

# INELASTIC NEUTRON SCATTERING AS A PROBE OF THE STATES OF HYDROGEN IN CARBON MATERIALS

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## Abstract

Inelastic neutron scattering (INS) has proven to be an effective tool for the study of the microscopic properties of H<sub>2</sub> adsorbed on nanotube bundles. In particular, this technique provides insight on the orientational dependence of the interaction potential between the tubes and H<sub>2</sub> through its effects on the rotational energy levels of H<sub>2</sub>. We have performed INS experiments on as-prepared single-walled nanohorns and opened single-walled nanotubes dosed with hydrogen gas.

## Introduction

Neutron scattering has been used extensively to probe the local potential at an adsorption site. In the solid, hydrogen behaves as a three dimensional quantum rotor with energy levels given by  $E = BJ(J+1)$ , where  $J$  is the rotational quantum number and  $B$  is the rotational constant having a value of 14.7 meV (59 cm<sup>-1</sup>) for H<sub>2</sub>. In principle, relatively weak interactions will give rise to deviations from this simple model and especially a splitting of the  $J=1$  rotational level. Given sufficient spectroscopic resolution one can ultimately deduce accurate information about the adsorbate site symmetry and nature of the intermolecular hydrogen guest interaction. The initial study of hydrogen adsorbed on bundles of laser produced, un-purified, nanotubes [Brown, 2000] identified a broadened rotational peak shifted slightly from the free rotor value. Two following studies on different types of nanotubes had clear multi-peaked feature being rationalized in terms of the hydrogen experiencing a stronger rotational hindering potential [Georgiev 2004; Schimmel 2004; Georgiev 2005]. Even though the data analysis concluded different orientations of the hydrogen molecule both groups concluded that the hydrogen lies in what is most likely the groove sites as compared to hydrogen on the exterior surfaces of the bundles. Recent work has, however, raised the possibility that the hydrogen preferentially binds to defect or impurity sites and this is the origin of the clear multi-peaked feature [Liu, 2007].

## Experimental

Single-walled carbon nanohorns (SWNHs) were synthesized by the laser ablation method at Oak Ridge National Laboratory using a high-power (600 W) industrial neodymium:yttrium aluminum garnet (Nd:YAG) laser [Puzos, 2000]. SWNHs were produced from pure carbon targets without metal catalysts under Argon [Cheng, 2007]. SEM and TEM images show SWNH aggregates are composed of radially oriented individual SWNHs with conical tips and have a uniform spherical morphology with diameters varying from 50 nm to 100 nm [Hu, 2007]. Elemental compositions and adsorption isotherms are also presented in these proceedings [Hu, 2007]. The excess hydrogen adsorption capacity of this SWNH sample is 0.87 mass at 77 K and 10 bar.

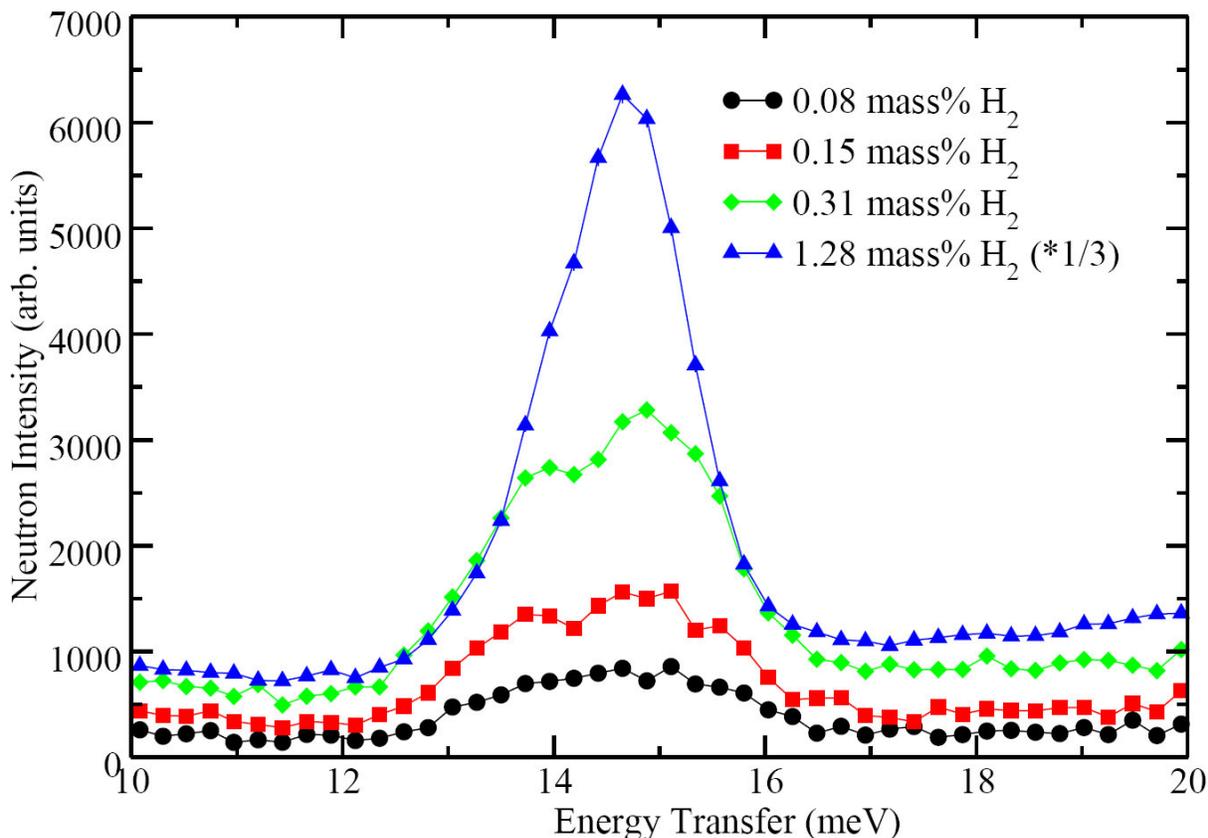
A chemically purified sample of open-ended single-walled nanotube (SWNT) bundles [Mer] was used as the alternative carbon substrate. The multistage purification process is described elsewhere [Chiang, 2001]. Evidence for the open nature and adsorption enthalpy and the structure of argon condensed in the various adsorption sites in this SWNT sample was

investigated previously [Rols, 2005]. Briefly, the sample is composed of bundles of  $\approx 50$  nanotubes. Neutron diffraction data did not reveal any diffraction lines from metal catalysts and a very small fraction of graphitized carbon. Prompt- $\gamma$  activation analysis (PGAA) was performed at the National Institute of Standards and Technology Center for Neutron Research (NCNR) facilities [Paul, 1997]. The SWNT sample was packaged in aluminum foil and suspended in the white neutron beam. Integrated count rates for the characteristic lines of carbon, boron, iron and cobalt were used to obtain atomic ratios. There are no contamination of the peaks of interest for the nanotube samples from the aluminum sample container [Liu, 2007].

Inelastic neutron spectra for both SWNHs (224 mg) and SWNTs (221 mg) were collected using the Filter Analyzer Neutron Spectrometer (FANS) at the NCNR. A pyrolytic graphite monochromator with two 20' collimators, before and after the monochromator, was used to condition the incident beam. Upon scattering from the sample, a band-pass filter of room temperature bismuth and cryogenically cooled beryllium-graphite was used to select the final neutron energy [Udovic, 2006]. The samples were packaged in aluminum foil and mounted in an aluminum cell capable of being loaded with gas while in a closed cycle refrigerator. All samples were degassed for  $\approx 20$  hrs at 473 K with a dynamic vacuum provided by a turbopump. Background data were recorded for all samples at a temperature of 3.5 K while under vacuum. Hydrogen dosing of the samples was performed with the temperature of the sample above 70 K. The sample was then cooled to 3.5 K after which a 30 minute equilibration was allowed before measuring any spectrum. Measurements were taken at a determined hydrogen loading amount taking into account the mass of the carbon samples.

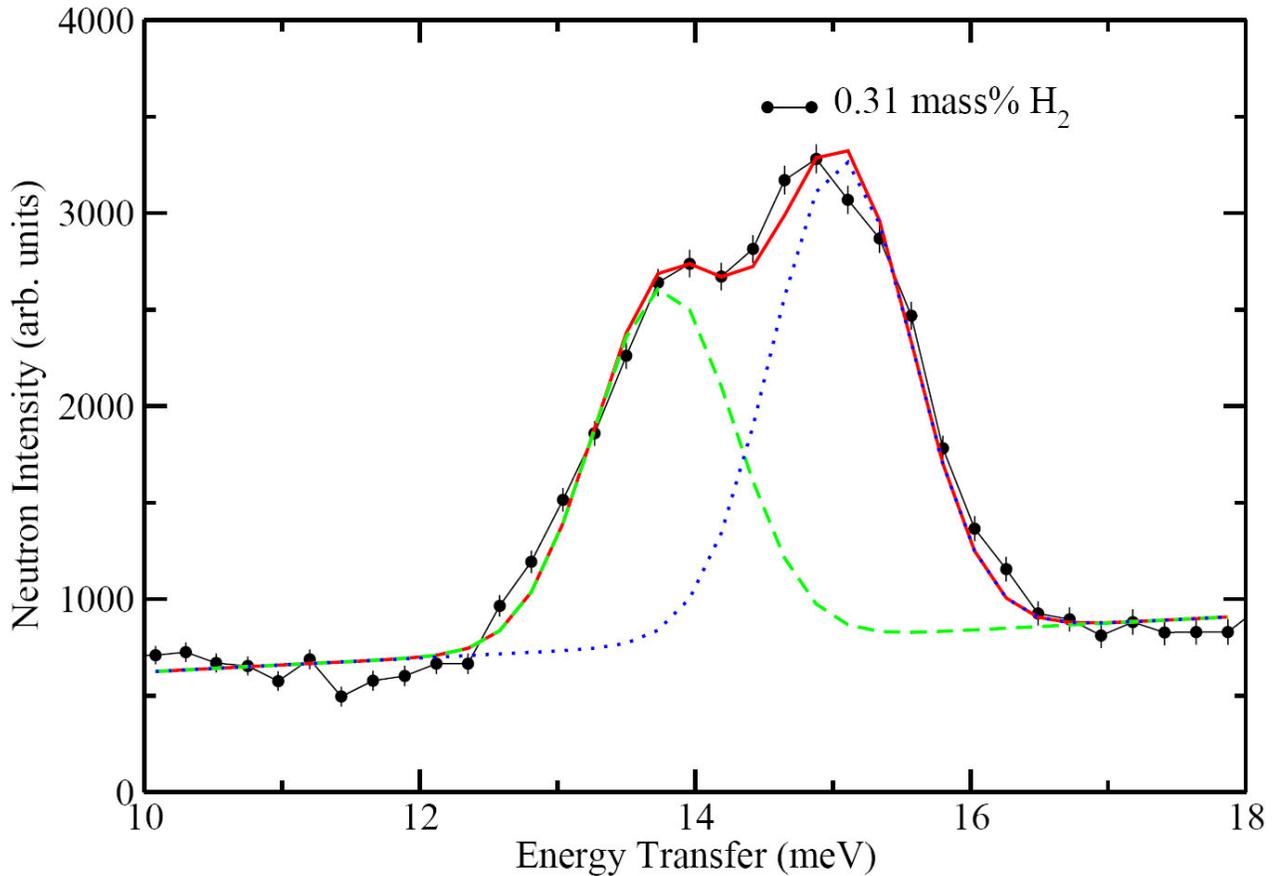
## Results

Neutron scattering can be used as a local probe of the hydrogen adsorption sites through the almost exponential dependence of the rotational transition upon the rotational barrier. Figure 1 shows the INS spectra for the as-prepared SWNHs as a function of hydrogen loading with the bare material subtracted as a background. The characteristic features close to the free rotor line for hydrogen are similar to those seen previously for hydrogen in other arc produced nanotubes and gas phase synthesized nanotubes [Georgiev 2004; Schimmel 2004; Liu 2007] and much broader than laser produced materials [Brown 2000; Liu 2007]. There are at least two peaks observable within the resolution of the FANS instrument, with the higher energy peak becoming proportionately more intense compared to the lower energy peak with increasing hydrogen content.



**Figure 1.** Inelastic neutron scattering spectra of the quantum rotational transition of hydrogen adsorbed on as-prepared single walled nanohorns. Note that the highest loading data have been scaled by one-third to facilitate comparison. Error bars representing one standard deviation are shown as the vertical lines.

The result of fitting these features to a function consisting of two resolution limited Gaussian peaks and a sloping background is displayed in figure 2 in the case of 0.31 mass% hydrogen loading. For the Gaussian functions, the full-width at half-maximum,  $\Gamma$ , was fixed at the instrument resolution value of 1.2 meV. The Gaussian peak parameters are given in table 1. As can be seen in figure 2, this description of that data is fairly reasonable, however, similar quality fits can be achieved using more Gaussian peaks. For a single adsorption site, it is expected that there may be one, two or three peaks corresponding to progressive lifting of the degeneracy of the  $J = 1$  rotational level. The ratio of intensities for the two peaks observed is not in the expected 1:2 ratio and may reflect the need for considering more than one type of adsorption site. A clear resolution to this question would require a spectrometer with higher resolution than used here. We have speculated [Liu, 2007] that the origins of the split hydrogen rotational peak observed for low hydrogen loadings in some SWNT materials is due to hydrogen adsorption at impurity or defect sites rather than the external groove sites. Since, we would not expect the packing of SWNHs to be regular, it is unlikely that the observed splitting here is a result of a regular inter-nanohorn adsorption site.



**Figure 2.** Decomposition of the inelastic neutron scattering spectrum of 0.31 mass% hydrogen adsorbed on single walled nanohorns (black circles) into two resolution limited Gaussian peaks. The continuous line is the total fit and each Gaussian component is shown by a dash or dotted line. Error bars representing one standard deviation are shown as the vertical lines.

**Table 1.** Fitted peak profile parameters for the two resolution limited Gaussian peaks used to describe the hydrogen rotation features in the INS spectra of SWNH at 0.31 and SWNT at 0.19 mass % hydrogen loadings, respectively.

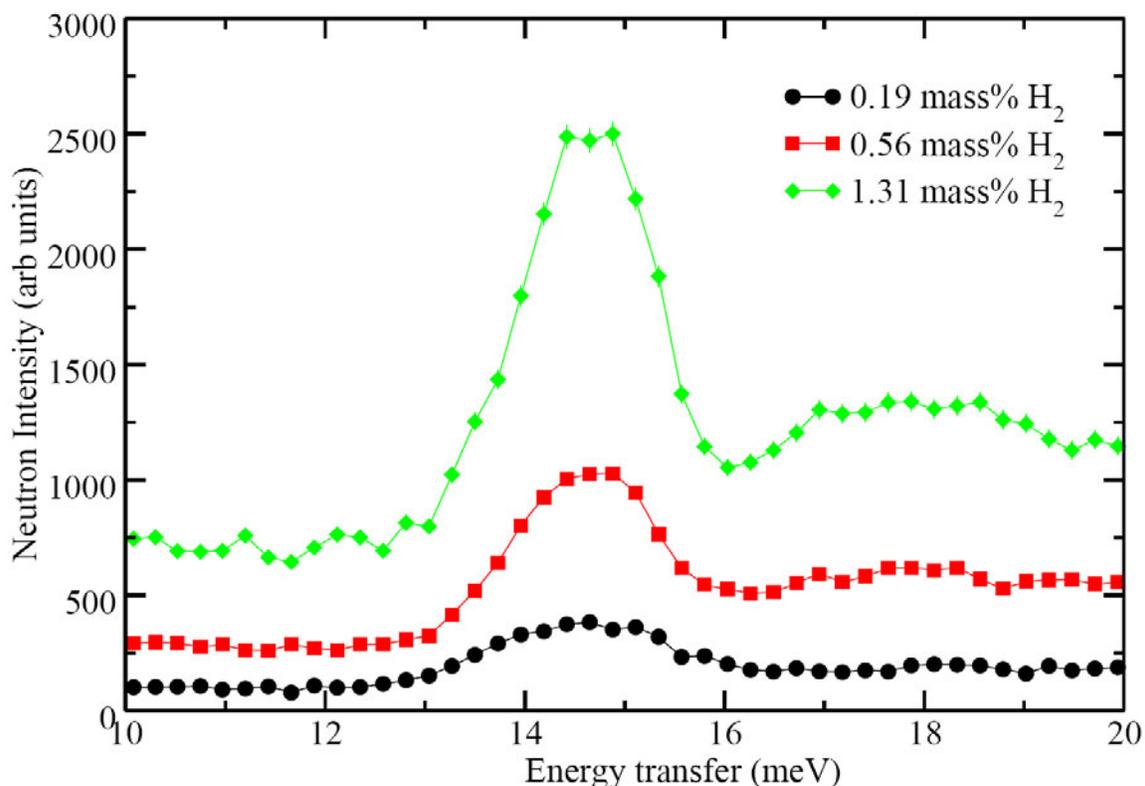
Sample	Gaussian 1			Gaussian 2		
	Area (A.U)	Center (meV)	$\Gamma$ (meV)	Area (A.U)	Center (meV)	$\Gamma$ (meV)
SWNH	2370±57	12.77±0.02	1.2	3151±60	15.06±0.01	1.2
SWNT	226±14	14.01±0.04	1.2	245±14	15.02±0.04	1.2

For the open SWNTs, even though there was no observation of crystalline catalyst particles using diffraction [Rols, 2005], elemental analysis using PGAA indicates that there are some residual catalysis components. Table 2 lists the mass ratios, relative to carbon, for select elements. Thus, there is approximately one iron atom for every 5000 carbon atoms.

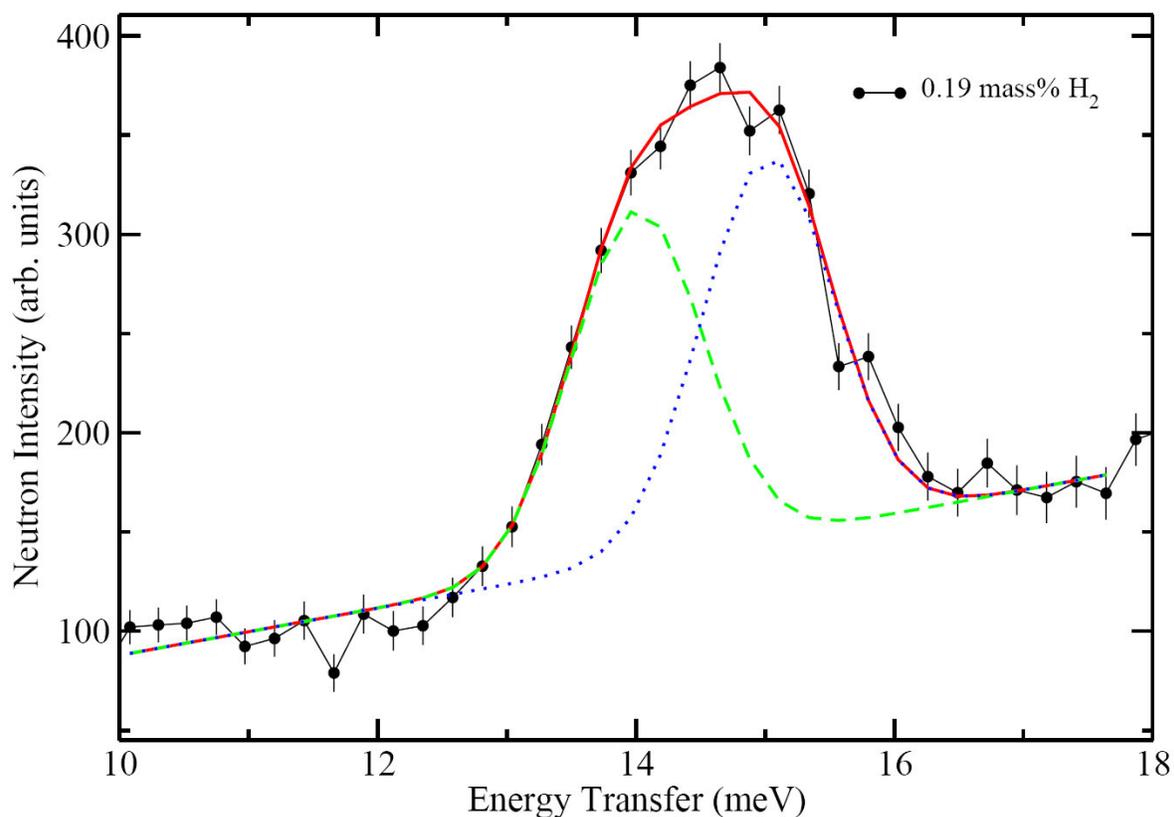
**Table 2.** Elemental composition of the open SWNT sample obtained from neutron PGAA. Ratios are referenced to the mass of carbon in the sample. Values in parentheses indicate the estimated standard deviation.

Elements	Mass ratio
B:C	0.025(4) %
Fe:C	0.9(3) %
Co:C	0.32(6) %

The INS spectra for the hydrogen loaded SWNTs with the background subtracted are shown in figure 3. Unlike the SWNH material, there is no distinct shoulder to define multiple peaks at any hydrogen loading level reminiscent of laser produced SWNTs [Brown, 2000; Liu 2007]. Though the peak width is somewhat broader than the nominal instrumental resolution of the instrument and a very good fit may be achieved using the methodology used for the SWNH sample. The two Gaussian fitting is shown in figure 4 for the lowest loading level studied with the peak parameters reported in table 1. Since we expect these SWNTs to be open and their internal volume accessible to hydrogen, we would expect there to be multiple types of adsorption sites each providing a rotational potential that may alter the degeneracy of the rotational levels from that of the free molecule. From this data it would be difficult to separate effects from hydrogen *inside* the nanotube or from hydrogen in the grooves of the bundles. It is clear that there is no gross splitting of the rotational levels as has been observed in arc produced SWNTs or even in the SWNHs of this study. We consider this as additional evidence [Liu 2007] against the assignment of the low energy shoulder as arising from the tunnel splitting of hydrogen inside the external groove sites as suggested by Georgiev *et al.* (2004;2005) and Schimmel *et al.* (2004). To further refine our understanding would require higher resolution measurements.



**Figure 3.** Inelastic neutron scattering spectra of the rotational transition of hydrogen adsorbed on opened single walled nanohorns as a function of loading level. Error bars representing one standard deviation are shown as the vertical lines.



**Figure 4.** Decomposition of the inelastic neutron scattering spectrum of 0.19 mass% hydrogen adsorbed on/in opened single walled nanotubes (black circles) into two resolution limited Gaussian peaks. The continuous line is the total fit and each Gaussian component is shown by a dash or dotted line. Error bars representing one standard deviation are shown as the vertical lines.

## Conclusion

We have measured inelastic neutron scattering spectra of hydrogen adsorbed on as-prepared single-walled nanohorns and open single-walled nanotubes. The spectra in both cases are broadened compared to that of bulk hydrogen, and in the case of the SWNHs can be resolved into two peaks. The SWNH data resemble the INS data previously ascribed to hydrogen rotations adsorbed in the external grooves of nanotube bundles but it is unlikely to be the case here. The opened SWNT data closely resemble data previously taken on laser produced material. Even though this sample could be expected to adsorb hydrogen in the tube center, there are no strong characteristics of the data to indicate that this is the case. Further work using high resolution would be needed to address these issues further.

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