



Halogens Substitution Effects on Electronic and Spectral Properties of Carbon Nanotube Molecules studying with the DFT method

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Abstract

The carbon nanotubes (CNTs) in a zigzag (4, 0) shape before and after substituted with F, Cl, and Br atoms were used as a basic computer model depending on the Quantum Espresso package DFT process) in the present work. This method demonstrated that the electronic structure, bandgap, total energy, FTIR spectrum, Raman spectrum, and depolarization spectrum can all being calculated. The simulated results are discovered that the increase in impurity atom size from F to Br as donor groups on nanotubes reduce the energy gaps from 0.959 eV to 0.674 eV, the ionization potentials from 6.088 eV to 5.729 eV, the electron affinities from 5.129 eV to 5.054 eV, and the firm energies from 5.609 eV to 5.392 eV. As a result, these substituted compounds have a high activity to act as a catalyst with broad absorption bands of the solar spectrum in the following order: Br+CNTs > Cl+CNTs > F+CNTs > CNT. This behavior will provide a better output for the solar cells and photovoltaic devices. The increment in HOMO, LUMO, and total energy magnitudes with increasing the impurity atom size from F to Br is given maximum changes, decreases band gaps, and elevated entropy values because of elevating in random.

Keywords: Carbon nanotubes; CNTs; DFT method; FTIR spectra; Raman spectra; depolarization spectra.

1. Introduction

Carbon nanotubes (CNTs) offer several unique and special properties, which suggest great promise for applications in nanoelectronics. In the high electrical, the conductivity of quantum wires provides a potential solution for on-chip interconnect metals, particularly, and transistors of future integrated circuits [1]. Carbon nanotubes have attracted much attention from researchers worldwide due to their pseudo exceptional mechanical, 1D structure, thermal and electrical properties, and many applications such as solar cells, gas sensors, chemical sensors, and nanoelectronic devices so forth [2,3]. Carbon has various chemistry and abundant forming compounds with almost every other known element of the Periodic Table. Bulk carbon materials, such as graphite and diamond, have been known for centuries; more recently, quasi low- dimensional allotropes of carbon have been discovered. The two-dimensional graphene [4,5] has several essential characteristics of carbon nanotubes that have been described. Graphene is including mechanical strength, which is higher than that of the other materials [6], and the good thermal conductivity an

order of magnitude is higher than that of copper [7]. Many commercial applications have been proposed, from molecular electronic devices to sensors [8]. It is more difficult to assess if these can be realized [9]. In theory, several approaches have been employed to study the electronic properties and bandgap, such as chemical doping and electric fields [10-16]. The effect of the carbon impurities on the electronic properties and the density of states of (10,10) and (16,0) SWBNNTs[17] was examined. The present research aims to study the optimized structure, electron affinity, ionization potential, energy gap, total energies, and use the DFT for CNTs, CNTs+F, CNTs+ Cl, and CNTs+Br molecules.

2. Experimental

Computational details

In the present study, the DFT calculations were performed using the package Gaussian 09 [18]. DFT calculations are a vital method to investigate the FTIR, Raman, and depolarization spectra of studied molecules. Moreover, the thermal properties were measured. Becke three parameters Lee–Yang–Parr

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(B3LYP) functional [19,20] with 3-21G basis set were used, to investigate the effect of defects for the halogens (F, Cl, and Br) impurity on the total energy, ionization potential, Fermi energy, bandgap, electron affinity, highest occupied and lowest unoccupied molecular orbital, and density of state of zigzag (4, 0) CNTs. These calculated functions were chosen because they provide this work in relatively good geometries of halogen-CNTs molecular systems. The mechanism is provided by the energy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of CNTs. Due to having an excess of electrons, the HOMO can be defined as an electron donor, whereas the LUMO lacks electrons and therefore has the power to accept electrons. The CNTs optimized structures are shown in **Figure 1**.

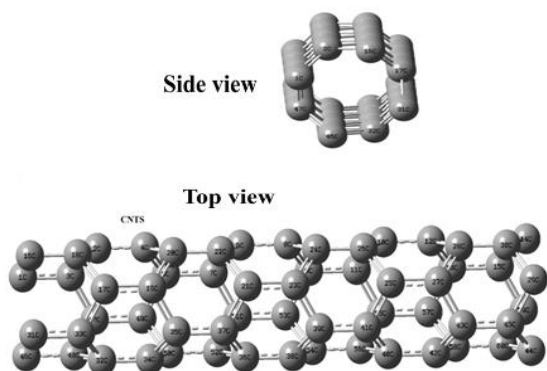


Figure 1. The optimized structures of CNT.

The ionization potential (IP) and electron affinity (EA) in the framework of Koopmans' theorem could be calculated from the energies of HOMO and LUMO as follows by Equations 1 and 2 [21].

$$IP = -EHOMO \quad (\text{Eq. 1})$$

$$EA = -ELUMO \quad (\text{Eq. 2})$$

The energy gap (E_{gap}) may be calculated from [22]:

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

The Fermi energy (E_f) has been calculated by Equation 4 [23, 24]:

$$E_f = \left(\frac{EHOMO + ELUMO}{2} \right) \quad (\text{Eq. 4})$$

3. Results and Discussion

Electronic Structure

The calculated electronic and structural properties of CNTs as clarified in **Figure 2** and **table 1**. The

optimized bond lengths for C–C, and C=C in CNT are equal to 1.4581 Å and 1.4834 Å. The bond lengths for C–C, C=C decrease with impurity CNT by F to form a C-F bond and equal to 1.4581 Å, 1.4834 Å, and 1.3508 Å, respectively. The impurity of CNT by Cl gives the reduction in the bond lengths of C-C and C=C also, during formed C-Cl bond and equal to 1.40443 Å, 1.4524 Å, and 1.7866 Å respectively. Moreover, the impurity of CNT by Br leads to depressing in the bond lengths of C-C and C=C after formed C-Br bond, which equals 1.4001 Å, 1.4551 Å, and 1.8917 Å respectively. From the above-mentioned results, the bond lengths (BL) for C-halogen are increment with increased atomic size and decreased electronegativity and following the sequences:

$$BL \text{ for } C-F > B.L \text{ C-Cl} > B.L \text{ C-Br}$$

In this case, the effect of halogens (F, Cl, Br) impurity, which is small different than that of C–C and C=C bond length in CNTs, as shown in figure 2. The bond angle magnitude of CNT reduces with adding halogens as CNTs+F, CNTs+ Cl, and CNTs+Br with the following order:

$$CNTs+F < CNTs+ Cl < CNTs+Br$$

This behavior indicates the most electron affinity for F compared with the electron affinities of Cl and Br [25].

The 3D plot of the HOMO and LUMO orbitals of CNTs+F, CNTs+ Cl, and CNTs+Br from DFT with 3-21G basis set calculations are shown in **Figure 3**. In this figure it can be seen that the majority of the molecular orbital density in HOMO and LUMO orbitals is localized along the C-C backbone. Additionally, the addition of halogen allows the charge to be distributed along the length of all CNTs.

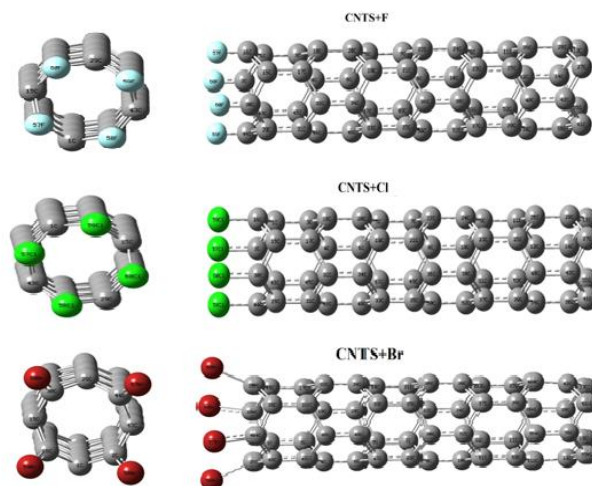


Figure 2. The optimized structures of CNTs+F, CNTs+ Cl, and CNTs+Br molecules using the DFT method with a 3-21G basis set.

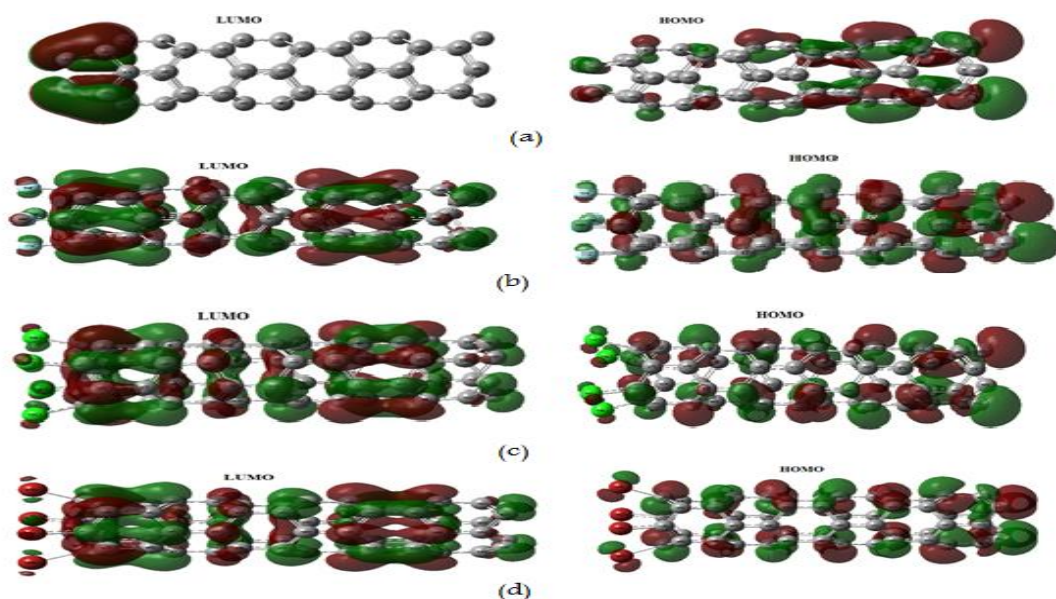


Figure 3. Shapes HOMO and LOUMO for (a) CNTs, (b) CNTs+F, (c) CNTs+ Cl and (d) CNTs+Br molecules using DFT with 3-21G basis set.

Table 1

Optimized geometrical parameters for CNTs, CNTs+F, CNTs+ Cl, and CNTs+Br molecules using the DFT method with a 3-21G basis set.

Molecules	Bond Types	Bond length (B.L)/ (Å)	Bond Types	bond angles A (°)
CNTS	(C-C)	1.4581	A(C=C-C)	119.3613
	(C=C)	1.4834	A(C-C=C)	119.1575
		1.374 ,1.48342	A(C=C=C)	107.7132
CNTS +F	(C=C)	1.4451	A(C=C-C)	117.4773
	(C-F)	1.3508	A(C=C=C)	106.4301
	(C-C)	1.4065	A(C=C-F)	119.8342
			A(C-C=C)	119.2252
CNTS +Cl	(C=C)	1.4524	A(C=C-C)	116.4618
	(C-Cl)	1.7866	A(C=C=C)	107.9047
	(C-C)	1.4043	A(C=C-Cl)	122.3495
			A(C-C=C)	119.2195
CNTS +Br	(C=C)	1.4551	A(C=C-C)	117.0513
	(C-C)	1.4001	A(C=C=C)	108.5654
	(C-Br)	1.8917	A(C=C-Br)	123.7254
			A(C-C=C)	119.2201

Electronic properties

Table 2 presents the values of the calculated quantum chemical parameters such as the electronic properties (ionization potential(I), electron affinity (E), energy gap(E_g), energy Fermi(E_f), and total energy(ET) [21, 23, 26], in (eV) units for CNTs+F, CNTs+Cl and CNTs+Br molecules using DFT with 3-21G basis set. The results noted that the HOMO, LUMO, and the total energy rise with an impurity by (F, Cl, Br), while I , E , E_g , and E_f decrease for (4, 0) tubes. The I for CNTs+F, CNTs+Cl, and CNTs+Br are less than that for the pristine tube; this indicated to the CNTs being studied may need a small amount of energy to become a cation comparing with a pristine tube, and

confirming their electron-donating properties. This small value of I will make CNTs+F, CNTs+Cl, and CNTs+Br useful for detectors of high-energy particles or as catalysis.

According to **Figure 4**, the results demonstrate that the energy gap of CNTs after substituted by halogens reduced from 0.959 eV to 0.674 eV with increasing the atom sizes as order F, Cl, and Br. That attitude to increase the number of trap levels with defect, which leads to increase the HOMO energy and decrease the LUMO energy. Because the HOMO energy is directly proportional to the ionization potential (I)

that due to increment the oxidation reaction, while, the LUMO energy is directly related with the electron affinity and the redaction reaction has closely happened.

The interaction between these orbitals mostly produced new bond via chemical reaction [26, 28]. Moreover, the Fermi level values and total energy The FTIR spectra of the C–C, and C=C are stretching studied in the region 162.36 cm^{-1} and 105.88 cm^{-1} for CNTs, which can be seen in **Figure 5**. The vibration modes were computed for CNTs+F, CNTs+Cl, and CNTs+Br molecules using the DFT method with a 3-21G basis set. Molecules have the C–C and C=C bonds studied in the region $1572.47\text{--}1575.07\text{ cm}^{-1}$ and $1840.84\text{--}122.27\text{ cm}^{-1}$, which can note in Figure 4. The impurity (F, Cl, Br) leads to a decrease in the values of C–C and C=C and new vibration modes for molecules under study. The

decrease with defect CNTs by halogen and cause the elevated activity of CNTs in a different application. However, this feature is hardly useful in various applications, such as energy devices, and good anode material for creating biology.

FTIR spectra

CNTs+F has C-F stretching studied in the region 831.87 cm^{-1} , while the CNTs+Cl found C-Cl stretching, and out of the plan in the region 419.3 cm^{-1} and 251.78 cm^{-1} . The C-Br stretching in region 619.723 cm^{-1} is an assignment to CNT+Br. From this figure, it can show the effect of (F, Cl, Br) impurity atoms are led to a high-Intensity vibration mode compare with the pure CNTs, which also led to a weak harmonic vibration.

Table 2 HOMO, LUMO energies and electronic properties (*I*, *E*, *E_g*, *E_f*, and *ET*) in (eV) units for CNTs, CNTs+F, CNTs+ Cl, and CNTs+Br molecules using the DFT method with a 3-21G basis set.

Molecules	HOMO	LUMO	<i>E_g</i> eV	<i>I</i> eV	<i>E</i> eV	<i>E_f</i> eV	<i>ET</i> eV
CNTs	-6.08873	-5.12955	0.959188	6.088733	5.129546	5.609139	-2272.04
CNTs+F	-5.98751	-5.18125	0.806262	5.987508	5.181247	5.584377	-2517.87
CNTs+Cl	-6.01554	-5.31077	0.704765	6.015536	5.310771	5.663153	-3952.62
CNTs+Br	-5.72982	-5.05499	0.674833	5.72982	5.054987	5.392404	-12367.2

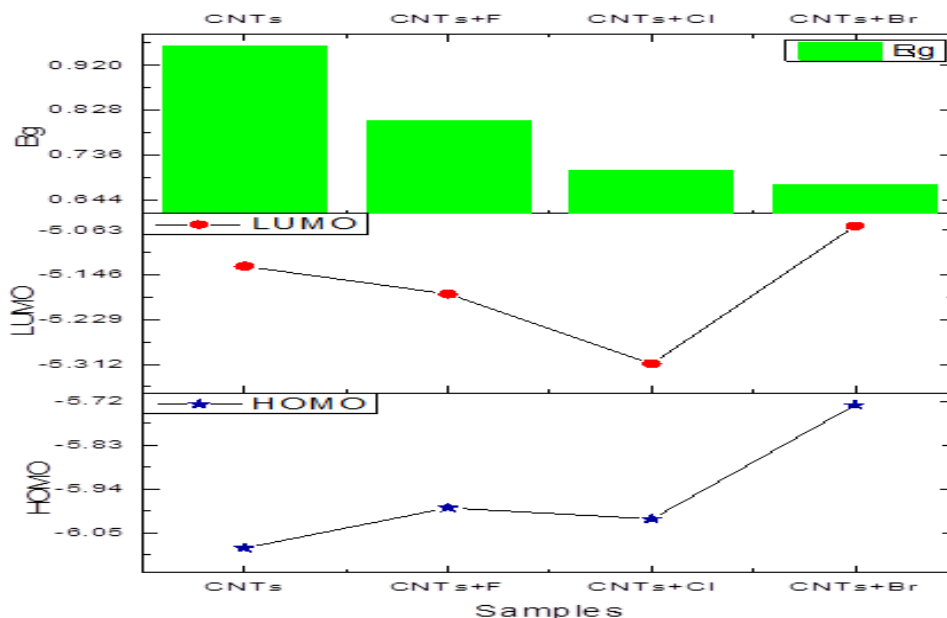


Figure 4. Relationship of the HOMO, LUMO, Bg with CNTS before and after substituted by haloge

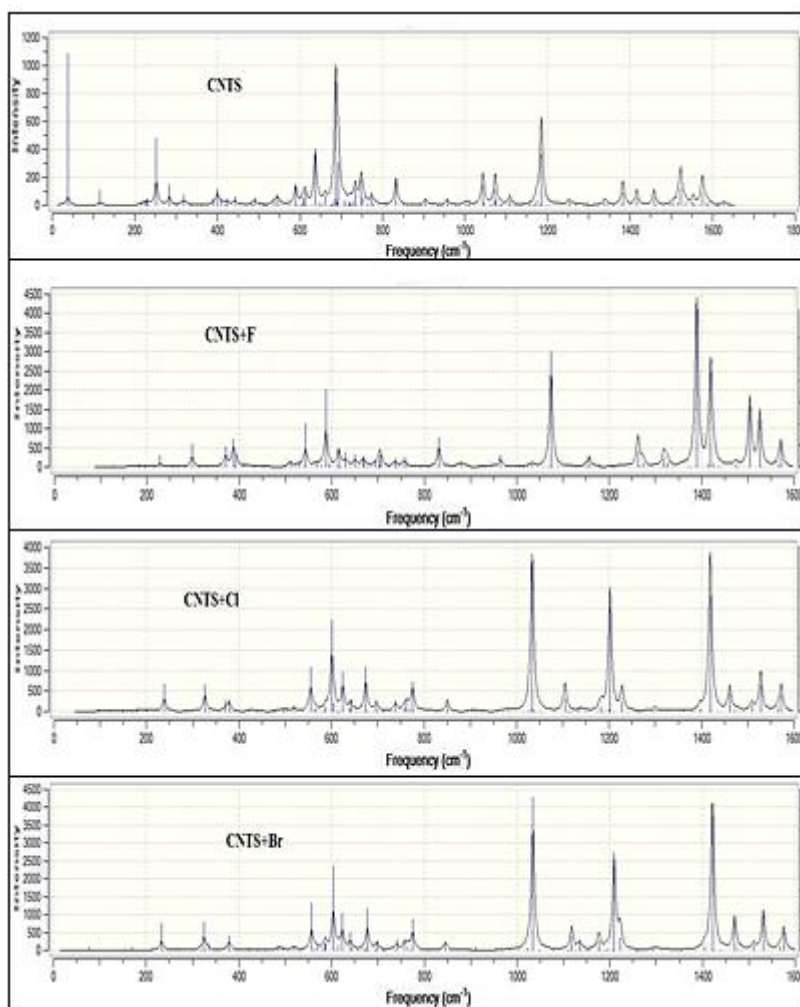


Figure 5. FTIR spectra for CNTs, CNTs+F, CNTs+ Cl, and CNTs+Br molecules using the DFT method with a 3-21G basis set.

Raman and Depolarization spectra

Figure 6 illustrates the Raman spectra of stretching are active at (5102.5 and 815.21) $\text{Å}^4/\text{AMU}$ with vibration at the (1627.36 and 1584.47) cm^{-1} . In addition, the p-Depolarization spectrum at 0.75 with the frequency equal to (1589.31-423.254) cm^{-1} and the u-Depolarization spectrum at 0.857 with the frequency equal to (1627.36-423.254) cm^{-1} are found for pristine CNT, while the magnitudes for CNTs+F, CNTs+Cl, and CNTs+Br have stretching active at 1768.59 $\text{Å}^4/\text{AMU}$ and vibration at the 1515.88 cm^{-1} . On the other hand, the p-Depolarization spectrum and u-Depolarization spectrum at 0.75, 0.8571 and vibration in the region (157.47-111.268) cm^{-1} for CNTs+F and CNTs+Cl, which has stretching active (2512.77) $\text{Å}^4/\text{AMU}$ and vibration in the region 1527.99 cm^{-1} , also has the p-Depolarization spectrum and u-Depolarization

spectrum at 0.75, 0.8571 and vibration in the region 1572.14-69 cm^{-1} and the stretching active 2543.84 $\text{Å}^4/\text{AMU}$ vibrations in the region 1531.23 cm^{-1} , and the p-Depolarization spectrum and u-Depolarization spectrum at 0.75, 0.8571 and vibration in the region 38.1947-1156.76 cm^{-1} for CNTs +Br. From this **Figure 6**, it can be seen that the effect of impurity (F, Cl, Br) atoms in place of the carbon atom lead to decreasing the stretching actively and the vibration for CNTs understudy, for the effect of impurity (F, Cl, Br) atoms on the (p and u) depolarization spectra lead to decrease the degeneracy for tube being studied compared with pristine CNT. This indicated to these molecules are active in FTIR and Raman spectra. The vibrational transition would have appeared in FTIR and Raman spectra as allowed transitions, However, the intensity of these bands will vary depending on the changes in the magnitude of dipole moment for infrared

spectrum, and the alters in magnitude or/and direction of polarizability terms for Raman spectrum [12,13].

Thermal properties:

Table 3 and Figure 7 display the calculated values of thermal properties such as a thermal correction to energy (E_{th}), heat capacity at constant volume (C_v), and entropy (S) using the DFT method with B3LYP. From this Table, it is clear that the effect of impurities (F, Cl, Br) atoms in place of the carbon after halogen-substituted on the CNTs surface indicate a tendency to elevate randomly on the CNTs surface. atom cause a decrease in the values of E_{th} , while C_v and S are increasing. The elevated entropy values. these atoms have a high electronegativity and low steric effect than the Br atom, therefore; it is attracted to charge toward them.

Table 3 E_{th} , C_v and S in Kcal/mol and cal/mol.K units for nanotube molecules CNTs, CNTs+ F, CNTs+Cl, and CNTs+Br using DFT with a 3-21G basis set.

Molecules	E_{th} Kcal/mol	C_v Kcal/mol	S cal/mol.K
CNTs	227.133	127.551	155.116
CNTs+F	221.579	133.538	161.226
CNTs+Cl	217.229	139.054	173.461
CNTs+Br	216.905	139.990	183.333

As compared with pristine CNTs, the CNTs+Br have a high C_v and S being analyzed often have high values of (E_{th}), indicating that the attitude to Br has a large atomic size with high electronic levels.

Electron density surfaces (EDS):

The electron density surfaces for CNTs, CNTs+F, CNTs+ Cl, and CNTs+Br molecules using the DFT method with a 3-21G basis set are shown in **Figure 8**. The distribution of electron density surfaces depends

on the type of substitution atoms; also depends upon the negative and the positive charges. From this figure, the density distribution on CNTs, CNTs+F, and CNTs+ Cl molecules is homogenous, while in CNTs+Br molecules is different than CNTs, CNTs+F, and CNTs+ Cl molecules.

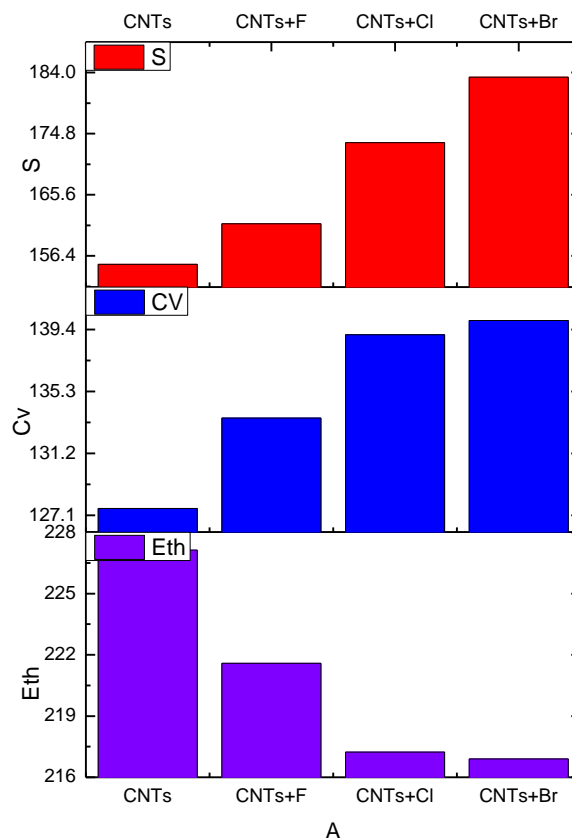


Figure 7. Relationship of the E_{th} , C_v and S with CNTS before and after substituted by halogens

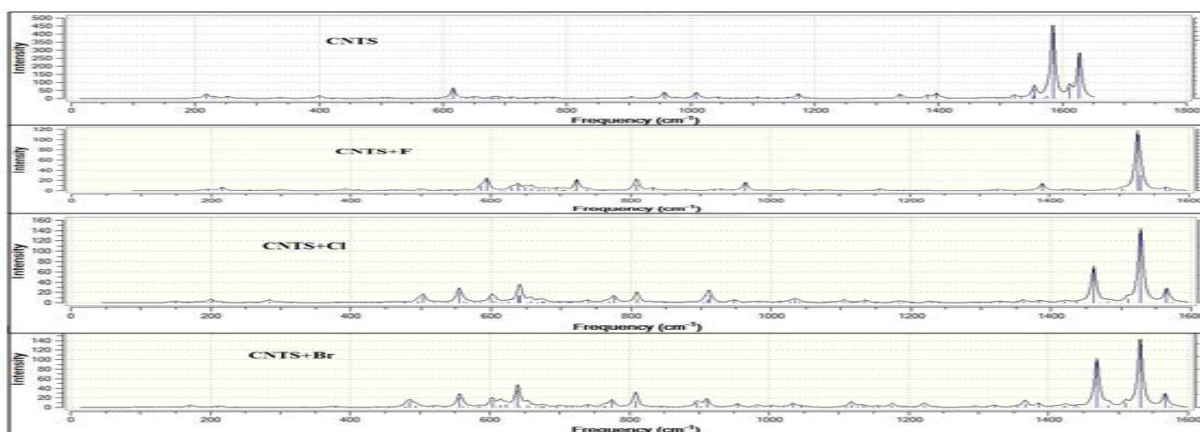




Figure 6. Raman and Depolarization spectra for CNTs, CNTs+F, CNTs+ Cl and CNTs+Br molecules using the DFT method with a 3-21G basis set.

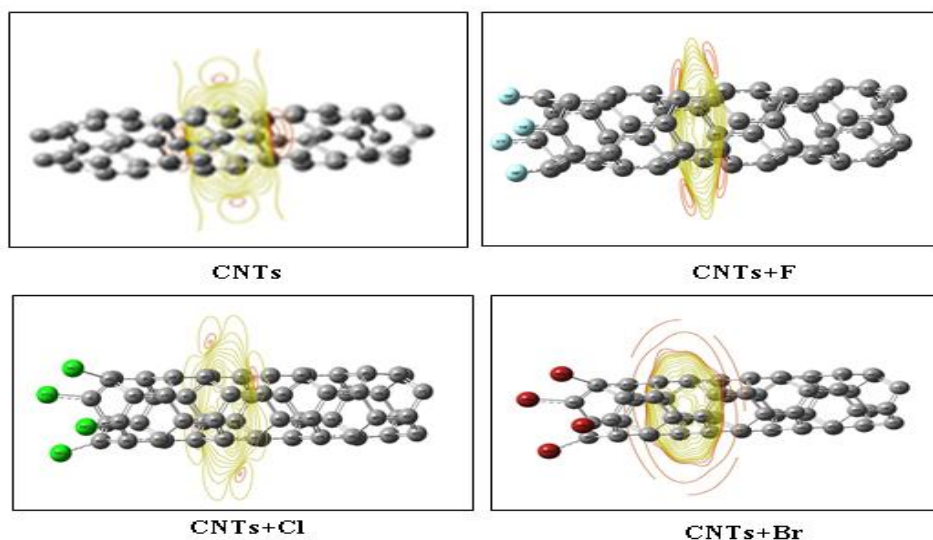


Figure 8. The electron density surfaces for CNTs, CNTs+F, CNTs+ Cl, and CNTs+Br molecules using the DFT method with a 3-21G basis set.

4. Conclusions

The key findings are summarized in this work based on the output results of Gaussian 09, (B3LYP) functional and 3-21G basis, and it is discovered that there are three halogens substituted on CNTs zigzag (4,0) molecules group examined. The electronic properties of pure CNTs and they are substituted with a halogen such as F, Cl, and Br are altered depending on the shape and size of impurity atoms. The values

of bond angle magnitude of CNT depress with substitution F, Cl, and Br. The magnitudes of HOMO, LUMO, and total energy rise with the impurity atom size by F, Cl, and Br, whereas the values of I , E , E_g and E_f decrease, corresponding to the more reactive molecule in the reactions with electrophiles size. The decrease of ionization with substituted halogen atoms F, Cl, and Br leads to produce the cations of their compounds, which elevated the probability to use them as catalysts. In

Raman spectra, the substitution with F, Cl, and Br lead to new vibration modes with small different stretching vibration; the modes of vibration are high Intensity compared with the pure CNTs. Moreover, it leads to weekly harmonic vibration, also, the substituted by (F, Cl, Br) on CNTs is caused to decrease the stretching actively and the vibration for CNTs understudy, for the effect of the impurity (F, Cl, Br) atoms on the (p and u) Depolarization spectra lead to decrease the degeneracy for tube under study compared to pristine CNT. On the other hand, in FTIR and Raman spectra, the vibrational transitions happened as allowed transitions. The intensity of bands in Raman and FTIR spectra alters with changes in the magnitude of dipole moment for infrared spectrum and direction of polarizability terms for Raman spectrum. The values of E_{th} , decrease, while C_V and S increase with substitution by halogen atoms (F, Cl, Br) atoms in place of the carbon atom. The CNTs+Br molecule has a low energy gap value of 0.674833 eV. This small energy gap indicated to increment in the activity of the molecule, thereby the impurity (F, Cl, Br) in place of the carbon atom of CNTs are essential in the industry for multiple uses, such as in the biochemistry of all living things, whereas photovoltaic, solar cells, thin-film transistors and organic light-emitting diodes (OLEDs).

5. Conflicts of interest

"There are no conflicts to declare".

6. Formatting of funding sources

Self

7. Acknowledgments

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