Density Functional Theory (DFT) Study of O₂, N₂ Adsorptions on H-Capped (5, 0) Single-Walled Carbon Nanotube (CNT)

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Abstract: CNT_s are one of the most significant achievements of nano-technology with important applications in the design of electronic nano-devices. Nano-tubes with small size, physical stability and sensitivity of their electric properties to adsorption of N₂ and O₂ make them ideal materials for use in gas sensors. In this investigation the (DFT) method is utilized to study the adsorption of oxygen, nitrogen molecules on the surface of (5,0) CNT. The electronic structure, NMR spectrum, dipole moment of nitrogen, oxygen and carbon nuclei's are thoroughly studied. The computational results indicate that rich adsorption patterns may result from the interaction of oxygen and nitrogen with the CNT_s. Sometimes, C-O bounds are formed via breaking C-C bounds and sometimes a carbon atom in the nanotube is replaced with an oxygen atom. Sometimes oxygen and nitrogen molecular are attracted to a C-C bound. In summary, the optimized adsorption rates are calculated. The nitrogen molecules adsorb with a comparatively lower rate and almost never a chemical binding is formed with the CNT. Gaussian 98 software has been used to carry out quantum chemistry calculations.

Keyword: Density functional theory (DFT), NMR spectrum, single-walled CNT, electronic structure, Gaussian 98 software.

Introduction

Carbon nanotubes have many fascinating properties^{1,2} and numerous studies have been conducted on their synthesis^{3,4}, treatments^{5,6} and physical properties^{7,8}. However, only a limited number of studies have been made on the adsorption of gases in carbon nanotubes; these include theoretical studies^{9,10}, experimental work^{11,12}. Many researchers studied endohedral adsorption of nitrogen in single walled nanotubes of 10.2 Å of diameters^{13,14}. A large number of experimental studies have been carried out thus far on the adsorption of nitrogen^{15,16}, oxygen^{17,18}, carbon nanotubes single-walled.

Sensitivity of CNTs to oxygen and nitrogen exposure has been also demon-started by

means of quantum mechanics calculations. Difficulties in CNTs production and spectroscopic characterization have made computational studies of these systems indispensable. Even though experimental techniques have advanced, theoretical calculations have preserved their significant role in predicting geometries and energy levels and interpreting spectroscopic data¹⁹. Pathways to oxygen macular chemisorptions on the (5,0) CNTs were probed by George E. Froudakis *et al*²⁰ and L.S. Cahill *et al*²¹, based on density functional theory, adsorption of O₂ molecule on the (8,0) CNT^{22,23}, was studied. Binding energies, charge transfer and density of states corresponding to O₂ chemisorption and physisorption on (8, 0) SWCNT also was studied²⁴. The effect of adsorbed oxygen molecule on the outer surface of a (10, 0) CNT was analyzed in more detailed by S. Peng *et al*²⁵, which considered adsorption of O₂ molecule on graphite and (8,0) nano-tube, also the similar studies was performed^{26,27}. Both local density approximation and gradient-corrected approximation (GGA) methods predict that O₂ molecular is physisorbed at perfect and defect sites of CNT, studies on physisorption and chemisorptions of O₂ on the outer surface of (4,2) CNT, performed by Liu *et al*²⁸, indicating that (4,4) tube is less air-stable than (5,0) tube.

In this study, electronic structure properties of (5,0) SWCNT involved with an O₂ and N₂ molecules are investigated. Nuclear magnetic resonance NMR properties are calculated in order to obtain useful information about the nature of interactions in nano-tubes. Consequently, the bond strength of O₂ is greater than N₂ species adsorbed on CNTs. In our study, oxygen and Nitrogen electronic structure modification effects on NMR chemical shielding and dipole moment (5,0) of CNT, the influence of hydrogen doping (H-doping) on the electrostatic properties of the zigzag SWCNTs is studied by means of the CS tensor calculations at the sites of ¹³C nuclei in representative model including H-doped of 7.1 nm long (5,0) zigzag SWCNTs²⁹, (Table 2 and Figure 1).

Experimental

This study was performed in Payame Noor University, Sari center, Sari, Iran, as a research project over carbon nanotubes adsorption property in 2009 and 2010.

Computational details

In the present study, O₂ and N₂ molecules adsorption behaviors on the SWCNT is taken in to consideration. A (5, 0) CNT containing 40 carbon atoms with length of 7.1 Å has chosen for the purpose. Due to the absence of periodic boundary conditions in molecular calculations, it is necessary to saturate the carbon dangling bonds with hydrogen atoms. All calculations were carried out at all-electron level using Gaussian 98 suite of programs.³⁰ It has been established that DFT is able to accurately treat such systems due to incorporation of the exchange-correlation effects^{31,32}. Geometry optimizations were performed using 6-311G* basis set with B3LYP functional^{29,33}. We see that greater dipole moments are associated with higher absolute values of energy, this seems reasonable because greater dipole moments means larger shifts in the probability distribution of electrons and hence a larger change in energy levels. NMR chemical shielding calculations were carried out of theory using gauge independent atomic orbital's (GIAO) approach³⁴. We have performed experiments on single-wall carbon nanotube SWCNT networks and compared with DFT calculations to identify the microscopic origin of the observed sensitivity of the network conductivity to physisorbed O₂ and N₂.

Figure 1. (A) The(5,0)SWCNT,(A₁) and (A₂) adsorption configurations of an N₂ molecule (sites A₁ and A₂, respectively) (A₃) and (A₄) adsorption configurations of an O₂ molecule (sites A₃ and A₄, respectively).

NMR chemical shielding calculations were carried out of theory using gauge independent atomic orbital's (GIAO) approach³⁴. We have performed experiments on single-wall carbon nanotube SWCNT networks and compared with DFT calculations to identify the microscopic origin of the observed sensitivity of the network conductivity to physisorbed O₂ and N₂. Previous DFT calculations of the transmission function for isolated pristine SWNTs have found physisorbed molecules have a little influence on their conductivity. However, by calculating we show that, physisorbed O₂ and N₂ 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 O₂ than for N₂ SWNTs junctions, in agreement with experiment³⁵. This may be understood as an increase in tunneling probability due to hopping via molecular orbitals. We find the effect is substantially larger for O₂ than for N₂ SWNTs junctions, in agreement with experiment³⁶. Components of CS tensor are defined by following relation³⁷:

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

Where E is energy of the 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) ($\sigma_{33} > \sigma_{22} > \sigma_{11}$) is diagonal and thus, principal values for specification of shielding is defined for this coordinate system:

$$\sigma_{iso} = \frac{\sigma_{11} + \sigma_{22} + \sigma_{33}}{3}, \Delta\sigma = \frac{3}{2}(\sigma_{33} - \sigma_{iso})$$

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

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

Results and Discussion

In this study, geometries and binding energies, ¹³C NMR chemical shielding tensors, and total dipole moment of states of H-capped (5,0) SWCNT in terraced with O₂ and N₂ molecules, are taken in Tables(1&2). In the following sections, molecular geometries and binding energies, NMR chemical shielding resulted from O₂ and N₂ adsorptions are discussed, separately.

Molecular geometries and binding energies

The optimized geometries of calculated configurations of O₂ and N₂ molecules adsorbed on (5, 0) SWCNT are schematically displayed in Figure 1. Geometrical parameters, binding energies and dipole moment are summarized in Table1. The nature of stationary points are confirmed by vibrational frequency calculations at the B3LYP/6-311G* level. For nitrogen and oxygen molecules we have considered distinct adsorption sites, marked as CNT (A, A₁, A₂, A₃ and A₄ (Table1). CNT, CNT–O₂ and CNT–N₂ binding energies, ΔE_{ab}, are calculated using:

$$E_{ad} = E_{tot}(\text{moleculeO}_2 + \text{CNT}_S) - E_{tot}(\text{CNT}_S) - E_{tot}(\text{moleculeO}_2)$$

$$E_{ad} = E_{tot}(\text{moleculeN}_2 + \text{CNT}_S) - E_{tot}(\text{CNT}_S) - E_{tot}(\text{moleculeN}_2)$$

Where, E_{tot}(CNT), E_{tot}(O₂) and E_{tot}(CNT+O₂), E_{tot}(N₂) and E_{tot}(CNT+N₂) are the energies of the optimized tubes, that are adsorbate and tube–adsorbate systems, respectively. Zigzag (5, 0) tube has two different C–C bonds ((C–C)₁=1.401 Å and (C–C)₂=1.465Å) and thus offers two distinct adsorption sites. Such a structure has also been observed for other SWCNTs, using DFT-GCA method^{12, 13, 38, 39}. For the molecular O₂–CNT system, O₂ is constrained to lie parallel to the outer surface of the tube. Two different types of adsorbed O₂, N₂ molecules were identified (Figure 1. A, A₁, A₂, A₃ and A₄). The calculated binding energies were predicted to be -1111.617 and -1110.745 eV at the sites A₁ and A₂ and the sites A₃ and A₄ 1.737 and 2.858 eV, respectively. Such adsorptions of O₂ molecule are known as cycloaddition which is very similar to those found for larger diameter tubes⁴⁰. The nitrogen molecules adsorb with a comparatively lower rate and almost never formed a chemical binding with the carbon nanotube. Once such oxidation occurs and physisorbed product is formed, the geometry of (5,0) tube is considerably modified. However, this is not the case for the (4,2) tube as reported previously.³⁸ The electron configuration of O₂ is KK (σ_{2s})² (σ_{2s}^{*})² (σ_{2pz})² (π_{2px})² (π_{2py})² (π_{2px}^{*})¹ (π_{2py}^{*})¹, The electron configuration of N₂ is KK (σ_{2s})² (σ_{2s}^{*})² (π_{2px})² (π_{2py})² (π_{2pz})², and the transferred electron is filled in the half-filled anti-bonding orbital of O₂, hence weaken the O–O bond. The binding orbital of N₂ molecule is filled, so that the electron can't enter into this binding orbital. The O₂-tube and N₂-tube equilibrium distances for adsorption sites A₁, A₂, A₃ and A₄ illuminate the interaction of O₂ and N₂ with CNT belongs to physisorption. The C–C distance increases from (C–C)₁=1.401Å to (C–C)₁=1.50 and (C–C)₂=1.465Å to (C–C)₂=1.49Å and hence C–O bond in A₂ site shows better adsorption, which is very similar to literature^{24,40}.

It was found that O₂ binding energy decreases as the diameter of (n, 0) CNT increases. It is well known that the tendency for sp²–sp³ rehybridization upon O₂ adsorption is strong for thin nanotubes, because highly bent sp² bonding of thin nanotubes is favored for the transition to sp³ bonding.

This is an essential reason for the binding performed studies, show that the values of energies of nitrogen molecules adsorption on armchair model with determined diameter and length have the differences about twice in grandeur. In addition, all these energies are positive

which show the reaction is improbable. Based on these results we can conclude that the physical adsorption over the surface area of nanotube occurs very difficultly and so this is not a suitable case. We approach that, the adsorption carry out over open ends of nanotubes, based on performed calculations, has more advantages.

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Table 1. Calculated structural parameters and adsorption energies of N₂ and O₂ adsorbed on the (5, 0) SWCNT^a.

Model (configuration)	r _{C-C}	r _{C-O}	r _{O-O}	r _{C-N}	R _{N-N}	Δ E _b	dipole moment
CNT(A)	(C-C) ₁ =1.401 (C-C) ₂ =1.465	-	-	-	-	-	1.0977
CNT(5,0)- O ₂ (A ₁)	(C-C) ₁ =1.51 (C-C) ₂ =1.51	(C-O) ₂ = 1.456 (C-O) ₂ = 1.456	1.488	-	-	-1111.617	2.4530
CNT(5,0)- O ₂ (A ₂)	(C-C) ₁ =1.50 (C-C) ₂ =1.49	(C-O) ₂ = 1.474 (C-O) ₂ = 1.498	1.429	-	-	-1110.745	2.4704
CNT(5,0)- N ₂ (A ₁)	(C-C) ₁ =1.51 (C-C) ₂ =1.51	-	-	(C-N) ₁ = 1.511 (C-N) ₂ = 1.511	1.256	1.737	2.5970
CNT(5,0)- N ₂ (A ₂)	(C-C) ₁ =1.50 (C-C) ₂ =1.49	-	-	(C-N) ₂ =1.574 (C-N) ₂ = 1.553	1.246	2.858	2.5764

^aAll calculated distances in Å°. All calculated binding energies in electron volt (eV). All calculated dipole moment in Debye.

Table 2. Calculated ¹³C NMR parameters for CNT, N₂-CNT, O₂-CNT system^a

Model	atoms	σ ¹¹	σ ²²	σ ³³	iso σ	Δσ	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	48.7700	48.7700	127.2600	74.9305	78.4943	0.0000
	C ₂	34.5201	76.2487	118.0313	76.2667	62.6469	0.9991
	C ₂						

^a Calculated σ_{ii}, σ_{iso}, Δ σ values in ppm.

¹³C NMR chemical shielding

Tables 2 exhibit the calculated ¹³C chemical shielding for CNTs. O₂ and N₂ adsorption on the CNT has a remarkable influence on ¹³C 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 ¹³C chemical shielding value at the ends is smaller than in the tube's center if the carbon is directly bound to a hydrogen; otherwise it is larger³⁸. 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 ¹³C chemical shielding values in the middle of the (5,0) CNT seem to approach values 149.1757 and 149.1663 ppm (Table 2). It may be noted that ¹³C chemical shielding tensor at the carbon sites depends remarkably on the tube size and nature of frontier orbitals³⁸.

DFT study of ¹³C chemical shielding tensors on small-to-medium diameter infinite SWCNTs revealed that chemical shielding decreases roughly inversely proportional to the tube diameter²⁹. The NMR chemical shielding of finite SWCNTs were found to converge very slowly, to the infinite 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 orbitals have carbon p-s character, they are localized at each end of the tube³⁸. 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 O₂, ¹³C NMR parameters of those interacted carbon atoms are also modified. As understood by comparison of sites A₁, A₂, A₃ and A₄, the carbon atoms included in O₂ adsorption become more shielded. Among the two NMR principal components, intermediate shielding component, σ_{22} , shows more change from nanotube to the O₂-CNT system. The results are consistent with strong interaction between the tube and O₂ molecule. The discrepancy between the ¹³C chemical shielding tensor for the site CNT, A₁, A₂, A₃ and A₄ systems must be attributed to the different nature of the frontier orbitals.

Conclusion

According to DFT calculations, adsorption of O₂ molecules dramatically influences geometrical and electronic structure properties of (5,0) SWCNT. For the molecular oxygen adsorption, the binding energy at the A₂ site is found to be 1110.745 eV, which is stable than A₁ site. It is found that ¹³C chemical shielding is appropriate parameter to investigate the nature of interactions in (5,0) SWCNT. The ¹³C chemical shielding isotropy and anisotropy values vary remarkably from CNT to the CNT-O₂ and CNT-N₂ systems for two O₂, N₂ adsorption sites.

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