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Effect of Monovacancy Defects on Adsorbing of CO, CO₂, NO and NO₂ on Carbon Nanotubes: First Principle Calculations

Ahlam A. EL-Barbary[1,2*], Gehan H. Ismail[1,2], Afaf M. Babeer[2]

[1]Physics Department, Ain Shams University, Cairo, Egypt; [2]Physics Department, Faculty of Science, Jazan University, Jazan, KSA.
Email: [*]ahla_eg@yahoo.co.uk

ABSTRACT

We have applied density functional theory to investigate different types of carbon nanotubes (armchair (4,4)CNT and zig-zag (7,0)CNT) as sensors of some pollutant gas molecules, especially CO, CO_2, NO and NO_2. We show, for the first time, that the adsorption of pollutant gas molecules on carbon nanotubes are improved by introducing the monovacancy defects on the surfaces of (7,0)CNT. The adsorption energies, the optimal adsorption positions and the orientation of these gas molecules on the surfaces of carbon nanotubes are studied. It is found that the most adsorbed pollutant gas is NO molecule on (7,0)CNT.

Keywords: Carbon Nanotubes; DFT; Sensor; Monovacancy Defects

1. Introduction

More than a decade after the discovery of carbon nanotubes (CNT) by Iijima in 1991 [1], they are still one of the hottest research areas in all of science and engineering. The specific geometry and unique properties of carbon nanotubes suggest important potential applications including transistors, hydrogen storage devices, quantum dots, gas sensors, and so many other applications [2-5]. Gas adsorption on carbon nanotubes is a great issue for both essential research and applied application of nanotubes. The adsorptive characteristics of SWCNTs in the gas phase caused their use as gas sensors of pollutant gases, and storage of fuels [6,7].

The most widely used consideration of atomistic modeling of a CNT is by reference to rolling up graphene sheet to form a hollow cylinder with end caps. The cylinder is composed of hexagonal carbon rings, while the end caps of pentagonal rings. In terms of the roll-up vector, the armchair nanotubes are defined by (n, n) and the zigzag nanotubes by (n, 0). Due to the highly regular atomic structure of CNTs and the large degree of the structure, purity makes it accessible to accurate computer modeling using a variety of theoretical techniques. The interaction between sp2-bonded carbon materials and mo-

lecular species has been extensively investigated for carbon nanotubes and fullerenes for sensor applications and chemical functionalization.

Furthermore, there are evidences indicating the great importance of molecular gaseous orientation on the energy of adsorption [8,9]. However, the effect of monovacancy defects is one of the major aspects of gas-nanotube interactions that has not been studied yet. Therefore, in this study we will investigate the effect of chiralities of CNTs on adsorption energy, as well as the effect of monovacancy defects.

2. Computational Methods

All calculations were performed with the DFT as implemented within G03W package [10-12], using B3LYP exchange-functional and applying basis set 6 - 31 g(d,p). In the basis set 6 - 31 g(d,p), number 6 represents the number of primitive Gaussians comprising each core atomic orbital basis function. Numbers 3 and 1 indicate that the valence orbitals are composed of two basis functions each, the first one composed of a linear combination of 3 primitive Gaussian functions, the other composed of a linear combination of 1 primitive Gaussian functions, however (d, p) are polarization (correlating) functions. This corresponds to the approximation method that makes use

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*Corresponding author.

of Becke-style 3-parameter density functional theory with the Lee-Yang-Parr correlation functional [12,13]. Pure carbon nanotubes (4,4) and (7,0) are fully optimized with spin average. However, the adsorption energies are calculated from single point calculations. The obtained diameters (D) [14] and the adsorption energies of gas on CNTs (E_{ads}) [13] are calculated from the following relations:

$$D = 0.73\left(n^2 + nm + m^2\right)^{1/2}$$

where n and m are integral numbers, the composition of chiral vector.

$$E_{ads} = E_{nanotube+gas\ molecules} - E_{nanotube} - E_{gas\ molecules}$$

where $E_{nanotube\ +\ gas\ molecules}$ is the total energy of nanotube and gas molecules, $E_{nanotube}$ is the energy of the carbon nanotube, and $E_{gas\ molecules}$ is the energy of gas molecules.

For each gas molecule, there are two adsorption energies corresponding to orientation of gas molecules. Also, the carbon monovacancy is created by removing a carbon atom, then the gas molecules are adsorbed on surface of carbon nanotubes at three positions: first on the vacant position of removing a carbon atom, second on one of the three dangling carbon atoms and the third position on one carbon atom far away from the vacancy position.

3. Results and Discussion

We will investigate the adsorption of gas molecules, CO, NO, CO_2 and NO_2, on two different types of carbon nanotubes, armchair (4,4)CNT, $C_{80}H_{16}$, with diameter 5.06 Å and zig-zag (7,0)CNT, $C_{70}H_{14}$, with diameter 5.11 Å, as shown in **Figure 1**.

3.1. Adsorption of CO and NO Gas Molecules

3.1.1. On Pristine Armchair (4,4)CNT Surfaces
We have adsorbed CO and NO gas molecules vertically on different three positions of pristine armchair (4,4) CNT: above a carbon atom, above a bond between two carbon atoms and above a center of a hexagon ring. Also, we have studied the effect of gas molecules orientation by adsorbing CO and NO, once when the oxygen atom is faced the surface of (4,4)CNT (refer by OC and ON symbols) and the other when the carbon/nitrogen atom is faced the surface of carbon nanotube (refer by CO and NO symbols).

We have calculated the adsorption energies and optimal adsorption distances of OC and CO gas molecules on armchair (4,4)CNT and are found to be (−32.97 meV, 3.2 Å and −19.10 meV, 3.9 Å) above a carbon atom, (−1.20 meV, 3.2 Å and 0.26 meV, 3.4 Å) above a bond between two carbon atoms and (−30.80 meV, 2.8 Å and
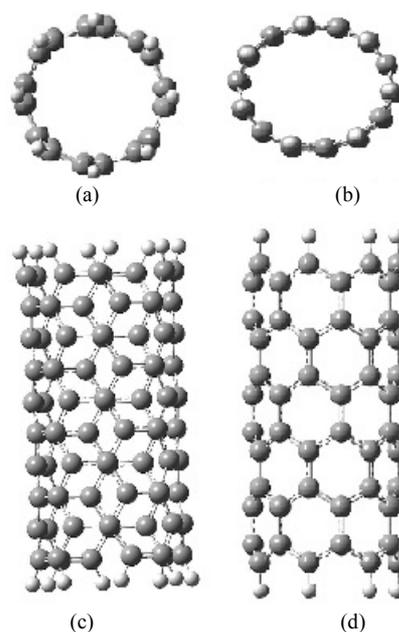
Figure 1. The fully optimized structures of (4,4) CNT, $C_{80}H_{16}$, and (7,0) CNT, $C_{70}H_{14}$, (a) and (b) top views, (c) and (d) side views, respectively.

−20.21 meV, 3.4 Å) above a center of a hexagon ring, respectively. Also, we have calculated the adsorption energies and optimal adsorption distances of ON and NO gas molecules on armchair (4,4)CNT and are found to be (−161 meV, 3.6 Å and −138 meV, 3.4 Å) above a carbon atom, (−98 meV, 3.6 Å and −54.8 meV, 3.2 Å) above a bond between two carbon atoms and (−241 meV, 3.4 Å and −98 meV, 3.0 Å) above a center of a hexagon ring, respectively.

It is clear that the adsorption of NO molecule on the surface of pristine (4,4)CNT is preferred than the adsorption of CO molecule. Also, the adsorption energy is dependent on the orientation of the adsorbed gas molecules. We have found that the adsorption energies of OC and ON are preferred than the adsorption energies of CO and NO on the surfaces of (4,4)CNTs, respectively. Also, the adsorption energies are dependent on the adsorption sites where the gas molecules are adsorbed on the surfaces of (4,4)CNTs. Our calculations show that the order of adsorption energies for ON and OC on (4,4)CNTs are E_{ads}(carbon site) < E_{ads}(vacant site) < E_{ads}(bond site), however NO and CO have the order E_{ads} (vacant site) < E_{ads} (carbon site) < E_{ads} (bond site). The best adsorption gas molecule is found to be ON molecules with adsorption energy (−241 meV) and optimal adsorption distance (3.4 Å). All these results are shown in **Figures 2(a**, **b**, **c)** and **3(a, b, c)** and **Table 1**.

3.1.2. On Pristine Zig-Zag (7,0)CNT Surfaces
We have adsorbed CO and NO gas molecules vertically

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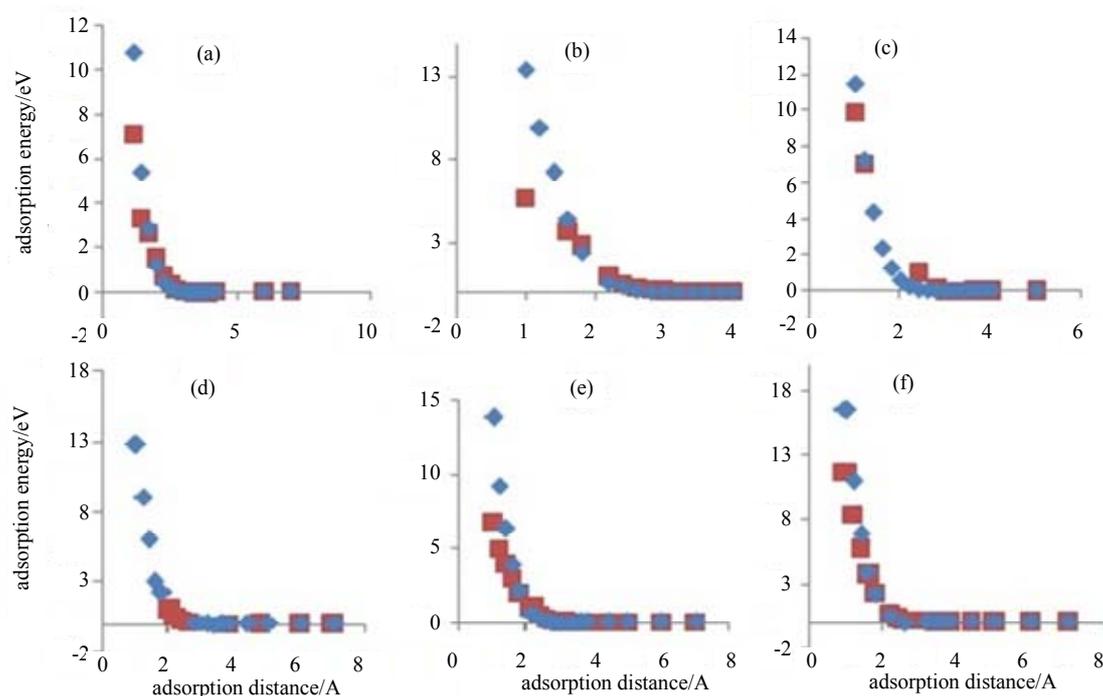
Figure 2. Adsorption energies of CO and OC gas molecules on pristine (4,4)CNT surfaces (a) above a carbon atom, (b) above a bond between two carbon atoms, (c) above a center of hexagon ring. Adsorption energies of CO and OC gas molecules on pristine (7,0)CNT (d)above a carbon atom, (e) above a bond between two carbon atoms (f) above a center of hexagon ring. The blue marks are corresponding to the CO molecules and the red marks referred to OC molecule.
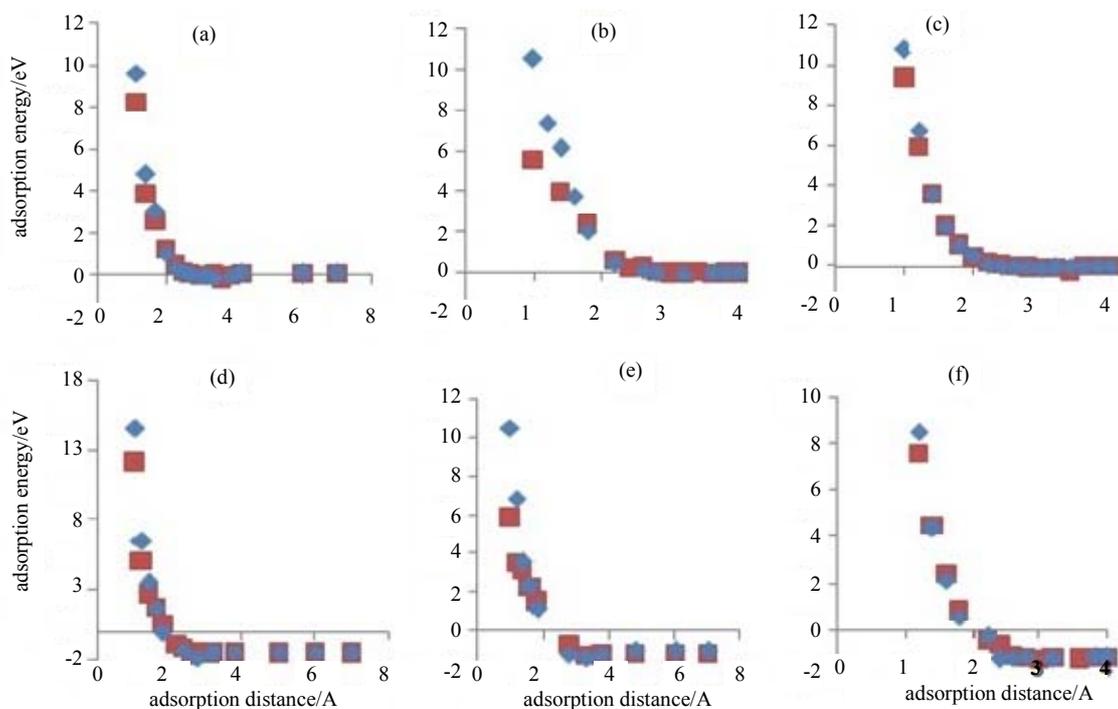
Figure 3. Adsorption energies of NO and ON gas molecules on pristine (4,4)CNT surfaces (a) above a carbon atom, (b) above a bond between two carbon atoms, (c) above a center of hexagon ring. Adsorption energies of NO and ON gas molecules on pristine (7,0)CNT (d)above a carbon atom, (e) above a bond between two carbon atoms (f) above a center of hexagon ring. The blue marks are corresponding to the NO molecule and the red marks are referred to ON molecule.

Table 1. The calculated adsorption energies (E_{ads}) and optimal adsorption distances (R) of CO, and NO above a carbon site, bond site and vacant site of pristine (4,4)CNTs and (7,0)CNTs. All energies are given by meV and distance by Å.

		Carbon site		Bond site		Vacant site	
		OC	CO	OC	CO	OC	CO
(4,4)CNT	E_{ads}/meV	−32.97	−19.1	−1.2	0.26	−30.8	−20.21
	R/Å	3.2	3.9	3.2	3.4	2.8	3.4
		ON	NO	ON	NO	ON	NO
	E_{ads}/meV	−161	−138	−98	−54.8	−241	−98
	R/Å	3.6	3.4	3.6	3.2	3.4	3.0
(7,0)CNT		OC	CO	OC	CO	OC	CO
	E_{ads}/meV	−95	1.4	28.1	68.8	−73.9	39.1
	R/Å	3.4	3.8	3.2	3.8	2.6	3.4
		ON	NO	ON	NO	ON	NO
	E_{ads}/meV	−1863.9	−1765.3	−1344.2	−1284.3	−1372.1	−1310.4
	R/Å	2.8	2.6	3.3	3.3	3.0	3.6

on the same three positions of pristine zig-zag (7,0) CNT: above a carbon atom, above a bond between two carbon atoms and above a center of a hexagon ring. Also, we have studied the effect of gas molecules orientation by adsorbing CO and NO, once when the oxygen atom is faced the surface of (7,0)CNT (OC and ON) and the other when the carbon/nitrogen atom is faced the surface (CO and NO).

We have calculated the adsorption energies and optimal adsorption distances of OC and CO gas molecules on armchair (7,0)CNT and are found to be (−95 meV, 3.4Å and 1.4 meV, 3.8 Å) above a carbon atom, (28.1 meV, 3.2 Å and 68.8 meV, 3.8 Å) above a bond between two carbon atoms and (−73.9 meV, 2.6 Å and 39.1 meV,3.4 Å) above a center of a hexagon ring, respectively. Also, we have calculated the adsorption energies and optimal adsorption distances of ON and NO gas molecules on zig-zag (7,0)CNT and are found to be (−1863.9 meV, 2.8 Å and −1765.3 meV, 2.6 Å) above a carbon atom, (−1344.2 meV, 3.3 Å and −1284.3 meV, 3.3 Å) above a bond between two carbon atoms and (−1372.1 meV, 3.6 Å and −1310.4 meV, 3.0 Å) above a center of a hexagon ring, respectively.

It is clear that the adsorption of NO on the surface of (7,0)CNT is preferred than the adsorption of CO. Also, the adsorption energy is dependent on the orientation of the adsorbed gas molecules. We have found that the adsorption energies of OC and ON are preferred than the adsorption energies of CO and NO on the surfaces of (7,0)CNTs, respectively. Also, the adsorption energies are dependent on the adsorption sites where the gas mo-

lecules are adsorbed on the surfaces of (7,0)CNTs. Our calculations show that the order of adsorption energies for adsorbing CO, OC, NO and ON are E_{ads}(carbon site) < E_{ads}(vacant site) < E_{ads}(bond site), see **Figures 2** and **3(d**, **e**, **f)** and **Table 1**.

3.2. Adsorption of CO₂ and NO₂ on (4,4)CNT and (7,0)CNT Surfaces

We have calculated the adsorption energies and the optimal distances of CO_2 and NO_2 above a carbon atom site, a bond site, and a vacant site of pristine (4,4)CNT. They are found to be (−33 meV, 3.7 Å), (−80 meV, 3.4 Å) and (−38 meV, 2.2 Å) for CO_2, respectively, and (−37 meV, 3.1 Å), (−146.6 meV, 2.4 Å) and (−81 meV, 2.8 Å) for NO_2, respectively. The calculated adsorption energies and the optimal distances of CO_2 and NO_2 above a carbon atom site, a bond site, and a vacant site of pristine (7,0)CNT are found to be (−169.3 meV, 3.4 Å), (−23.9 meV, 3.8 Å), (−77.7 meV, 2.8 Å) for CO_2, respectively, and (−1602.7 meV, 2.6 Å), (−972.8 meV, 2.2 Å) and (−1218.9 meV, 2.8 Å) for NO_2, respectively.

One can see that the adsorption of NO_2 on the surface of (4,4)CNT is preferred than the adsorption of CO_2. Also, the adsorption energy is dependent on the type of CNTs. We have found that the adsorption energies of NO_2 on (7,0)CNT are preferred than the adsorption energies NO_2 on (4,4)CNT. Also, the adsorption energies are dependent on the adsorption sites where the gas molecules are adsorbed on the surfaces of (4,4)CNTs and (7,0)CNTs. Our calculations show that the order of adsorption energies for adsorbing CO_2 and NO_2 on (4,4)

CNTs are E_{ads}(bond site) < E_{ads}(vacant site) < E_{ads}(carbon site), however for adsorbing CO_2 and NO_2 on (7,0)CNTs have the order E_{ads}(carbon site) < E_{ads}(vacant site) < E_{ads}(bond site). All these results are shown in **Figure 4** and **Table 2**.

3.3. Adsorption Energies of CO, NO and CO₂ on Monovacancy Defected (4,4)CNTs

We have studied the adsorption energies and optimal adsorption energies of CO, NO and CO_2 of the monovacancy defected (4,4) CNT on three different sites. The calculated adsorption energies and optimal adsorption energies for CO molecules are found to be (39 meV, 3.0 Å), (−88 meV, 3.9 Å) and (40 meV, 3.2 Å) on a vacant site, on one dangling carbon atom site, and on a carbon atom far away from the position of monovacancy defects, respectively. The optimal adsorption energies for NO molecules are (−770 meV, 3.4 Å), (−560 meV, 3.0 Å) and (−280 meV, 3.9 Å) on a vacant site, on one dangling carbon atom site, and on a carbon atom far away from the position of monovacancy defects, respectively.

The calculated adsorption energies and optimal ad-

sorption distances for CO_2 molecules are (−1 meV, 2.7 Å), (−10 meV, 3.0 Å) and (47 meV, 3.2 Å) on a vacant site, on one dangling carbon atom site, and on a carbon atom far away from the position of monovacancy defects, respectively, as shown in **Figure 5** and **Table 3**. One can see that the adsorption of CO on the monovacancy defected surface of (4,4)CNT is enhancement only on the position of dangling carbon atom (the adsorption energy is changed from −32.97 meV to −88 meV). For NO adsorption, the enhancement is achieved on the three positions from −138 meV to −770 meV above the vacant site, to −560 meV above the dangling carbon atom site and to −280 meV above the carbon atom site. However, for the CO_2 there is no enhancement on any adsorption site.

3.4. Adsorption Energies of CO, NO and CO₂ on Monovacancy Defected (7,0)CNTs

We have calculated the adsorption energies and the optimal adsorption distances of CO, NO and CO_2 of the monovacancy defected (7,0) CNT on the same three sites, above a vacant site due to a removing carbon atom site, above one dangling carbon atom site, and a carbon atom
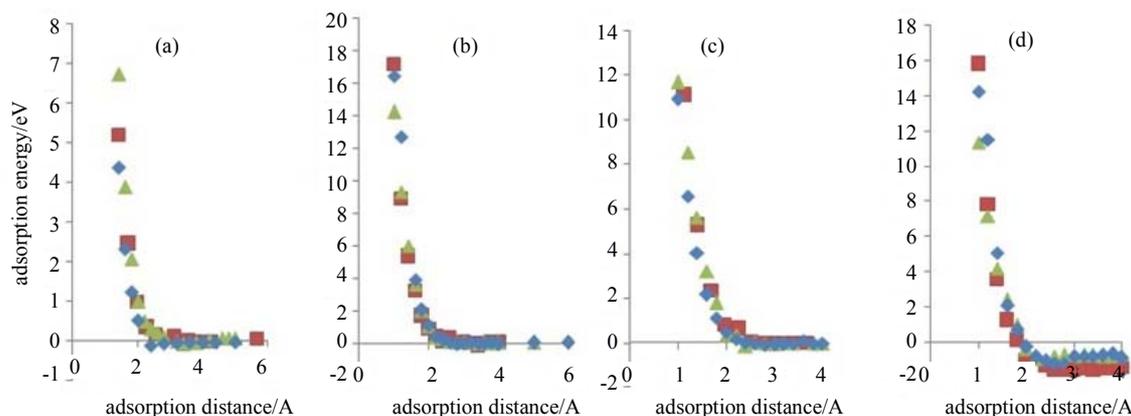
Figure 4. The calculated adsorption energies above carbon atom site (blue marks), above bond site (red marks) and above vacant site (green marks) of (a) CO_2 on (4,4)CNT, (b) NO_2 on (4,4)CNT (c) CO_2 on (4,4)CNT and (d)NO_2 on (7,0)CNT.

Table 2. The calculated adsorption energies and optimal adsorption distances of CO_2 and NO_2, above a carbon site, bond site and vacant site of pristine (4,4)CNTs and (7,0)CNTs. All energies are given by meV and distance by Å.

		Carbon site		Bond site		Vacant site	
		CO₂	NO₂	CO₂	NO₂	CO₂	NO₂
(4,4)CNT	Eads/meV	−33	−37	−80	−146.6	−38	−81
	R/Å	3.7	3.11	3.4	2.4	2.2	2.8
		CO₂	NO₂	CO₂	NO₂	CO₂	NO₂
(7,0)CNT	Eads/meV	−169.3	−1602.7	−23.9	−972.8	−77.7	−1218.9
	R/Å	3.4	2.6	3.8	2.2	2.8	2.8
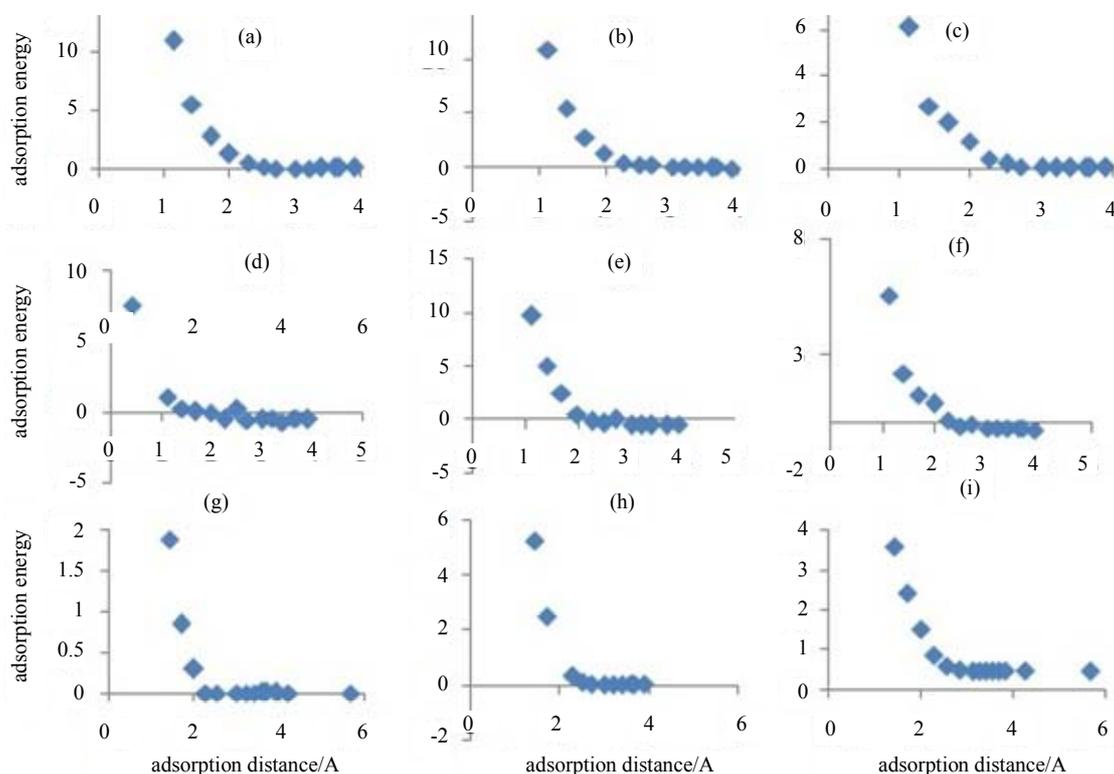
Figure 5. Adsorption energies of CO, NO and CO₂ gas molecules on the monovacancy defects of (4,4)CNTs. (a, d, g), above the vacancy site for CO, NO and CO₂, respectively. (b, e, h) above one of three dangling carbon atoms for CO, NO and CO₂, respectively, and (c, f, i) above a carbon atom far away from the vacancy defect for CO, NO and CO₂, respectively.

Table 3. The calculated adsorption energies and optimal adsorption distances of CO, NO and NO₂, on monovacancy defected (4,4)CNTs and (7,0)CNTs. All energies are given by meV and distance by Å.

		Vacant site			Dangling carbon atom site			Carbon atom site		
		CO	NO	CO₂	CO	NO	CO₂	CO	NO	CO₂
(4,4)CNT	Eads/meV	39	−770	−1.0	−88	−560	10	40	−280	47
	R/Å	3.0	3.4	2.7	3.9	3.0	3.0	3.2	3.9	3.2
(7,0)CNT	Eads/meV	90	−2410	7	−220	−2410	−99	−240	−2420	−12
	R/Å	2.6	2.6	2.8	3.8	3.8	3.8	2.6	3.8	3.0

site far away from the position of monovacancy defects. The calculated adsorption energies and optimal adsorption energies for CO molecules are (90 meV, 2.6 Å), (−220 meV, 3.8 Å) and (−240 meV, 2.6 Å) on a vacant site, on one dangling carbon atom site, and on a carbon atom site, respectively.

The calculated adsorption energies and optimal adsorption distances for NO molecules are (−2410 meV, 2.6 Å), (−2410 meV, 3.8 Å) and (−2420 meV, 3.8 Å), respectively. The calculated adsorption energies and the optimal adsorption distances for CO₂ molecules are (7 meV, 2.8 Å), (−99 meV, 3.8 Å) and (−12 meV, 3.0 Å) on a vacant site, on one dangling carbon atom site, and on a

carbon atom site, respectively, as shown in **Figure 6** and **Table 3**. One can see that there is no enhancement of CO₂ adsorption on any adsorption site. However, the adsorption of CO and NO is improved by applying the monovacancy defects on (7,0)CNTs.

3.5. Mulliken Atomic Charges

To understand more about the surface reactivity, the Mulliken atomic charges are calculated for adsorbing some selected gas molecules on pristine (4,4)CNT and (7,0)CNT. As shown in **Figure 7**, the carbon atom or nitrogen atom of CO and NO possess always positive
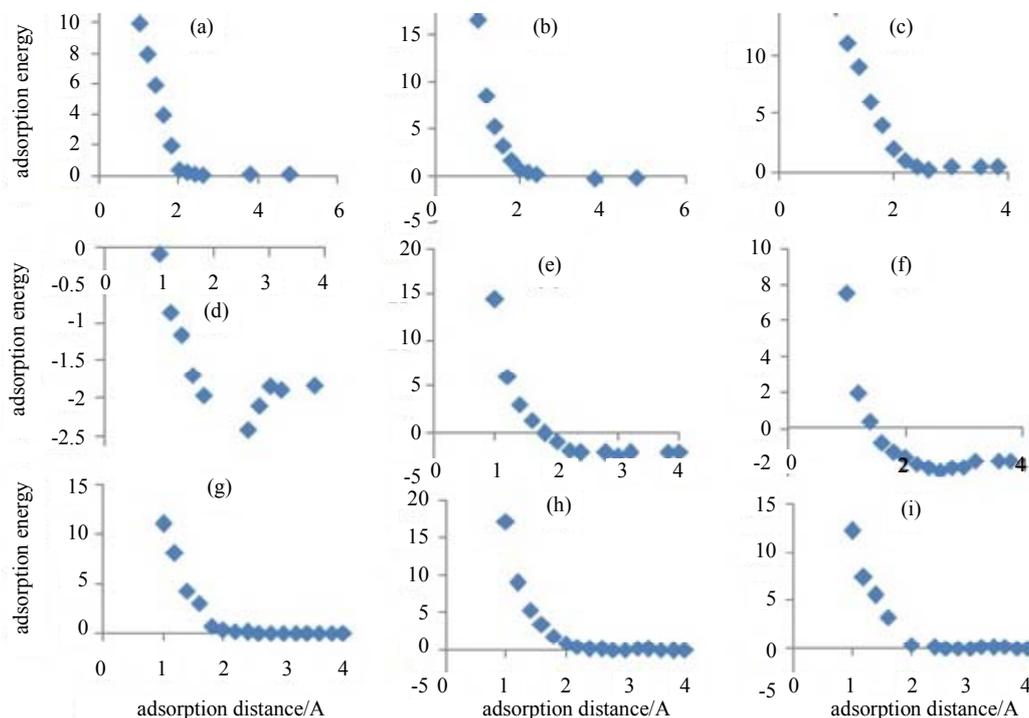
Figure 6. Adsorption energies of gas molecules on the monovacancy defects of (7,0)CNTs. (a, d, g) for CO, NO and CO₂ above the vacancy site, respectively. (b, e, h) for CO, NO and CO₂ above one of three dangling carbon atoms, respectively, and (c, f, i) for CO, NO and CO₂ above a carbon atom far away from the vacancy defect, respectively.
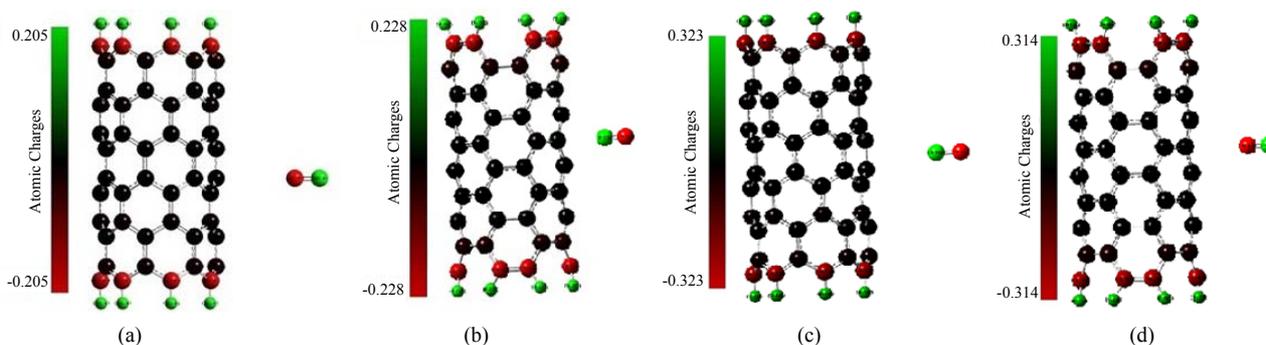
Figure 7. Mulliken atomic charges of (a) ON gas molecule adsorbed on (7,0)CNT, (b) NO gas molecules adsorbed on (4,4)CNT, (c) CO gas molecules adsorbed on (7,0)CNT and (d) OC gas molecules adsorbed on (4,4)CNT.
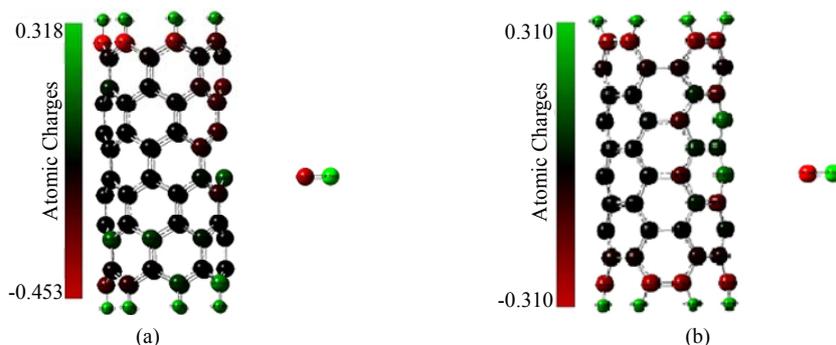
Figure 8. Mulliken atomic charges of (a) OC gas molecule adsorbed on (7,0)CNT and (b) CO gas molecules adsorbed on (4,4)CNT.

charge, however, oxygen atom possesses always negative charge. This can be explained in terms the electron infinity of the oxygen is more than the electron infinities of carbon and nitrogen. Therefore, the adsorption energies of OC and ON are preferred than the adsorption energies of CO and NO on the surfaces of carbon nanotubes.

Also, the Mulliken atomic charges are calculated for adsorbing some selected gas molecules on monovacancy defects of (4,4)CNT and (7,0)CNT. As shown in **Figure 8**, introducing the monovacancy defects leads to change the zero charge of carbon atom in case of pristine nanotubes into partially negative and positive charges, especially three dangling carbon atoms. Therefore, introducing the monovacancy defects on carbon nanotubes surfaces is caused the enhancement of adsorption energies.

4. Conclusion

We have studied the adsorption energies of some pollutant gas molecules as CO, NO, CO₂ and NO₂ on (4,4) CNT and (7,0)CNT. We have investigated the effects of different adsorbed sites and the orientation of adsorbed gas molecules, in addition to introducing the monovacancy defects on (4,4) CNT and (7,0) CNT surfaces. One can conclude that the zig-zag (7,0) CNT is better than the armchair (4,4)CNT for adsorbing pollutant gas molecules, especially, NO gas molecules. Also, we have found that introducing the monovacancy defects is improved the adsorption only on the (7,0)CNT of CO and NO gas molecules.

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