Neutron spectroscopy study of single-walled carbon nanotubes hydrogenated under high pressure

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Abstract

Single-walled carbon nanotubes (SWNT) were loaded with 5.2 wt% hydrogen at a hydrogen pressure of 3 GPa and $T = 620$ K, quenched to 80 K and studied at ambient pressure and 15 K by inelastic neutron scattering (INS) in the range of energy transfers 3–400 meV. An analysis of the measured INS spectra showed that the quenched SWNT & H sample contained hydrogen in two different forms, as H atoms covalently bound to the carbon atoms ($\sim$4.7 wt%) and as H_2 molecules ($\sim$0.5 wt%) exhibiting nearly free rotational behavior. Annealing the sample in vacuum at 332 K removed about 65% of the H_2 molecules and annealing at 623 K removed all of them. This demonstrates that H_2 molecules were kept in this sample more tightly than in earlier studied SWNT & H samples that were hydrogenated at lower pressures and temperatures and lost all molecular hydrogen on heating in vacuum to room temperature.

1. Introduction

Single-walled carbon nanotubes (SWNT) reversibly absorb and desorb considerable amounts of hydrogen at moderate hydrogen pressures below 20 MPa and room or lower temperatures [1]. The dominating mechanism of hydrogen sorption at these *P–T* conditions is physisorption of H_2 molecules on the graphene layers of SWNT [2]. The hydrogenation of SWNT at $P = 9$ GPa and $T = 450\,°C$ with following quenching under pressure down to $-140\,°C$ produced a new C–H compound containing 6.8 wt% H [3]. On heating this compound in vacuum, about 0.5 wt% H left the sample by room temperature whereas the intense release of the main quantity of hydrogen began only above 500 °C.

An effective means for studying the hydrogen bonding in carbon nanomaterials is using inelastic neutron scattering (INS). The INS technique has already been successfully applied for the investigation of low-pressure hydrogenated SWNT [4–12] and fullerenes [13], and also for the C_{60} fullerenes hydrogenated under high pressure [14–17]. The present paper describes results of an INS investigation of SWNT and, for comparison, of C_{60} hydrogenated at 3 GPa and $T = 620$ K. To analyze the nature of hydrogen bonding in these high-pressure compounds, the spectra were measured for the SWNT & H and C_{60} & H samples in the quenched state and after partial removal of hydrogen by vacuum annealing.

2. Experimental details

The SWNT was prepared by direct current arc vaporization of graphite/metal composite rods (contained Co/Ni catalyst in a 3:1 mixture). The raw SWNT material was purified by leaching out the metal catalyst with hydrochloric acid followed by oxidation of nontube carbon components by air at 300–600 °C,

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similar to the known procedure [18]. The purification procedure yields nanotubes about 14 ± 1 Å in diameter and about $10\,\mu m$ in length as revealed by electron microscopy observation using HRTEM, SEM, X-ray and neutron diffraction. The C_{60} sample of 99.99 wt% purity was prepared as described previously [19] and sublimed in a vacuum better than 10^{-5} Torr at 870 K.

The SWNT (weight of $\sim 0.6\,g$) and fullerenes C_{60} ($\sim 0.5\,g$) were hydrogenated at a hydrogen pressure of 3 GPa and 620 K, quenched to 80 K and then studied by INS. INS data were measured using the TOSCA instrument at the ISIS pulsed neutron source [20]. TOSCA is an inverse geometry time-of-flight spectrometer with fixed energy for registered neutrons, $E_r \approx 4$ meV. The data were recorded over a wide range of energy transfer, 3–400 meV, with a resolution of 2% of the energy transferred. The time-of-flight spectra were converted into dynamical structure factor $S(Q, E)$ versus energy transfer using the standard ISIS data analysis programs. The background spectrum for the empty container was measured under the same conditions and subtracted from the original data.

INS spectra were measured first on the quenched hydrogenated samples and then on the same samples annealed in vacuum (~ 10 Torr) at 332 K (for 40 min) and then at 623 K (60 min) for SWNT and at 300 K for C_{60} (90 min). All INS data were collected at 15 K in order to minimize the multiphonon neutron scattering and the Debye–Waller factors. The hydrogen content in the heated $C_{60}H_x$ was $x = 38$ (determined by burning the sample in an oxygen flow), and H/C atomic ratio for SWNT & H sample heated at 623 K was 0.56 (or 4.7 wt%) as estimated from the ratio of total intensities of INS spectra for the $C_{60}H_{38}$ and the annealed SWNT & H.

3. Results and discussion

The measured INS spectra for hydrogenated SWNT and C_{60} samples are shown in Figs. 1a and 2a. The peak at ~ 355 meV can be assigned to stretching C–H modes [16,17], revealing the existence of C–H covalent bonds in the quenched and annealed samples. The widths of the peaks are smaller (FWHM ≈ 12 meV) for the SWNT & H spectra than for C_{60} & H (FWHM ≈ 20 meV). According to [21], the C–H stretching peak should be expected around 360–365 meV for hydrogen connected to sp^3 hybrid atom and around 375–380 meV for sp^2 hybridization. The observed values for the stretching C–H peaks clearly indicate the $sp^2 \rightarrow sp^3$ rehybridization in SWNT and C_{60} during hydrogenation.

The bands between 125 and 180 meV are due to bending C–H modes [14–17]. There is a clear splitting of the band for two peaks at 146 meV (FWHM ≈ 27 meV) and 166 meV (FWHM ≈ 9 meV) in the INS spectra for SWNT & H sample (Fig. 1a), and only one broad peak is observed for hydrogenated C_{60} at 155 meV (FWHM = 25 meV). The clear splitting of the bending mode peak for SWNT & H is due to strong anisotropy of the potential well for covalently bound H, presumably, in the directions along and perpendicular to the SWNT axis.

Fig. 3 shows the calculated multiphonon neutron scattering contributions for the INS spectra of the annealed samples. A harmonic isotropic approximation was used with assumption that all hydrogen atoms are similar. A good agreement of the calculated and experimental data in the range of the two-phonon band between 280 and 340 meV in the INS spectrum of SWNT & H indicates that two peaks in the bending mode range (at 146 and 166 meV) originate from neutron scattering on the same hydrogen atoms. In the case that the origin of the two bending peaks arises from hydrogen atoms of different type (placed on different symmetry positions), there would be two peaks at 292 and 332 meV. Thus, we can conclude that covalently bound hydrogen atoms occupy equivalent positions in SWNT & H, presumably
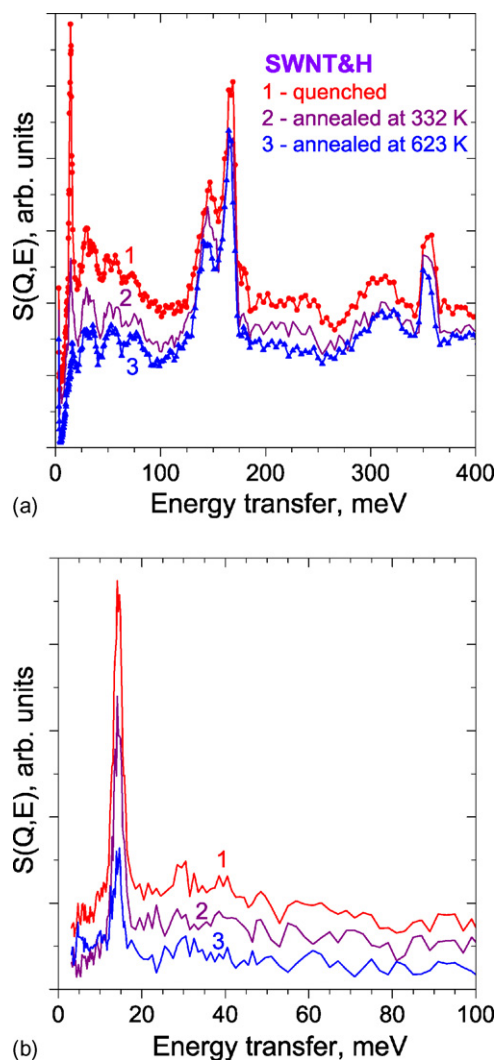

Fig. 1. (a) INS spectra at 15 K of SWNT & H measured for the following sample states: 1-quenched, 2-annealed at 332 K, 3-annealed at 623 K. (b) INS spectra of the molecular H_2 in SWNT & H obtained as difference between the spectra for the sample states: 1-quenched and annealed at 623 K, 2-quenched and annealed at 332 K, 3-annealed at 332 and 623 K.

on the outer surface of the tubes, thus forming exohydrogenated SWNT & H.

The difference spectra between the quenched and annealed hydrogenated SWNT samples are shown in Fig. 1b. A narrow peak at ~ 14.5 meV in the difference spectra is a direct proof of the presence of molecular hydrogen in the quenched SWNT & H sample as well as in the sample after annealing at 332 K. This peak is close to the energy 14.7 meV of the $J = 0 \rightarrow J = 1$ transition for a free H_2 rotor, which is the transition of *para*-hydrogen, *p*-H_2, to *ortho*-hydrogen, *o*-H_2. Rotational states for a quantum rotor are characterized by quantum number J and its z-component m. The rotational energy for a free rotor can be described by $E_J = BJ(J + 1)$, where $B = 7.35$ meV is the rotational constant for hydrogen molecule; and the z-component is not included because the levels are degenerate for a free rotor. Other peaks in the difference spectra for hydrogenated SWNT have small intensity and low statistics to be unambiguously assigned. The content of molecular hydrogen in quenched hydro-
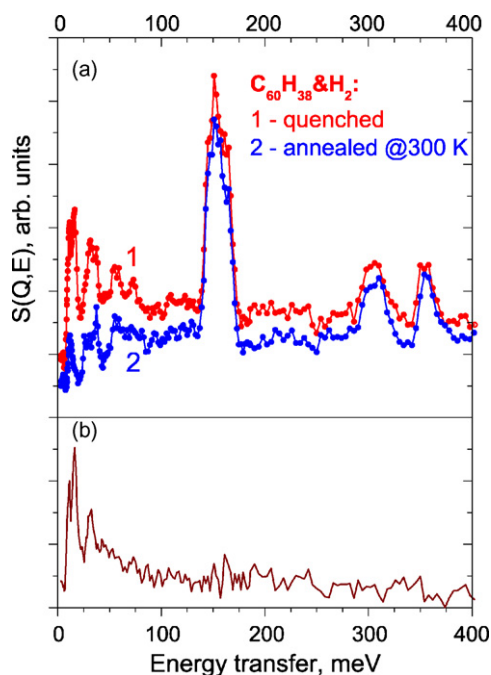
Fig. 2. (a) INS spectra at $T = 15$ K of the quenched $C_{60}H_{38}$ and H_2 (curve 1) and that after annealing at 300 K (curve 2). (b) INS spectrum of molecular H_2 in $C_{60}H_{38}$ obtained as difference between the above curves.

genated SWNT estimated from intensity change in INS spectra after annealing was about 11 wt% compared to covalently bound hydrogen, or ∼0.5 wt% of initial SWNT.

As seen from Fig. 2b, the spectrum of H_2 in $C_{60}H_{38}$ (the difference between the spectra for the quenched and annealed hydrogenated fullerenes) has two broad peaks with maxima at about 10 and 16 meV. The splitting of the $J = 0 \rightarrow J = 1$ peak for
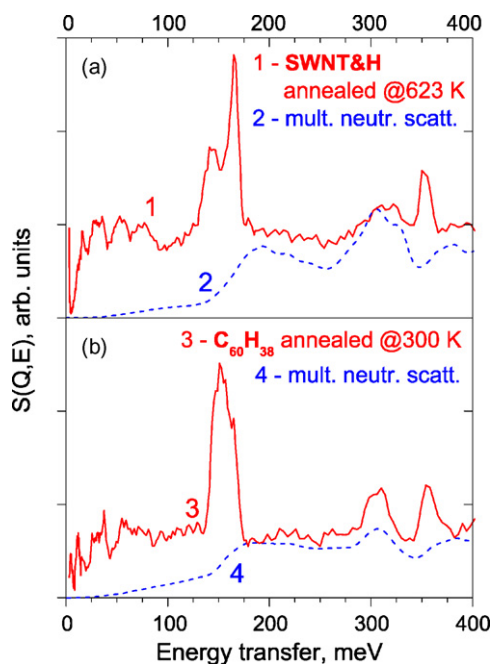

Fig. 3. INS spectra for the annealed states of SWNT & H (a) and $C_{60}H_{38}$ (b) samples; the calculated multiphonon neutron scattering contributions are shown by dashed curves.
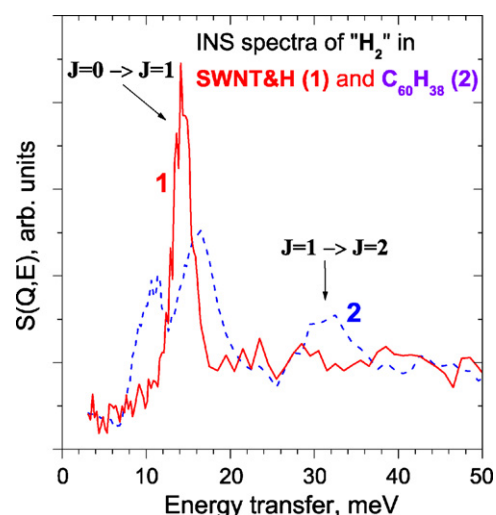

Fig. 4. INS spectra of the molecular H_2 in SWNT & H (curve 1) and in $C_{60}H_{38}$ (curve 2) obtained as difference between the INS spectra for the quenched and annealed sample states.

H_2 in hydrofullerenes indicates that the H_2 molecules occupy the sites in the $C_{60}H_{38}$ unit cell which strongly affect the rotational behavior of hydrogen. Assuming an orientationally dependent potential for H_2 in the form $V(\theta) = V_0(1 - \cos(2\theta))$ [22] and using the shifts of rotational energy levels calculated in [22], we can estimate the strength of the orientational potential for H_2 in $C_{60}H_{38}$ as being about $V_0 = 15$ meV. In addition, the H_2 spectrum in $C_{60}H_{38}$ shows a broad intense peak at ∼31 meV which can be attributed to the $J = 1 \rightarrow J = 2$ transition due to the presence of o-H_2 (the corresponding value for free H_2 rotor is 29.4 meV). The absence of a clear peak at 29.4 meV (see Figs. 1b and 4) in the difference spectra for SWNT indicates a negligible amount of o-H_2 in the quenched SWNT & H sample. This is probably due to the presence of residual catalytic particles in SWNT, which accelerates conversion of o-H_2 to p-H_2 at low temperature.

From the 14.5 meV peak intensity change in the INS spectrum of SWNT & H (Fig. 1) we can conclude that about 65% of H_2 molecules left the sample after the first annealing (at 332 K), but the remaining H_2 molecules (∼35%) were still contained in SWNT & H. After the second annealing at 623 K there were nearly no H_2 molecules left in the sample. The presence of the peak at 14.5 meV after annealing of SWNT & H at 332 K is a direct proof of the existence of molecular hydrogen in SWNT & H sample at temperatures above room temperature (59 °C). In the case of hydrogen adsorption in SWNT at lower pressures (<15 MPa) and temperatures (<300 K), hydrogen molecules completely leave the sample after heating to room temperature in vacuum.

4. Conclusions

Our measurements show that hydrogenated SWNT and fullerenes quenched to 80 K under high hydrogen pressure ($P = 3$ GPa) consist of SWNT & H or $C_{60}H_{38}$ molecules with covalently bound hydrogen, and interstitial molecular hydrogen that leaves the sample on heating. The molecular hydrogen is

almost rotationally free in SWNT & H, but it exhibits a highly perturbed rotational behavior in the hydrofullerenes.

Acknowledgements

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