

Heteronuclear carbon nanotubes

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Abstract. The physical properties of double-wall carbon nanotubes (DWCNT) with highly ¹³C enriched inner walls were studied with Raman spectroscopy and nuclear magnetic resonance (NMR). An inhomogeneous broadening of the vibrational modes is explained by the random distribution of ¹²C and ¹³C nuclei based on *ab-initio* calculations. The growth of DWCNTs from natural and ¹³C enriched fullerene mixtures indicates that carbon does not diffuse freely along the tube axis during the inner tube growth. The high curvature of the small diameter inner tubes manifests in an increased distribution of the NMR chemical shift tensor components.

INTRODUCTION

Isotope engineering (IE) of materials provides an important degree of freedom for both fundamental studies and applications. The change in phonon energies upon isotope substitution, while leaving the electronic properties unaffected, has been used repeatedly to identify vibrational modes¹ and gave insight into underlying fundamental mechanisms, such as phonon-mediated superconductivity². The SWCNT specific enrichment of SWCNTs was reported recently^{3,4}. In brief, highly ¹³C enriched fullerenes are encapsulated inside SWCNTs. After a high temperature heat treatment, the inner fullerenes are transformed to an inner tube that is also highly ¹³C enriched. It was also shown that there is no carbon exchange between the inner and outer shells during the synthesis. The advantage of this method is that other carbonaceous phases, such as amorphous carbon or graphite are not expected to be ¹³C enriched. This would be particularly advantageous for NMR studies, where a high contrast between the highly ¹³C enriched inner tubes and other carbon phases, thus a highly SWCNT specific signal is expected.

Here, we study further this heteronuclear carbon nanotube system. An inhomogeneous, isotope distribution related broadening is observed that is explained by *ab-initio* calculations. It is shown that inner tube growth can be studied with the help of carbon isotopes. The NMR studies on the material indicate that other carbon phases are not ¹³C enriched and the NMR signal is indeed specific to the inner tubes. A curvature related anomalous distribution of chemical shift tensor components is observed.

EXPERIMENTAL

The sample preparation was described previously^{3,4}. In brief ¹³C isotope enriched fullerenes and commercial SWCNT samples were used to prepare fullerene peapods C₆₀,C₇₀@SWCNT. We used two grades of ¹³C enriched fullerene mixtures: 25 and 89 %. Fullerene filling and DWCNT transformation was performed following Ref. 5 and 6, respectively. DWCNTs with different ¹³C enrichment grades are denoted as ^{Nat}C-, ¹³C_{0.25}- and ¹³C_{0.89}-DWCNT. Vibrational analysis was performed on a Dilor xy triple Raman spectrometer. First principles calculations were performed with the Vienna ab initio Simulation Package (VASP)⁷. Magic angle spinning (MAS) and static ¹³C-NMR spectra were measured at ambient conditions using a Chemagnets (Varian Inc.) MAS probe at 7.5 Tesla. The ¹³C-NMR spectra were obtained by a Fourier transformation of the free induction decay following the excitation pulse.

RESULTS AND DISCUSSION

The Raman modes, including the radial breathing (RBM) and the G modes of DWCNTs with highly ¹³C enriched inner walls were discussed previously^{3,4}. In brief, an overall downshift of all the modes was observed for the enriched inner tubes. In the simplest continuum approximation, the shift originates from the increased mass of the inner tube walls. This gives $(\nu_0 - \nu)/\nu_0 = 1 - \sqrt{\frac{12 + c_0}{12 + c}}$, where ν_0 and ν are the original and downshifted phonon energies, respectively, c is the ¹³C enrichment of the inner walls, $c_0=0.011$ is the natural abundance of ¹³C in carbon.

The validity of the continuum approximation for the RBM was verified by performing first principles calculations on the $(n,m)=(5,5)$ tube as an example. In the calculation, the Hessian was determined by DFT. A large number of random ¹³C distributions were generated and the RBM frequencies were determined from the diagonalization of the dynamical matrix for each individual distribution. We observed that the distribution of the RBM frequencies can be approximated by a Gaussian whose center and variance determine the isotope shifted RBM frequency and the spread in these frequencies. The difference between the shift determined from the continuum model and from the *ab-initio* calculations is below 1 %.

The broadening for the ¹³C enriched inner tubes was observed previously^{3,4} and is explained by calculations herein.

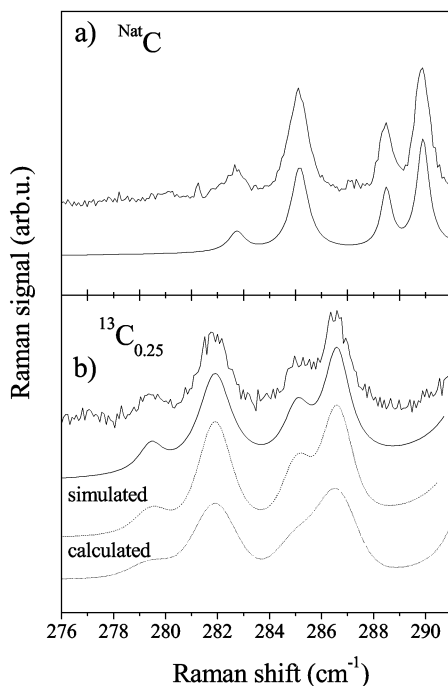


Figure 1. RBMs of some inner tubes at 676 nm laser excitation at 90 K with 0.5 cm^{-1} spectral resolution. a) ^{12}C , b) $^{13}\text{C}_{0.25}$. Smooth solid curves are the line-shapes after deconvolution by the spectrometer response. The dashed curve is a simulated line-shape with an extra Gaussian broadening to the intrinsic lines of the ^{12}C material. The dotted curve (lowest) is calculated line-shape (see text).

In Fig. 1a-b. we show the RBMs of some inner tubes for the ^{12}C and $^{13}\text{C}_{0.25}$ samples. Smooth solid curves are the line-shapes after deconvolution with the Gaussian response of our spectrometer. In Fig. 1a, this is a Lorentzian, but in Fig. 1b, the line-shape still contains a Gaussian component, as discussed below. The FWHMs of the resulting line-shapes are 0.76(4), 0.76(4), 0.44(4), 0.54(4) and 1.28(6), 1.30(6), 1.12(6), 1.16(6) for the inner tube RBMs shown in Fig. 1 of the ^{12}C and $^{13}\text{C}_{0.25}$ materials, respectively. The origin of the extra broadening is due to the random distribution of ^{12}C and ^{13}C nuclei. We found that the ratio between the half width of extra broadening and the shift, $\Delta\nu/(\nu_0-\nu)$, is approximately 0.19 for a 30 % ^{13}C enriched sample. The corresponding broadened line-shapes are shown by dotted curves in Fig. 1b. When the magnitude of the Gaussian randomness related broadening was fit (shown as dashed curve in Fig1b), we found that $\Delta\nu/(\nu_0-\nu)=0.15$. Similar broadening was observed for the 89 % sample which can also be reproduced by the calculation.

The freedom to manipulate the carbon enrichment on the inner walls allows to study the mechanism of inner tube growth. In Fig. 2. we show the RBMs for ^{12}C -, $^{13}\text{C}_{0.25}$ -DWCNTs, together with a ^{13}C -DWCNT sample that was produced from a peapod containing mixed ^{12}C - C_{60} and $^{13}\text{C}_{0.25}$ - C_{60} . The downshift of the inner RBMs for the ^{13}C -DWCNT sample lies half-way between the corresponding modes for the ^{12}C - and $^{13}\text{C}_{0.25}$ -DWCNT samples reflecting the $\sim 12\%$ overall enrichment of the inner walls that is a result of the 1:1 mixing of natural and enriched fullerenes.

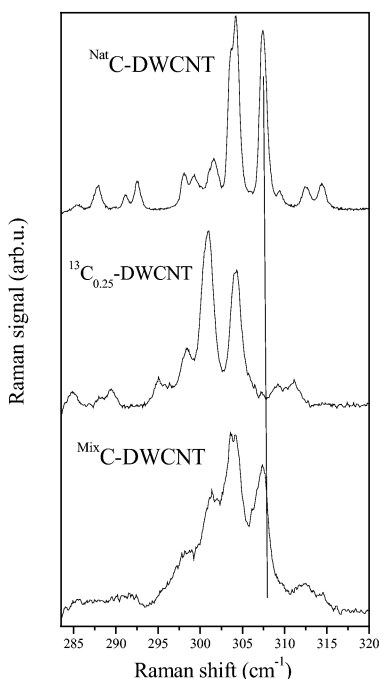


Figure 2. Inner tube RBMs at 676 nm laser excitation with 0.5 cm^{-1} spectral resolution for ^{12}C -, $^{13}\text{C}_{0.25}$ -, and ^{13}C -DWCNT. The vertical solid line is a guide to the eye to show the downshift of a mode for the ^{13}C -DWCNT sample.

However, the widths of the inner tube modes are larger than expected from the homogeneously random distribution of ^{12}C and ^{13}C nuclei. This suggests that the two types of nuclei cannot form a homogeneously random mixture for such inner tubes, and instead ^{13}C rich and poor region alternates along the tube axis that gives rise to an increased inhomogeneity in the isotope distribution. This is supported by cluster-model simulations where the ^{13}C rich and poor regions with 60 randomly distributed nuclei vary randomly along the tube axis⁸. This proves that carbon cannot diffuse along the tube axis during the growth of the inner tube from fullerenes, and is stuck to its original position. This supports the growth model of inner tubes from pre-formed dimers with Stone-Wales transformations⁹ rather than e.g. their growth through a complete evaporation into C_2 gas units.

The ^{13}C isotope enrichment of the inner wall of the DWCNTs allows NMR measurements with unprecedented contrast with respect to non-enriched carbon phases³. In Fig. 3, we show the static and MAS spectra of ^{13}C enriched DWCNTs, and the static spectrum for the SWCNT starting material. The typical chemical shift anisotropy (CSA) powder pattern is observed for the SWCNT sample in agreement with previous reports^{10,11}. However, the static DWCNT spectrum cannot be explained with a simple CSA powder pattern even though the spectrum is dominated by the inner tube signal. The structure of the spectrum suggests that the chemical shift tensor parameters are distributed for the inner tubes. It is the result of the higher curvature of inner tubes as compared to the outer ones: the variance of the diameter distribution is

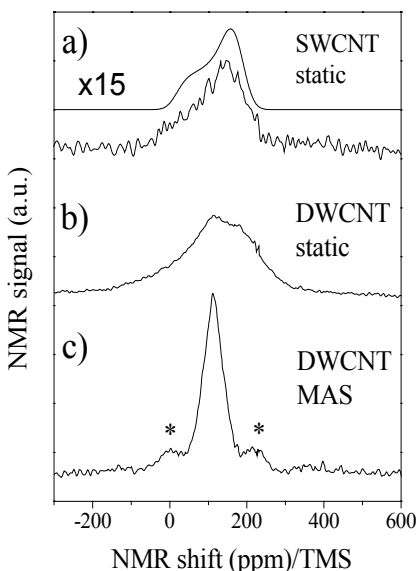


Figure 3. NMR spectra normalized by the total sample mass, taken with respect to the tetramethylsilane shift. (a) Static spectrum for non-enriched SWCNT enlarged by a factor 15. Smooth solid line is a CSA powder pattern simulation with parameters published in the literature. (b) Static and (c) MAS spectra of $^{13}\text{C}_{0.89}$ -DWCNT, respectively. Asterisks show the sidebands at the 8 kHz spinning frequency.

the same for the inner and outer tubes but the corresponding bonding angles show a larger variation. In addition, the residual line-width in the MAS experiment, which is a measure of the sample inhomogeneity, is 60(3) ppm, i.e. about twice as large as the ~ 35 ppm found previously for SWCNT samples^{10,11}.

ACKNOWLEDGMENTS

This work was supported by the Austrian Science Funds (FWF) project Nr. 17345, by Hungarian State Grant (OTKA) Nr. T038014, and by the EU projects BIN2-2001-00580 and MEIF-CT-2003-501099 grants.

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