CO and CO₂ Adsorptions on H-Capped (6, 0) Single-Walled Carbon Nanotube: A Density Functional Study

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Abstract: The adsorption of monoxide (CO) as well as the adsorption of CO_2 on *(6,0)* carbon nanotube surface was studied by using density functional theory (DFT). Zigzag *(6,0)* CNT was used to simulate the surface. Parallel and Perpendicular bonding geometries of CO and CO_2 adsorbed on *(6,0)* carbon nanotube (CNT) surface are considered. The calculated adsorption energies for CO and CO_2 molecules on the carbon nanotube (CNT) were positive or near of zero. Therefore, absolute the carbon nanotube (CNT) cannot detect CO and CO_2 molecules because they could not be adsorbed on the pure *(6,0)* carbon nanotube (CNT) surface. In the CO-CNT system, the C-O distances in the parallel adsorption configurations were longer than the Perpendicular adsorption configurations because of further electron transfers from carbon nanotube (CNT) to anti-bonding orbital of CO.

Key words: Carbon nanotube (CNT) · Adsorption · DFT methods

INTRODUCTION

After discovery of carbon nanotubes (CNTs) [1], single-walled carbon nanotubes (SWCNTs) have been attracting great interest for their physical and chemical properties [1-3]. Numerous works have been performed to study the properties and applications of this fascinating novel material [4, 5]. They have a wide range of application in nanoelectronics, nanoscaling biotechnology and biosensors [3, 6-9]. Because of their size, large surface area and hollow geometry of single-walled carbon nanotubes are being considered as prime materials for gas adsorption [10-14], biological, chemical, electromechanical sensors and nanoelectronic device [15-17]. For example, carbon nanotubes (CNTs) have been experientially investigated for the detection of gas molecules [18-20], organic vapors [21-22], biomolecules and different ions [23-25].

Sensitivity of carbon nanotubes (CNTs) to CO has been also indicated by means of quantum mechanics calculations. Carbon monoxide oxidation is one of the most extensively studied heterogeneous catalytic reactions [26].

In this work, we report that the sensitivity of carbon nanotubes (CNTs) *(6,0)* system to CO and CO_2 gases can be enhanced to a higher level based on density functional theory (DFT) calculations.

Computational Details: In the present work, adsorption behaviors of CO and CO_2 molecules on the single-walled carbon nanotube (SWCNT) were taken into consideration. In first step, single-walled carbon nanotube (SWCNT) with chiralitie *(6,0)* and length 6 Å had been selected. Due to the absence of periodic boundary conditions in molecular calculations, it was necessary to saturate the C dangling bonds with H atoms.
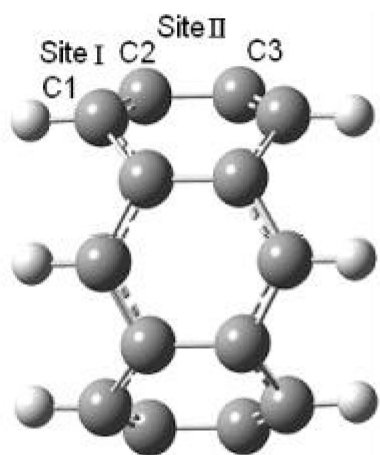
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Fig. 1: Two distinct adsorption sites (I, II) of the (6, 0) single-walled carbon nanotubes (SWCNT)

The hydrogenated *(6,0)* carbon nanotube (CNT) had 36 atom ($C_{24}H_{12}$). The optimized *(6,0)* carbon nanotube (CNT) structure had the diameter ~4.80 Å. The optimized carbon nanotube (CNT) *(6,0)* had two distinct adsorption sites (I, II) (Fig. 1). The sites considered for CO and CO_2 adsorptions on the carbon nanotube (CNT) *(6,0)* were site I and site II (Fig. 1). All calculations have been carried out by using the Gaussian 98 suite of programs [27]. The density functional theoretical method with the B3LYP functional and the 6-31G* basis set was used for all the calculations. Adsorption energies were calculated as the different between the total energy for carbon nanotube (CNT), CNT-CO, CNT-CO_2 and the isolated CO and CO_2 molecules. Adsorptions energies, the vibrational frequencies, NBO, thermodynamic changes, HOMO, LUMO and density of state (DOS) have been carried out with the B3LYP/631G*.

RESULTS AND DISCUSSION

Adsorption of CO on the *(6,0)* Carbon Nanotube (CNT):
Zigzag (6, 0) tube has two different C-C bonds (C1-C2= 1.418 Å and C2-C3= 1.452 Å) (Fig. 1) and thus offers two distinct adsorption sites. Therefore we had considered two distinct adsorption sites, marked as I and II (Fig.1).

For the molecular CO-CNT system, parallel and Perpendicular bonding geometries of CO adsorbed on the carbon nanotube (CNT) *(6,0)* surface are raised. The optimized geometries of calculated configurations of CO molecule adsorbed on *(6,0)* single-walled carbon nanotubes (SWCNT) are schematically displayed in Fig. 2. Geometrical parameters, binding energies, NBO atomic charges and stretching frequencies for the parallel
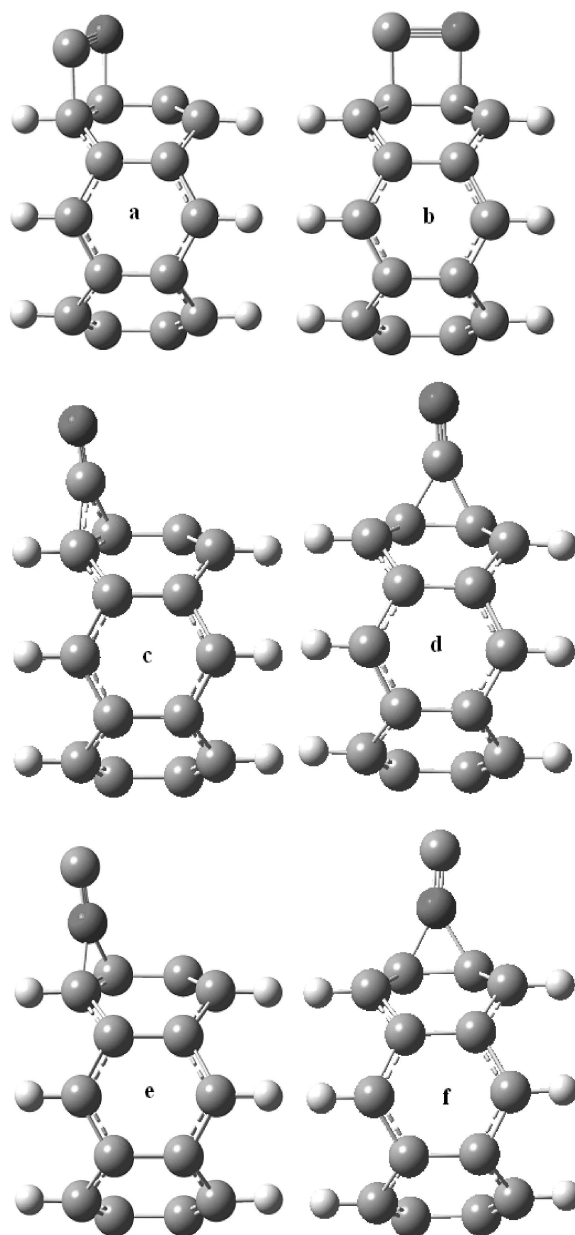

Fig. 2: (a) and (b) The parallel adsorption configurations of an CO molecule on the sites (I, II), (c) and (d) perpendicular adsorption configurations of an CO molecule to the carbon nanotubes (CNT) surface via C down on the sites (I, II), (e) and (f) perpendicular adsorption configurations of an CO molecule to the carbon nanotubes (CNT) surface via O down (sites I and II, respectively).

and Perpendicular chemisorbed CO (C-down and O-down) on I and II sites are summarized in Table 1. The notation C down and O down denotes a CO perpendicular to the surface via C and O, respectively (Figs. 2c-f).

Table 1: The equilibrium geometries (Å), adsorption energies (kcal/ mol), charge transfer (e), thermodynamic changes (kcal/ mol) and stretching frequencies (cm^{-1}) for CO adsorbed on the (6, 0) carbon nanotubes (CNT) surface

Model→	CO	CO-CNT parallel		CO-CNT Perpendicular C_{down}		CO-CNT Perpendicular O_{down}	
Parameters →	-	site1	site2	site1	site2	site1	site2
	-	Fig. 2a	Fig. 2b	Fig. 2c	Fig. 2d	Fig. 2e	Fig. 2f
$r_{(C1-C2)}$	-	1.605	1.501	2.491	1.419	1.418	1.418
$r_{(C2-C3)}$	-	1.500	1.484	1.439	1.452	1.451	1.452
$r_{surface-CO}$	-	1.555	1.480	0.740	3.730	3.733	4.390
$r_{(C=O)}$	1.138	1.324	1.359	1.235	1.139	1.138	1.138
ΔE_b	-	57.468	41.617	-0.956	-0.890	-0.045	0.089
ΔH	-	58.574	43.965	0.015	0.019	-0.921	-0.783
$T\Delta S$	-	-11.036	-12.240	-4.585	-4.747	-8.96	-7.854
ΔG	-	69.610	56.205	4.600	4.766	8.039	7.943
q_{CO}		-0.197	-0.169	-0.119	-0.012	0.0	0.0
q_c (in CO)	-	0.301	0.320	0.462	0.498	0.502	0.502
q_o (in CO)	-	-0.498	-0.489	-0.581	-0.510	-0.502	-0.502
v_{CO}	2210.94	1300.32	1176.72	1678.63	2156.76	2209.64	2208.63

The CNT-CO binding energies, ΔE_b, were calculated using:

$$\Delta e_b = E_{CNT-CO} - (E_{CNT} + E_{CO}) \tag{1}$$

That E_{CNT-CO}, E_{CNT} and E_{CO} were the total energies of the fully optimized CNT-CO structure, nanotube alone and CO molecule, respectively.

The calculated Eads indicated that CO may be absorbed very weak on the carbon nanotubes (CNT) with the perpendicular adsorption configurations and the calculated Eads of the parallel adsorption configurations at the sites were very less than the perpendicular adsorption configurations [Table 1]. Moreover, the calculated adsorption energies of C-down were more favorable than the obtained adsorption energies of O-down on the same adsorption sites. Similar result were also found for CO on Rh-decorated *(8,0)* single-walled carbon nanotube [28]. Except the perpendicular adsorption configurations of CO-adsorption (C-down) (Figs. 2c and 2d) that its binding energy was very weak, in other stats, the calculated adsorption energies were positive or near of zero [Table 1]. Therefore, absolute the carbon nanotubes (CNT) could not detect CO molecule because they could not be adsorbed on the pure *(6,0)* carbon nanotubes (CNT) surface. Similar results were also obtained for CO-adsorption on other carbon nanotubes (CNT) [29, 30].

The configuration of CO-adsorption on the site I (Fig. 2c) by using C atom (C-down) was the most with the binding energy of-0.956 kcal/mol and the bonding distance from the C-O axis to the surface was 0.740 Å. At Perpendicular bonding geometries, the calculated Eads of

C-down was more than the Eads of O-down. But in the geometries, the calculated R_{CNT-OC} was longer than the R_{CNT-CO} bond distance in C-down. In addition, the present calculations showed that CO molecule absorbed on siteI of the *(6,0)* carbon nanotube (CNT) was the most stable site.

The C-O distance in the parallel adsorption configurations were longer than the Perpendicular adsorption configurations because of further electron transfers from carbon nanotubes (CNT) to anti-bonding orbital of CO.

The calculated C-O frequencies in the range of 1100-2111 cm^{-1} indicated the triplet bonding characteristic between C and O atoms and the calculated C-O stretching frequencies were red-shifted, comparable with the calculated gaseous value at 2210.94 cm^{-1}. As shown in Table 1, the C-O distance in the parallel adsorption configurations were increased for CO on the carbon nanotubes (CNT) surface, which is consistent with the decreasing of the C-O frequency.

For the most stable CO adsorption site (Fig. 2c), the NBO population analysis showed that the total charge transfer from the tube to CO molecule was-0.119e. The electron configuration of CO is KK $(\sigma_{2s})^2$ $(\sigma_{2s}^*)^2$ $(\pi_{2py})^2$ $((\pi_{2px})^2 (\pi_{2pz})^2$ and the transferred electron was filled in the half-filled anti-bonding orbital of CO, hence the C-O bond was weaken. Adsorbed CO species on the *(6,0)* carbon nanotubes (CNT) surface had not significant negative charge and it indicated that the bonding between CO and the carbon nanotubes (CNT) surface was not possibly ionic.
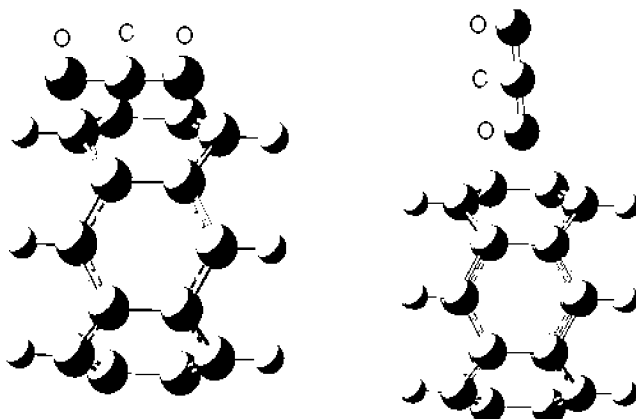
Fig. 3: The CO_2 adsorption configurations on the (6, 0) carbon nanotubes (CNT) in sites I (parallel) and in site II (Perpendicular)

Table 2: The equilibrium geometries (Å), adsorption energies (kcal/ mol) and charge transfer (e) for CO_2 adsorbed on the carbon nanotubes (CNT) surface

Model→	CO_2-CNT (site1) (parallel)	CO_2-CNT (site2) (perpendicular)
r (C_1-C_2)	1.418	1.418
r (C_2-C_3)	1.452	1.452
r($CNT_{surface}$-CO_2)	1.328	3.628
r C=O	1.169	1.169
ΔEb	0.361	0.122
qc	1.240	1.020
qo_1	-0.623	-0.513
qo_2	-0.617	-0.507
qco_2	0.0	0.0

Adsorption of CO_2 on (6, 0) CNT: As shown in previous section, the optimized carbon nanotubes (CNT) (6, 0) had two distinct adsorption sites (I, II). So, in this part, the sites considered for CO_2 adsorptions on carbon nanotubes (CNT) (6, 0) were site I and site II. For the CO_2-carbon nanotubes (CNT) system, parallel and Perpendicular bonding geometries of CO_2 adsorbed on the sites of the carbon nanotubes (CNT) (6, 0) surface were considered. In the first step, the structures were allowed to relax by all atomic geometrical optimization at the DFT method. After structural relaxation, we found the adsorption of CO_2 molecule for parallel state at site I and for Perpendicular state at site II was the more stable state (Fig. 3). According to the results of (6, 0) single-walled carbon nanotubes, we focus on the configurations for other studies in the following sections.

Binding Energy, ΔE_b, Were Calculated Using:

$$\Delta e_b = E_{CNT-CO2} - (E_{CNT} + E_{CO2}) \qquad (2)$$

The calculated adsorption energies of CO_2 on the different sites of the carbon nanotubes (CNT) surface are presented in Fig. 3 and the calculated results of CO_2 adsorption on the SWCNT are shown in Table 2.

In Fig. 3 are seen two stable configurations of one-CO_2-adsorption on the carbon nanotubes (CNT). The configuration of CO_2-adsorption on the carbon nanotubes (CNT) for Perpendicular state at site II (Fig. 3b) was the most with the binding energy of 0.122 kcal/mol. In the configuration described Fig. 3b, the C-O and C_{CNT}-CO_2 distances were 1.169 and 3.628 Å, respectively (see Table 2).

The calculated Eads indicated that the calculated adsorption energies between CO_2 molecule and the *(6,0)* carbon nanotubes (CNT) were positive. When a CO_2 molecule was adsorbed on the carbon nanotubes (CNT), the system could not become more stable. Therefore, absolute the carbon nanotubes (CNT) could not detect CO_2 molecule because they could not be adsorbed on the pure *(6,0)* carbon nanotubes (CNT) surface. Similar results were also found for CO-adsorption on the *(6,0)* carbon nanotubes (CNT).

CO_2 molecule has two same C=O bonds (C=O: 1.169 Å). The NBO population analysis showed that the total charge transfer from the tube to CO_2 molecule for the parallel and perpendicular adsorption configurations were

zero, therefore the physical parameters of CO_2 (C=O bonds) had not changed and in CO_2 adsorption on the carbon nanotubes (CNT), CO_2 molecule has symmetry center, so in IR spectrum had not been activated.

Electronic Properties: Finally, we studied the influence on the electronic properties of the carbon nanotubes (CNT) by CO and CO_2 molecule adsorption. The calculated band-gap of the clean perfect *(6,0)* single-walled carbon nanotubes (CNT) was about 0.59eV which is very close to DFT simulated for the other small diameter zigzag tubes [31, 32]. The effects of CO and CO_2 molecules on adsorptions energies in the CNTs relate to their electronic structure. When CO and CO_2 molecules were adsorbed on the carbon nanotubes (CNT), the interaction of them became very weak. Therefore, the band gaps were calculated 0.61 and 0.60 eV and for the systems, significant changes in the band gap were not observed.

CONCLUSION

We had theoretically studied the adsorptions of CO and CO2 molecules on the Zigzag of (6, 0) carbon nanotubes (CNT) through the DFT calculations. Based on our calculations, it seems that the pristine CNTs could not detect CO and CO2 molecules because the molecules could not be adsorbed on the pure (6, 0) carbon nanotubes (CNT) surface and in this systems, significant changes in the band gap were not observed. The present theoretical work indicates that the adsorption of CO (C-down) on site I the carbon nanotubes (CNT) was most favorable. Moreover, the C-O distances in the parallel adsorption configurations were longer than the Perpendicular adsorption configurations because of further electron transfers from carbon nanotubes (CNT) to anti-bonding orbital of CO.

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