density of hydrogen inside the pores is twice the density of liquid hydrogen
  - Its overall storage per volume at room temperature is twice that of 3K

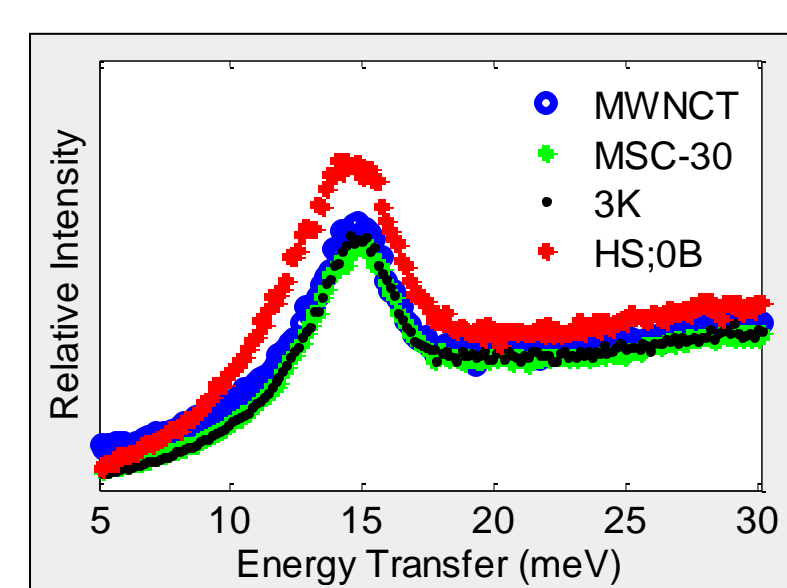


Figure 2. Inelastic neutron scattering spectra of HS;0B, 3K, and two other carbon adsorbents

Classical adsorption theory is entirely unable to explain the characteristics of this sample, indicating the presence of some as yet undiscovered adsorption mechanism. Understanding it may lead to further improvements in the performance of carbon adsorbents. Inelastic neutron scattering (INS) probes the quantum states of adsorbed hydrogen. INS spectra (Fig 2.) collected from hydrogen adsorbed in several carbons show that the quantum states of HS;0B are significantly different than any other sample, suggesting quantum mechanics plays an important role in understanding the phenomena at work in this material.

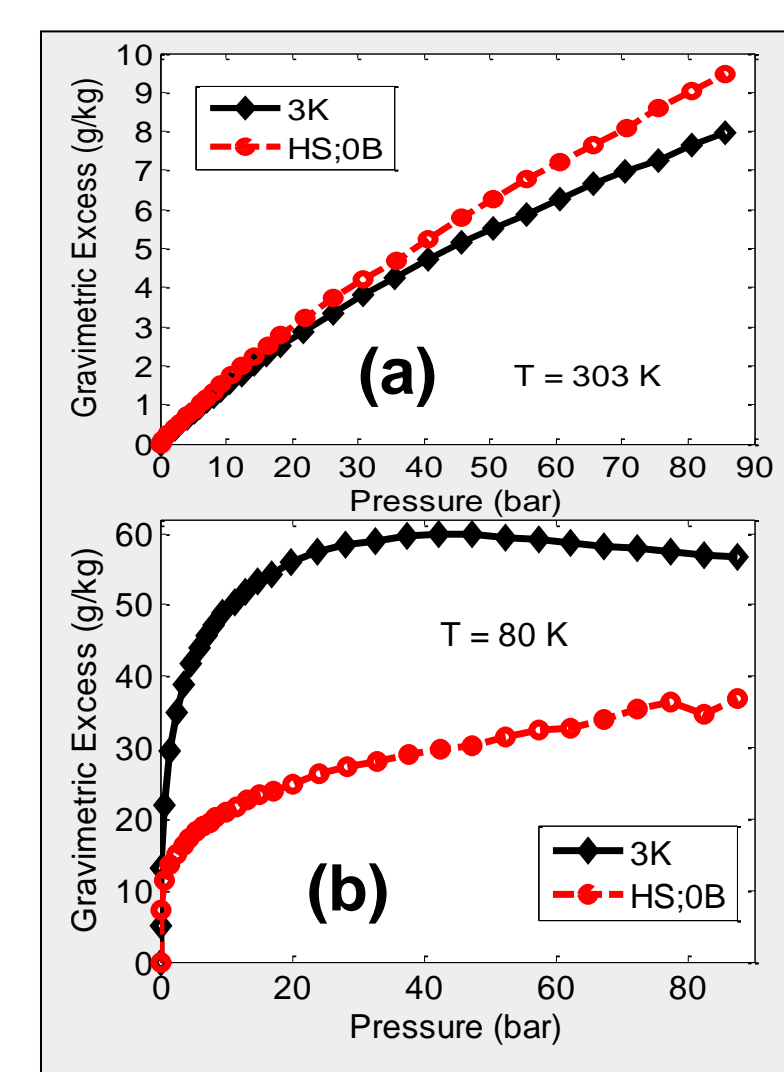


Figure 1. Excess gravimetric hydrogen adsorption at (a) room and (b) cryogenic temperatures, for PVDC carbon HS;0B (surface area 700 m<sup>2</sup>/g, pore volume 0.34 cc/g) and activated carbon 3K (surface area 2500 m<sup>2</sup>/g, pore volume 1.68 cc/g).

## Approach

The goals of proposed work are twofold. Firstly several variants of HS;0B will be studied experimentally in an effort to identify relationships between performance and other sample characteristics. There is no evidence that HS;0B has a significantly different binding energy than similar carbon samples, but it does have significantly different quantum states and preliminary images of the sample (Fig. 3) show unusual structures. Thus the focus of this work will be on understanding the structure and quantum states of the samples using TEM, X-ray diffraction, Raman scattering, CO<sub>2</sub> adsorption, and INS.

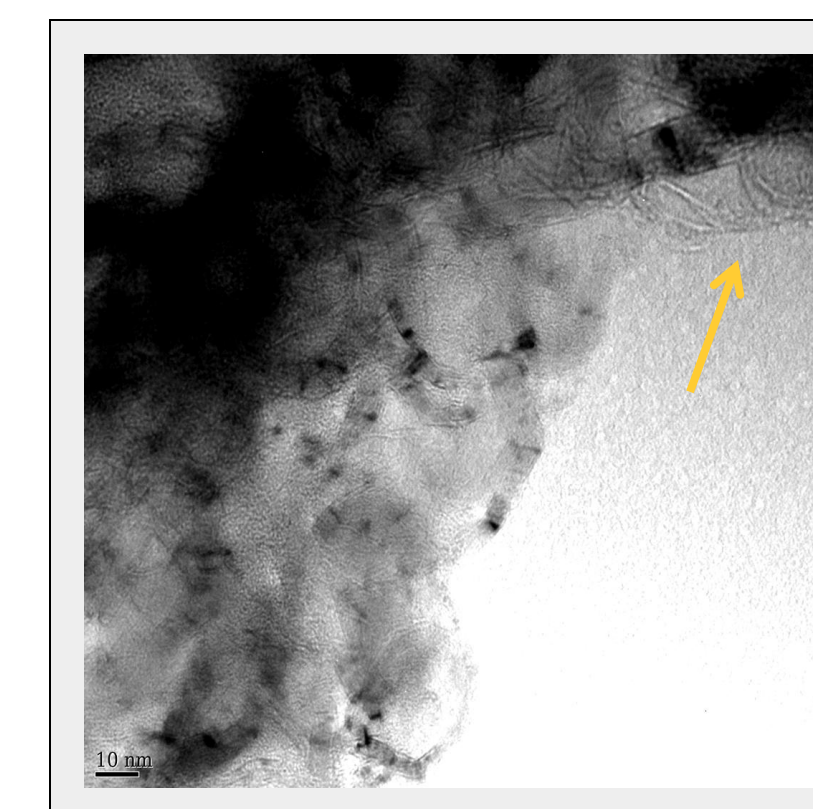


Figure 3. Transmission Electron Microscopy (TEM) image of HS;0B, showing long curved pores

The second purpose of the proposal is to gain a theoretical understanding of the mechanism(s) at work in this sample. The quantum states of adsorbed hydrogen will be studied numerically and analytically as a function of pore structure, with this work governed by experiment and the current proposed mechanism.

Classically, we understand each molecule as having a definite location on the surface of the adsorbent. At low coverage, adsorption is primarily controlled by the binding energy. As coverage increases, interactions between adjacent molecules present important corrections to the energy. Ultimately, the molecules are pushed as close together as allowed by interactions, and the surface saturates. However in any real system, the underlying physics is truly governed by quantum mechanics.

Traditional models of many body systems of this type would expect the quantum states of the molecules at low coverage to be quite similar to the single particle solutions of the system: highly delocalized states, essentially plane waves, in which the wavefunctions are extended over the entire surface. In the classical equivalent, this situation represents molecules free to diffuse across the surface. As coverage increases, interactions between molecules in overlapping states result in the quantum states becoming more localized. In the classical equivalent, this situation represents molecules prevented from diffusing freely across the surface by interactions with their neighbors. Solution of this problem involves the balance of two effects: the increase in energy of the states themselves as the particles become more confined, and the decrease in the interaction energy due to the reduction in the overlap of states with one another.

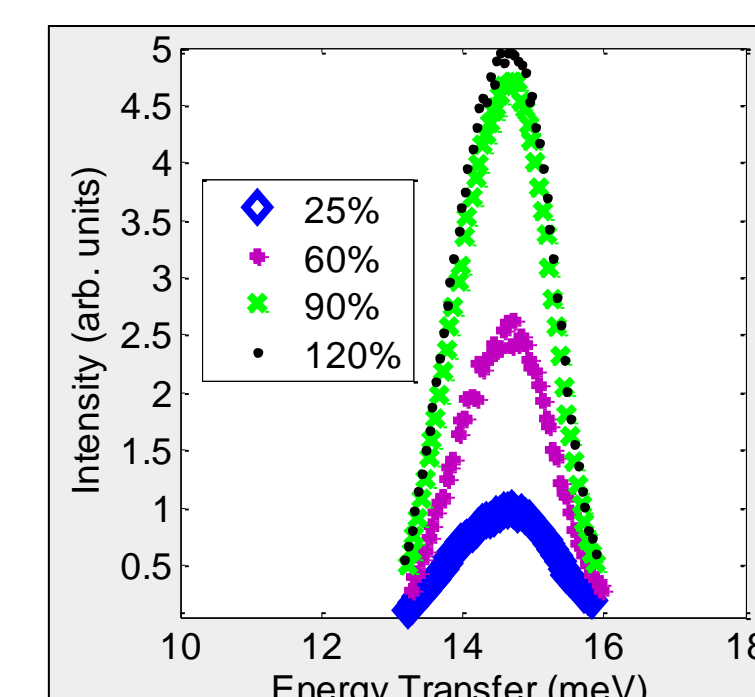


Figure 4. Narrow peak extracted from INS spectra of 3K as a function of coverage. This peak represents molecules which don't move along the adsorption plane.

However, the measured quantum states are not consistent with this picture. Each INS spectrum can be split into two parts: a broad peak representing molecules which move along the plane, and a narrow peak representing molecules which do not move along the plane. The energies and shapes of these peaks remain quite constant as a function of coverage. Instead their relative proportions change, with the narrow peak growing faster than the coverage (Fig. 4) and the broad peak growing more slowly.

Thus a reasonable hypothesis is that some single particle states are already localized, and as coverage grows the interaction energy is minimized by preferentially occupying these localized states. In this model, the adsorption is significantly affected both by the number of these states and to what degree they are localized. Theoretical work will explore how these states are created and how they are affected by the structure of the pore.

## Impact

If successful, this project will result in a theoretical understanding of the important features of an unusually high performing carbon adsorbent. This understanding can then be used in the manufacture of samples with the same adsorption characteristics, but threefold larger surface areas, resulting in hydrogen storage systems with nearly an order of magnitude improvement over similar adsorbent systems, but which retain the low cost and safety of a carbon material. However it is also possible that the mechanism at work in this material may be exploited further, resulting in more significant improvements than those which have been currently demonstrated experimentally.

## Acknowledgments

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## To Identify Novel Techniques to Increase Adsorption in Carbon Materials by Controlling Structure