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Adsorption of NO_2 molecules on single-walled carbon nanotubes: A Computational Electronic Energies and Relative Stabilities Study

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ABSTRACT

The combining processes of adsorption on all different sites of surface and open ends of SWCNTs are mainly exothermic and the relaxed geometries are generally less stable. The obtained results reveal that the interaction between NO_2 molecule and the open-ended armchair (4, 4) SWCNT is weak and may be considered as chemisorption process.. In the contrary, the interaction between NO_2 molecule and the open ended zigzag (5,0) SWCNT is rather strong and can be concluded as a physisorption process. The chemisorption of NO_2 molecule has appreciable adsorption energy. This may be attributing to electronic configuration of p electrons on the surface and carbon doped atoms on the open ends of these models of SWCNTs. Thus, the adsorption of NO_2 molecule over the surface and on the open ends of the SWCNTs would affect their electronic conductance and mechanical properties, which could serve in the gas sensor signal. It can be concluding that the remarkable charge transfer from SWCNTs to NO_2 molecule falls out due to the decrease of the gap of HOMO–LUMO energy.

Keywords: Physisorption, chemisorptions, conductance, energy gap, HOMO – LUMO energy.

INTRODUCTION

The first researcher who has found carbon nanotubes was Ijima, which produced by graphite and reported this ushered in a new and phenomenal research field in compressing gases by physisorption methods [1]. The changes in electrical resistance by adsorption of certain gas molecules, also were studied by certain authors and are considerable [2- 4]. For example the adsorption of NO_2 depicts $C_{40}H_{10}$ and $C_{72}H_{16}$ tubes modeling a zig-zag (5,0) and armchair (4, 4) SWCNTs (Figure 1) which demonstrates the stated effect on the electronic structure of SWCNTs [5-7]. Electronic properties of SWCNTs have been studied in numerous computational and theoretical studies and optimized forms of nanotubes can be designed by a precise positioning of NO_2 gas on considered carbon atoms [8,9]. Although, some studies have investigated the adsorption of other gases such as O_2, NH_3, N_2, CO_2, CH_4, H_2O, H_2 and Ar [10-14], the adsorption of NO_2 on SWCNTs has not been clearly studied.

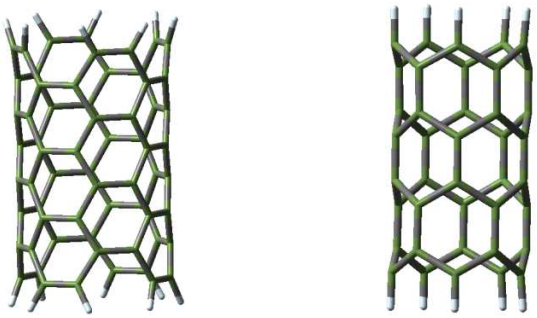
In this paper, we report the results of density functional calculations that investigates the changes in the electronic structure of CNTs when exposure NO_2 molecule. This observation motivated us to undertake calculations aimed at elucidating the mechanism by which NO_2 molecules adsorbed over SWCNTs.

In this study NO_2, adsorption mechanism on the surface and on the open ends of SWCNTs investigated. It was found that NO_2 can be adsorbed on the surface and open on the ends of zigzag (5, 0) and armchair (4, 4) SWCNTs that makes active nitrite group. The obtained computational results in this work, can lead to a new comprehension to the nanotechnology of gas sensing and monitoring.

MATERIALS AND METHODS

Computational details

The interactions of CO_2 gas molecules on the surface and on the open ends of zigzag (5, 0) and armchair (4, 4) SWCNTs were evaluated within the framework of density functional theory [13-15]. In order to avoid the boundary effects, hydrogen atoms doped the atoms at the open ends of SWCNTs. The performed calculations based on DFT in this investigation the gauge-included atomic orbital (GIAO) approach [16-20]. Therefore, structures of SWCNTs are allowed to fully relax during the base series B3PW91/6-311++G (*d*, *p*) optimization process and properties of the structures considered models of SWCNTs armchair (4,4) (constructed of 64 C and 16 H atoms), and zigzag (5,0) (constructed of 40 C and 10 H atoms), types (Fig. 1) were calculated.



(a) (b)

Fig.1. Pristine structure of single walled carbon nanotubes (a) armchair (4, 4), (b) Zigzag(5,0)

To confirm that, all of the stationary points are relate to true minima on the surface of the potential energy, the vibration frequencies also calculated at the same level. Geometry and density of states (DOS) of zigzag (5, 0) and armchair (4, 4) SWCNTs of the optimized tubes which are shown in Fig. 1, indicate that the tubes are either semi-conductor or conductor with HOMO/LUMO energy gaps (E_g) of 0.122 eV and 0.131 eV, respectively. The diameters and the lengths of the optimized pristine SWCNTs, zigzag (5, 0) and armchair (4,4), were calculated and were about 4.02 A and 7.08 A, 5.67A and 7.34A, respectively. The adsorption energy (E_{ads}) is determined as the energy difference between the adsorbate and the adsorbent in the interaction process. Thus, E_{ads} of the gas onto nanotubes defined as:

$$E_{ads} = E_{SWCNTs-NO_2} - (E_{SWCNTs} - E_{NO_2}) \quad (1)$$

Where $E_{SWCNTs-NO2}$ denotes the total energy of the (5,0) zigzag and (4,4) armchair SWCNTs with the corresponding adsorbed gas molecule and E_{SWCNTs} and E_{NO2} are the total energies of the isolated nanotubes and gas molecules, respectively. Based on the equation (1), negative adsorption energy means that the formed (NO_2-SWCNTs) complex is stable and positive adsorption energy indicates that the local minimum belongs to the adsorption of gas molecules onto the nanotubes, which debarred by a barrier. Where E_{SWCNTs} in NO_2-SWCNTs /E_{NO2} in NO_2-SWCNTs is the total energy of SWCNTs /E_{NO2} and E_{def} SWCNTs /E_{def} gas is the deformation energy of tube/gas in its relaxed geometry.

By this explanation, $E_{ads}<0$ corresponds to exothermic adsorption which results in local minima perdurable for adsorption of gas molecule on the open end of zigzag (5,0) SWCNT.

The electronic structure of the most energetically favorable complexes analyzed according to the partial and net charge transfers, which obtained from natural bond orbital (NBO) and Mulliken analysis to estimate the sensing capability [21]. The quantum molecular descriptors [22, 23] for SWCNTs defined as following:

$$\mu = -(I + A)/2 \quad (2)$$

$$\chi = -\mu \quad (3)$$

$$\eta = (I + A)/2 \quad (4)$$

$$S = \frac{1}{2}\eta \quad (5)$$

$$\omega = \left(\frac{\mu^2}{2\eta}\right) \quad (6)$$

Where, I ($-E_{HOMO}$) is the ionization potential, A ($-E_{LUMO}$) is the electron affinity of the molecule, E_{HOMO} is the energy of the Fermi level, E_{LUMO} is the first given value of the conduction band and χ is defined as the negative of chemical potential ($\chi = -\mu$). Furthermore, hardness (η) can be approximated using the Koopmans' theorem [24] as: $\eta = (E_{LUMO} - E_{HOMO})/2$. Softness (S) [25] and electrophilicity (ω) [26] defined by equations (5) and (6). The maximum amount of electronic charge, ΔN_{max} (a.u.), that the electrophile system may accept given by Eq. (7) [27]:

$$\Delta N_{max} = \frac{-\mu}{\eta} \quad (7)$$

Method

In this study we used the Gassian03 software using DFT method for research on the adsorption mechanism of NO_2 on the carbon nanotubes (zigzag (5, 0) and armchair (4, 4) SWCNTs) and determination the properties of bond lengths, dipole moments, binding energies, HOMO–LUMO energy gaps and Fermi level energies by theoretical methods.

The SWCNTs was initially constructed maintaining the C–C distance at 1.42 A, and the structure was then optimized (Fig. 1). After optimization, one NO_2 molecule attached to the tube wall in each unit cell, as shown in Fig.2. Two rotational geometries of NO2 on the surface and on the open ends of the zigzag (5, 0) and armchair (4, 4) SWCNTs considered respectively, as shown on Figs. 2. In the present study, also the results of density functional calculations on the pristine and NO_2-SWCNTs models reported. The electronic structure, properties of bond lengths, dipole moments, binding energies, energy gaps, Fermi level energies and in addition, the electronic properties of NO_2 adsorbed onto the nanotubes have investigated.

RESULTS AND DISCUSSION

Firstly, the structure of pristine SWCNTs including zigzag (5, 0) and armchair (4,4) models which were used for NO_2 adsorption, are optimized and are shown in Fig. 1. The structure of NO_2 also, optimized. Four adsorption states of NO_2 molecule on the zigzag (5,0) and on the armchair (4,4) SWCNTs for the most stable configurations were studied via its expected active sites (C-C) over SWCNTs surface and open ends. The optimized geometrics of perfect zigzag(5, 0) and armchair (4,4) SWCNTs were found to be with C-C bond lengths about 1.396A and 1.435A on the surface and 1.443A, 1.358A on the open ends, and the diameters of the nanotubes about 3.986A and 5.670A, respectively. After NO_2 chemisorption on the open end of (5,0) SWCNT and NO_2 physisorption on the open end of (4,4) SWCNT, there is not efficient change of the diameters and C-C bond lengths of the nanotubes.

But after NO_2 adsorption on the surface (5,0) and (4,4) SWCNTs, N-C bond lengths were about 3.999A and 4.286A in the open end adsorption and 1.583A and 1.638A in the surface adsorption of (4,4) SWCNT and (5,0) SWCNT, respectively. Investigation on the adsorption of NO2 through -CNTs bond represented the stronger interaction on the surface of (5,0) and (4,4) SWCNTs than on the open ends of zigzag (5,0) and armchair (4,4) SWCNTs with the energy values of -0.027 eV, 0.750 eV and 9.450 eV, 0.270 eV, respectively (see table 1). The net charge-transfer (Q_T) from NO_2 molecule to zigzag (5,0) and armchair (4,4) SWCNTs was calculated by using Mulliken population analysis, which is defined as the charge difference between NO_2 molecule adsorbed on the doped nanotube and an isolated NO_2 molecule. Also, NBO analysis shows that the natural charges of N atom in NO_2 and C atom over the surface and on the open end of zigzag (5,0) and armchair (4,4) SWCNTs are about –0.165 esu, −0.499 esu and 0.271 esu, 0.081 esu, respectively (table 2). We have found that the electron charge transfer is an important mechanism of change in conductivity of CNTs while adsorption of NO_2 gas.

The charge transfer behavior affects the whole concentration of CNTs, giving rise to a change in conductivity. This strongly suggests that NO_2 molecule is electron acceptor from CNTs or electron donor to CNTs, in accordance with the results of electron charge transfer above discussed. From our calculations, we can explain the difference in

adsorption mechanism of NO_2 molecule on the surface and on the open ends of SWCNTs. The obtained data summarized in Tables 1 and 2. Remind that the electronic structures of these SWCNTs are approximately independent of diameter and chirality of CNTs because of enormous ionicity of these bindings. Hence, it seems that the adsorption of NO_2 molecule on the open ends of armchair (4,4) and zigzag (5,0) SWCNTs could be weaker than on the surface of these nanotubes. This can attributed to the *p* orbitals electrons configuration on the surface and H doped atoms on the open ends of nanotubes and spatial orientation of NO_2 molecule.

Table 1. Calculated adsorption energies (E_{ads}), HOMO (E_{HOMO}) and LUMO energies (E_{LUMO}), HOMO–LUMO energy gap (E_g), Q_T (esu) and dipole moment (Debye) of the NO_2 adsorption on the surface and on the open ends of zigzag (5,0) and armchair (4,4) SWCNTs.

System	E_{ads} (eV)	Dipole moment (Debye)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)	ΔE_g (%) [b] (eV)	Q_T [a] (esu)
NO_2	-	0.355	-0.395	-0.120	0.276	-	-
CNT (5, 0)	-	0.003	-0.242	-0.120	0.122	-	-
CNT (4, 4)	-	2.361	-0.230	-0.099	0.131	-	-
NO_2-CNT(4, 4)-D	0.750	4.5415	-0.188	-0.113	0.075	57.251	0.181
NO_2-CNT(5, 0)-D	-0.027	11.5356	-0.192	-0.138	0.053	43.442	0.271
NO_2-CNT (4, 4)-S	0.270	3.0463	-0.175	-0.101	0.073	55.725	-0.499
NO_2-CNT (5, 0)-S	9.450	2.0026	-0.166	-0.118	0.048	39.344	-0.165

[a] *Q_T is defined as the average of total Mulliken charge on the molecule.*
[b] *The change of HOMO–LUMO gap of SWCNTs after NO_2 adsorption.*

Considering the orientation of NO_2 on the surface and on the open ends of the SWCNTs, a number of different starting structures have used for optimization, containing carbon atoms of SWCNTs.

After careful structural optimizations, re-orientation of NO2 molecule has predicted in some cases, and finally four stable NO_2/SWCNTs complexes obtained (see Fig. 2). More detailed information including values of E_{ads}, dipole moments, Mulliken charge transfers (Q_T) and electronic properties listed in Table 2. All these calculations performed using Gaussian03 software package [28].

Table 2. Chemical potential (μ), hardness (η), softness (S), ΔN_{max} (a.u.), and electrophilicity (ω) of NO_2, pristine CNTs and NO_2 adsorption on CNTs surface and on CNTs open ends at the B3PW91/6-311++G level.**

Property	NO_2	CNT(4,4)	CNT(5,0)	CNT(4,4)- NO_2-S	CNT(4,4)-NO_2-D	CNT(5,0)-NO_2-S	CNT(5,0)-NO_2-D
[I = $-E_{HOMO}$] (eV)	-0.395	-0.230	-0.242	-0.175	-0.188	-0.166	-0.192
[A = $-E_{LUMO}$] (eV)	-0.120	-0.099	-0.120	-0.101	-0.113	-0.118	-0.138
[η = (I−A)/2] (eV)	-0.138	-0.065	-0.061	-0.037	-0.037	-0.024	-0.027
[μ = −(I + A)/2] (eV)	0.024	0.329	0.181	0.138	0.150	-0.142	-0.165
[S = 1/2 η] (eV)	-0.069	-0.033	-0.031	-0.019	-0.018	-0.012	-0.013
[ω = μ^2/2η] (eV)	-0.002	-0.833	-0.269	-0.257	-6/627	-0.420	-0.888
ΔN_{max} = −μ/η] (a.u.)	0.174	5.061	2.967	3.729	4.054	5.916	6.111

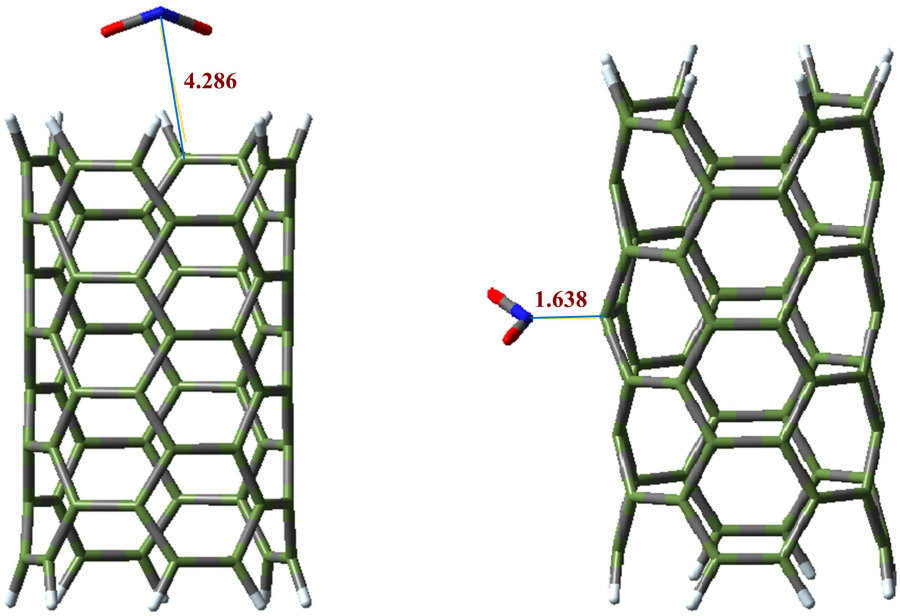
As shown in Fig. 2, the interaction occurs between N atom of NO_2 molecule and C atom of the SWCNT. After optimization of above CNTs, the large difference between these four sites may be interpreted by the nature of the newly formed bonds between NO_2 with the surface and the open end of zigzag (5,0) and armchair (4,4) SWCNTs. The lengths of C-C bonds increased from 1.435 A, 1.358 A in the pristine nanotube on the surface and on the open end of armchair (4,4) SWCNT to 1.516 A, 1.359 A when NO_2 was adsorbed over these positions. Also the lengths of C-C bonds increased from 1.396 A and 1.443 A in the pristine nanotube on the surface and on the open end of zigzag (5,0) SWCNT to 1.540 A and 1.433 A when NO_2 was adsorbed over these positions. These calculations were performed using base series of B3PW91/6-31++G (*d*, *p*).

The calculations of NO_2 adsorption on the surface of SWCNTs indicate that the geometric structure of the adsorbent distorted. In this configuration, a Mulliken charge of -0.445 esu and -0.086 esu transferred from the zigzag (5,0) and armchair (4,4) SWCNTs, respectively, to NO_2 molecule and the calculated E_{ads} values are about -9.450 eV and 0.270 eV (Table 1). The smallest distance of NO_2 molecule from nanotube found to be about 1.583A and a charge of -0.445 esu transferred from the molecule to the NO_2-CNT (5, 0)-S. The sensitivity of the response to gas molecule seems be related to the amount of electron charge transfer and the binding energy. In addition, it concluded that SWCNTs respond more quickly and sensitively to NO_2 gas on the surface than on the open end of SWCNTs. All above results indicate that there are stronger interaction on the surface of zigzag (5,0) and armchair (4,4) SWCNTs

than on the open ends and may be considered as chemisorption. These behaviors may attribute to the comportment of *p* orbitals on the surface and the behavior H doped carbon atoms on the open ends of SWCNTs.

Effect of NO_2 adsorption on the electronic properties of SWCNTs

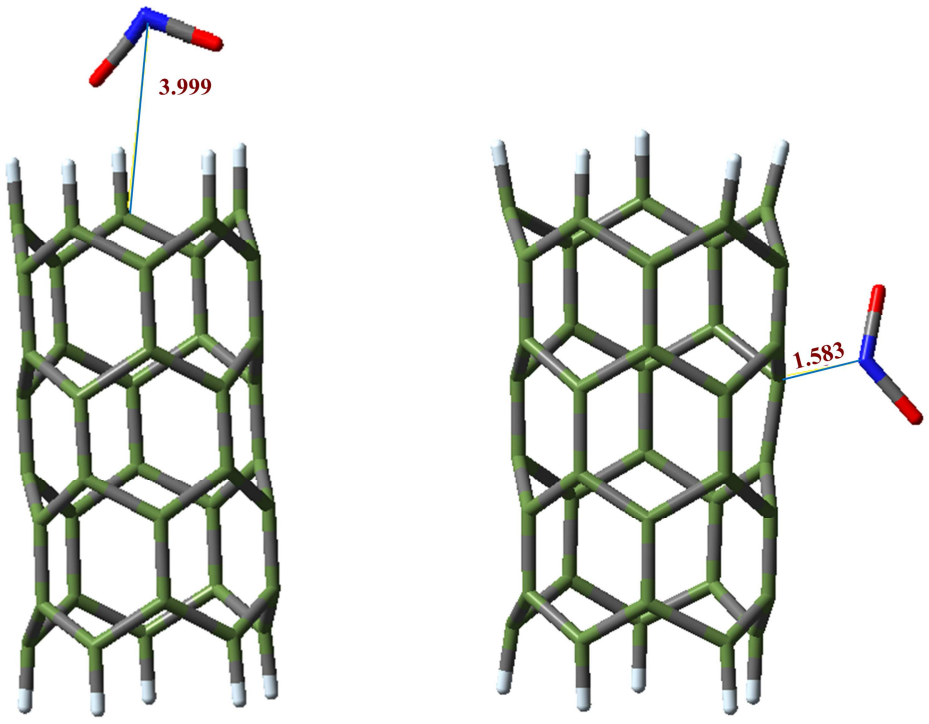
The influence of the NO_2 adsorption on the electronic properties of nanotube was studied. Uniform distribution of HOMO and LUMO orbitals is shown in Fig. 3 and the Charge distribution of HOMO and LUMO orbitals on the (5,0) and (4,4) SWCNTs loaded with one NO_2 at B3PW91/6-311++G (*d*, *p*) level are shown in Fig. 4. The difference in energy between the HOMO and the LUMO (E_g) calculated from DOS plots (see Fig. 5). For the bare SWCNTs as shown in Fig. 1, it can be concluded that NO_2 adsorption on the surface and on the open end of zigzag (5,0) nanotube gives a semi-conductor with an E_g of 0.048 eV and 0.053 eV respectively. Also, NO_2 adsorption on the surface and on the open end of armchair (4,4) nanotube gives a conductor with an E_g of 0.073 eV and 0.075 eV, respectively. The sensing mechanism is to detect the conductance change of $SWCNT_S$ induced by charge transfer from NO_2 molecules to SWCNTs.



NO_2-CNT (4, 4)-D **NO_2-CNT (4, 4)-S**

Calculated DOS plots (Fig. 5) show that NO_2 adsorptions through physisorption on the open ends of NO_2-CNT (4,4)-D and NO_2-CNT (5,0)-D and the NO_2 adsorptions through chemisorption on surfaces of NO_2-CNT (4,4)-S and NO_2-CNT (5,0)-S, the valence and conduction levels of the SWCNTs are slightly changed and therefore the E_g of SWCNT is preserved. The E_g of nanotubes after NO_2 adsorption on the (5,0) nanotube and (4,4) nanotube show a decrease from 0.122 eV and 0.131eV in the pristine nanotube to 0.048 eV on the surface and 0.053 eV on open end of (5,0) nanotube and 0.073 eV on the surface and 0.075 eV on the open end of (4,4) nanotubes (see table 1). The DOS plots for chemisorption cases show a considerable change in electronic properties that indicate these properties of SWCNTs are very sensitive to NO_2 molecule adsorption on these structures, in comparison with the physisorption cases. It revealed from DOS plots that their conduction levels in both complexes, adsorbed on the surface and adsorbed on the open end, are approximately similar to SWCNTs, while the valence levels are significantly shifted upwards. A new peak appeared just beneath the Fermi level. This peak indicates that after adsorption of NO_2 molecule, the system becomes either a semiconductor (zigzag (5,0) SWCNT) or a conductor with smaller E_g (armchair (4,4) SWCNT), and thus, a significant increase in electrical conductivity is expected in comparison with the pristine nanotubes. In order to interpret the NO_2 interaction with SWCNTs, it concluded that the HOMO of NO_2-adsorbed nanotubes more localized on both of the adsorption sites occupied by NO_2 molecules. The energy level of HOMO is about -0.188eV in NO_2-CNT (4,4)-D and about -0.192 eV NO_2-CNT (5,0)-D in , that indicates it becomes less stable by NO_2 adsorption because of the charge transfer from NO_2 to nanotubes (E_{HOMO} of non adsorbed (4,4)

and (5,0) SWCNT, is -0.230 eV and -0.242 eV, respectively). On the other hand, as shown in Fig. 4, the LUMO of NO2 adsorbed on nanotubes surface remains nearly constant and indicates that the LUMO not contributed in adsorption process. The considerable change about 39.344% to 57.251% in the E_g value, demonstrates the high sensitivity of electronic properties of SWCNTs towards adsorption of NO_2 molecule. Calculated E_g values for the complexes of NO_2-adsorbed on the surface and on the open ends of SWCNTs indicates that the E_g of the complexes decreased by increasing of adsorbed NO_2 molecules. It suggests that NO_2 can transform the presence of this molecule directly into an electrical signal, and therefore it may potentially use in NO_2 sensors. As a result, this nanotube can monitor NO_2 molecule in its pristine type without manipulating its structure through doping, making defect, etc. In addition, the response of nanotube may be dependent on the concentration of NO_2.



NO_2-CNT (5, 0)-D **NO_2-CNT (5, 0)-S**

Fig.2: Optimized geometries of NO_2 adsorptions on the open end and on the surface of zigzag (5,0) and armchair (4,4) SWCNTs

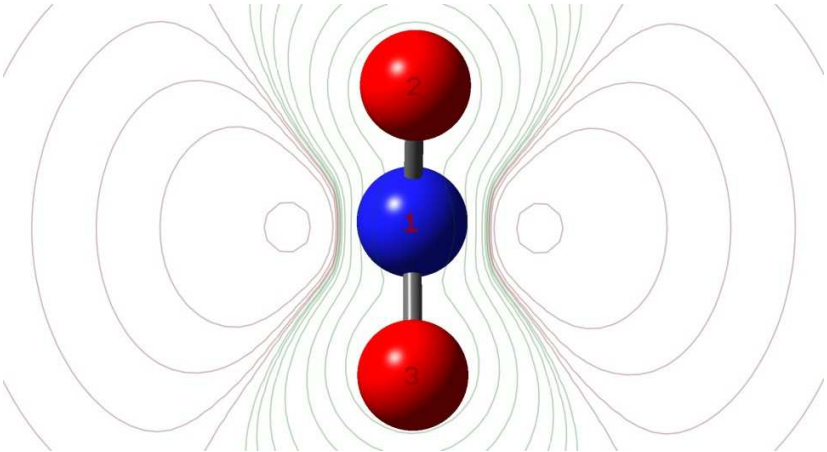
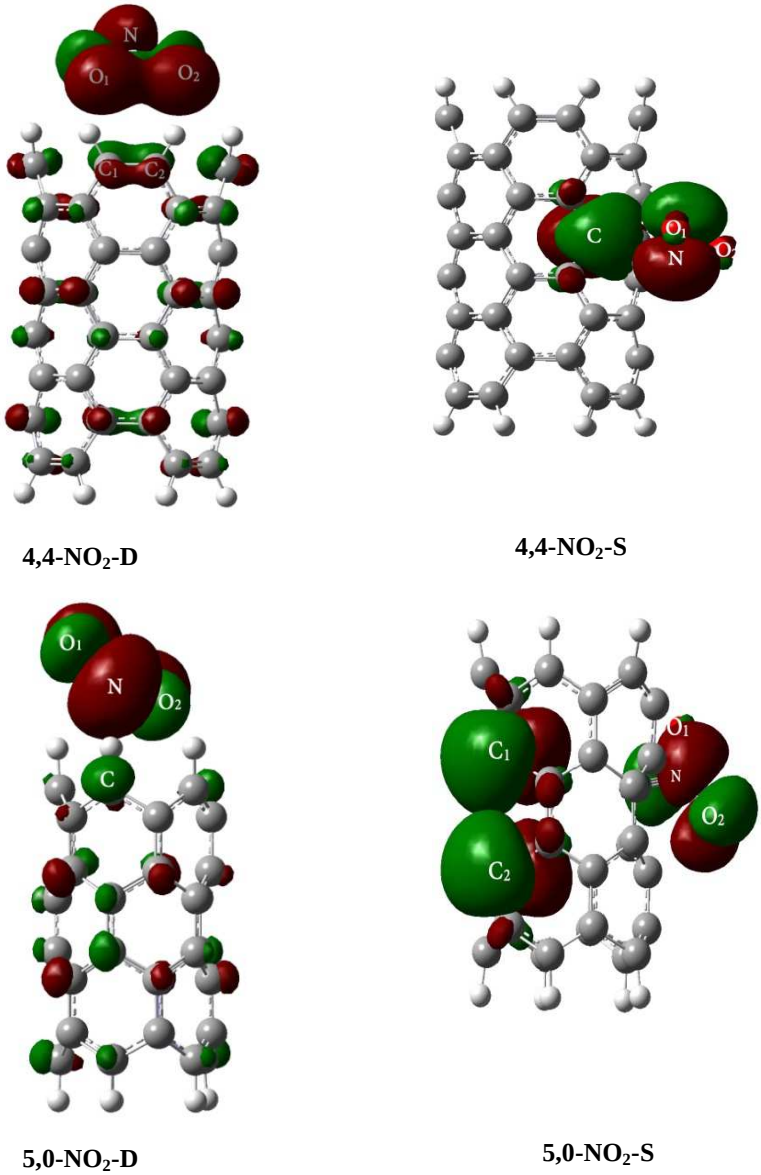


Fig. 3. Uniform distribution of HOMO and LUMO orbitals

Electronic energies and relative stabilities

To further investigate the adsorption properties of NO_2 on (5,0) and (4,4) SWCNTs, the electronic energies of NO_2 adsorption on these nanotubes have examined. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in NO_2 adsorption on the (5,0) and (4,4) SWCNTs were studied (see Table 1).

Table 2 presents the results of LUMO and HOMO energies of NO_2 adsorption on the (5,0) and (4,4) SWCNTs top site, obtained by DFT calculations. This study indicates that by adsorption of NO_2 on the surface and on the open ends of SWCNTs, E_{LUMO} and E_{HOMO} for whole models decreased. Therefore, both groups of occupied and unoccupied molecular orbital are more stable than these groups of pristine SWCNTs. Furthermore, HOMO and LUMO orbitals uniformly distributed throughout nanotubes, which illustrates that covalent functionalization is preferable throughout the nanotubes (see Fig. 3).



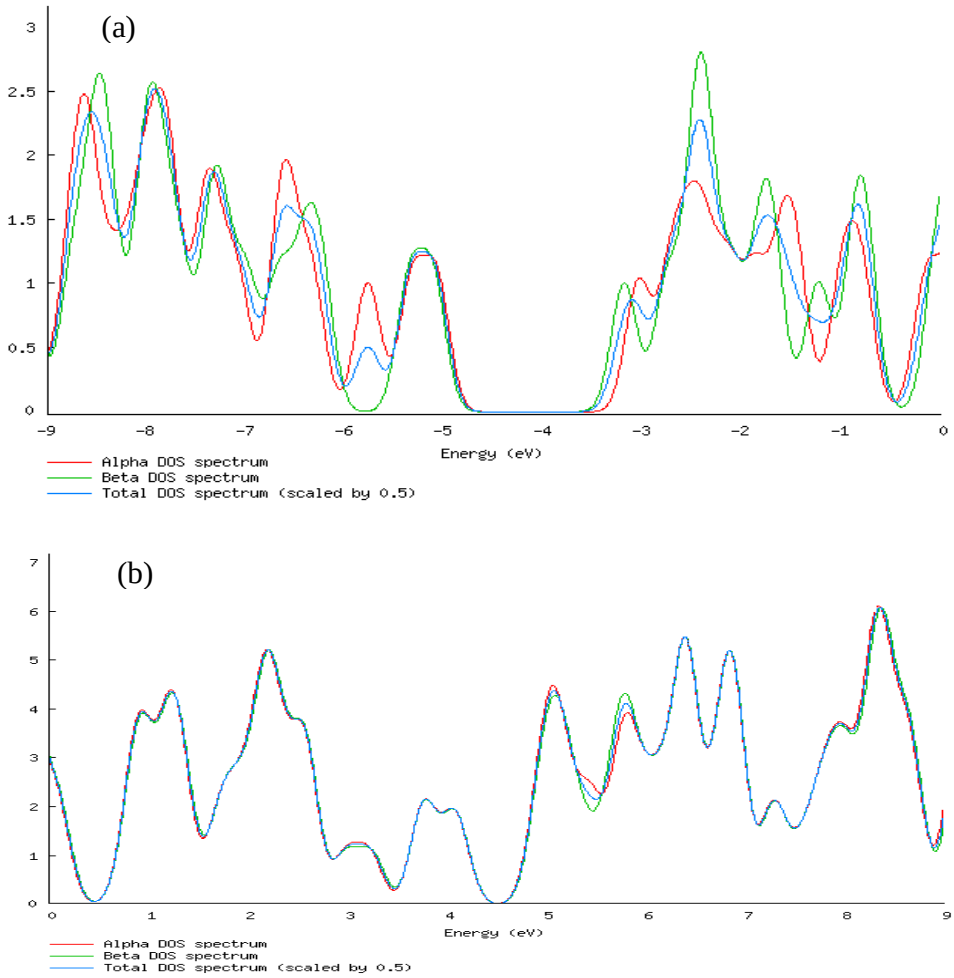
4,4-NO_2-D **4,4-NO_2-S**

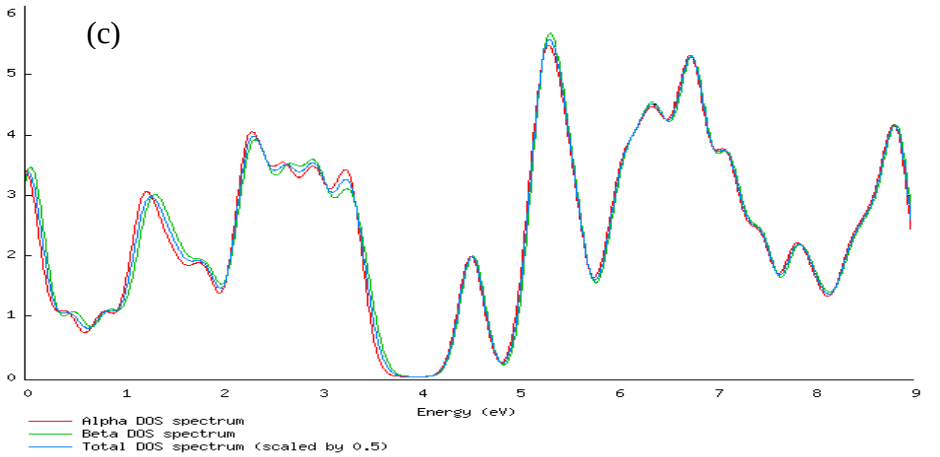
5,0-NO_2-D **5,0-NO_2-S**

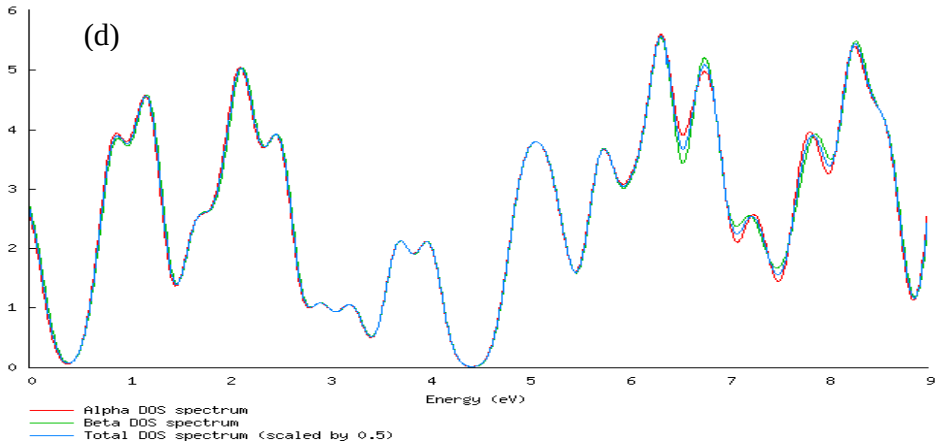
Fig. 4. Distribution of charges of HOMO and LUMO orbitals on the (5,0) and (4,4)SWCNT loaded with one NO_2 at the B3PW91/6-311++G (*d*, *p*) level.

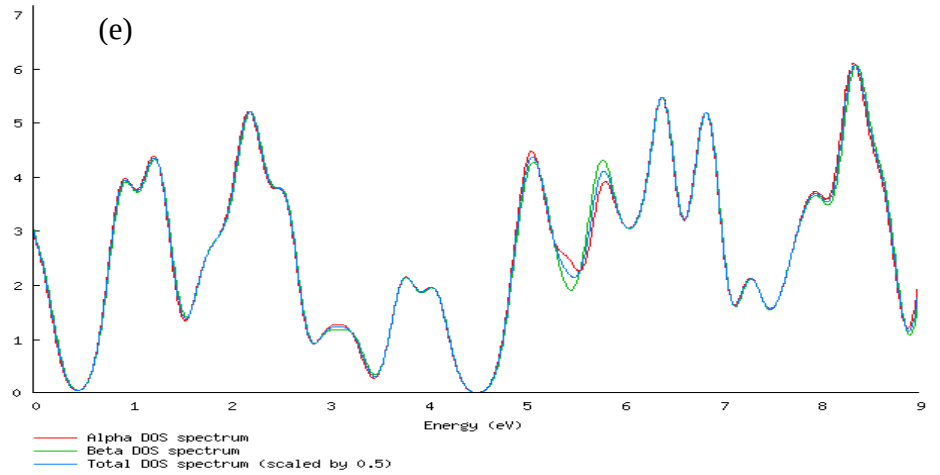
The distribution of frontier orbital in the perfect (5,0) SWCNTs model, show that the HOMO is localized on the most electronegative carbon atoms on the surface and on the open end of nanotube, which corresponds to *p* electron on carbon atoms, Whereas, the LUMO is more localized on the surface of nanotubes. In NO_2 molecule, the HOMO and the LUMO are uniformly distributed on O = N = O orbitals which are summarized in Fig. 4. It can found that the HOMO localized on the carbon orbitals on the surface and on the open end of nanotubes, while the LUMO more localized on carbon atoms on the surface in SWCNTs and on NO_2 orbital.

The chemical activity of SWCNTs can characterized by the HOMO–LUMO energy gap, which is a significant parameter relying on HOMO and LUMO energy levels. Typically, a small HOMO–LUMO energy gap means a high chemical activity and a low chemical stability. The calculated gap energies for zigzag (5, 0) and armchair (4,4) SWCNTs are in the range of 0.12 to 0.13 eV at B3PW91/6-311++G (d, p) level (see Table 1). When NO_2 is adsorbed on the surfaces and on the open ends of (5,0) and (4,4) SWCNTs in stable configuration (N-side), the gap of energies decreases (see table 1). Chemical stability of zigzag (5,0) and armchair (4,4) SWCNTs will be decreased and hence chemical activity of such system will be slightly increased. Fig. 5 shows the influence of NO_2 on the electronic properties of the (5,0) and (4,4) SWCNTs. Also, the density of state (DOS) plots corresponding to adsorption of the NO_2 by (5,0) and (4,4) SWCNTs have computed.




(c)
Energy (eV)
Alpha DOS spectrum
Beta DOS spectrum
Total DOS spectrum (scaled by 0.5)


(d)
Energy (eV)
Alpha DOS spectrum
Beta DOS spectrum
Total DOS spectrum (scaled by 0.5)


(e)
Energy (eV)
Alpha DOS spectrum
Beta DOS spectrum
Total DOS spectrum (scaled by 0.5)

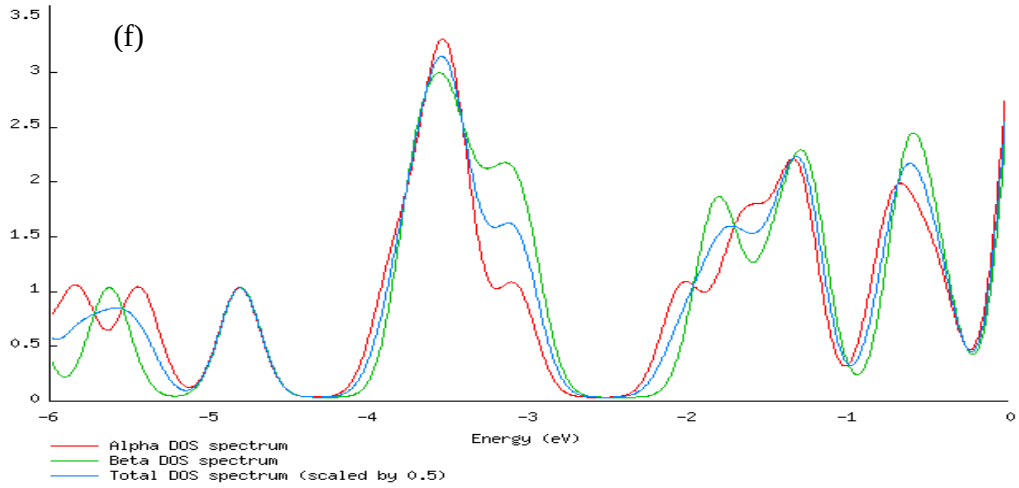


Fig. 5. Total density of states (DOS) for an pristine (5, 0) and (4,4) SWCNTs (a and b), NO_2/(5, 0) SWCNTs surface (c) and open ended (d), NO_2/(4,4) SWCNT surface (e) and open ended (f).

Revealing slightly effect of NO_2 molecule in electronic conductivity of SWCNTs, the DOS plots of NO_2 on (5,0) and (4,4) SWCNTs displays more reasonable changes than the DOS plots of pristine (4,4) SWCNTs. This result states that the DOS plots of NO_2 adsorption on (5,0) and on (4,4) SWCNTs systems near Fermi level is not affected by this adsorption. In fact, there is the slightly difference of the DOS between three combined systems of NO_2/ SWCNTs. These results show that after adsorption of NO_2 on SWCNTs the HOMO–LUMO energy gap of nanotubes have not considerable change that is an evidence of the weak interaction between NO_2 and related to the SWCNTs.

Electric dipole moment

Electric dipole moment vector of species has important properties which shows the charge distribution when gases were adsorbed on the surface and on open end of nanotubes. While a NO_2 molecule approaches the surface of (5,0) and (4,4) SWCNTs, the size and direction of the electric dipole moment vector will change depending on configuration of NO_2 molecule in adsorption process. The related computation indicates that while NO_2 adsorption in the case of all complexes, the total dipole moment increases (see table 1). The dipole moments of (5,0) and (4,4) SWCNTs were calculated and are about 0.003 and 2.361 Debye, respectively. This considerable difference in dipole moment values can attribute to physisorption and chemisorption status. In the case of NO_2 adsorption on the surface and on the open ends of SWCNTs, the dipole moments are 2.0026 Debye on the surface and 11.5356 Debye on the open end for zigzag (5,0) and 3.0463 Debye on the surface and 4.5415 Debye on the open end for armchair (4,4) SWCNTs. In fact, both electron transfers and dipole moment implies this concept that SWCNTs with absorption of NO_2 caused increasing of polarization and this will lead to the change of dipole moments.

Overall indices

The overall hardness of a substance defined as its resistance against deformation in presence of an electric field. Increasing in overall hardness, results in increase of stability and decrease in reactivity of the substance (see table 2). In this study, the global indices of reactivity according to the DFT computations for NO_2 adsorption on zigzag (5, 0) and armchair (4,4) SWCNTs are presented in Table 2. While NO_2 adsorption on SWCNTs, the hardness, electrophilicity and electronic chemical potentials of SWCNTs decreased, and on the contrary, softness increased (see table 2). The results of this work also show that when NO_2 is chemisorbed on the outer surface of SWCNTs, a slight charge transfer to NO_2 can be occur, which may be attributed to high electronegativity of N and O atoms. The direction of electron flow can characterize by the effect of this electronegativity.

When NO_2 approaches SWCNTs, the electrons is transferred from higher chemical potential to the lower electronic chemical potential, until the electronic chemical potentials achieve an equilibrium [22]. This study shows also the same results (table 2).The energy lowering of a ligand due to maximum flow of electron from donor to acceptor can determined by global electrophilicity index and this will provide information about structural stability.

The results obtained in this investigation confirm the above discussion (see table 2).

CONCLUSION

Studying the adsorption of NO2 through -CNT bond represented the stronger interaction on the surface than on the open ends of zigzag (5,0) and armchair (4,4) SWCNTs. This may attributed to electronic configuration of *p* orbitals of carbon in the surface of SWCNTs.

It was found that the electron charge transfer is an important mechanism of change in conductivity of CNT_S when adsorption of NO_2 gas. In this case, the charge transfer behavior affects the whole concentration of CNTS, giving rise to a change in conductivity. The obtained results show that the adsorption of NO_2 molecule on the open ends of armchair (4,4) and zigzag (5,0) nanotubes may be weaker than on the surface of these nanotubes.

Considering the orientation of NO_2 on the surface and on the open end of the SWCNTs, four stable NO_2/SWCNTs complexes obtained (Figs. 2). The large difference between these four sites, after optimization, may be interpreted by the nature of the newly formed bonds between NO_2 with the surface and the open ends of (5,0) zigzag and armchair (4,4) SWCNTs.

The lengths of C-C bonds in the pristine nanotube on the surface and on the open end of armchair (4,4) and in zigzag (5,0)SWCNTs, increased when NO_2 was adsorbed over these positions on nanotubes.
The calculations of NO_2 adsorption on SWCNTs indicate that the geometric structure of the adsorbent distorted and a Mulliken charge transferred from the SWCNTs to the NO_2 molecule. In addition, it concluded that CNTs respond more quickly and sensitively to NO_2 gas on the surface than on the open ends of SWCNTs.

By calculation the difference of energy between the HOMO and the LUMO (E_g) from DOS plots, it can be concluded that NO_2 adsorption on the surface and on the open ends of zigzag (5,0) nanotubes, for the bare SWCNTs, gives a semi-conductor, whereas NO_2 adsorption on the surface and on the open end of armchair (4,4) nanotubes gives a conductor. It revealed from DOS plots that their conduction levels in both complexes, adsorbed on the surface and adsorbed on the open end, is approximately similar to that of SWCNTs, while the valence levels is significantly shifted upwards.

The peak appeared just beneath the Fermi level indicates that after adsorption of NO_2 molecule the system becomes either a semiconductor or a conductor (with smaller E_g), and so that, a considerable increase in electrical conductivity is expected comparing with the pristine nanotubes. It illustrates that NO_2 can transform its presence directly to an electrical signal, and therefore it may potentially use in NO_2 sensors.

The studies performed by DFT calculations indicate that by adsorption of NO_2 on the surface and on the open ends of SWCNTs, E_{LUMO} and E_{HOMO} for whole models decreased.

When NO_2 adsorbs on the surfaces and on the open ends of (5,0) and (4,4) SWCNTs in stable configuration (N-side), the gap of energies decreases, therefore, chemical stability of zigzag (5,0) and armchair (4,4) SWCNTs will be decreased and hence chemical activity of such system will be increased.

The results of DOS plots show that after adsorption of NO_2 on SWCNTs, the HOMO–LUMO energy gap of nanotube has not considerable change that is an evidence of the weak interaction between NO_2 and related to the SWCNTs.

The results suggest that both electron transfers and dipole moment implies this concept that SWCNTs with absorption of NO_2 caused increasing of polarization and this will lead to the change of dipole moments.

It can conclude that while NO_2 adsorption on SWCNTs, the hardness, electrophilicity and electronic chemical potentials of SWCNTs decreased, and on the contrary, softness increased.

Finally, the results of this study also, show that when NO_2 is chemisorbed on the outer surface of SWCNTs, a slight charge transfer to NO_2 can be occur which may be attributed to high electronegativity of N and O atoms.

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