Structural properties of carbon nanotubes derived from ^{13}C NMR

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We present a detailed experimental and theoretical study on how structural properties of carbon nanotubes can be derived from ^{13}C NMR investigations. Magic angle spinning solid state NMR experiments have been performed on single- and multiwalled carbon nanotubes with diameters in the range from 0.7 to 100 nm and with number of walls from 1 to 90. We provide models on how diameter and the number of nanotube walls influence NMR linewidth and line position. Both models are supported by theoretical calculations. Increasing the diameter D, from the smallest investigated nanotube, which in our study corresponds to the inner nanotube of a double-walled tube to the largest studied diameter, corresponding to large multiwalled nanotubes, leads to a 23.5 ppm diamagnetic shift of the isotropic NMR line position δ. We show that the isotropic line follows the relation $\delta = 18.3/D + 102.5$ ppm, where D is the diameter of the tube and NMR line position δ is relative to tetramethylsilane. The relation asymptotically tends to approach the line position expected in graphene. A characteristic broadening of the line shape is observed with the increasing number of walls. This feature can be rationalized by an isotropic shift distribution originating from different diamagnetic shielding of the encapsulated nanotubes together with a heterogeneity of the samples. Based on our results, NMR is shown to be a nondestructive spectroscopic method that can be used as a complementary method to, for example, transmission electron microscopy to obtain structural information for carbon nanotubes, especially bulk samples.

I. INTRODUCTION

Since their discovery in 1991,[1] carbon nanotubes (CNTs) have attracted attention due to their extraordinary structural, mechanical, and electronic properties,[2] which make them interesting for various applications in our daily life.[3] However there are two main problems in developing nanotube applications: as-synthesized samples usually contain a mixture of CNTs with different structural, physical, and chemical properties,[4–6] and there is a lack of experimental techniques that can be used to achieve information on bulk CNT materials. In recent years some progress has been made to improve the purification process[7] and to increase the selectivity in diameter and chirality in the synthesis process of carbon nanotubes.[8] Also methods to selectively postpurify carbon nanotubes according to their electronic properties,[9,10] or their diameter[11] have been developed. Still however, the information about bulk samples relies on techniques such as tedious statistical electron microscopy studies,[12] x-ray diffraction,[13,14] optical absorption,[15] or Raman scattering.[16] However, it appears that even a combination of these experimental techniques, which is very time consuming, still results in insufficient structural information for a given bulk sample.[17] Also few of the techniques mentioned above can be used to get information on both multiwalled (MWNTs) and single-walled carbon nanotubes (SWNTs). The need of a new or a complimentary information source would therefore be advantageous. ^{13}C NMR has shown to be an excellent tool for characterizing fullerenes,[18–23] fullerenes inside carbon nanotubes,[24,25] graphite,[26] and

conducting polymers.[27,28] For carbon nanotube studies, ^{13}C NMR has not been used as frequently although some studies have been reported recently to study their electronic properties,[29–31] their magnetic properties,[32] or the dynamic properties of molecules encapsulated inside carbon nanotubes.[25,33] In particular, theoretical studies have been performed to investigate the electronic structures and dynamics of SWNTs[30,34,35] and MWNTs.[36] The results have revealed interesting features of the response of CNTs in magnetic fields. Latil *et al.* reported that ^{13}C NMR can be able to distinguish between the metallic and insulator character of SWNTs,[34] although a later study[37] claims that the difference in line position is smaller than claimed in the previous report by Latil *et al.* The study of ^{13}C-enriched single-wall carbon nanotubes by Hayashi *et al.* reveals that the linewidth of the main isotropic peak in magic angle spinning (MAS) spectra is about 30 ppm, which reflects a distribution of diameter and helicity.[35] An even fewer number of studies are reported for MWNTs. Yamamoto *et al.* studied the magnetic response of MWNTs together with the calculated field distribution of the NMR line shape in MWNTs and concluded that the NMR line is broadened roughly proportional to the number of walls.[36]

In this work, we provide additional data in the first detailed study of how diameter and number of walls of the nanotubes influences NMR linewidth and line position. Our results are based on the experimental and theoretical results obtained on different CNTs with a wide range of diameters and wall numbers.

TABLE I. Structural parameters: diameters and number of walls extracted from statistics on High resolution transmission electron microscopy (HRTEM) images and ^{13}C NMR parameters: $\delta = M_1$ and parameter $\Delta = \sqrt{M_2}$ calculated from ^{13}C NMR isotropic lines.

Samples	Outer diameter distributions (*nanometers*)	Number of walls	δ (*part per million*)	Δ (*parts per million*)
DWNTs (DW1) inner CNT 25% ^{13}C	0.7 ± 0.1	$1+1$ (25% ^{13}C)	125.8	19.5
SWNTs HiPCo (SW2)	1.1 ± 0.2	1	123.8	18.9
SWNTs Carbon Solution (SW1)	1.4 ± 0.2	1	118.8	16.8
DWNTs Swan (DW2)	$(1.3 - 3.5) \pm 0.4$	2 or 3	116.3	25.8
MWNTs Nanocyl (MW4)	$(4 - 17) \pm 2$	15 ± 5	106.1	44.8
MWNTs CoMgO (MW1)	$(4 - 20) \pm 2$	15 ± 5	104.7	44.2
MWNTs CoNaY (MW2)	$(8 - 50) \pm 2$	90 ± 20	103.4	54.7
MWNTs Pyrolysis (MW3)	$(10 - 100) \pm 2$	60 ± 10	102.3	51.6

II. EXPERIMENTAL SECTION

In our study, eight CNT samples with different structural characteristics, particularly with respect to their diameter and number of walls, were selected. The characteristics of the samples are presented in Table I. The SWNT sample (SW1) was purchased from Carbon Solutions, Inc., and was filtered through a magnetic field of 1.1 T to remove residual catalyst.[7] The SWNT sample (SW2) was produced by high-pressure CO disproportionation over Fe catalyst (HiPco technique) at CNI, Houston, Texas.[38] A double-walled CNT (DWNT) sample (DW1) was fabricated by annealing peapods under dynamic vacuum for 48 h at 1250 °C. The peapods were prepared using 25% ^{13}C enriched C_{60} vapor during 10 h at 650 °C for filling CNTs, followed by 1 h postannealing in dynamic vacuum to remove nonencapsulated fullerenes.[39–41] A high-purity DWNT sample (DW2), synthesized by the catalytic carbon vapor deposition (CCVD) technique, was purchased from Thomas Swan and Co., England. The MWNT samples named (MW1) and (MW2) were provided by CRMD Laboratory in Orleans, France. They were prepared, respectively, by catalytic decomposition of acetylene diluted in nitrogen at 600 °C on $Co_x Mg_{1-x}$[42] and over Co incorporated zeolite NaY as described elsewhere.[43] After synthesis, MW1 and MW2 were posttreated to remove the catalysts by dissolution in 40% HF. After repeated washings in distilled water followed by filtration, the remaining carbon phase was annealed for 1 h at 2400 °C under flowing argon.

The MWNT sample (MW3) provided by Laboratoire Francis Perrin, CEA Saclay in France was synthesized using liquid aerosol pyrolysis containing both carbon and catalyst sources, which enables clean and well-aligned carbon nanotubes.[44] The MWNT sample (MW4) was synthesized using the CCVD and was purchased from Nanocyl (3100 grade) with a purity higher than 95%.

For each CNT sample, the diameter distribution and the number of walls have been estimated with the help of statistical measurements on transmission electron microscopy (TEM) micrographs as presented in Fig. 1. Entangled CNTs have not been counted, and only parts of the images where CNTs are isolated have been considered in the statistics. CNTs were segmented into several measured sections where the diameters and number of walls are similar.

The TEM micrographs were obtained using a Philips CM20 microscope with LaB_6 filament. The operating voltage was set to 200 kV, and the magnification to 200,000. Images were collected in bright field mode. ^{13}C NMR experiments were carried out using Bruker ASX200 and Tecmag Apollo spectrometers at a magnetic field of 4.7 T and at Larmor frequency of 50.3 MHz. All NMR line positions are relative to tetramethylsilane (TMS).

III. RESULTS AND DISCUSSION

The estimated structural parameters using the statistical method described above are summarized in Table I. The diameters of our investigated samples and the number of walls were found to range from 0.7 to 100 nm and from 1 to 90, respectively. The number of walls was estimated by considering the graphitic interlayer spacing of 0.335 nm.

Figure 2 shows high-resolution MAS ^{13}C NMR measurements on the eight different CNT samples. With higher number of walls in the nanotube samples, a diamagnetic shift is observed, as seen by, for example, comparing the spectra for samples SW2 and MW3. The particular case of sample DW1 in Fig. 2(a) needs special attention. It reveals two peaks
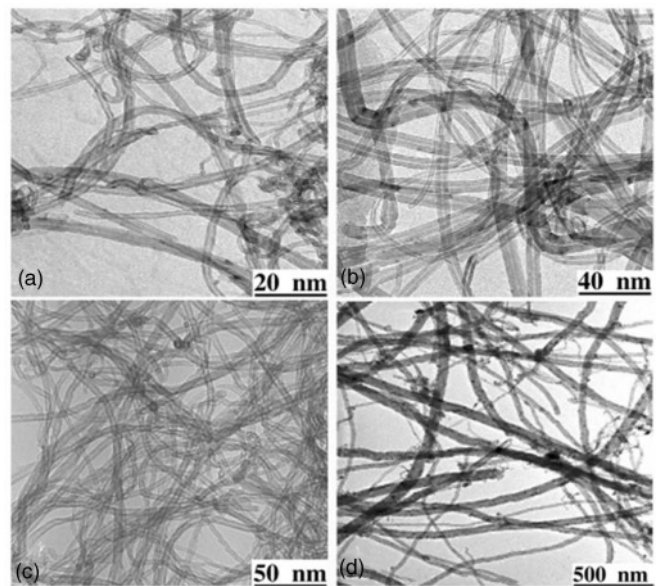

FIG. 1. High resolution transmission electron microscopy (HRTEM) of different MWNTs: (a) MW1, (b) MW2, (c) MW4, and (d) MW3.
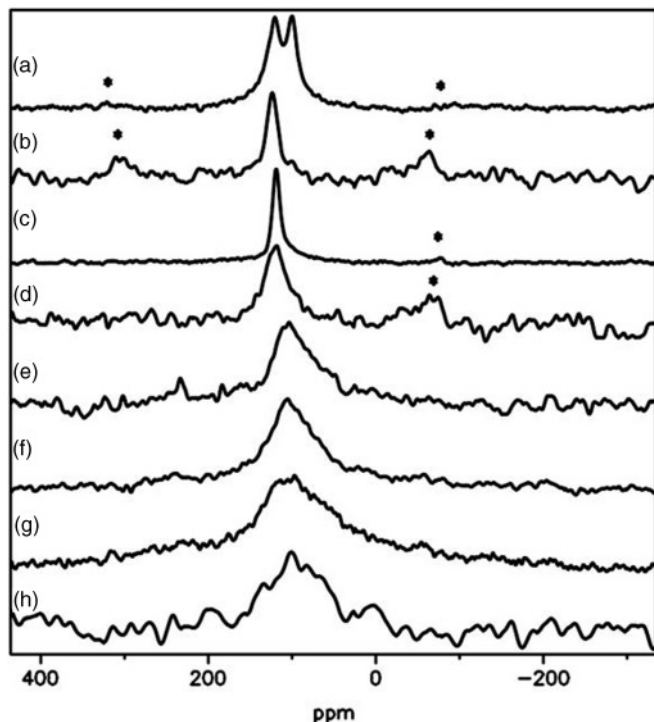
FIG. 2. ^{13}C high-resolution MAS NMR spectra on single-, double-, triple-, and MWNTs. (a) DW1, (b) SW2, (c) SW1, (d) DW2, (e) MW4, (f) MW1, (g) MW2, and (h) MW3. The structural characteristics of each sample are listed in Table I. (sidebands are denoted by *).

FIG. 3. ^{13}C NMR isotropic chemical shifts for CNTs versus the inverse of their diameter (D): experiments (circles), *ab initio* calculation (squares) and calculation performed by Sebastiani and Kudin *et al.* for different tube diameters (triangles).[48] The dashed line corresponds to δ (see Eq. (1)), the best fit of the experimental data.

that are both signatures of the 0.7-nm inner CNTs. The NMR signals for this double-walled nanotube sample are strongly dominated by the 25% ^{13}C enriched inner tube since the signal of the outer CNT with natural abundance of 1% is very weak, in agreement with the study by Simon *et al.*[45] and Singer *et al.*[46] As predicted by Marques *et al.*,[47] the peak at 99.2 ppm can be assigned to the diamagnetically shifted NMR line of inner CNTs due to ring currents from π electrons circulating on the outer CNTs. The second peak at 125.8 ppm is also attributed to the inner CNTs but represents carbons in the vicinity of defects on the outer CNTs, which are known to cancel this diamagnetic shielding.[25,32,48] Hence, the latter line position (125.8 ppm) can be considered as a good estimation of the chemical shift for a free-standing CNT with a diameter of 0.7 nm. For each sample, the average isotropic chemical shift was estimated from the first moment of the isotropic lines. These are listed in Table I. First moment were found to range from 125.8 ppm for the CNTs with the smallest diameter to 102.3 ppm for the largest nanotubes. The latter line position is in good agreement with the value expected for a single graphene sheet, which can be seen as a CNT with an infinite diameter.[49,50] The experimental data are presented in Fig. 3 and can be fitted by the following expression:

$$\delta = \frac{18.3}{D} + 102.5 \text{ (ppm relative to TMS)}, \qquad (1)$$

where δ is the ^{13}C NMR isotropic chemical shift, and D is the average diameter of the CNTs in nanometers. The relation above allows estimating the diameter and the diameter
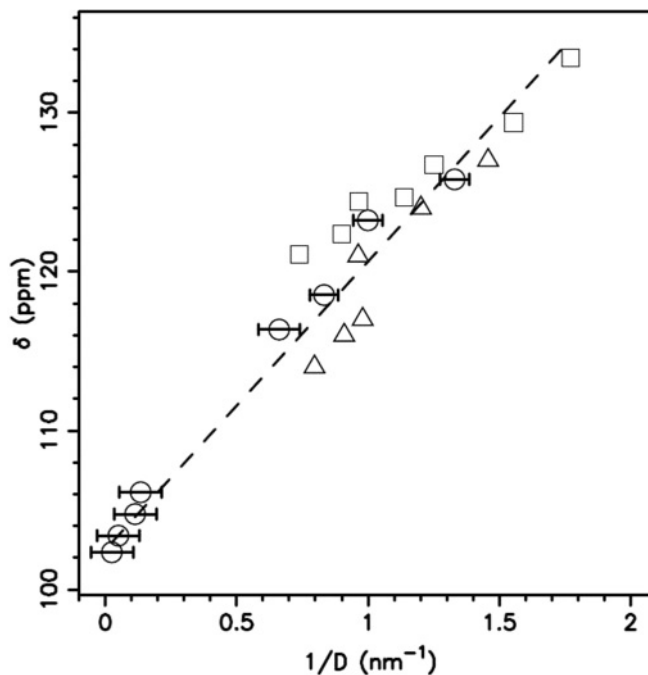
distribution of an unknown CNTs sample by measuring δ, the average ^{13}C NMR isotropic line position.

We now focus on the broadening of the ^{13}C NMR isotropic lines as observed when passing from single to MWNTs. From the second moment M_2 of the isotropic lines, an important parameter $\Delta = \sqrt{M_2}$, can be estimated for each CNT spectrum. The results are listed in Table I, and in Fig. 4 Δ versus the number of walls is presented. Several effects contribute to the line broadening. It has been shown that residual catalysts used for the synthesis have a dramatic effect[51] on the isotropic NMR linewidth. However, in our experiments, careful effort has been made to select and purify samples in order to investigate CNT samples with a minute quantity of impurities.[7] Hence, the main contribution to Δ is expected to be due to diamagnetic shielding[47,48,52] related to the encapsulation of CNTs inside other CNTs and due to a mixture of CNTs with different structural characteristic.[36,52] For single-walled nanotubes, Δ was found to be about 18 ppm, while for double-walled nanotubes, it is about 26 ppm. For N > 10 a linear dependence $\sim 45.2 + 0.14$ N can be fitted, where N is number of walls of the CNT sample and $\Delta = \sqrt{M_2}$, with the second moment measured in parts per million. The inset of Fig. 4 shows the fit with principal values of the chemical shift tensors of sample DW2 and MW3 (the resulting parameters are indicated by arrows). The tensors fits were performed following the procedure described in Refs. 47 and 53. In this procedure the δ_{11} component is a principal value of the tensor, as a consequence of their uniaxial character, while the two other components δ_{22} and δ_{33} are the orthoradial and radial directions, respectively. The uniaxial and orthoradial
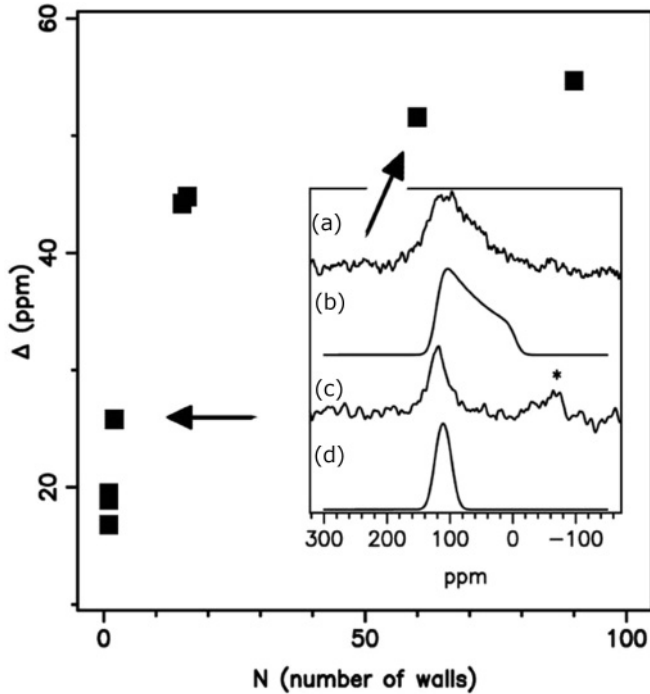
FIG. 4. The parameter Δ versus the number of walls. Inset shows (a) NMR spectrum of sample MW3 with (b) the corresponding tensor fit and (c) NMR spectrum of DW2 with (d) the corresponding tensor fit. The arrows indicate where in the plot the two samples can be found.

directions correspond to the in-plane directions of a graphene sheet and the radial component corresponding to the direction perpendicular to the sheet. The tensor fits shown in the inset of Fig. 4 reveal a good agreement between experiment and calculations.

In order to support our findings theoretically, first-principles calculations were performed within the density functional theory (DFT) as implemented in the plane-wave pseudopotential PARATEC.[54] To reduce the computational cost, we have restricted our study to zigzag (n,0) SWNTs with a small diameter, $7 \leqslant n \leqslant 17$. This particular nanotube geometry allows reasonably tractable calculations due to the relatively small number of atoms in the unit cell, as well as a moderately fine grid needed to accurately sample the reciprocal Brillouin zone. A sufficiently large supercell size was chosen so that isolated SWNTs are separated by a vacuum distance of at least 0.9 nm, making intertube interactions negligible. Exchange-correlation effects were described in the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional,[55] which already proved to give accurate results for a large range of systems, including CNTs. A norm-conserving Troullier-Martins pseudopotential with a core radius of 1.75 a.u. was used to model the valence and core interaction. The plane-wave basis set contained components with energies up to 40 Ry. The one-dimensional irreducible Brillouin zone was sampled using 13 k-points. The nanotube geometry was fully optimized with a force criterion of 0.01 eV/Å. The magnetic susceptibility and ^{13}C NMR shielding tensors of the infinite SWNT were calculated using the recent gauge-including projector-augmented plane-wave

(GIPAW) approach proposed by Pickard and Mauri.[56] Due to the current limitations of its implementation in PARATEC, we have focused on the two families of nonmetallic (n, 0) SWNTs defined by l=1 and l=2, where l=n {mod 3}. To be able to compare the calculated chemical shifts with the experimental data, we have used the same method as in Ref. [47], i.e., using the experimental isotropic chemical shift of benzene $\delta_{benzene}^{TMS}$, which itself is usually given relative to TMS, according to

$$\delta_{CNT} = \delta_{CNT}^{unref} - \delta_{benzene}^{unref} + \delta_{benzene}^{TMS}, \qquad (2)$$

where δ_{CNT}^{unref} and $\delta_{benzene}^{unref}$ are the unreferenced calculation results and $\delta_{benzene}^{TMS} = 126.9$ ppm the experimental reference.[57] Following our convergence studies in cut-off energy, k-point sampling, supercell size, we estimate the calculated NMR chemical shifts to be converged within 1 ppm. As mentioned, *ab initio* computations on large-diameter CNTs or MWNTs are not accessible. Therefore, the comparison was feasible only in a relatively small window of diameters in the range from 0.7 to 1.4 nm. The optimized structural parameters obtained in the present work are consistent with earlier reports.[47,58–62] The results of *ab initio* calculation for isolated CNTs are presented in Fig. 3 (squares) together with the line shifts obtained in experiments (circles). In addition to our calculation for tubes with diameters from 0.7 to 1.4 nm, the data obtained for different diameters by Sebastiani and Kudin[52] by first-principles studies are also presented (triangles). The agreement between the experimental data and the theoretical calculations is very good and validates the use of NMR experiments for structural characterization of CNTs.

IV. CONCLUSION

In conclusion, high-resolution ^{13}C NMR was used to study the structural properties of SWNT and MWNT bulk samples. We have shown that the line position can be exploited to measure the average diameter of the CNTs, while the linewidth provides information on the number of walls and/or homogeneity of the samples. Our experimental results are supported by *ab initio* calculations, and two empirical relations for the structural parameters of CNTs over a wide range of diameters are proposed. Our current results demonstrate the benefit of using NMR as a complementary and reliable source of information for bulk samples of CNTs. Our study also gives further insight into the magnetic properties of CNTs.

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