

Density Functional Theory (DFT) Study Adsorptions On Single-Walled Carbon Nano Tube-A Review

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Abstract: Carbon nanotubes (CNTs) are one of the most significant achievements of nano-technology because of its important applications in the design of electronic nano-devices. The study of their properties is therefore important. In this study, Density Functional Theory (DFT) was used to investigate the adsorption of gas molecules on the surface of carbon nanotubes. Theoretical studies have found that this single-walled carbon nanotube has novel electronic properties, which can be semiconducting; optimization of a sample system includes relaxation of atoms to lower forces from other constituents on each atom. Calculations were carried out with Gaussian98 suite of programs at all-electron level ¹.

Keywords: DFT, CNTs, Adsorption, Electronic properties, Gaussian98 program.

Introduction

Since their discovery in 1993 ²⁻³, single-wall carbon nanotubes (SWNTs) have been extensively studied because of their unique structure and properties ⁴⁻⁵. Studying the interaction between CNTs and chemical gases could, from fundamental point of view, significantly deepen our understanding on nanoscale device physics. CNTs have a variety of superior properties including well-defined nanodimensional structure, high electronic and thermal conductivity, good mechanical stability, etc. These structures provide a large specific surface area per unit weight; higher than graphite, but are lower in density due to their hollow interior. Single-walled carbon nanotubes (SWNTs) are of interest as gas adsorbents because of their unique structural properties. Four different adsorption sites have been identified on bundles of SWNTs, internal (endohedral), interstitial channels (ICs), external

groove sites, and external surfaces ⁶⁻⁷. Proposed method for this study is DFT which gives the values approximately approach to real ones. The studies on structural variations during oxygen adsorption and comparing with studies performed on adsorption of small molecules and atoms on surface areas of graphite and nanotubes and present study was approved that the chemical adsorption over C-C bond is most probable C-C bond ⁸⁻⁹. The length of nanotube have selected with respect to the length of unit cell of nanotube. Then, after selection this length for nanotube, the carbon atoms situated in both ends of this length will have negative charge because of carbon bonds breaking. For saturation of carbon bond in two ends of nano wire and create a model similar to a real wire of nanotube, hydrogen atoms were added to the In our zigzag nanotube, 10 hydrogen atoms were added to basic structure of nanotube

and 16 hydrogen atoms were added to the end links of nanotube wire, in armchair model of nanotube, for obtaining a model so similar to a real one. Molecules and atoms can attach themselves onto surfaces in two ways. In physisorption (physical adsorption), there is a weak van der Waals attraction of the adsorbate to the surface. In chemisorption (chemical adsorption), the adsorbate sticks to the solid by the formation of a chemical bond with the surface. This interaction is much stronger than physisorption, and, in general, chemisorption has more stringent requirements for the compatibility of adsorbate and surface site than physisorption. The chemisorption may be stronger than the bonds internal to the free adsorbate which can result in the dissociation of the adsorbate upon adsorption (dissociative adsorption). Gas adsorption in carbon nanotubes and nanotube

Materials And Methods

2.1. Software

GAUSSIAN 98 package program

2.2. Computational details

In this work, we studied zigzag, (8, 0) (10, 0), (17, 0), (5, 0) and armchair (5, 5), (10, 10) tubes. In this approach we use DFT for calculation over (8, 0), (5, 0) SWCNT. The calculations are performed by hybrid functional B3LYP density functional theory (DFT) based method and 6-311G* standard basis set by GAUSSIAN 98 package of program. The calculations are performed by The self-consistent field (SCF) electronic structure calculations are performed based on density functional theory (DFT) with either localized basis (DMol) or plane-wave basis (CASTEP) over both zigzag (10, 0), (17, 0), and armchair (5, 5), (10, 10) tubes. DMol is a density functional theory

Results And Discussion

3.1. Adsorption energies

Primary structures of nanotubes have optimized in length and diameter by nanotube modeler software. The calculation was performed for a zigzag (5, 0) nano-tube of 7.10 length and 2.26 diameter. The optimized geometries of calculated configurations of O₂ and N₂ molecules adsorbed on (5, 0) SWCNT are schematically displayed in Figure 1¹⁴. Geometrical parameters, binding energies and dipole moment are summarized in Table1. Optimization was

performed by atoms were added to the end links of nanotube wire and by GAUSSIAN 98 software, calculation method of B3LYP and 6-311G* basis set. The best proposed method for this study is DFT which gives the values approximately approach to real ones. 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, E_{ab}, are calculated using:

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

(DFT) package based on an atomic basis distributed by MSI. More accurate electronic band structure and electron density are the choice of adequate model leads us to reasonable results which are calculated by a SCF plane-wave pseudo potential technique (CASTEP)¹². CASTEP is a density functional theory (DFT) package based on plane-wave pseudo potential technique distributed by MSI. Comparable with experimental results. Minimum length of nanotube in SWCNTs model is unit cell's representative, which characterizes the compartment of this nanotube adsorption, similar to a real nanotube. It is appointed that, if the length of selected model is 32 and equal to unit cell, the model is an adequate one for calculation. Determination of the length of this unit cell with respect to its hexagonal rings is simple¹³.

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

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

Where, $E_{tot}(\text{CNT})$, $E_{tot}(\text{O}_2)$ and $E_{tot}(\text{CNT}+\text{O}_2)$, $E_{tot}(\text{N}_2)$ and $E_{tot}(\text{CNT}+\text{N}_2)$ are the energies of the optimized tubes, that are adsorbate and tube–adsorbate systems, respectively. 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.

Table 1. Calculated structural parameters and adsorption energies of N_2 and O_2 adsorbed on the (5, 0) SWNTs¹⁴.

Model (configuration)	rC-C	rC-O	rO-O	rC-N	rN-N	E_b	Dipole moment
CNT(A)	(C-C)1=1.401 (C-C)2=1.465	-	-	-	-	-	1.0977
CNT(5,0)-O ₂ (A1)	(C-C)1=1.51 (C-C)2=1.51	(C-O)2 =1.456 (C-O)2 =1.456	1.488	-	-	-0.103	2.4530
CNT(5,0)-O ₂ (A2)	(C-C)1=1.51 (C-C)2=1.49	(C-O)2 =1.474 (C-O)2 =1.498	1.429	-	-	-0.071	2.4704
CNT(5,0)-N ₂ (A1)	(C-C)1=1.51 (C-C)2=1.51	-	-	(C-N)1=1.511 (C-N)2=1.511	1.256	0.063	2.5970
CNT(5,0)-N ₂ (A2)	(C-C)1=1.50 (C-C)2=1.49	-	-	(C-N)1=1.574 (C-N)2=1.553	1.246	0.105	2.5764

Table 2 summarizes our results on the equilibrium tube–molecule distance, adsorption energy, and charge transfer for various molecules (NO_2 , O_2 , H_2O , NH_3 , CH_4 , CO_2 , H_2 , N_2 , Ar) on (10, 0), (17, 0) and (5, 5) SWCNTs¹⁵. In general, all these gas molecules are weakly bonded to the nanotube and the tube–molecule interaction can be identified as physisorption. Most molecules studied (with exception of NO_2 and O_2) are charge donors with small charge transfer (0.01 ~ 0.035 electron per molecule) and

weak binding (0.2 eV). For O_2 and NO_2 , both of which are charge acceptors, the charge transfer is not negligible. This is also reflected in their larger adsorption energies. The tube–molecule interactions are comparable to the van der Waals-like interactions between these molecules and graphite surfaces¹⁶. Our results show that there is no clear dependence of adsorption on the tube size and chirality (table 2).

Table 2. Equilibrium tube–molecule distance (d), adsorption energy (E_a) and charge transfer (Q) of various molecules on (10, 0), (17, 0) and (5, 5) individual SWNTs^a. The optimal adsorption sites are given in the table: T (top of an carbon atom), B (top of the centre of the C–C bond), C (top of the centre of carbon hexagon)¹⁵.

	NO2	O2	H2O	NH3	CH4	CO2	H2	N2	Ar
(10, 0) SWNT d (Å)	1.93	2.32	2.69	2.99	3.17	3.20	2.81	3.23	3.32
E_a (meV)	797	509	143	149	190	97	113	164	57
Q (e)	-0.061	-0.128	0.035	0.031	0.027	0.016	0.014	0.008	0.01
Site	T	B	T	T	C	C	C	C	C
(5, 5) SWNT d (Å)	2.16	2.46	2.68	2.99	3.33	3.54	3.19	3.23	3.58
E_a (meV)	427	306	128	162	122	109	84	123	82
Q (e)	-0.071	-0.142	0.033	0.033	0.022	0.014	0.016	0.011	0.011
Site	T	B	T	T	C	C	C	C	C
(17, 0) SWNT d (Å)	2.07	2.50	2.69	3.00	3.19	3.23	2.55	3.13	3.34
E_a (meV)	687	487	127	133	72	89	49	157	82
Q (e)	-0.089	-0.096	0.033	0.027	0.025	0.015	0.012	0.006	0.01
Site	T	B	T	T	C	C	C	C	C

(a Tube–molecule distance d is defined as the nearest distance between atoms on the molecule and the nanotube for T site, or the distance between the centre of the gas molecule and the centre of the carbon hexagon (carbon–carbon bond) for the C (B) site. The adsorption energy E_a (d) is defined as the total energy gained by molecule adsorption at equilibrium distance: $E_a(d) = E_{tot}(\text{tube} + \text{molecule}) - E_{tot}(\text{tube}) - E_{tot}(\text{molecule})$. Charge transfer Q denotes the total Mulliken charge number on the molecules, positive Q means charge transfer from molecule to tube.)

The calculated tube–molecule distance, adsorption energy and charge transfer for the different sites are given in table 3. The atomic structure and total charge density of valence electrons for a H₂O molecule adsorbed on (10, 0) SWCNT. No substantial electron density overlap is found in the region between the gas molecule and nanotube, indicating that no chemical bond is formed. As shown in figure 2, four possible sites (surface, pore, groove, interstitial) for the H₂ adsorption in the tube bundle have been considered. We find that the adsorption energy and charge transfer of H₂ in the interstitial and groove sites of the tube bundle are considerably larger than those on the surface sites. The pore site is also energetically more favorable than the surface site. Similar results are obtained for the other gas molecules studied. The enhancement of molecule adsorption on the groove and interstitial sites can be understood by the increased number of carbon nanotubes interacting with the molecule¹⁴. Our present results compared well with a previous empirical force field simulation⁷. Interaction of (8, 0) zigzag SWCNT with a single NH₃ molecule

and NH₃ (H₂O) n=1, 2, 3 complexes is considered¹⁷. To evaluate the interaction behavior between the NH₃ (H₂O) n=0, 1, 2, 3 complexes and CNT, we use the binding energy (E_B) and the coupling energy (E_C), respectively. E_B measures the average interaction between an ammonia molecule and its surroundings, including the intermolecular interaction within the water molecules and the interaction between ammonia molecule and the nanotube. E_B can be calculated using the following equation:

$$E_B = - (E_{\text{complex}} - E_{\text{tube}} - E_{\text{NH}_3} - nE_{\text{water}}) \quad n = 0, 1, 2, 3$$

Where E_{complex} is the total energy of the NH₃ (H₂O)_n/tube hybrid complex; E_{tube} is the total energy of tube; E_{water} is the total energy of an individual water molecule; E_{NH₃} is the total energy of an individual ammonia molecule and n is the number of water molecules. To differentiate between the ammonia–water molecular interaction and the tube–ammonia coupling interaction, here we define the coupling energy (E_C) as:

$$E_C = - (E_{\text{complex}} - E_{\text{tube}} - E_{\text{NH}_3}(\text{H}_2\text{O})_n) \quad n = 0, 1, 2, 3$$

Table 3. Equilibrium tube–molecule distance (*d*), adsorption energy (*E_a*) and charge transfer (*Q*) of the H₂ molecule on different adsorption sites (see figure 3) in the (10, 10) SWNT bundle[14].

Site	<i>d</i> (Å)	<i>E_a</i> (meV)	<i>Q</i> (e)
Surface	3.01	94	0.014
Pore	2.83	111	0.012
Groove	3.33	114	0.026
Interstitial	3.33	174	0.035

Table 4 displays that E_B and E_C are functions of n (number of water molecules) and they decrease upon increasing it. The coupling energy E_C is not sensitive enough to the number of water molecules, except for the first water molecule added to the system in which the energy is reduced from -2.0 kcal/mol to -4.1 kcal/mol.

However, table 5 shows that when the n is increased, the contribution of each water molecule in energy reduction is lessened. The equilibrium tube–NH₃ distance (R) also exhibits sensitivity to the n. Results reveal that R is shortened to 0.25 by changing the n from zero to three.

Table 4. Binding energy (E_B), coupling energy (E_C) and equilibrium tube–molecule distance (R) of the tube–NH₃ (H₂O) n=0, 1, 2, 3 systems as calculated by X3LYP¹⁷.

System	EB (kcal/mol)	EC (kcal/mol)	R (Å)
NH ₃	-2.0	-2.0	3.50
NH ₃ (H ₂ O)	-9.2	-4.1	3.42
NH ₃ (H ₂ O) 2	-13.2	-4.4	3.33
NH ₃ (H ₂ O) 3	-18.7	-4.9	3.25

Table 5. Binding energy (E_B) and coupling energy (E_C) per water molecule as a function of number of water molecules (0, 1, 2, and 3).

System	E_B (kcal/mol)	E_C (kcal/mol)
NH3	-2.0	-2.0
NH3 (H2O)	-9.2	-4.1
NH3 (H2O) 2	-6.6	-2.2
NH3 (H2O) 3	-6.3	-1.6

3.2. Electronic properties

The electronic density of states (DOS) of individual (10, 0) SWCNTs adsorbed with NO₂, NH₃, along with that of the pure SWCNT. Except for the slight modification on DOS shape due to band splitting, we find that the DOS of NH₃ adsorbed nanotube is very close to that of the pure nanotube. Similar behavior is obtained for all charge donor molecules studied (N₂, H₂O, and CO₂ etc)¹⁵. Therefore, we suggest that the interaction between the nanotube and these gas molecules is weak and does not have a significant influence on the electronic structures of SWCNTs. The electrical conductance of an individual semiconducting tube increases dramatically upon NO₂ gas exposure and the NO₂ is identified as charge acceptor¹⁸. Collins *et al* found that the oxygen gas has dramatic effects on conductivity, thermo power, and local DOS of individual semiconductor nanotubes, while Ar, He, and N₂ have no noticeable doping effect. Oxygen exposure generally converts semiconducting tubes into apparent conductors¹⁹. Based on present calculations, we propose that the effects from most gas molecules in the air, such as N₂, CO₂, H₂O, are relatively weak. The air exposure effect should be dominated by O₂, which is a charge acceptor and make all nanotubes p-type conductors. Weak coupling between NO₂ and the carbon nanotube is found. The carbon bonds near the molecule are weakened due to the charge transferred from carbon to NO₂. Influence of NH₃

adsorption on the electronic properties such as on-site charge transfer, charge density, molecular orbitals, and dipole moments are computed to get more details about the interaction between NH₃ and tube in each system (Table 6)¹⁶. As shown in table 6, the computed energy-gap (E_g) is insensitive to the n except for tube–NH₃ (H₂O)₃ system in which a slight change of about 0.003 eV is observed. It is known that the changes in the dipole moments affect the intermolecular interactions. In table 6, the amplitude of dipole moments for the tube–NH₃ (H₂O)_{n=0, 1, 2, 3} complexes are listed. With the exception of adding the first water molecule, the system dipole moments are increased by addition of more water molecules. However, dipole moments direction from tube–NH₃ to tube–NH₃ (H₂O)_{n=1, 2, 3} systems are inverted (Fig 3). The coupling between the electrons of the CNT and the valence electrons of the NH₃ molecule are increased. However, there is still weak coupling between the electrons of the CNT and the valence electrons of the ammonia molecules. However increasing the n in the NH₃ (H₂O)_n cluster leads to a dissociated (ion-pair) structure for large n [NH₄⁺ ... (H₂O)_n ... OH⁻] as a local minimum where a proton is transferred from a water molecule to the ammonia molecule²⁰⁻²¹. At the ammonia–water solution (instead of NH₃ alone) this changes the conductance of CNTs.

Table 6. Energy-gap (E_g), dipole moment $|\mu|$, and nitrogen atom charge of the tube–NH₃ (H₂O)_{n=0, 1, 2, 3} systems as calculated by B3LYP.

System	E_g (eV)	$ \mu $ (Debye)	Nitrogen atom charge	Average hydrogen atom charge
NH3	0.220	2.16	-0.628	+0.213
NH3 (H2O)	0.220	1.83	-0.645	+0.205
NH3 (H2O) 2	0.220	3.89	-0.659	+0.198
NH3 (H2O) 3	0.223	6.51	-0.688	+0.197

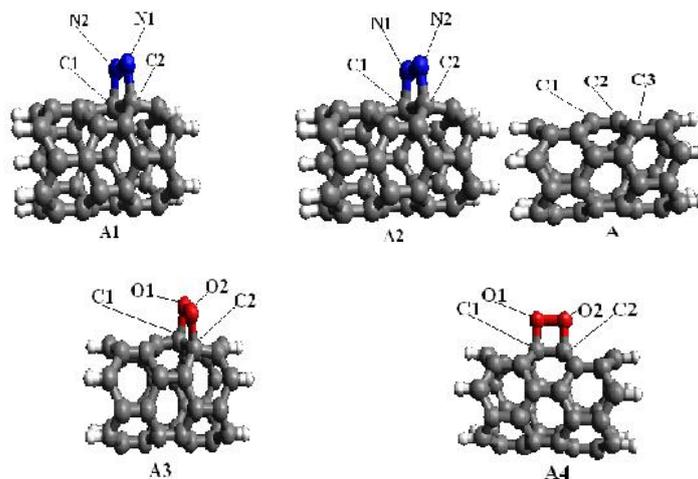


Figure 1. (A) The(5,0)SWCNT,(A1) and (A2) adsorption configurations of an N₂ molecule (sitesA1 and A2,respectively) (A3) and (A4) adsorption configurations of an O₂ molecule (sites A3 and A4,respectively)¹⁴.

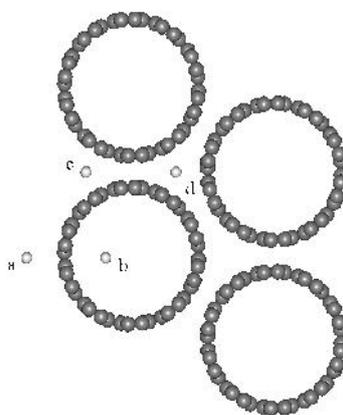


Figure 2. Illustration of several adsorption sites for the H₂ molecule in the nanotube bundle. (a) Surface; (b) pore; (c) groove; (d) interstitial.

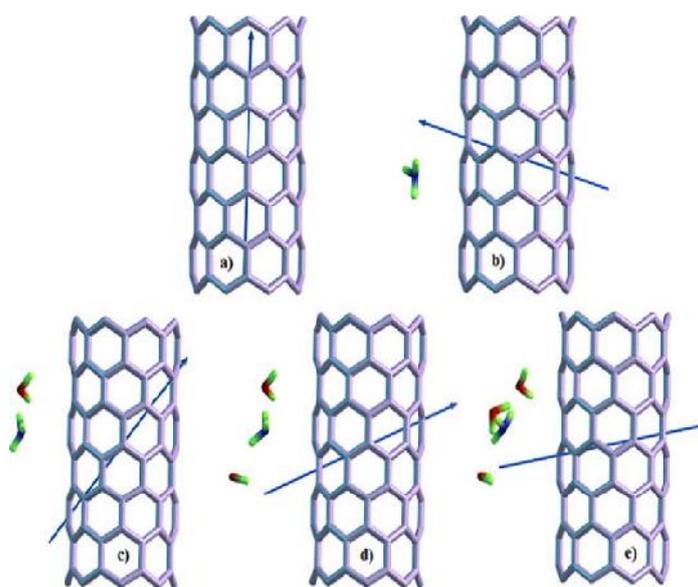


Figure 3. Dipole moment orientation for (a) pristine tube (8, 0), (b) tube-NH₃, (c) tube-NH₃(H₂O) (d) tube-NH₃(H₂O)₂ (e) tube-NH₃(H₂O)₃¹⁷.

Conclusion

In this work the structures of (O₂, N₂, CH₄, CO₂, NH₃, NO₂, H₂, Ar, H₂O) molecules adsorption over zigzag, (8, 0) (10, 0), (17, 0), (5, 0) and armchair (5, 5), (10, 10) tubes were studied by using density functional theory (DFT). It is found that interaction of nitrogen molecule with surface of nano-tube is an exothermic chemical reaction in which the amount of liberated energy varies with adsorption site of nitrogen molecule (table 1)¹⁴. We found that all molecules are weakly adsorbed on SWCNT with small charge transfer, while they can be either a charge donor or an acceptor of the nanotube. The adsorption of some

gas molecules on SWCNTs can cause a significant change in electronic and transport properties of the nanotube due to the charge transfer and charge fluctuation. The molecule adsorption on the surface or inside of the nanotube bundle is stronger than that on an individual tube¹⁵. The energy values and equilibrium distances between NH₃ molecule and tubes obtained from DFT calculations are typical of physisorption. The current results clearly indicate that addition of water molecules to tube–NH₃ system increases the interaction between tube and ammonia molecule¹⁷.

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