The Influencing of Toxic Gases on Structural, Electronic and Optical Features of CNTs Molecules: Computation Study

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Abstract

The electronic properties of carbon nanotubes CNTs, such as ionization potential (IP), electron affinity (EA), energy gap (Eg), Fermi energy (Ef), binding energy (Eb), the density of state (DOS), and IR spectral properties, investigated after substituted the OH, SO, SiO_2, H_2O, and N_2 groups on the optimization structure of CNT (3,3). The lengths of C=C for zigzag CNT (3,3) slight altered with substituted the mention groups and given the depress in bond length during the substituted –OH, -SO, and $–SiO_2$ that attitude to bond orders for these substituted groups and different in electronegativity power for an oxygen atom in these groups. Moreover, the C-C bond for zigzag CNT (3,3) changed also, and gave a slight increase during the substituted OH group, but decreased during substituted So and SiO_2 groups. The substituted of –SO and $–SiO_2$ on the structure of CNT (3,3) demonstrated, fewer values of total energies that will increase the stability of CNT. The CNT_S-SiO_2 has a less value for bandgap compared with other substituted materials, this behaver has given it a good electronic conductivity. The B3LYP functional theory has been used to conduct the DFT approach. The analyzed Nano species agree well with the experimental results based on the measured values of HOMO and LUMO energies. The Gaussian 09 program was used to calculate all feature values.

Key Words: Electronic Structure, Band Gap, CNTs, B3LYP Functional Theory, HOMO and LUMO Energies.

DOI Number: 10.14704/nq.2022.20.5.NQ22174 **NeuroQuantology 2022; 20(5):298-303**

Introduction

Carbon Nanotubes (CNTs) were raised as the materials of the new era where such materials have many Nano-electronics, optics, and material applications [1-3]. The (CNTs) represent carbon's allotrope with a cylindrical Nanostructure. Such molecules of cylindrical carbon possess special and more features than any material [4]. These features are very important for optics, electronics, and the field of nanotechnology and significantly in materials science [5]. Nanotube represents a kind among the toughest material ever recognized for humans in each term of elastic modulus as well as tensile strength. Such strengthen the result of the covalent bond that exists in the single carbon atom. Since nanotube has comparatively little density, the strengths against weight rate can be extraordinary [6]. Raman and fluorescence spectroscopic features give useful information's about the structural features of these spices. There are many demands for this characterizing according to the industry perspective. The nanotubes' structure features could be altered. Raman, photoluminescence, and optical spectra permit fast as well as dependable characterizing for good nanotubes product according to nanotubes and non-tubular carbonic contents.

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Relevant conflicts of interest/financial disclosures: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Received: 13 March 2022 **Accepted:** 18 April 2022

These features determine the electrical, mechanical, and optical features [7]. One application of individual-Walled Carbon Nanotube (SWCNTs) is its usage in a panel of solar nature because of its strength and robust absorption in the wide range of UV visible-NIR spectra [8].

Large numbers of displayed preparations SWCNTs hybrid solar panel is utilized to achieve high competence. Such hybrids were produced via using SWNTs combined with a Photo-expiating electron donor for increasing the generating electron. The results of the previous study show that the combination between photo-excited porphyrin and SWNTs increases the generating of electron- holes pairs on the surface of SWNTs, and therefore it will contribute practically to increase the efficiency [9].

The nanotubes are potentially replacing the indium tin oxide within a cell of solar nature to conduct films within a solar cell for allowing light to go towards an active layer then to generate the photocurrents [10]. Within this work, the DFT method was employed for examining the electronic band structuring, states' total density, and local of (7,7) Carbonic nanotubes. However, the findings foresee that the nanotube metallically behaves. The carbonic nanotube geometries can be carried out and hence discussed subsequently upon connected electronic features and other physical features [11]. The examination of the electronic features of carbonic nanotube fabric composite material will be produced by utilizing dual easy producing procedures [12]. Carbon nanotubes will have large applications in the future for molecular electronics, so the experiment, along with theory studies for the electronic and structural features of carbon nanotubes are very important [13]. Also, studying the influence of zigzag on the bandgap, local-density-functional, density of state, and electronic features of CNTs is significant [14].

The theoretical and experimental analyses covering the physical, structural, chemical electronic as well as vibrating features for carbonic nanotube should be conducted by using first principles. It should be started with electronic features of zigzag carbon nanotubes [15, 16]. An experimental study of superconductivity, thermoelectricity, photoconductivity, and electroluminescence has been carried out [17]. The theoretical results of pure and doped SWCNTs that contain zigzag, zigzag (16, 0), (10, 0), and (8, 0) nanotubes using DFT methods well agree with the published experiment outcomes [18]. The previous theoretical study of the mechanical, vibrational, thermal, electronic, dielectric, and optical features for SWCNTs shows a good agreement compared with the experimental values [19]. The theoretical efforts have been directed to understand the interesting mechanical, electronic, vibrating, thermic, and optical features for the nanotubes. The nanotube still has an extensive range of undiscovered potential applications within different fields of technology, for instance, medicine, automobiles, the chemical industry, or aerospace and renewable energy [20, 21].

The purpose of this work is to investigate how the OH, SO, SiO_2, H_2O, and N_2 groups influencing electronic features such as ionization potential(IP), electrons affinity(E_A), energy gap E_g), Fermi energy(E_f), binding energy (E_b), the density of state (DOS), and IR spectral properties as well as the optimization structure of carbon nanotubes CNTs (3,3), DFT technique was conducted by using the B3LYP functional theory.

Computational Methods

The calculation was carried out using DFT/B3LYP, where the geometrical structure was optimized using the method of the Gaussian 09 program. [22]. E_{HOMO} represents the energy for the largest engaged molecular orbital, while E_{LUMO} represents the lowermost unengaged molecular orbital of CNT_S that gives the interacting methodology. The definition for HOMO could be given as an electronic donor due to its excessive electrons; while the LUMO lacks electrons, thus it possesses a force to attract electrons [23]. The ionizing potential (IP) and the electronic affinity (E_A) in the outline theorem for Koopmans could be measured from the energies of HOMO and LUMO as follows by Eqs. (1) and (2) [21, 23, 24]:

$$IP = -EHOMO \quad (1)$$

$$EA = -ELUMO \quad (2)$$

The energy gap E_g has been determined using Eq. (3)[21]:

$$E_{gap} = ELUMO - EHOMO \quad (3)$$

The E_f has been calculated by Eq.(4) [25,26]:

$$Ef = \left(\frac{EHOMO + ELUMO}{2}\right) \quad (4)$$

The binding energy E_b is calculated by Eq. (5)

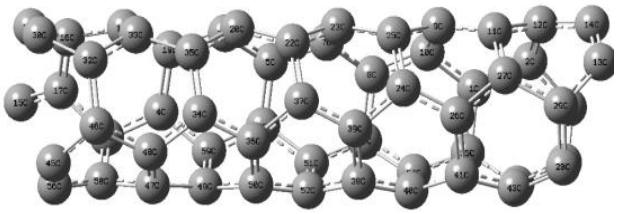
$$E_g = \left(\frac{E_{tot.}}{N}\right) - 1027.868 \quad (5)$$

Where $E_{tot.}$ is the total energy, and N refers to the atoms' quantity within the system, and E_{carbon} refers to the calculated total energy of an isolated carbon atom=1027.868 eV.

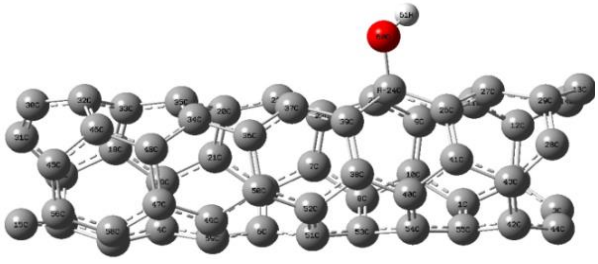
Results and Discussion

1. The Electronic Structure

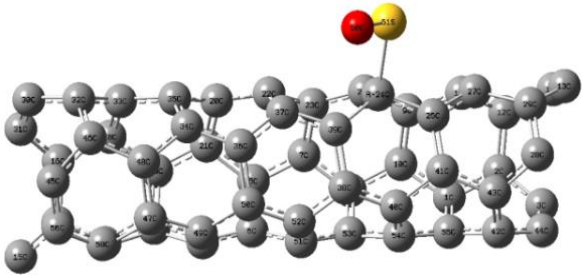
The calculated electronic and structural features of the nanomaterials studied are shown in fig.(1). The optimized bond lengths for C–C, and C=C of CNTs are found to be about 1.476 Å and 1.4423 Å, respectively. Such results agree well with other calculations for CNTs [2]. The C–C bond lengths for CNT_S-OH, CNTs-SO, CNTs-SiO_2, CNTs-$H_2O$and CNTs-N_2 are found to be 1.4785 Å, 1.4717 Å, 1.4768 Å, 1.4769 Å, and 1.4768 Å, respectively, which slightly differ from that of C–C bond lengths in CNTs that may be too slight alter in bond order for substituted groups. The value of C=C bond lengths for OH, SO, SiO_2, H_2O, and N_2 are 1.4105 Å, 1.4311 Å, 1.4279 Å, 1.4426 Å, and 1.4424 Å, respectively. It should be mentioned that all C=C bond lengths were slightly decreased and the less value found with addition OH that attitude to the high electronegativity for oxygen atom compared with hydrogen in the hydroxyl group, which will draw with the high electronic densities for C=C. While the bond lengths for H_2O and N_2 were slightly increased that may be beyond the dissemination of the electronic cloud from the unpaired electrons for nitrogen and oxygen.



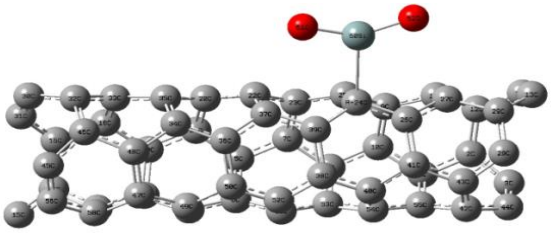
(a) CNT_S



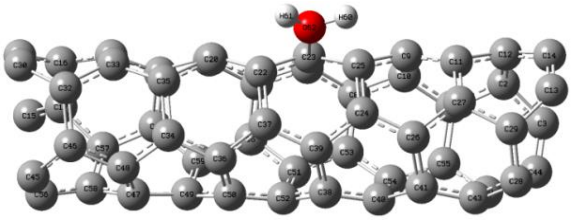
(b) CNT_S-OH



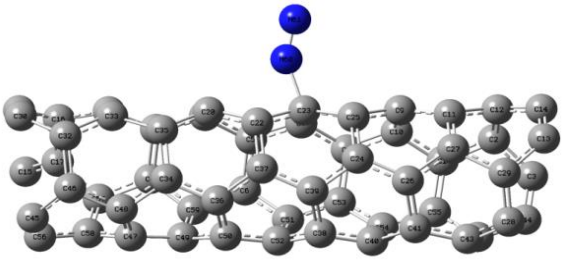
(c) CNT_S-SO



(d) CNT_S-SiO_2



(e) CNT_S-H_2O



(f) CNT_S-N_2

Fig. 1. Optimized structure for (a) CNT_S, (b) CNT_S-OH, (c) CNT_S-SO, (d) CNT_S-SiO_2, (e) CNT_S-H_2O and (f) CNT_S-N_2

The calculated natural bonds were performed to derive the HOMO plus LUMO energies, E_g, and Fermi energy (E_f). It is well known that CNTs are a semiconductor with Eg= 0.64354 eV. The values of these calculated physical quantities are listed in Table 1.

2. Electronic Features

All the physical features have been computed by utilizing the DFT/B3LYP 3-21G technique to CNT_S. Table 1 explains the calculated energy values of HOMO plus LUMO and electronic features values of IP and E_A Eg and E_f. It is clear from Table 1 the substituted OH, SO, SiO_2, H_2O, and N_2 lead to a decrease in the energy values of HOMO, LUMO, E_f, E_b, E_g, and E_{tot}, but they elevate the energy values of IP and E_A. CNT_S-OH has a high HOMO, and this value depends on the type of substituted; also, the (CNT_S-SiO_2) has a small energy Gap and E_f, this indicated to increase the activity of this molecule, CNT_S-SO has low E_{tot}, this factor would be very vital for the estimation the stability for those molecules. Consequently, this increase in total energy gives lower reactive and more stability for these structures. The HOMO-LUMO gap is significantly changed in all the cases. This change is very important in many applications since a small change of bandgap can modify the electrical conductivity.

Table 1. The electronic features ionization potential (IP), electron's affinity (E_A), energy gap(E_g),Fermi energy(E_f), values in eV units ,while binding energy (E_b) values in (a.u) units. of CNT_S, CNTS-OH, CNT_S-SO, CNT_S-SiO_2, CNTS-H_2O and CNT_S-N_2

Property (eV)	IP (eV)	E_A(eV)	E_g (eV)	EHOMO (eV)	ELUMO (eV)	E_f (eV)	E_b (eV)	$E_{tot.}$(a.u)
CNT_S	5.341791	4.69825	0.64354	-5.34179	-4.69825	-5.02002	-1065.94	-2246.08
CNT_S-OH	6.157577	4.20954	1.948035	-6.15758	-4.20954	-5.18356	-1065.93	-2321.91
CNT_S-SO	5.782882	4.87974	0.903133	-5.78288	-4.87975	-5.33132	-1072.45	-2719.35
CNT_S-SiO_2	5.722473	5.13117	0.591295	-5.72247	-5.13118	-5.42683	-1071.19	-2685.91
CNT_S-H_2O	5.220158	4.56877	0.651431	-5.22016	-4.56873	-4.89444	-891473	-2322.47
CNT_S-N_2	5.331723	4.68818	0.64354	-5.33172	-4.68818	-5.00995	-1066.48	-2355.55

3. Density of States

The density of states (DOS) is essentially used to understand and analyze the electronic properties; in this section, DOS contains the difference of energy for the HOMO, LUMO, and the structures. Fig. 2 (a-f) illustrates the Density of States of CNT_S as a task of energy levels. The DOS of the enhanced nanotubes, which indicate the CNT_S represent semiconductors with E_g ranging from (0.591295-1.948035) eV before and after substituted. The largest quantity of degenerating states within the valence and conduction bands can be shown as follows: 4.74, 4.69, 5.514, 4. 98, 5.080 and 5.23 for (CNT_S), (CNT_S-H_2O), (CNT_S - N_2), (CNT_S-SiO_2),(CNT_S-OH) and, (CNT_S-SO), respectively. From fig. 2, the DOS for all molecule structures have the same shape, and there are few differences in values the HOMO, LUMO, and energy gap, except fig. 2 (b) is different, Hydroxide (OH) consists of oxygen and a hydrogen atom that held together by a covalent bond, and carries a negative electric charge. It is an important but usually minor constituent of water. It functions as a base, a ligand, a nucleophile, and a catalyst. The hydroxide ion forms salts, some of which dissociate in an aqueous solution, liberating solvated hydroxide ions.

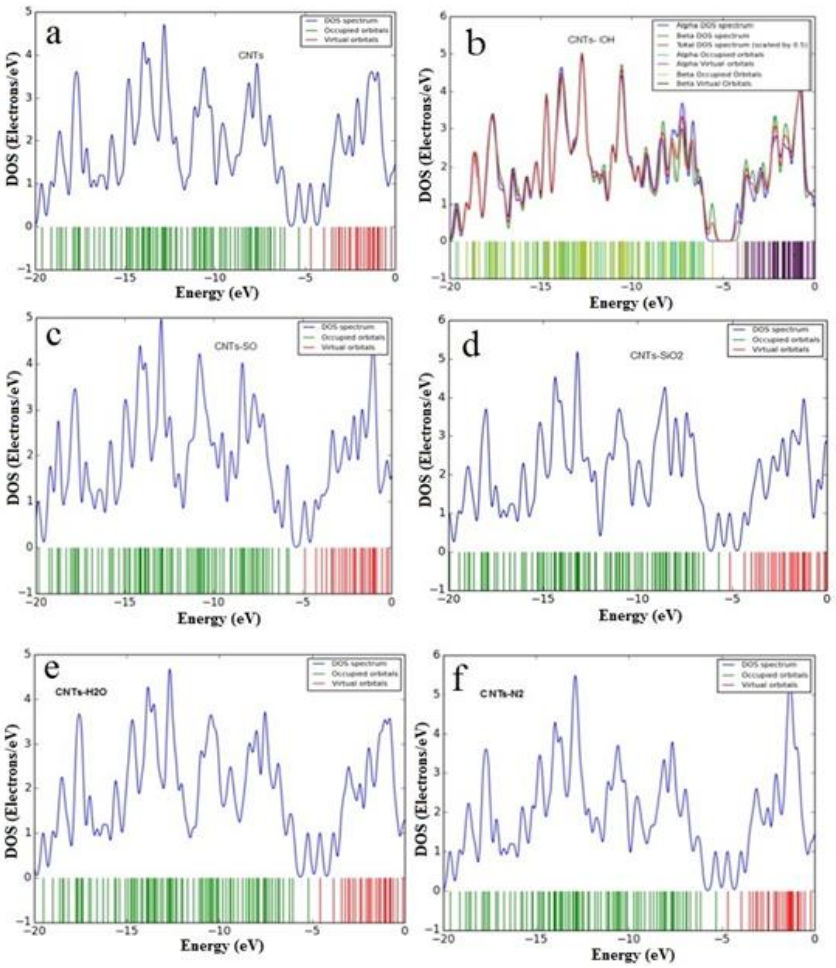


Fig. 2. The States of Density for the structure for (a) CNTS, (b) CNTS-OH, (c) CNTS-SO, (d) CNTS-SiO2, (e) CNTS-H2O and (f) CNTS-N2 structures for energy

There are many fundamental peaks in DOS. A large DOS with a certain energy level refers to the existence of several states which are available for the occupation. A zero-density of states indicates that no occupation for any state at that level of energy. The DOS of SO, SiO_2, H_2O, and N_2 nanotubes shows an increment within the largest DOS's quantity within the valence bands as well as conduction bands compared with CNTs.

4. Thermal Energy

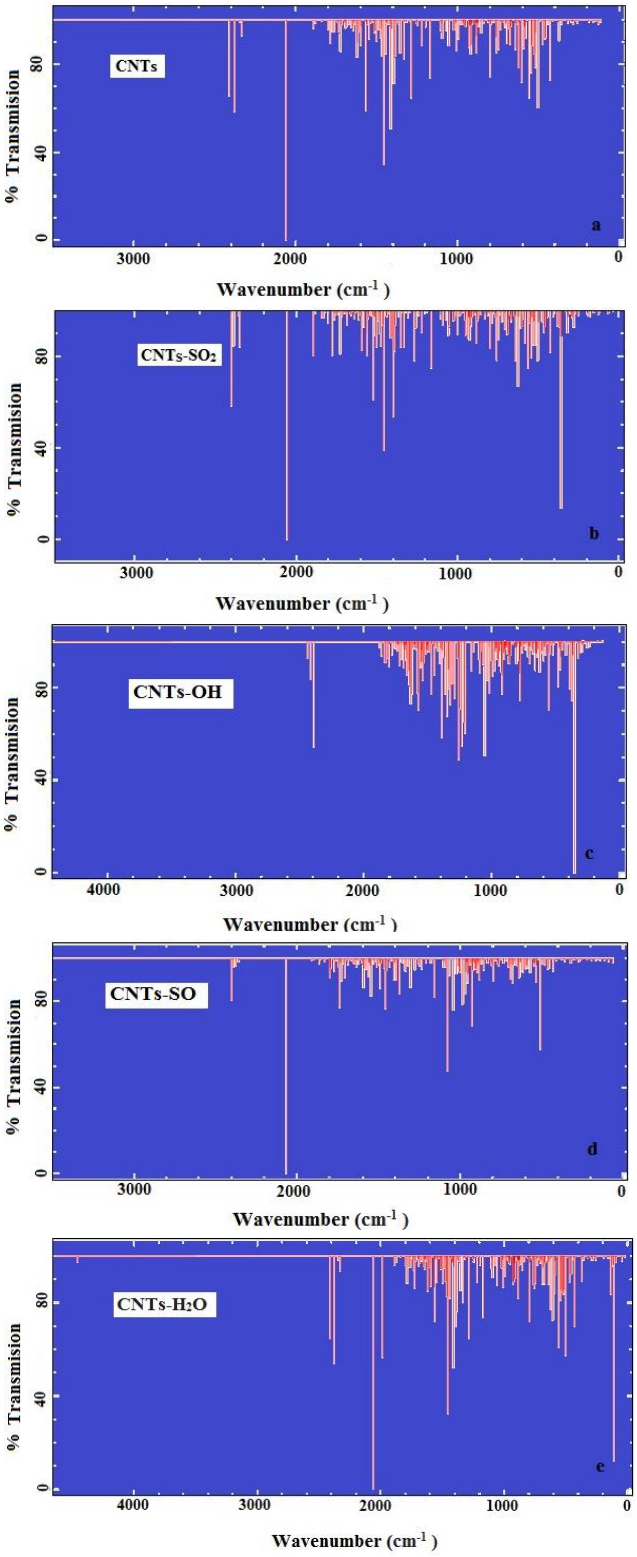
Table 2 illustrates the calculated values of enthalpy (E_{th}), calorific capacity (C_V) with entropy (S) using the DFT method with B3LYP. It is clear from this table that the existence of OH, SO, SiO_2, H_2O, and N_2 groups leads to elevate in the values of E_{th}, C_V, and the values of S increase. The CNT_S-H_2O has a maximum value in E_{th}, and The CNT_S-SiO_2 has a maximum value in C_V, while CNT_S-N_2 has a maximum value in S. That may be due to the chemical and physical nature of this substituted such as bond order, steric effect, reduced mass and effective charge of this groups.

Table 2. E_{th}, C_V, and S for CNT_S.CNT_S-OH, CNT_S-SO, CNTs-SiO_2, CNTs-H_2O, and CNTs-N_2 using DFT with 3-21G basis set

Molecules	E_{th} (kcal/mol)	C_V (kcal/mol)	S (cal/mol.K)
CNT_S	230.45	129.766	161.068
CNT_S-OH	240.464	133.763	162.904
CNT_S-SO	234.735	139.875	177.517
CNT_S-SiO_2	237.713	143.846	186.248
CNT_S-H_2O	246.897	141.685	188.184
CNT_S-N_2	236.777	139.699	197.591

5. IR Spectra

Fig. 3 (a- f) explains the computed IR spectra for CNT_S, CNT_S-OH, CNT_S-SO_2, CNT_S-H_2O, and CNT_S-N_2, respectively. For the studied nanotubes, the harmonic vibrational frequencies were determined using the B3LYP method with a 3-21G basis set. The (C–C) symmetrical stretchable vibrating has been placed at the center of 2406.06 cm^{-1}, and the (C=C) asymmetric stretching vibration is centered at 2372.62 cm^{-1}. The(C-C=C) in-plane vibration has been calculated at 1560.53 cm^{-1}. The out-of-plane (C-C=C) bending vibration is found at 423.395 cm^{-1}, which is in good agreement with the experiment value that equals 552.90 cm^{-1} [1]. The OH, SO, SiO_2, H_2O, and N_2 groups have new vibrational stretching modes of (O-H), (C-OH), (S-O), (C-SO), (Si–O_2), (C-SiO_2), and (O-H_2) at 1561.99.1258.89, 318.5.929.959, 270.73 and 822.977 cm^{-1}, respectively. However, the waging vibrations C-OH, S-O, and Si–O_2 are centered at (349.609, 877.868, and 226.69)cm^{-1}, respectively, while the rocking vibration is centered at 290.900 cm^{-1} for C-SiO_2, the bending vibration of O-H_2 is centered at 1613.5cm^{-1}, the N-N stretching vibration is at 2352.4cm^{-1}. Finally, the weak bond centered at 332.4cm^{-1} is due to the CN_2 bending vibration.



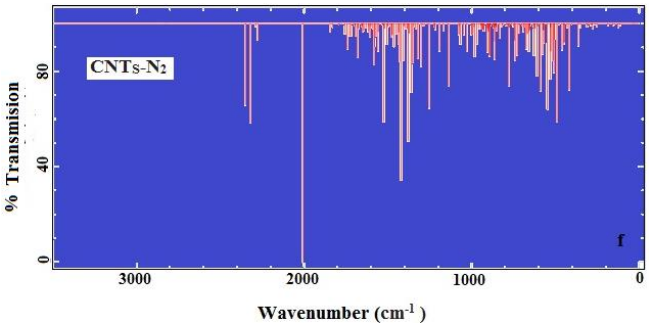


Fig. 3. Calculated IR spectra for (a) CNTS, (b) CNTS-OH, (c) CNTS-SO, (d) CNTS-SiO2, (e) CNTS-H2O and (f) CNTS-N2 structures

Conclusions

The electronic features of substituted OH, SO, SiO_2, H_2O, and N_2 groups on CNTs have been studied. The vibrational bands of these groups have been assigned. The DOD of these groups has also been calculated. The values of HOMO, LUMO, IP, C_V, E_A, S, E_{th}, E_f, E_b, E_g, and E_{tot} have been calculated by using the DFT method depending on the B3LYP functional and Gaussian 90 program and found the less E_g for substituted SiO_2 on CNT with less total energy, hence, it regards as a good semiconductor that favors used in electronic devices. The CNT_S-SO and CNT_S-SiO_2 have low E_{tot}, therefore they are stable compounds. The maximum entropy found with substituted with $-N_2$, that due to steric effect for orbitals because nitrogen bond as triple bond with the other nitrogen atom. All the above physical quantity values agree well with the ones of the experiment outcomes as reported in the results.

Acknowledgment

The authors appreciate the assistance of the University of Technology's Applied Science Department, Kerbala University's Physics and Chemistry Departments, and University of Babylon, in completing this project.

Conflict of Interest

The authors confirm that this manuscript content has no conflict of interest.

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