Journal of Engineering and Applied Sciences 14 (Special Issue 8): 10325-10330, 2019
ISSN: 1816-949X

Theoretical Study the Structure, Electronic and Spectra Properties for Nanotube Molecules by using DFT Method

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Abstract: DFT method has been carried out to studying the effects of NH_3, SO_2, CO_2, O_2 and CH_3 on the nanotube (2, 2) using the B3LYP functional and the 3-21 G basis set, the optimization structure, properties such as Ionization potential (I), Electron affinity (E), Energy gap (Eg), thermal properties (Eth, CV and S), EPS and IR spectra. The CNTs (1 and 2) is semiconductor with Eg ranging from 0.98-0.90 eV. All properties are calculated by using Density Function (DFT) method with basis set 3-21 G.

Key words: DFT calculation, electronic properties, IR spectra, nanotube molecules, optimization, structure

INTRODUCTION

Carbon Nanotubes (CNTs) represent a new group of materials with new application in technologies. Carbon nanotubes have several structures, differing in thickness, length and in the type of number of layers and helicity. n and m denote the number of unit vectors along two directions (Odem *et al*.,1998). If m = 0, the nanotubes are called zigzag which is named for the pattern of hexagons as we move on circumference of the tube while if n = m the nanotubes are called armchair or chirala which describes one of the two confirmers of cyclohexene of carbon atoms (Ganesh, 2013). Carbon nanotubes may have impact on semiconductor physics because of its the special electronic properties and very small size that are unique to carbon nano tubes. Because of the variety of possible helical geometries called as chirality, carbon nanotubes provide a family of structures with different chiralities and diameters (Saito *et al*., 1998).

Carbon Nanotubes (NTs) have been exhibit promising behavior for many application. One of the interesting facts is that their performance is completely dependent on the atomic geometrical organization. Ayala *et al*. (2010) many other materials as more results that are experimental became available and theoretical investigations, CNT was found to be not as perfect as it seems. These defects can significantly change the electrical, electronic, mechanical and thermal properties of CNTs (Meyyappan, 2005; Cahangirov *et al*., 2012). There are many approaches have been used to adjust the chemical doping electronic gap such as filling as an external stimulus and electric fields (Khoo and Louie, 2004; Ishigami *et al*., 2005; Kim *et al*., 2001; Zhi *et al*., 2005; Tang *et al*., 2005; Chen *et al*., 2007; Wei *et al*., 2010; Mickelson *et al*., 2003; Bando *et al*., 2001; Sirikumara *et al*., 2016).

For of seven different Carbon Nanotubes (CNTs) study the effect of physical properties and of surface chemistry carbon nanotubes on the adsorption of polycyclic aromaticin aqueous solutions (Al-Abboodi *et al*., 2017). Using DFT to study the electron properties, optical phonons and Raman spectroscopy of graphene: their relationship with carbon nanotubes (Charlier *et al*., 2007). Study the mechanical properties, chemical properties, optical properties and aplecation of carbon nanotubes (Varshney, 2014). Study the structure, symmetry, DOS physical and electronic properties and discussions related physical properties of carbon nanotubes also other electronic properties (Teng, 2010). Electrical, mechanical and thermal properties of carbon nanotube are study by using Chemical Vapor Deposition (CVD) (Kaushik and Majumder, 2015). The oretical and experimental analyses the topics covering the physical, structural, chemical electric properties and vibrational properties of carbon nanotubes (Suzuki, 2013).

MATERIALS AND METHODS

Computational approach: DFT calculations were performed using Gaussian 09 package (Frisch *et al*., 2009). The investigate the effect of NH_3, SO_2, CO_2, O_2 and CH_3 on the nanotube (2, 2) have been performed with B3LYP/3-21G level in the gas phase. The B3LYP hybrid functional has shown to be highly successful for calculation the electronic properties such as I, E and Eg because the calculation of the energy interaction effects between electrons and exchange-correlation also shows most accurate results. Figure 1 shows the structure of (1-4) nanotube molecules at gas phase using DFT method with B3LYP. The energy E^{HOMO} of the highest occupied orbital, energy E^{LUMO} of the lowest unoccupied orbital. The Ionization potential (I) and Electron affinity (E) have been computed by Eq. 1 and 2 (Al-Yasari, 2017):

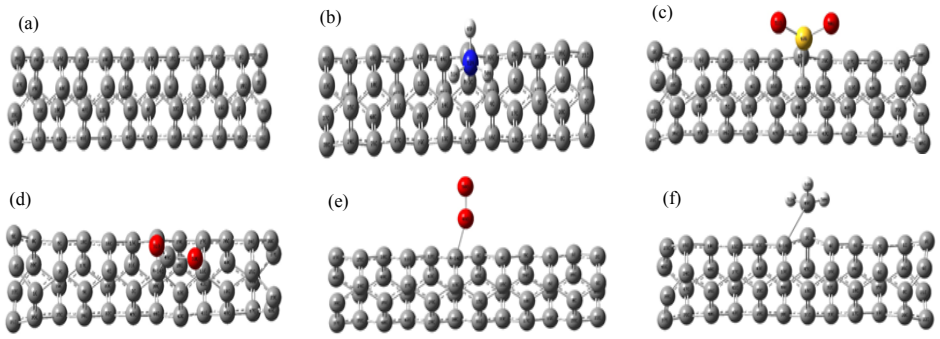

Fig. 1(a-f): The structures of (1-6) CNTS (2, 2) using DFT with B3LYP/3-21G bases set

$$I = E^{HOMO} \quad (1)$$

$$E = E^{LUMO} \quad (2)$$

$$E_g = (E^{LUMO} - E^{HOMO})$$

The Fermi energy has been calculated by Eq. 3 (Al-Yasari, 2016):

$$E_L = -(I+E)/2 \quad (3)$$

Cohesive energy (Ecoh) can be calculated by Eq. 4 (Sahin *et al*., 2013):

$$Ecoh = (ETot / n) - Ecarbon \quad (4)$$

Where:

ETot : The total energy of the system
n : The number of atoms in the system
Ecarbon : The calculated total energy of an isolated carbon atom = 1027.868 eV

RESULTS AND DISCUSSION

Electronic properties: All properties are computed by DFT/B3LYP 3-21G method for (Eq. 1-4) nanotube (2, 2) molecules. Table 1 shows the calculated values of HOMO and LUMO and electronic properties (I, E values (Eq. 1 and 2) while Ef values (Eq. 3) and EB values (Eq. 4). It is clear from Table 1 and Fig. 2-4 that the NH_3, SO_2 and CO_2 gropes lead to decreasing the values of HOMO and increasing the vales of LOUMO. From this figure shows the electronic could distribution on along therings C-C and the different parts of nanotube molecules, all molecules the HOMO shows a bonding character and LOUMO shows antibonding. The variation of LUMO and HOMO as the number of atoms of tube grows up in size.

While the values of I, Ef, EB and Eg are increasing while E are decreasing with the doping. From Table 1 and Fig. 2 indicating that the CNTs (1 and 2) is semiconductor with Eg ranging from 0.98-0.90 eV.

Electrostatic Potential and density Surfaces (EPS): The electrostatic potential and density surfaces nanotube molecules 2-6 using DFT with 3-21G basis set and are shown in Fig. 3. The distribution of electrostatic potential and electron density surfaces depends on the type of dobing group atoms; also depend on negative and positive charges. From this figure the density distribution on nanotube molecules is homogenous while in nanotube molecules 2-6 distribution on the NH_3, SO_2, CO_2, O_2 and CH_3. It is because these gropes have a high electronegativity, hence, it is engage charge toward them.

IR spectra: Figure 4 shows the IR spectra of nanotube molecules 1-6 using DFT method. The harmonic vibrational frequencies rotational constant, degree of freedom and vibration mod were calculated for study molecules by using B3LYP level with 3-21G basis set. NH_3, SO_2, CO_2, O_2 and CH_3 lead to new vibration mod such as (N-H), (S-O), (C-S) and (C-O), (C-CO_2) is weak and increasing of vibrational modes. From this fiuger found the Nts (2-4) have high values of harmonic vibrational frequencies (C-C), (C = C) and (C-C-C) compared pristine CNTs. According to the rule of 3N-6 where N is the number of atoms in nanotube molecules are calculated degree of freedom for CNTs from Table 2. Found the NH_3, SO_2, CO_2, O_2 and CH_3 groups lead to increasing of rotational constant, degree of freedom.

Thermal properties: Table 3 shows the calculated values thermal properties (Eth, CV and S) using DFT method with B3LYP. It is clear from this table that the NH_3, SO_2 and CO_2 gropes lead to decreasing the values of Eth, CV and S. The 3 has high CV and S while 2 has high values of Eth. Also the CNTs under study have high values of (Eth, CV and S) compered pristine CNTs.

Table 1: HOMO, LUMO energies and electronic properties (I, E, Eg, Ef and EB) in (eV) units for nanotube molecules 1-6 using DFT with 3-21 G basis set

Molecules	HOMO	LOUMO	I	E	Eg	Ef	EB
1	-5.34669	-4.35703	5.346689	4.357025	0.989664	-4.85186	-1065.72
2	-4.71594	-3.80954	4.715938	3.809540	0.906398	-4.26274	-1063.90
3	-5.99518	-4.24356	5.995179	4.243555	1.751624	-5.11937	-1074.20
4	-5.67594	-4.40437	5.675942	4.404372	1.271570	-5.04016	-1067.18
5	-5.51104	-4.27104	5.511044	4.271039	1.240005	-4.89104	-1067.20
6	-5.81445	-3.84818	5.814446	3.848180	1.966267	-4.83131	-1063.58

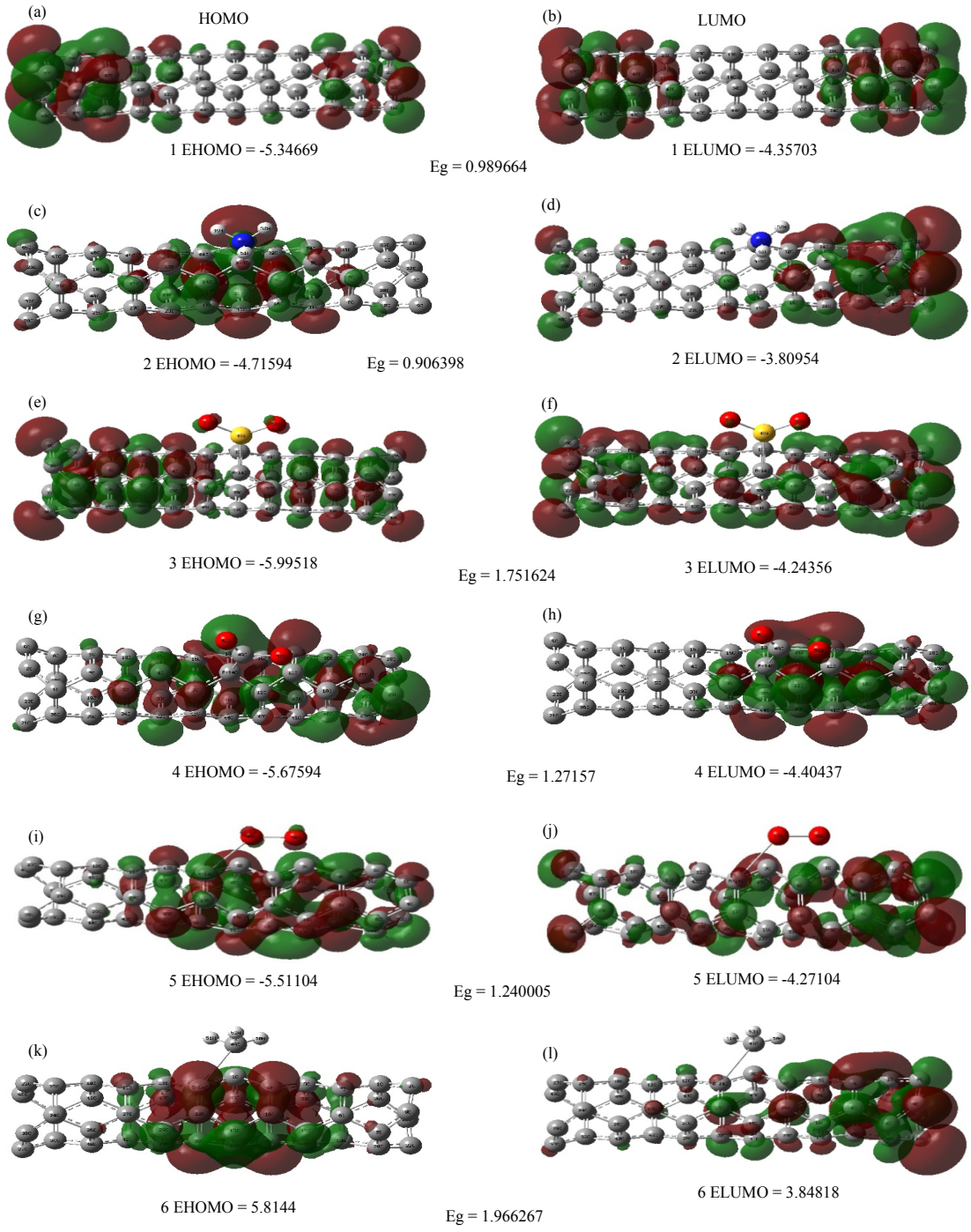

Fig. 2(a-l): Shapes HOMO and LOUMO for nanotube molecules 1-6 using DFT with 3-21G basis set

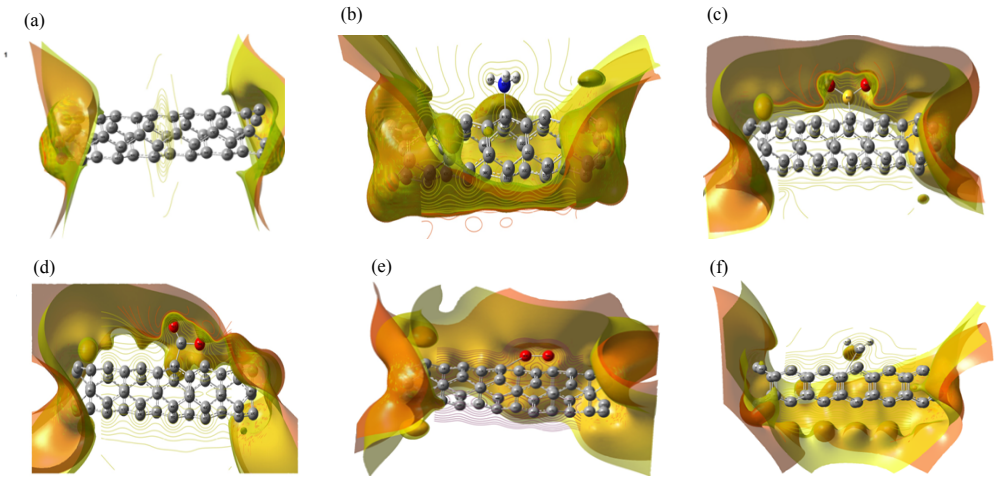

Fig. 3(a-f): The electrostatic potential and density surfaces for nanotube molecules 1-6 using DFT with 3-21G basis set

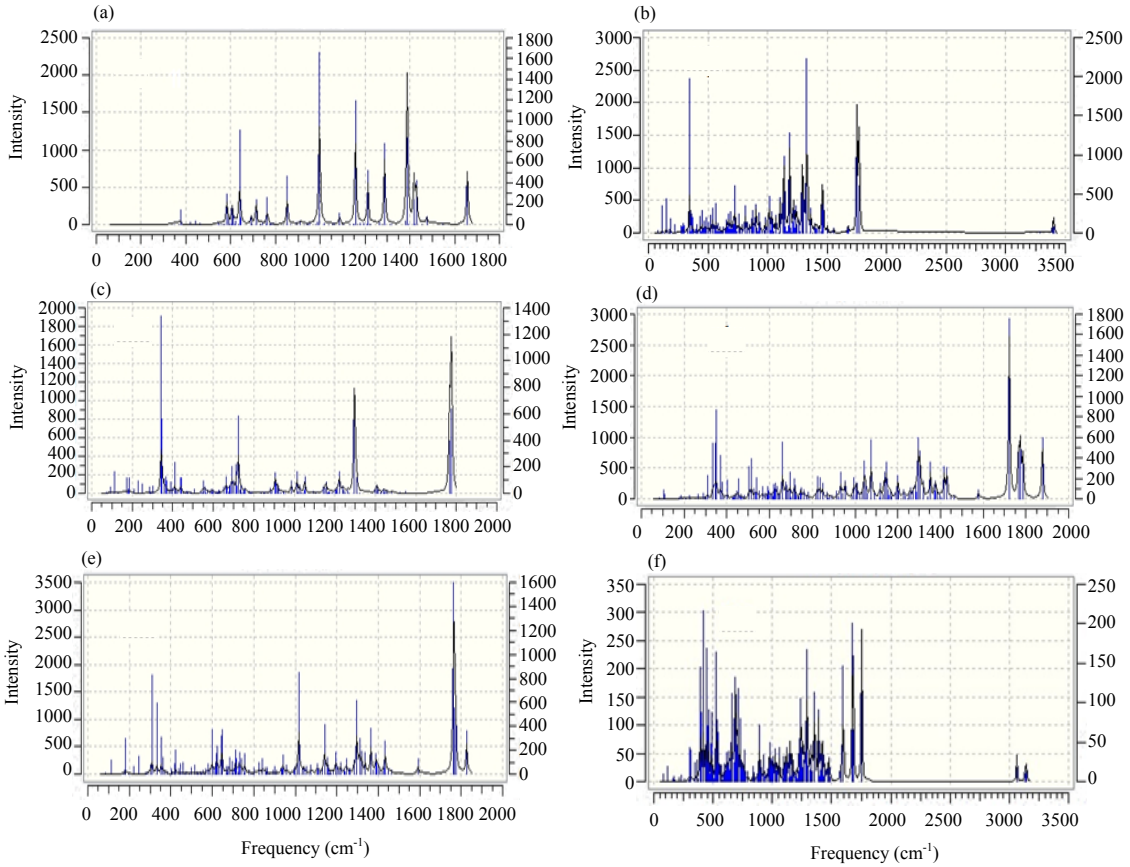

Fig. 4(a-f): Shapes IR spectra for nanotube molecules 1-6 using DFT with 3-21G; IR spectrum

Table 2: Vibration frequencies rotational constant in (Gl), degree. of freedom and vibration mod for nanotube molecules 1-6 using DFT with 3-21 G basis set

Molecules	Vibration mode	Frequency (cm^{-1})	Degree of freedom	Rotational constant
1	C = C, C-C stretching	1657.2, 1165.27	35	0.4254143
2	N-H stretching C = C, C-C stretching	3404.48; 1529.04, 1330.16	150	0.3666001

Table 2: Continue

	$N-H_3$ rocking ,waging	1674.46, 1128.69		
3	S-O stretching C = C, C-C stretching	1052.55; 1459.62, 1322.13	147	0.2628798
	C-S set reaching S-O sesoring	1012.9, 416.082		
4	C-O stretching C = C, C-C stretching	1877.54; 1786.04, 1318.98	147	0.2947358
	$C-CO_2$ rocking	482.308		
5	$C-O_2$ stretching C = C, C-C stretching	309.533; 1826.27, 1374.8	144	0.3354019
	O-O waging, stretching	5482.308; 931.77, 801.587		
6	C = H stretching C = C, C-C stretching	3145.8; 1755.05, 1598.3	150	0.3663494
	$C-H_3$ bending, rocking, waging	3064.45, 1060.77, 1153.89		

Table 3: Eth, CV and S in Kcal/mol and cal/mol-Kelvin units for nanotube molecules 1-4 using DFT with 3-21 G basis set

Molecules	Eth	CV	S
1	174.194	105.283	141.199
2	209.194	114.894	152.055
3	190.578	119.497	160.388
4	191.863	116.922	153.508
5	187.121	114.918	150.911
6	205.670	116.460	154.183

CONCLUSION

In this study found the NH_3, SO_2 and CO_2 gropes lead to decreasing the values of HOMO and increasing the vales of LOUMO. From this figure shows the electronic could distribution on along the rings C-C and the different parts of nanotube molecules the CNTs (1 and 2) is semiconductor with Eg ranging from 0.98-0.90 eV and lead to decreasing the values of Eth, CV and S. The 3 molecule has high CV and S, NH_3, SO_2 and CO_2 lead to increasing of vibrational modes such as (N-H) at 3404.48 cm^{-1} for 2 molecule, (S-O) at 1052.55 cm^{-1} an (C-S) at 1012.9 set reaching cm^{-1} and (C-O) at 1877.54 cm^{-1} and ($C-CO_2$) rocking 482.308 cm^{-1}. The density distribution on nanotube molecules is homogenous while in nanotube molecules 2-6 distribution on the NH_3, SO_2 CO_2, O_2 and CH_3. It is because these gropes have a high electronegativity, therefore, it is attract charge toward them.

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