Influence of hydrogen doping on the ^{15}N and ^{17}O NMR parameters in zigzag and armchair single wall nanotube: A DFT study

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ABSTRACT

Density functional theory (DFT) calculations were performed to calculate nitrogen-14 and oxygen-17 Nuclear magnetic resonance (NMR) spectroscopy parameters in the representative considered models of zigzag and armchair single wall nanotubes (SWNTs) for the first time. The considered models consisting of 7.1 and 4.8nm length of H-capped (5,0) and (4,4) single-walled nanotube respectively, At first, the structural models were optimized and then the chemical-shielding (CS) tensors were computed in the optimized structures. Finally, the CS tensors were converted to isotropic chemical-shielding (ICS) and anisotropic chemical-shielding (ACS) parameters. The calculations were performed based on the B3LYP DFT method and 6-311G standard basis set using the Gaussian 98 package of program.*

Keywords: DFT, NMR, SWNT, CSI, CSA.
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INTRODUCTION

Interaction of oxygen with carbon nanotubes (CNTs) always has been an interesting and fascinating, subject for the scientific community for both fundamental and practical reasons, as well as for the possible applications in nanodevice technologies and in chemical sensors [1-3]. The electrical transport properties of entangled SWCNT mat samples have been found to be very sensitive to exposure to oxygen or ambient air [1]. Collins et al. [2] found that oxygen gas has dramatic effects on conductivity, thermoelectric power, and the local density of states of nanotubes. Theoretical studies have shown that N2 adsorption surface area of arrays of single-walled nanotubes (SWNTs) could be as high as 3000 m^2g^{-1} [4]. Nevertheless, it is known that the adsorption surface area and porosity results of SWNTs are usually specific to a particular study and are generally not reproducible by other researchers.

However, precise quantification of N2 adsorption properties of carbon nanotubes, which should be valid for a wide range of experimental conditions, is essential to understand how best to apply carbon nanotubes for alternative fuel storage [5] or development of nano scale sensors for detecting air pollutants [6] or removal of hazardous air pollutants and other contaminants from gas streams [7,8] or any other adsorption related application. Nuclear magnetic resonance (NMR) spectroscopy is among the most versatile techniques to study the electronic structure properties of matters [9 –14]. The chemical-shielding (CS) tensors originating at the sites of half-spin nuclei, magnetic nuclei, reveal important trends about the electronic properties at the sites of these nuclei. The CS tensors are either measured experimentally or reliably reproduced by high-level quantum chemical calculations [14,15].

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MATERIALS AND METHODS

2.1. Software
GAUSSIAN 98 package program

2.2. Computational details
Our representative H-doped model of armchair and zigzag CNTs in the present study (Fig.1, 2 and 3) have 4.88 nm and 7.1 nm length for (4,4) (fig 1) and for (5,0) (fig 2), respectively; single-walled CNT consisting of 40 C atom . The calculations are performed by hybrid functional B3LYP and DFT based method and 6-311G* standard basis set by GAUSSIAN 98 package program [16]. The calculated CS tensors in principal axes system (PAS) are converted to measurable NMR parameters, chemical shielding isotropic and chemical shielding anisotropic using CNTs (A, A_1, A_2, A_3 and A_4) are shown in Tables 2 and 3, respectively [17]. London [18] initially suggested local gauge origins to define the vector potential of the external magnetic field in the study of molecular diamagnetism. The idea was then adapted by Ditch field [19] in the gauge independent atomic orbitals (GIAO) method for magnetic shielding calculations. We have performed experiments on single-wall carbon nano tube SWCNT networks and compared with DFT calculations to identify the microscopic origin of the observed sensitivity of the network conductivity to physisorbed O_2 and N_2. First DFT calculations of the transmission function for isolated previous SWCNTs have found that the physisorbed molecules have a little influence on their conductivity. However, by calculating we show that, physisorbed O_2 and N_2 affect the junction's conductance. This may be understood as an increase in tunneling probability due to hopping via molecular orbitals. We find the effect is substantially larger for O_2 than for N_2 SWCNTs junctions, in agreement with experiment [20].

RESULTS AND ISCUSSION

3.1. ^{13}C NMR chemical shielding (4,4)
Table 2 shows the calculated ^{13}C chemical shielding tensors for CNTs O_2 and N_2 molecules adsorption on the CNT has a remarkable influence on ^{13}C NMR tensors, which is in complete accordance with the facts mentioned above. It is also explain that, chemical shielding components converge in a way similar to that of the chemical shifts which increasing the tube length however, not as monotonous as the isotropy shielding. On the other hand, the calculated ^{13}C chemical shielding values in the middle of the (4,4) CNT seem approach the values 53.8 and 57.3ppm.
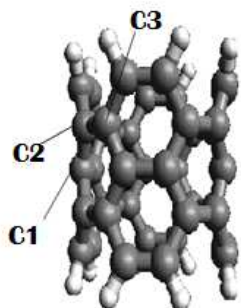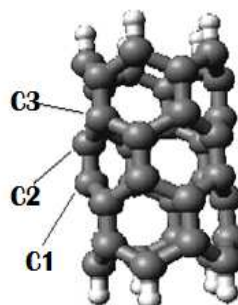

Figure 1: (4,4) SWCNT   **Figure 2: (5,0) SWCNT**

Table1: Calculated ^{13}C NMR parameters for CNT, N_2–CNT, O_2–CNT systems

Model	atoms	$\sigma 11$	$\sigma 22$	$\sigma 33$	σ_{iso}	$\Delta \sigma$	η_σ
CNT(A)	C_1	-35.3100	13.8404	175.9600	51.4968	186.69481	0.3949
	C_2	-35.9811	13.5591	176.0667	51.2149	87.2777	0.3968
	C_3	0.0252	0.0252	163.8800	53.8495	165.0308	0.0000
CNT(4,4)-	C_1	-80.4572	10.7847	102.7393	11.0223	137.57551	0.9948
$O_2(A_1)$	C_2	-80.8301	10.9026	102.4569	10.8431	37.4207	1.0013
CNT(4,4)-	C_1	40.2230	40.2230	141.8900	96.4600	68.1450	0.0000
$O_2(A_2)$	C_2	64.9425	91.1836	133.1339	96.4200	55.0709	0.7147
CNT(4,4)-	C_1	-88.7059	38.8741	95.3872	15.1851	120.3032	1.5907
$N_2(A_3)$	C_2	-88.7419	38.8274	95.3910	15.1588	120.3483	1.5900
CNT(4,4)-	C_1	62.8717	62.8717	120.5500	97.2764	34.9100	0.0000
$N_2(A_4)$	C_2	64.1611	64.1611	125.8100	99.3120	39.7400	0.0000

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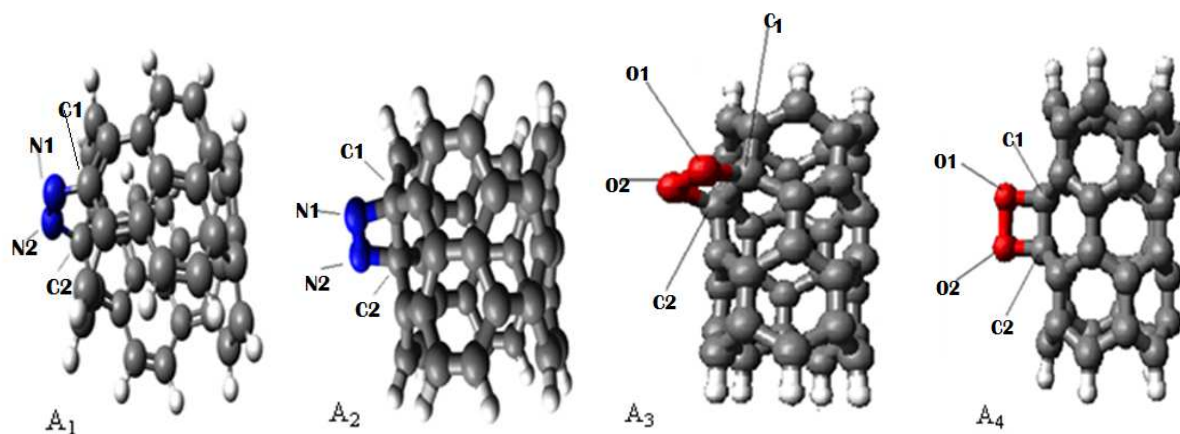
Figure 3. (A₁) and (A₂) adsorption configurations of an Oxygen.
(A₃) and (A₄) adsorption configurations of a Nitrogen molecule.

According to GIAO calculations performed after adsorption of oxygen and nitrogen molecules, the isotropy value of the ^{13}C NMR shielding tensor decreased in A₁ and A₃ (fig 3) sites (about 11.0223 ppm, and10.8431 ppm at C₁ and C₂ of site A₁ and 15.1851 ppm, 15.1588 ppm at C₁ and C₂ of site A₃) and increased in A₂ and A₄ (fig 3) sites (about 96.4565 ppm, 96.4200ppm at C₁ and C₂ of site A₂ and 99.3120 ppm and 97.2764 ppm at C₁ and C₂ of site A₄) (Table2). The associated anisotropy value decreases for both carbons.

However, the effect is more significant for C₁ and C₂ nuclei. Results reveal that electronic charge distribution around the carbon atoms becomes more symmetric as a result of oxygen adsorption. The anisotropy value of the ^{13}C NMR shielding tensor increased approximately about 137.5755ppm and 137.4207ppm, at C1 and C₂ of site A₁.

In this case, anisotropy values for both carbons decrease by adsorption, while the reduction is more evident for C1 and C2. Due to O_2 adsorption, the calculated ^{13}C NMR parameters of those interacted carbon atoms are also modified. As deduced from comparison of sites A₁ and A₂, the carbon atoms contributed in O2 adsorption, become more shielded. Among the two NMR principal components, intermediate shielding component, $\sigma 22$, shows more change from nano-tube than O_2–CNT system, which is in contrast with N_2-CNT. The results are consistent with strong interaction between nano-tube and O_2 molecule. The discrepancy between ^{13}C chemical shielding tensor for the site A₁ and A₂ systems and A₃and A₄ systems must be attributed to the different nature of the frontier orbital. Components of CS tensor are defined by following relation [20].

$$\sigma_{ij} = (\frac{\partial^2 E}{\partial B_i \partial \mu_j})_{\mu_j B_i}$$

Where E is energy of system and μ_j and B_i are components of magnetic moment and external magnetic field, respectively. CS tensor in the principal axes system (PAS)($\sigma_{33} \succ \sigma_{22} \succ \sigma_{11}$) is diagonal and thus, principal values for specification of shielding are defined by this coordinate system as following:

$$\sigma_{iso} = \frac{(\sigma_{11} + \sigma_{22} + \sigma_{33})}{3}$$

$$\Delta\sigma = \frac{3}{2}(\sigma_{33} - \sigma_{iso})$$

$$\eta_\sigma = \frac{3}{2}(\frac{\sigma_{22} - \sigma_{11}}{\Delta\sigma})$$

Where σ_{iso}, $\Delta\sigma$ and η_σ are isotropic, anisotropic and asymmetric parts of CS tensor, respectively and in certain cases vanishes.

3.2. ^{13}C NMR chemical shielding (5, 0)
Tables2 exhibit the calculated ^{13}C chemical shielding for CNTs. O_2 and N_2 adsorption on the CNT has a remarkable influence on ^{13}C NMR tensors which is in complete accordance with the facts mentioned above. Previously, it has been indicated that for the H-capped CNTs, the calculated ^{13}C chemical shielding value sat the ends are smaller than
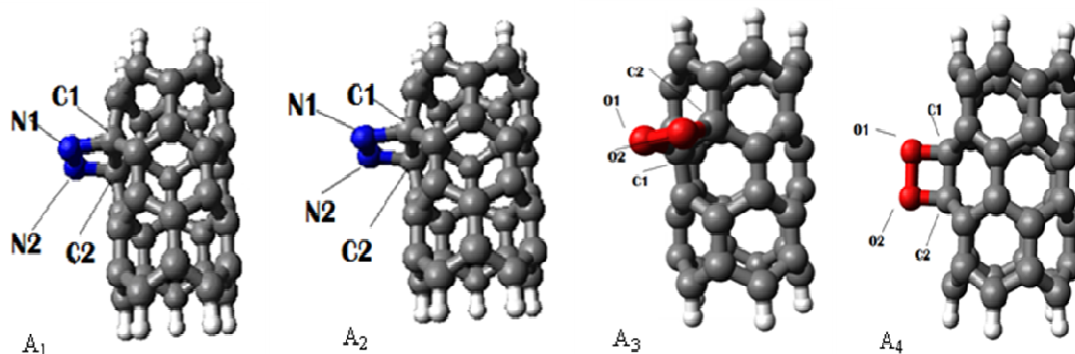
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in the tube's center if the carbon is directly bound to hydrogen; otherwise it is larger [21]. It is also depicted that chemical shielding components converge in a way similar to that of the chemical shifts when increasing the tube length albeit not as smoothly as the isotropic shielding.

On the other hand, the calculated ^{13}C chemical shielding values in the middle of The (5,0) CNT seem to approach values 149.1757and149.1663 ppm (Table2). It may be noted that ^{13}C chemical shielding tensor σ_{ii} shows the carbon sites depends remarkably on the tube size and nature of frontier orbital's [19, 21, 22].

Table2: Calculated ^{13}C NMR parameters for CNT, N_2–CNT, O_2–CNT system [a]

Model	atoms	$\sigma 11$	$\sigma 22$	$\sigma 33$	$_{iso}\,\sigma$	$\Delta\sigma$	η_σ
CNT(A)	C_1	27.4749-	155.3869	319.6152	149.1757	255.6593	1.0729
	C_2	-27.4737	155.3875	319.5851	149.1663	255.6282	1.0730
	C_3	-166.2046	-4.1528	153.1572	-5.7334	238.3359	1.0199
CNT(5,0)-O_2(A_1)	C_1	74.4312	77.7044	155.3112	102.4823	79.2434	0.0620
	C_2	74.6323	77.7154	155.0228	102.4568	79.2720	0.0637
CNT(5,0)-O_2(A_2)	C_1	42.8507	97.3469	149.1738	96.4571	79.0751	1.0338
	C_2	47.6078	104.8761	127.8227	93.4355	51.5808	1.6654
CNT(5,0)-N_2(A_3)	C_1	76.1071	96.5323	143.1071	105.2245	56.8239	0.5411
	C_2	76.0659	96.4950	143.0751	105.2120	56.7946	0.5396
CNT(5,0)-N_2(A_4)	C_1 C_2 C_2	48.7700 34.5201	48.7700 76.2487	127.2600 118.0313	74.9305 76.2667	78.4943 62.6469	0.0000 0.9991

[a] *Calculated $\sigma\,ii$, $\sigma\,iso$, $\Delta\sigma$ values in ppm*

Figure 4. (A_1) and (A_2) adsorption configurations of an N_2 molecule (sitesA_1 and A_2,respectively), (A_3) and (A_4) adsorption configurations of an O_2 molecule (sites A_3 and A_4,respectively)

DFT study of ^{13}C chemical shielding tensors on small-to-medium – diameter infinite SWCNTs reveals that chemical shielding decreases roughly inversely proportional to the tubes diameter [22]. The NMR chemical shielding of finite SWCNTs were found to converge very slowly, to the in finite limit, indicating that hydrogen capped tube fragments are not necessarily good models of infinite systems. For the hydrogen capped (9,0) tube case, all of the frontier orbital's have carbon p-s character, they are localized at each end of the tube [23]. As the length of the fragment increases, these orbitals do not yield a contribution to the electron density along the tube (except at the ends) and must therefore be regarded as artifacts due to treating the finite sized systems. According to GIAO calculations performed after adsorption of O_2 ^{13}C NMR parameters of those interacted carbon atoms are also modified. As understood by comparison of sites A_1, A_2, A_3 and A_4, the carbon atoms included in O_2 adsorption become more shielded (fig 4). Among the two NMR principal components, intermediate shielding component, σ_{22}, shows more change from nano-tube to the O_2–CNT system.

The results are consistent with strong interaction between the tube and O_2 molecule. The discrepancy between the ^{13}C chemical shielding tensor for the site CNT, A_1, A_2, A_3 and A_4 (fig 4) systems must be attributed to the different nature of the frontier orbitals.

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CONCLUSION

In this work, geometries, binding energies and ^{13}C NMR chemical shielding tensors of H-capped (4,4) and (5,0) SWCNT interacted with molecule O_2 and N_2 species, have studied. The calculated ^{13}C chemical shielding tensors have been shown in Tables1and 2. In the following sections, molecular geometries and NMR chemical shielding tensors, the data obtained from O_2 andN_2 molecules adsorptions were discussed, separately.

According to DFT calculations, adsorption of, O_2 and N_2 Molecules extremely influenced geometrical and electronic structure properties of (4,4) and(5,0) SWCNT. It is found that ^{13}C chemical shielding is appropriate parameters to investigate the nature of interactions in (4,4) and(5,0) SWCNT. The ^{13}C chemical shielding isotropy and anisotropy values vary remarkably from CNT to the CNT–O_2 and CNT–N_2 systems, for adsorption sites.

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