NMR of hydrogen adsorbed on carbon nanotubes

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Abstract

Hydrogen gas is introduced to multi-walled carbon nanotubes and ^{1}H nuclear magnetic resonances are measured as the functions of hydrogen gas pressure and temperature. The resonance frequency is shifted in inverse proportion to temperature due to the super-paramagnetic Fe catalysts remained in the nanotubes. By the differences in relaxation times, the signal from hydrogen adsorbed on carbon nanotubes is differentiated from that of gas phase hydrogen.

Key words: hydrogen adsorption; carbon nanotubes; ^{1}H NMR

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1. Introduction

Since the discovery of carbon nanotubes there have been explosive interests in using them for hydrogen storage purposes. [1] The curved surface and large surface area of carbon nanotubes make the material particularly attractive. [2] Much of the theoretical and experimental efforts are devoted to find out where the hydrogen goes and which form it takes. [3–5]

Nuclear magnetic resonance(NMR) is a valuable tool to examine the hydrogen adsorbed on the surface [6] or confined in a cage. [7] It is especially so since NMR is sensitive not only to the spin states but also to the rotational states of hydrogen molecules.

2. Experimental

We use the multi-walled carbon nanotube obtained from a local company. [8] Its outer diameter and length are about 50nm and $> 60\mu$m, respectively. About 1mg of the powder form sample is transferred snugly to a glass tube and placed inside a rf coil of 3mm diameter. A home made pulse NMR spectrometer is used with a 5T superconducting magnet(Oxford). The spectrometer is tuned to the proton resonance using water sample. The 90° pulse width is 4μs. The sample is evacuated to $< 10^{-5}$ Torr prior to introduction of hydrogen gas. Ultrapure hydrogen gas (impurity $<$ 1ppm) is introduced and the gas pressure is measured by a capacitance manometer(MKS). Sample temperature is controlled with a continuous gas flow cryostat(Oxford).

3. Results and discussions

At room temperature, the NMR signal intensity increases with the gas pressure, however, the spectrum does not change in its position nor width.

When temperature is changed, the resonance spectra changes as shown in Fig. 1. The sample was sealed in a can with 3atm of hydrogen gas at room temperature. As the temperature is lowered the resonance peak shifts to higher frequencies. The shift is inversely proportional to absolute temperature, indicating a paramagnetic shift.(Fig. 2) The intensity of signal increases almost following the Curie's law. The width of the spectrum also increases. The shift and width are due to the local field and its distribution, respectively, generated by the Fe catalysts remained in the carbon nanotubes. The catalysts are small particles and reveal super-paramagnetism.

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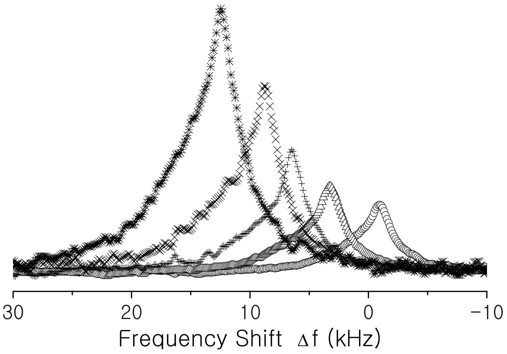

Fig. 1. The fast Fourier transform of free induction decay signals at T = 70(∗), 85(×), 96(+), 150(△), and 250K(○). Origin of the frequency corresponds to the resonance frequency of water at room temperature.

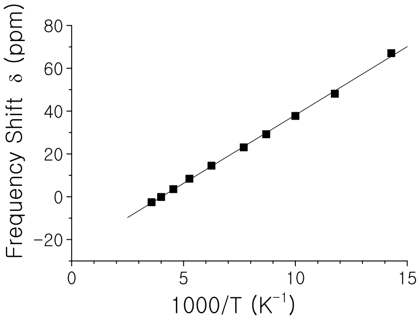

Fig. 2. The resonance frequency shift δ from that of water at room temperature as a function of inverse temperature. The straight line is a fit to the paramagnetic shift($\propto 1/T$).

The spin-lattice relaxation time T_1 and spin-spin relaxation time T_2 are measured by using the inversion-recovery and spin-echo techniques, respectively. Both relaxation measurements indicate double exponential recovery behavior due to the presence of gas phase hydrogen which bears shorter relaxation times. [9] Only about 10% of the signal intensity is from the adsorbed hydrogen on carbon nanotube. The spectrum of adsorbed hydrogen can be obtained by the difference in two spectra obtained by using long($t_r \gg T_{1,\ \mathrm{long}}$) and short($T_{1,\ \mathrm{long}} \gg t_r \gg T_{1,\ \mathrm{short}}$) repetition times t_r of the measuring pulse sequence(180° - t - 90° - t_r). The spectra are located at the same frequencies with the gas phase component but with broader widths.

The long and short components of the relaxation times are plotted as the functions of temperature in Fig. 3. The spin-lattice relaxation time $T_{1,\ \mathrm{long}}$ of the adsorbed hydrogen shows a Korringa type relation ($T_{1,\ \mathrm{long}}T$ = const) reflecting metallic nature of the multi-walled carbon nanotubes. T_2 of the gas phase hydrogen is known to be 0.8 T_1, [9] however, the data in Fig. 3 shows $T_{2,\ \mathrm{short}} \ll T_{1,\ \mathrm{short}}$ suggesting other relaxation mechanism. Both $T_{2,\ \mathrm{short}}$ and $T_{2,\ \mathrm{long}}$ show minima at around 160K and 140K, respectively, which might be provided by the diffusion of hydrogen molecules in both gaseous and adsorbed phases under the thermally fluctuating magnetic field from Fe catalysts.

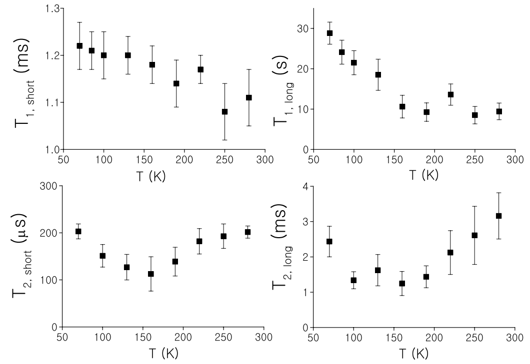

Fig. 3. Temperature dependence of the short and long components of the spin-lattice(T_1) and spin-spin(T_2) relaxation times.

Acknowledgements

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