

NMR chemical shifts of molecules encapsulated in single walled carbon nanotubes

Nicholas A. Besley^{a)} and Adam Noble

School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom

(Received 16 October 2007; accepted 12 February 2008; published online 14 March 2008)

We present density functional theory calculations of the nuclear magnetic resonance spectroscopy of molecules encapsulated within single walled carbon nanotubes. Ring currents in the nanotube induce shifts in the chemical shift of the nuclei comprising the encapsulated molecule. These changes in the chemical shifts are shown to have characteristic dependence on the chirality of the surrounding nanotubes. © 2008 American Institute of Physics. [DOI: 10.1063/1.2894538]

I. INTRODUCTION

In the years since the discovery and elucidation of the structure of multiwalled and single walled carbon nanotubes in the early 1990s,^{1,2} there has been an intensive effort toward understanding and exploiting their properties. A remarkable feature of carbon nanotubes is that their properties can depend on structural parameters, such as length or helicity.³ Many applications of nanotubes rely on their synthesis and manufacture with a high degree of uniformity and purity, and the controlled production of nanotubes is one of the biggest challenges in nanotube science. The development of techniques that provide quantitative information on the structural properties of nanotubes is central to this problem.

Nuclear magnetic resonance (NMR) spectroscopy would be an intuitive choice of technique to study nanotubes. NMR has several advantages over scanning tunneling microscopy since it provides a bulk measurement and is a noninvasive technique. Despite considerable progress,^{4–11} the application of ¹³C NMR to study nanotubes is problematic. The primary difficulty in the measurement of the NMR spectra of nanotubes is the large magnetic inhomogeneity arising from the residual metal catalyst in the sample. The measured spectra consist of a broadband centered on about 125 ppm, although more recent work has achieved narrower bands.^{7–10} The broadness of the band has been attributed to the nature of the nanotube sample that will contain a wide range of lengths, diameters, and helicities.⁶ Several theoretical studies of the ¹³C NMR spectroscopy of nanotubes have also been reported.^{6,12–16} These studies predict chemical shifts in agreement with the experiment, and illustrate a dependence of the chemical shift on the diameter of the nanotube. Other theoretical studies have focused on functionalized nanotubes¹⁷ and the Knight shift in metallic tubes.¹⁸

Another area of research of increasing prominence is the study of molecules encapsulated within nanotubes. The encapsulation of molecules in nanotubes adds another dimension to nanotube science. A range of molecules have been encapsulated within nanotubes, and a recent review provides a summary of this work.¹⁹ There has been a number of stud-

ies of the NMR spectroscopy of labeled noble gas atoms inside fullerenes. Through NMR spectroscopy of ³He encapsulated in fullerenes, it was shown that the magnetic field inside the cage was altered due to aromatic ring currents,²⁰ and this technique has been used to study the reaction of molecules with the fullerene.^{21,22} In this Communication, we report calculations of the NMR chemical shifts of molecules encapsulated in nanotubes. These calculations show that the NMR spectroscopy of molecules encapsulated within single walled carbon nanotubes show a characteristic dependence on the chirality of the surrounding nanotubes, with a weaker dependence on the nanotube diameter.

II. COMPUTATIONAL DETAILS

Isotropic nuclear shieldings were computed with the gauge-including atomic orbitals methodology implemented within Q-CHEM.^{23,24} In this work, nuclear shieldings were computed using density functional theory (DFT) with the B3LYP exchange-correlation functional.²⁵ A mixed basis set comprising 6-31G* for the atoms of the molecule and STO-3G for the atoms of the surrounding nanotubes, denoted 6-31G*_STO-3G, was used. The use of the 6-31G* basis set for all atoms for the larger diameter nanotubes is beyond our current computational resources. For the smaller (5,5) and (9,0) nanotubes, calculations with 6-31G* basis sets for all atoms and the cc-pVDZ basis set for the atoms of the encapsulated molecule are used to test the validity of the smaller basis set calculations. The structure of the nanotubes and molecules were optimized at the B3LYP/STO-3G and B3LYP/6-31G* levels, respectively. This does not account for changes in the molecular structure of the encapsulated molecule. However, for CO and C₂H₄ in the (5,5) and (9,0) nanotubes, the NMR for optimized structures are also reported. The molecules are placed at the center of the tube, such that the center of mass of the molecule and nanotube coincides. For acetylene, ethylene, and diatomic molecules, the C—C bond or molecular axis is aligned along the nanotube axis and for formaldehyde, the C=O bond is orientated along the nanotube axis. The nanotubes are modeled with finite hydrogen capped tubes (see Fig. 1), which are all 18.1 Å long. Details of these nanotubes are shown in Table I.²⁶

^{a)}Electronic mail: nick.besley@nottingham.ac.uk.

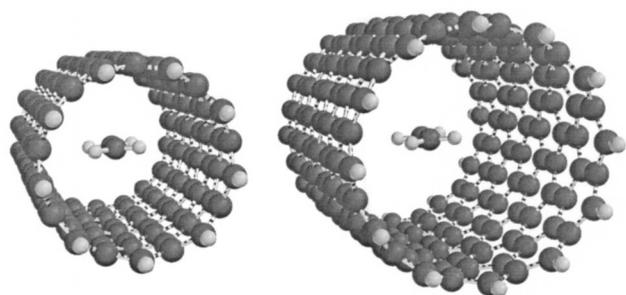


FIG. 1. Ethylene encapsulated in model (9,0) and (5,5) nanotubes.

III. RESULTS AND DISCUSSION

Table II shows the change in the chemical shift for a small set of molecules encapsulated within the (5,5) and (9,0) nanotubes compared to the isolated (gas phase) molecule for three basis set combinations. The change in chemical shift has the same magnitude but opposite sign as the change in isotropic nuclear shielding. On encapsulation there can be a small difference in the computed nuclear shieldings of atoms equivalent in gas phase. In this work, we report the average shift for these atoms. The calculations show that for most nuclei in a variety of molecules, there is a reduction in the chemical shift on encapsulation in the nanotubes. This change arises in the paramagnetic contribution to the shielding, while the diamagnetic component remains approximately constant. The results presented are for nanotube fragments capped with hydrogen atoms. However, we have also found similar results in analogous calculations on model nanotubes capped with fullerene fragments. The results predicted from the different basis sets are consistent. In particular, the cheapest basis set combination 6-31G*_STO-3G agrees well with results using a better quality basis set for the nanotube and the encapsulated molecule. It is currently not possible to use significantly better basis sets than cc-pVDZ containing higher angular momentum functions with our current code.

The change in chemical shift observed in these calculations is consistent with experimental measurements on related systems.^{20,27} A change in chemical shift of -6.3 and -28.2 ppm has been determined for ^3He in C_{60} and C_{70} , respectively.²⁰ Furthermore, recent experiments have measured the NMR spectrum of the inner wall of a double walled carbon nanotubes using selective isotopic enrichment of the inner tube.²⁸ The isotropic line position of the inner tube was

TABLE I. Dimensions of the nanotubes studied.

Nanotube	No. of carbon atoms	Diameter (Å)
(9,0)	144	7.1
(10,0)	160	8.0
(11,0)	176	8.7
(12,0)	192	9.6
(5,5)	140	6.9
(6,6)	168	8.2
(7,7)	196	9.7
(8,8)	224	11.0

TABLE II. Variation of the change in chemical shift on encapsulation with basis set (in ppm).

Molecule		6-31G*	cc-pVDZ_STO-3G	6-31G*_STO-3G
He@(5,5)	^3He	-3.4	-4.6	-4.6
He@(9,0)	^3He	-20.0	-17.9	-17.9
CO@(5,5)	^{13}C	-1.8	-0.2	-0.4
	^{17}O	-1.0	-0.7	-1.5
CO@(9,0)	^{13}C	-21.7	-18.3	-18.2
	^{17}O	-22.2	-23.3	-22.3
C_2H_2 @(5,5)	^{13}C	-0.3	-1.2	-1.4
	^1H	-3.8	-5.3	-5.2
C_2H_2 @(9,0)	^{13}C	-19.3	-18.4	-18.1
	^1H	-16.6	-17.8	-17.7
C_2H_4 @(5,5)	^{13}C	-4.6	-6.6	-6.6
	^1H	-3.6	-5.2	-5.0
C_2H_4 @(9,0)	^{13}C	-18.0	-16.8	-16.7
	^1H	-19.7	-17.9	-17.7

found to be 111 ppm, a change in chemical shift of -14 ppm from the value for the single walled nanotube sample. Calculations on a (8,0)@(16,0) double walled nanotube predicted a change in chemical shift in good agreement with the experiment.¹⁵

Since the calculations are consistent with the known experimental information, the dependence of the chemical shift of encapsulated molecules on the structure of the surrounding nanotube can be explored in more detail. Table III shows the computed changes in the chemical shifts of the encapsulated molecules for a range of zigzag and armchair nanotubes of varying diameter. These have been computed with the 6-31G*_STO-3G basis set combination. The calculations

TABLE III. Change in chemical shift on encapsulation (in ppm).

Molecule		(5,5)	(6,6)	(7,7)	(8,8)	(9,0)	(10,0)	(11,0)	(12,0)
He	^3He	-4.6	-5.3	-4.8	-3.7	-17.9	-26.2	-13.4	-18.1
HF	^{19}F	-3.0	-5.7	-5.2	-3.8	-15.7	-19.6	-14.0	-15.6
	^1H	-4.8	-5.3	-4.8	-3.7	-18.1	-19.8	-13.3	-15.0
CO	^{13}C	-0.4	-4.9	-5.1	-3.7	-18.2	-26.3	-12.6	-18.4
	^{17}O	-1.5	-4.9	-4.3	-3.6	-22.3	-27.9	-12.9	-17.7
N_2	^{15}N	-1.6	-4.6	-4.8	-3.7	-21.2	-21.1	-13.6	-18.2
CH_4	^{13}C	+0.3	-4.8	-5.4	-4.2	-14.8	-19.9	-13.4	-18.7
	^1H	-4.5	-5.2	-4.8	-3.8	-18.0	-20.9	-13.3	-18.3
C_2H_2	^{13}C	-1.4	-4.7	-4.8	-3.7	-18.1	-25.7	-13.4	-18.1
	^1H	-5.2	-5.4	-4.7	-3.6	-17.7	-25.6	-13.3	-17.7
C_2H_4	^{13}C	-6.6	-5.4	-6.4	-3.8	-16.7	-25.5	-13.2	-18.3
	^1H	-5.0	-5.5	-6.1	-3.7	-17.7	-26.0	-13.3	-18.0
H_2CO	^{13}C	-1.0	-4.0	-4.4	-3.6	-11.6	-17.4	-12.1	-15.6
	^1H	-5.4	-5.5	-4.8	-6.7	-17.6	-19.8	-13.3	-16.2
Mean		-3.2	-5.1	-5.0	-4.0	-17.5	-23.0	-13.3	-17.4

TABLE IV. Variation of the computed isotropic shielding of encapsulated ^3He with the length of the tube.

Tube length (Å)	Chirality	δ (ppm)	Band gap a.u.
7.1	(9,0)	+72.5	0.01
18.1	(9,0)	+77.7	0.01
28.6	(9,0)	+75.7	0.00
7.3	(5,5)	+68.9	0.10
18.1	(5,5)	+64.4	0.05
26.8	(5,5)	+60.7	0.04
38.4	(5,5)	+56.5	0.03

suggest that the change in chemical shift of the encapsulated molecules is dependent on the surrounding nanotube, and relatively independent of the molecule itself. This is consistent with the origin of the change in chemical shift arising from ring currents circulating in the nanotube. The most striking feature of the results is a significant difference in the predicted shifts for armchair and zigzag nanotubes. The change in chemical shift on encapsulation in the zigzag nanotubes is typically 10–20 ppm greater than that for the armchair nanotubes. This effect is generally larger than the variations arising from the diameter of the tubes. For the armchair tubes, there is little variation with the diameter of the nanotubes, although the results for the zigzag nanotubes are more sensitive to the diameter. This is reasonable since nanotube ring currents will be dependent on the detailed atomic positions of the surrounding tube, and there is a greater structural change between the nanotubes of different chirality than between similar tubes of different diameters.

In this study, finite models of nanotubes are used. With these models, it can be problematic to achieve convergence of the computed properties with respect to the length of the nanotubes. Table IV shows the computed isotropic shielding of ^3He in (9,0) and (5,5) nanotubes as the length of the nanotube model is increased. For (9,0) nanotube, there is only a weak dependence of the nuclear shielding with respect to the length of the nanotube. For nanotubes 7.1, 18.1, and 28.6 Å long, the computed isotropic shielding of encapsulated ^3He is +72.5, +77.7, and +75.7 ppm, respectively. For the (5,5) nanotube, poorer convergence is observed and the isotropic shielding decreases as the length of the nanotube is increased. Convergence is not achieved for the longest nanotube studied which comprises 320 carbon atoms and is 38.4 Å long. Also shown in Table IV is the computed band gaps of the nanotubes. For the (5,5) nanotube, as the band gap becomes smaller, the isotropic shielding decreases. This indicates a correlation between the band gap and the computed isotropic shielding. However, the band gaps for the (9,0) nanotubes which have a higher isotropic shielding are smaller suggesting that the structural effect is dominant. Furthermore, the trend of decreasing isotropic shieldings for the (5,5) nanotubes would increase the difference between the change in chemical shifts for armchair and zigzag nanotubes. Achieving convergence with respect to the length of the nanotube represents a limitation of studying these systems within finite models, and the extension of this work to infinitely long nanotubes is underway.

The changes in chemical shift computed do not account

for any changes in the structure of the molecule that may occur on encapsulation. For CO and C_2H_4 , optimization of the geometry of the molecule inside the (5,5) nanotube led to changes in the chemical shift of +0.3 and +0.2 ppm for the carbon and oxygen in CO, and –1.3 and –4.6 ppm for the carbon and hydrogen in C_2H_4 . Similar calculations for the (9,0) nanotube gave values of –17.3 and –20.4 ppm for carbon and oxygen in CO, and –12.0 and –17.4 ppm for carbon and hydrogen in C_2H_4 . For these molecules, structural changes on encapsulation do modify the observed chemical shift. This change due to the structure is similar for both nanotubes and the differences arising from the chirality of the nanotubes remain.

The NMR spectroscopy of encapsulated molecules can be contrasted with their infrared spectroscopy. Experimental studies have shown that a blueshift in infrared bands is often observed on encapsulation, and the magnitude of the blueshift is sensitive to the diameter of the nanotube.^{29,30} It is possible that the spectroscopy of molecules encapsulated within nanotubes may provide a probe of the structure of the surrounding nanotube, with different spectroscopies yielding different structural information. The measurement of the NMR spectroscopy of molecules in fullerenes has already been achieved and the measurement of the NMR of an encapsulated molecule has practical advantages over the direct measurement of the NMR of the nanotube itself since isotope enrichment can be exploited to enhance the sensitivity of the technique.

ACKNOWLEDGMENTS

This research was supported by the EPSRC through the award of an Advanced Research Fellowship to N.A.B. (No. GR/R77636). The authors are grateful to the University of Nottingham for access to its high performance computing facility. N.A.B. would like to thank Dr. Jeremy Titman and Dr. Andrei Kholobystov for useful discussions.

- S. Iijima, *Nature (London)* **354**, 56 (1991).
- S. Iijima and T. Ichihashi, *Nature (London)* **363**, 603 (1993).
- T. W. Odom, J. L. Huang, P. Kim, and C. M. Lieber, *Nature (London)* **391**, 62 (1998).
- X.-P. Tang, A. Kleinhammes, H. Shimoda, L. Fleming, K. Y. Bennoune, S. Sinha, C. Bower, O. Zhou, and Y. Wu, *Science* **288**, 492 (2000).
- C. Goze-Bac, S. Latil, P. Vaccarini, P. Bernier, P. Gaveau, S. Tahir, V. Micholet, R. Aznar, A. Rubio, K. Metenier, and F. Beguin, *Phys. Rev. B* **63**, 100302 (2001).
- C. Goze-Bac, S. Latil, P. Lauginie, V. Jourdain, J. Conrad, L. Duclaux, A. Rubio, and P. Bernier, *Carbon* **40**, 1825 (2002).
- S. Hayashi, F. Hoshi, T. Ishikura, M. Yumuar, and S. Ohshima, *Carbon* **41**, 3047 (2003).
- L. S. Cahill, Z. Yao, A. Adronov, J. Penner, K. R. Moonosawmy, P. Kruse, and G. R. Goward, *J. Phys. Chem. B* **108**, 11412 (2004).
- A. Kitaygorodskiy, W. Wang, S.-Y. Xie, Y. Lin, K. A. Shiral Fernando, X. Wang, L. Qu, B. Chen, and Y.-P. Sun, *J. Am. Chem. Soc.* **127**, 7517 (2005).
- C. Engrakul, M. F. Davis, T. Gennett, A. C. Dillon, K. M. Jones, and M. J. Heben, *J. Am. Chem. Soc.* **127**, 17548 (2005).
- L. B. Alemany, L. Zhang, L. Zeng, C. L. Edwards, and A. R. Barron, *Chem. Mater.* **19**, 735 (2007).
- S. Latil, L. Henrard, C. Goze-Bac, P. Bernier, and A. Rubio, *Phys. Rev. Lett.* **86**, 3160 (2001).
- E. Zurek and J. Autschbach, *J. Am. Chem. Soc.* **126**, 13079 (2004).
- N. A. Besley, J. J. Titman, and M. D. Wright, *J. Am. Chem. Soc.* **127**, 17948 (2005).

- ¹⁵M. A. L. Marques, M. d'Avezac, and F. Mauri, *Phys. Rev. B* **73**, 125433 (2006).
- ¹⁶E. Zurek, C. J. Pickard, B. Walczak, and J. Autschbach, *J. Phys. Chem. A* **110**, 11995 (2006).
- ¹⁷E. Zurek, C. J. Pickard, and J. Autschbach, *J. Am. Chem. Soc.* **129**, 4430 (2007).
- ¹⁸O. V. Yazyev and L. Helm, *Phys. Rev. B* **72**, 245416 (2005).
- ¹⁹D. A. Britz and A. N. Kholobystov, *Chem. Rev. (Washington, D.C.)* **35**, 637 (2006).
- ²⁰M. Saunders, H. A. Jimenez-Vazquez, R. J. Cross, S. Mroczkowski, D. I. Freedberg, and F. A. L. Anet, *Nature (London)* **367**, 256 (1994).
- ²¹A. W. Jensen, A. Khong, M. Saunders, S. R. Wilson, and D. I. Schuster, *J. Am. Chem. Soc.* **119**, 7303 (1997).
- ²²G.-W. Wang, M. Saunders, and R. J. Cross, *J. Am. Chem. Soc.* **123**, 256 (2001).
- ²³C. Ochsenfeld, J. Kussmann, and F. Koziol, *Angew. Chem., Int. Ed.* **43**, 4485 (2004).
- ²⁴Y. Shao, L. Fusti-Molnar, Y. Jung, J. Kussman, C. Ochsenfeld, S. T. Brown, A. T. B. Gilbert, L. V. Slipchenko, S. V. Levchenko, D. P. O'Neill, R. A. Distasio, Jr., R. C. Lochan, T. Wang, G. J. O. Beran, N. A. Besley, J. M. Herbert, Y. L. Lin, T. Van Voorhis, S. H. Chien, A. Sodt, R. P. Steele, V. A. Rassolov, P. E. Maslen, P. P. Korambath, R. D. Adamson, B. Austin, J. Baker, E. F. C. Byrd, H. Daschle, R. J. Doerksen, A. Drauw, B. D. Dunietz, A. D. Dutoi, T. R. Furlani, S. R. Gwaltney, A. Heyden, S. Hirata, C.-P. Hsu, G. Kedziora, R. Z. Khalliulin, P. Klunzinger, A. M. Lee, M. S. Lee, W. Lian, I. Lotan, N. Nair, B. Peters, E. I. Proynov, P. A. Pieniazek, Y. M. Rhee, J. Ritchie, E. Rosta, C. D. Sherrill, A. C. Simmonett, J. E. Subotnik, H. L. Woodcock III, W. Zhang, A. T. Bell, A. K. Chakraborty, D. M. Chipman, W. J. Hehre, A. Warshel, H. F. Schaefer III, J. Kong, A. I. Krilov, P. M. W. Gill, and M. Head-Gordon, *Phys. Chem. Chem. Phys.* **8**, 3172 (2006).
- ²⁵A. D. Becke, *J. Chem. Phys.* **98**, 1372 (1993).
- ²⁶See EPAPS Document No. E-JCPSA6-128-810810JCP for coordinates of the nanotubes. This document can be reached through a direct link in the online article's HTML reference section or via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>).
- ²⁷J. Autschbach and E. Zurek, *J. Phys. Chem. A* **107**, 4967 (2003).
- ²⁸F. Simon, C. Kramberger, R. Pfeiffer, H. Kuzmany, V. Zolyomi, J. Kürti, P. M. Singer, and H. Alloul, *Phys. Rev. Lett.* **95**, 017401 (2005).
- ²⁹O. Byl, P. Kondratyuk, S. T. Forth, S. A. FitzGerald, L. Chen, J. K. Johnson, and Y. T. Yates, Jr., *J. Am. Chem. Soc.* **125**, 5889 (2003).
- ³⁰J. Wang, M. K. Kuminova, M. Poliakoff, G. A. D. Briggs, and A. N. Kholobystov, *Angew. Chem., Int. Ed.* **45**, 5188 (2006).