13C NMR study of single-walled carbon nanotubes

Kyuhong Lee\textsuperscript{a,*}, K.H. Kang\textsuperscript{a}, B.J. Mean\textsuperscript{a}, Moohee Lee\textsuperscript{a,*}\textsuperscript{,1}, Jae-Kap Jung\textsuperscript{b,1,2}, Kwon-Sang Ryu\textsuperscript{b,1,2}, Young Hee Lee\textsuperscript{c}

\textsuperscript{a}Department of Physics and ReCOD, Konkuk University, #1 Hwayang-dong Kwangjin-gu, Seoul 143-701, Korea
\textsuperscript{b}Electric and Magnetism Group, Korea Research Institute of Standards and Science, Daejeon 305-600, Korea
\textsuperscript{c}Center for Nanotubes and Nanostructured Composites, Department of Physics, Sungkyunkwan University, Suwon 440-746, Korea

Abstract

We have performed 13C nuclear magnetic resonance (NMR) measurements on single-walled carbon nanotubes. Spectrum, shift, linewidth, and $T_1$ have been measured as a function of temperature from 4.6 K to 200 K under the magnetic field of 4.7 T. Spectrum shows a narrow lineshape for the 13C nucleus. Shift is very small around 100 ppm and shows no significant change in the whole temperature range. The linewidth becomes broader with decreasing temperature from 13 kHz at 200 K to 22 kHz at 4.6 K. The spin–lattice relaxation recovery is made of three channels of relaxation like other nanotubes. However, all three relaxation rates are very weakly dependent on temperature. While the fastest rate is found to come from remaining catalysts after synthesis, the other two rates from metallic and semiconducting parts of the nanotubes seem to be altered during exposure to the atmosphere.

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The recently discovered carbon nanotubes have amazing mechanical and electronic properties. These originate from their quasi-one-dimensional structure and the graphite-like arrangement of the carbon atoms in the shells. Very high chemical stability and mechanical strength have made the carbon nanotube preferable for composite materials in nanotechnology.

The single-walled carbon nanotubes (SWNTs) can be either metallic or semiconducting depending on its structural parameters [1,2]. This boosts up nanotubes as central elements in the vast area...
of applications such as nanodevices, field emitters, gas sensors, hydrogen storage in fuel cells, and DNA recognition technology.

Even though SWNTs have different electronic properties depending on their chirality and diameters [3], it is difficult to selectively synthesize SWNTs that have appropriate electronic properties for each application, namely, the chirality distribution and its dependence on synthesis conditions, are not known. The density of states and its dependence on tube diameters remain to be investigated. Furthermore, it should be explored how ambient conditions influence the properties of SWNTs. Since NMR is a sensitive probe for local electronic structures, we take $^{13}$C NMR measurements for SWNTs.

SWNTs were synthesized by the electric arc discharge of carbon rods in the helium gas environment at 100 Torr. The catalyst made of Fe: Ni: Co: S = 1: 1: 1: 0.227 was mixed with carbon graphite by an amount of 5%. The $^{13}$C isotope was enriched up to 30% by the nominal percent before the arc discharge. The thermal purification by annealing at 450°C was performed several times to get rid of amorphous carbons. The chemical purification by 6 mol of HCl acid was employed to remove the remaining catalysts. Scanning electron micrograph (SEM) images confirm that both amorphous carbons and catalysts were almost completely removed after the thermal and chemical purifications, respectively. $^{13}$C NMR measurements were carried out at 4.7T by using our home-made pulsed spectrometers with a quadrature detection scheme. $^{13}$C NMR shift, spectrum and the spin-lattice relaxation time $T_1$ were measured in the temperature range of 4.6 ~ 200 K.

The $^{13}$C NMR spectrum shows a narrow peak, as shown in Fig. 1. While the shift is independent of temperature around $\approx 100$ ppm, the linewidth increases from 13 kHz at 200 K to 22 kHz at 4.6 K.

The spin–lattice relaxation time $T_1$ is measured by the full recovery and the progressive saturation techniques. The spin–lattice relaxation recovery shows a non-exponential profile, as shown in Fig. 2, throughout the whole temperature range. The recovery is found to be made of three exponential parts; $1 - M(t)/M_0 = A_S \exp(-t/T_{1S}) + A_m \exp(-t/T_{1m}) + A_L \exp(-t/T_{1L})$, where S, m, and L stand for, respectively, short, middle and long components. Fig. 2 compares double and triple exponential fits for the full recovery of relaxation at 12 K. It is clear that three exponential parts are necessary to fit the full recovery at 12 K. Since $T_1$'s are long and the full recovery takes more time to measure, the progressive pulse sequence is utilized at other temperatures. The fitting formula is extended for the triple relaxation channels.

Analyzing the recovery, we find that all three channels are very weakly dependent on temperature. $T_{1S}$ is about 0.3 s and independent of temperature. $T_{1m}$ is about 3 s and almost

![Fig. 1. The $^{13}$C NMR spectra at 4.7T.](image1)

![Fig. 2. The spin–lattice relaxation recovery of $^{13}$C NMR.](image2)
independent of temperature whereas $T_{1L}$ is about 36 s throughout the temperature range. The relative intensity of the three channels is roughly same around $A_S:A_m:A_L = 3:4:3$ throughout the temperature range. Therefore, no temperature dependent channels in our $T_1$ recovery are observed.

In general, different relaxation channels are identified by magnitude and temperature dependence of relaxation rates. We note that other NMR measurements on SWTs reported that the recovery was made of three relaxation channels [4–6]. They also observed the fastest (shortest) channel coming from magnetic impurities, whose rate and intensity were consistent with our $T_{1S}$ and $A_S$ respectively. Therefore, we identify $T_{1S}$ as a relaxation channel due to magnetic impurities remaining after chemically removing the catalysts. SEM images confirm that the trace amount of magnetic impurities still persists.

However, other two channels, $T_{1m}$ and $T_{1L}$, are found to be different from previous measurements [4–6]. Their results suggest that the spin–lattice relaxation recovery shows metallic and semiconducting parts of SWTs. The metallic part with intermediate values of $T_1$ is measured to show the Korringa behavior, $1/T_1 \propto T$. Also, the semiconducting part is reported to follow the Korringa behavior at high temperature above 200 K with a small density of states. On the contrary, our $1/T_{1m}$ and $1/T_{1L}$ show almost no temperature dependence with higher rates. This behavior is commonly observed as relaxation to paramagnetic centers. The paramagnetic centers may be developed in the nanotubes whereas the magnetic impurities come from the remnant catalysts and are extrinsic to the nanotubes.

Thus our $T_{1m}$ and $T_{1L}$, otherwise exhibiting metallic and semiconducting behavior with strong temperature dependence, are obviously altered by exposure to the atmosphere [4]. Interaction of SWTs with oxygen in the atmosphere is highly possible. The reaction with oxygen is suggested. In detail, the adsorption of paramagnetic oxygen molecules on the surface of the SWT bundles or the chemical reaction of oxygen atom with carbon generating change in local electronic structure are possible scenarios.

References