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Investigation of the interaction of carbon dioxide fluid with internal and external single-wall carbon nanotubes by DFT

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Abstract

The effective parameters of (5, 0) and (5, 5) single-wall carbon nanotubes during the interaction with carbon dioxide as sensors are determined. The interaction of carbon dioxide molecules with internal and external walls of the nanotubes is studied using Gaussian 03 coding by density functional theory (DFT) at the B3LYP/6-311G level of theory. CO_2 rotation around tube axles vertically and parallel to the internal and external walls has been investigated. The carbon dioxide molecule is predicted to bind only weakly to nanotubes, and the tube-molecule interactions can be identified as physisorption. CO_2 adsorption is stronger on external wallsthan on internal walls, and adsorption on the external wall of (5, 0) is stronger than on the external wall of (5, 5); the adsorption energies are exothermic and equal to -0.8884 and -0.0528 kcal/mol, respectively. The rotation energy barrier for (5, 5) is lower than that for (5, 0) in all rotations, therefore in these interactions (5, 5) is more active. The energy gap significantly changes in the presence of carbon dioxide molecules on the inside surface of (5, 0) and the electric conductivity is affected, but no remarkable change is observed in the electronic structure of (5, 5).

1. Introduction

The special geometry and unique properties of carbon nanotubes offer great potential applications, including nanoelectronic devices, energy storage, chemical probes and sensors, field emission displays, etc. [1]. The electronic properties of single-wall carbon nanotubes (SWNTs) can be considerably affected by the presence of adsorbed molecules. This has important consequences for device applications that use SWNTs as the bases of chemical sensors. Advantages of carbon nanotubes (CNTs) over other materials as good sensors are due to their small size, high strength, high electrical and thermal conductivity, and high specific area. The effects of absorbance of gas on SWNTs were studied theoretically and experimentally [2–6].

The interaction of various gas molecules with carbon nanotubes has been investigated in several recent theoretical studies [7–11]. Zhao et al. [9] used self-consistent field (SCF) electronic structure calculations based on density functional theory (DFT) with either localized basis (DMol) or plane-wave basis (CASTEP) to study adsorption of various gases (NO_2, O_2, NH_3, N_2, CO_2, CH_4, H_2O, H_2, and Ar) on SWNTs and bundles. Most of the molecules adsorb weakly on (10, 0), (17, 0), (5, 5), and (10, 10) SWNTs and can be either charge donors or acceptors to the nanotubes. Short unit cell length, namely one molecule per two-unit cell, was used. The gas adsorption bundle interstitial and groove sites are stronger than those on individual tubes.

The electronic properties of SWNTs are sensitive to the adsorption of NO_2 and O_2 molecules, which are charge acceptors. Based on the calculations, the effects due to most charge donor molecules in the air, such as N_2, CO_2, and H_2O, are relatively weak. Therefore, the interaction between nanotubes and these gas molecules is weak and does not have significant influence on the electronic structure of SWNTs [9].

Adsorption of CO_2 on purified SWNTs was studied computationally and experimentally by Martin Cinke et al. [10]. The computational study was carried out using second-order Moller-Plesset perturbation theory (MP2), whereby several base sets ranging from the 6–31G* set to the augmented correlation-consistent polarized valence triple zeta set were used to study CO_2 interaction with (9, 0) SWNT. The computational results yielded a binding energy similar to the experimental value, 2303 J/mol (0.24 ev), and they showed that CO_2 was physisorbed side-on the nanotube.

Recently, Lithoxoos et al. [11] used Monte Carlo (MC) simulation of N_2, CH_4, H_2, CO, and CO_2 adsorbed gas on (9, 9) SWNT in the grand cononical ensemble. They reported that the experimental and the simulated adsorption showed the same qualitative behaviour, namely, it followed the order $CO_2 > CO > N_2$ and $CH_4 > H_2$ of the adsorption in SWNTs.

Although, there is a lot of published research about the interaction of long-diameter SWNTs with CO_2 molecules using supercomputers with large amounts of memory [9, 10], not

much research on this subject has been carried out using ordinary personal computers. In the present study, density functional calculation atthe B3LYP/6-311G level of theory is used to determine effective parameters of (5, 0) and (5, 5) SWNT as carbon dioxide sensors. Adsorption on both inner and outer surfaces of nanotubes and CO_2 rotation are examined.

2. Computational Method

The CO_2-nanotube interactions were studied using Gaussian 03 coding [12] by DFT at the B3LYP/6-311G level of theory [13–18]. The basis set superposition errors (BSSE) were estimated for the counterpoise correction [19]. The (5, 0) SWNT containing 50 carbon atoms of length 8.5 Å and diameter 4 Å, saturated with 10 hydrogen atoms, and the (5, 5) SWNT containing 80 carbon atoms of length 7.4 Å and diameter 6.8 Å, saturated with 20 hydrogen atoms were selected for this purpose. CO_2 molecule on the internal and external walls of the SWNTs was fully optimized without any symmetrical constraints in the parameters, such as the height above the surfaces or CO_2 location and orientation. The adsorption energies were determined according to the expression:

$$E_{ads} = E_{tot}(CO_2 - \text{nanotube}) - E_{tot}(\text{nanotube}) - E_{tot}(CO_2)$$

where $E_{tot}(CO_2\text{-nanotube})$ is the total energy of the optimized CO_2-nanotube system,

$E_{tot}(\text{nanotube})$ is the total energy of the optimized nanotube and $E_{tot}(CO_2)$ is the total energy of the isolated CO_2 molecule. By this explanation, $E_{ads} < 0$ corresponds to exothermic adsorption, which leads to a stable structure.

The rotation of carbon dioxide molecule in different directions on the internal and external walls of the carbon nanotubes was investigated. Active sites and stable structures were determined. Adsorption energy was estimated as a function of tube-molecule distance and tube-molecule angle.

3. Results and Discussion

Table 1 summarizes the results for the total energy (E_{tot}), equilibrium distance, energy gap, adsorption energy (E_{ads}), dipole moment, and some bond distances. The CO_2 molecule is weakly bound to nanotubes and the tube-molecule interactions can be identified as physisorption. The calculations show that the adsorption of carbon dioxide molecule on the outer surface of (5, 0) nanotube is stronger than on the inside surface of (5, 0) nanotube, with a calculated adsorption energy of -0.8884 kcal/mol, exothermic, and 304.9699 kcal/mol, endothermic, respectively. The energy gap changed significantly after CO_2 adsorption on the inside surface of (5, 0) nanotube, therefore there was a change in the conductivity due to CO_2 adsorption.

Table 1. Calculated structural parameters and adsorption energy values of CO_2 adsorbed on internal (a) and external (b) of (5, 0) and (5, 5) nanotubes surfaces.

System	E_{tot} (Hartree)	E_{ads} (kcal/mol)	Energy gap (ev)	d (A°)	Dipole moment (Debye)	Bond distance (A°)	
						R_{C1-C2}	R_{C3-H4}
(5,0)	-1910.5207		1.7244		0.0000	1.4215	1.0825
CO_2-(5,0)[a]	-2098.5919	304.9699	0.8310	2.00	0.0589	1.4154	1.0822
CO_2-(5,0)[b]	-2099.0794	-0.8884	1.7187	3.47	0.4359	1.3810	1.0819
(5,5)	-3060.4923		1.7571		0.0000	1.4152	1.0810
CO_2-(5,5)[a]	-3249.0461	2.1626	1.7522	3.40	0.0122	1.4159	1.0808
CO_2-(5,5)[b]	-3249.0496	-0.0528	1.7576	3.57	0.1673	1.4160	1.0810

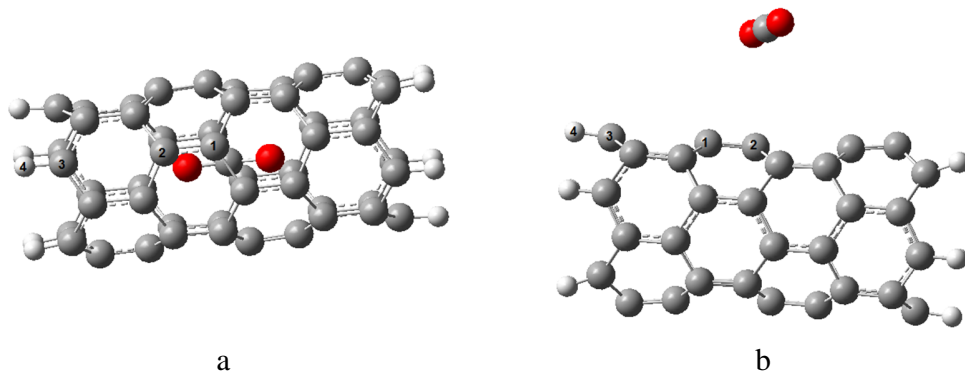a   b

Fig. 1. Adsorption configuration of CO_2 molecule on a) inside and b) outside surface of (5, 0) nanotube.
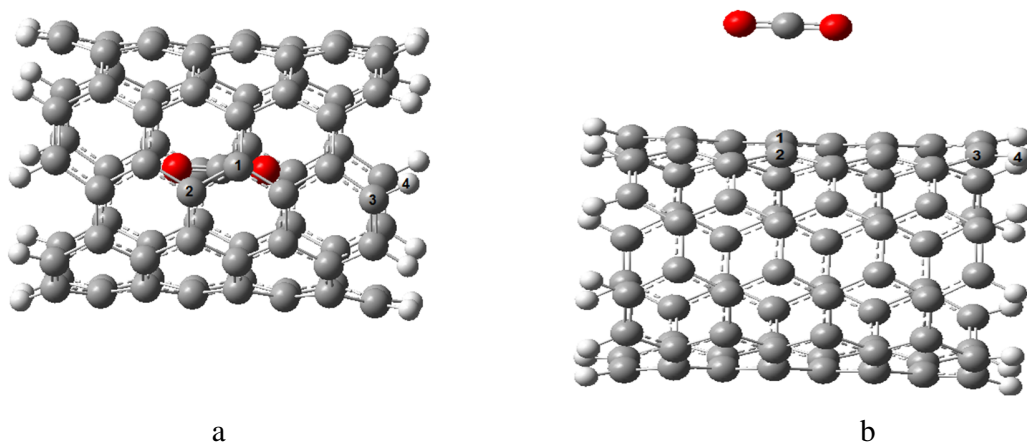

a   b

Fig. 2. Adsorption configuration of CO_2 molecule on a) inside and b) outside surface of (5, 5) nanotube .

The adsorption configuration of CO_2 molecule on the inside surface of (5, 0) nanotube is shown in Fig. 1a; the depicted CO_2 molecule is optimized in the middle of nanotubes, and the equilibrium distance from the internal wall is 2 Å. The adsorption configuration of CO_2 molecule on the outer surface of (5, 0) nanotube is shown in Fig. 1b, where the equilibrium distance from the external wall is 3.47 Å. The values of dipole moment significantly change after CO_2 adsorption on the outer surface of (5, 0) nanotube, with calculated values of 0.4359 Debye, with no significant changes for the inner surface. Bond distances beside interaction areas don't significantly change after CO_2 adsorption.

The values of the adsorption energy for the outer surface of (5, 5) nanotube are less than for the inside surface, corresponding to the calculated energy of -0.0528 kcal/mol, exothermic, and 2.1626 kcal/mol, endothermic, respectively. There are no significant changes in the energy gap values on the inner and outer surfaces of (5, 5) nanotube after CO_2 adsorption. The optimized adsorption configurations of CO_2 molecules on the inside and outside surfaces of (5, 5) nanotube are shown in Figs. 2a and 2b, respectively. The equilibrium distances from internal and external walls are 3.40 and 3.57 Å, respectively. The values of dipole moment don't change significantly after CO_2 adsorption, corresponding to the calculated values of 0.1673 Debye for the outer surface and 0.0122 Debye for the inner surface. Bond distances don't change significantly after CO_2 adsorption. Furthermore, the adsorption energy value for the outer surface of (5, 5) nanotube, -0.0528 kcal/mol, is less than for the inside surface, 2.1626 kcal/mol, which show exothermic and endothermic adsorption, respectively. There are no significant changes in energy gap values on the inner and outer surfaces of (5, 5) nanotube after CO_2 adsorption.

The variations of the adsorption energy as a function of CO_2 molecule angle and CO_2 molecule distances were investigated. After optimizing CO_2 distance to the tube walls, rotation of the carbon dioxide molecule invertical and horizontalto the tube axle were studied. We investigated four rotations as follows: rotations 1 and 2 are the rotations of CO_2 molecules on the internal wall vertically and horizontally around the tube axle, respectively; rotations 3 and 4 are the rotations of CO_2 molecules on the external wall vertically and horizontally around the tube axle, respectively, which are depicted in Fig. 3 at zero and 90 ^{o} angles.
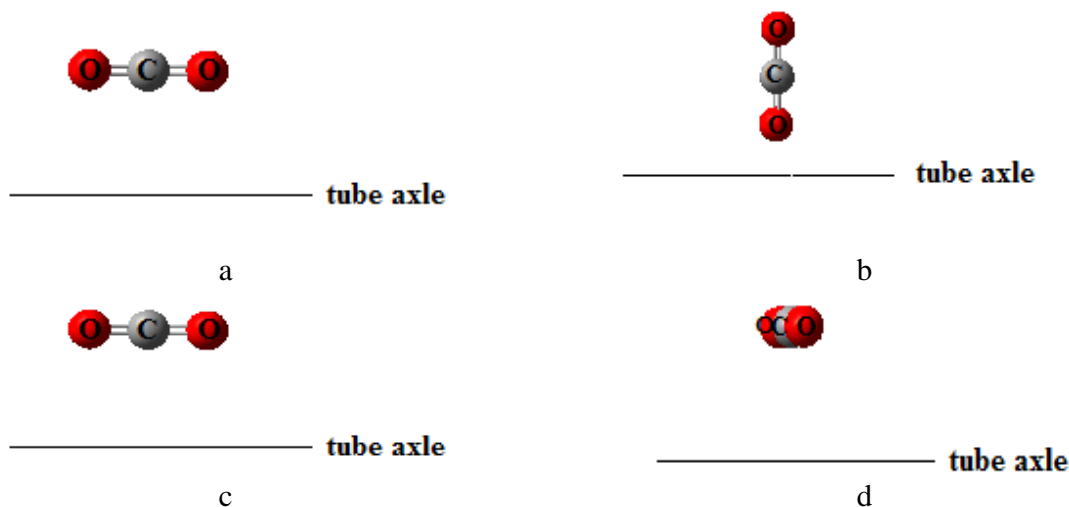
Fig. 3. Vertical (a, b) and horizontal (c, d) rotations around the tube axle at 0 $^{\circ}$ (a, c) and 90 $^{\circ}$ (b, d) angles.

Table 2 summarizes our results for the adsorption energy (Eads) with rotation of CO_2 molecule. In rotation 1, the adsorption energy has the minimum value, corresponding to the expression (1), and this leads to a stable structure. During the vertical rotation, the adsorption energy increases up to 80 $^{\circ}$ angle, the CO_2 molecule is close to the carbon atoms of the tube wall, and the repulsion energy increases, causing less stable structures, whereas the parallel rotations of the CO_2 molecule decrease the repulsion energy and the adsorption energy up to 180 $^{\circ}$ angle, which leads to a stable structure. In rotation 2, the adsorption energy has the maximum value, which leads to a less stable structure. During the parallel rotation, the adsorption energy decreases up to 100 $^{\circ}$ angle, the CO_2 molecule is far from the carbon atoms of the tube wall, and

the repulsion energy decreases, resulting in the minimum adsorption energy and the most stable structure, then the adsorption energy increases up to 180 $^{\circ}$ angle. In rotation 3, the adsorption energy increases up to 100 $^{\circ}$ angle, the CO_2 molecule is close to the carbon atoms of the tube wall, and the repulsion energy increases and causes less stable structures. After this point, the interaction of CO_2 decreased, thus the repulsion energy and the adsorption energy decreased up to 180 $^{\circ}$ angle, leading to a stable structure. In rotation 4, the adsorption energy increases up to 60 $^{\circ}$ angle, but the values are under zero, then the adsorption energy decreases up to 160 $^{\circ}$ angle, which leads to the most stable structure, and the adsorption energy has the minimum value, -1.6025 kcal/mol.

Table 2. Adsorption energy of CO_2 on internal (a) and external (b) of (5, 0) SWNT as a function of tube-molecule angle (°).

Rotation angle (degree)	Rotation1[a]			Rotation2[a]		
	E_{tot} (Hartree)	BSSE (Hartree)	E_{ads} (kcal/mol)	E_{tot} (Hartree)	BSSE (Hartree)	E_{ads} (kcal/mol)
0	-2098.2916	0.0293	493.4766	-2096.6042	0.0423	1552.2907
20	-2098.1972	0.0305	552.6577	-2097.3510	0.0388	1281.9984
40	-2097.9258	0.0331	722.9975	-2097.4895	0.0365	996.7865
60	-2097.5955	0.0381	930.2492	-2097.6566	0.0343	891.9312
80	-2097.2548	0.0397	1144.0639	-2097.8200	0.0334	789.3505
100	-2097.3050	0.0332	1112.5624	-2097.8741	0.0331	755.4090
120	-2097.4971	0.0333	991.9873	-2097.7219	0.0344	850.9124
140	-2097.8274	0.0320	784.7620	-2097.4768	0.0398	1004.7151
160	-2098.1655	0.0298	572.5541	-2097.1061	0.0439	1237.3291
180	-2098.2910	0.0292	493.7986	-2096.6584	0.0421	1518.1751

Table 3. Adsorption energy of CO_2 on internal (a) and external (b) of (5, 0) SWNT as a function of tube-molecule angle (°).

Rotation angle (degree)	Rotation3[b]			Rotation4[b]		
	E_{tot} (Hartree)	BSSE (Hartree)	E_{ads} (kcal/mol)	E_{tot} (Hartree)	BSSE (Hartree)	E_{ads} (kcal/mol)
0	-2099.0791	0.0024	-0.7130	-2099.0799	0.0014	-1.1974
20	-2099.0785	0.0014	-0.3694	-2099.0798	0.0013	-1.1488
40	-2099.0763	0.0020	1.0415	-2099.0795	0.0012	-0.9516
60	-2099.0716	0.0033	3.9990	-2099.0794	0.0011	-0.9025
80	-2099.0636	0.0032	8.9955	-2099.0794	0.0010	-0.9227
100	-2099.0609	0.0037	10.6992	-2099.0796	0.0010	-1.0271
120	-2099.0669	0.0036	6.9539	-2099.0796	0.0010	-1.0287
140	-2099.0740	0.0018	2.4975	-2099.0794	0.0015	-0.9322
160	-2099.0777	0.0014	0.1319	-2099.0805	0.0013	-1.6025
180	-2099.0791	0.0024	-0.7130	-2099.0802	0.0013	-1.3782

According to the results obtained for BSSE correction energy, it is negligible in all structures; its maximum value is 0.0439 Hartree for rotation 2, which proves that the selected basis set and the method are appropriate.

The same steps were repeated for (5, 5) nanotube and the results are reported in Table 3. During rotation 1, the adsorption energy change is similar to this rotation for the CO_2-(5, 0) system, but the adsorption energy and barrier energy values are less. In rotation 2, the adsorption energy has the maximum value, which leads to a less stable structure; the adsorption energy decreases up to 60 ° angle, the local minimum energy point, then the adsorption energy increases and reaches the minimum adsorption energy at 120 °, which it is the most stable structure in this rotation. Then, during this rotation, the adsorption energy increases up to 180 ° angle. The adsorption energy and barrier energy values are less than those for a similar rotation in the CO_2-(5, 0) system. In rotation 3, the adsorption energy increases up to 80 ° angle, the CO_2 molecule is close to the carbon atoms of the tube wall, and the repulsion energy increases, causing a less stable structure. After this point, the CO_2 molecule is parallel to the direction of the tube axle, the interaction of CO_2 and carbon atoms of the tube wall decreases, and the repulsion energy and adsorption energy decrease up to 180 ° angle, leading to a stable structure. Barrier energy

values are less than those for a similar rotation in the CO_2-(5, 0) system. Finally, in rotation 4, the system has local minimum energy values at 80, 120, and 160 ° and local maximum energy values at 60, 100, and 180 °. Maximum and minimum points are at 140 and 0 °, with calculated energy values of 0.7736 kcal/mol and -0.2838 kcal/mol, respectively. The BSSE correction energy in all structures is negligible; the maximum value is 0.0130 Hartree in rotation 2, which proves that the selected basis set and the method are appropriate.

Figs. 4 and 5 show the adsorption energy versus the tube-molecule distance for CO_2-(5, 0) and CO_2-(5, 5) systems, respectively. By scanning CO_2 molecule distance from the wall of the tube, the repulsion energy decreases, and the minimum adsorption energy and the most stable structures are found in the middle of (5, 0) and (5, 5) SWNT, as expected. The most stable interactions with CO_2 molecules occur in the middle of (5, 0) and (5, 5) SWNT (Table 1) with minimum adsorption energy values. The results of this work can be compared with the aforementioned theoretical and experimental investigations on gas adsorption on (9, 0) [10] and (9, 9) [11] SWNTs.

Table 4. Adsorption energy of CO_2 on internal (a) and external (b) of (5, 5) SWNT as a function of tube-molecule angle (°).

Rotation angle (degree)	Rotation1[a]			Rotation2[a]		
	E_{tot} (Hartree)	BSSE (Hartree)	E_{ads} (kcal/mol)	E_{tot} (Hartree)	BSSE (Hartree)	E_{ads} (kcal/mol)
0	-3249.0423	0.0067	4.5176	-3248.9671	0.0132	51.7658
20	-3249.0386	0.0070	6.8858	-3248.9833	0.0124	41.5482
40	-3249.0254	0.0089	15.1576	-3249.0127	0.0103	23.1283
60	-3248.9984	0.0113	32.0691	-3249.0311	0.0078	11.5617
80	-3248.9707	0.0129	49.4979	-3249.0263	0.0080	14.5941
100	-3248.9714	0.0129	49.0422	-3249.0256	0.0081	15.0412
120	-3248.9995	0.0112	31.4182	-3249.0332	0.0076	10.2614
140	-3249.0255	0.0088	15.0634	-3248.9812	0.0108	42.8760
160	-3249.0387	0.0070	6.8041	-3248.9542	0.0125	59.8283
180	-3249.0442	0.0067	3.3611	-3248.9468	0.0130	64.4588

Table 5 Adsorption energy of CO_2 on internal (a) and external (b) of (5, 5) SWNT as a function of tube-molecule angle (°).

| Rotation angle (degree)	Rotation3[b]			Rotation4[b]		
	E_{tot} (Hartree)	BSSE (Hartree)	E_{ads} (kcal/mol)	E_{tot} (Hartree)	BSSE (Hartree)	E_{ads} (kcal/mol)
0	-3249.0500	0.0012	-0.2838	-3249.0500	0.0011	-0.2838
20	-3249.0489	0.0011	0.4302	-3249.0495	0.0011	0.0465
40	-3249.0472	0.0008	1.4843	-3249.0493	0.0011	0.1246
60	-3249.0434	0.0023	3.8616	-3249.0486	0.0014	0.6207
80	-3249.0418	0.0028	4.8458	-3249.0489	0.0012	0.3948
100	-3249.0424	0.0056	4.4935	-3249.0489	0.0012	0.4209
120	-3249.0443	0.0022	3.3009	-3249.0490	0.0011	0.3705
140	-3249.0475	0.0045	1.3010	-3249.0483	0.0012	0.7736
160	-3249.0487	0.0012	0.5267	-3249.0496	0.0012	-0.0459
180	-3249.0495	-0.0060	0.0282	-3249.0495	0.0011	-0.0278
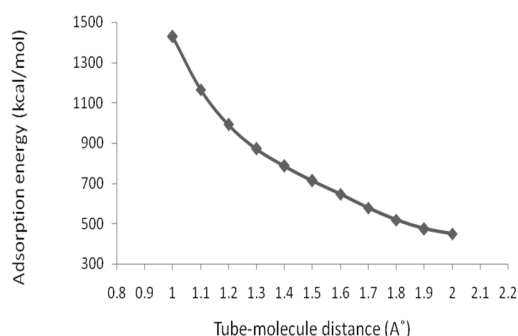
Fig. 4. Adsorption energy of CO_2 on internal of (5, 0) as a function of tube-molecule distance
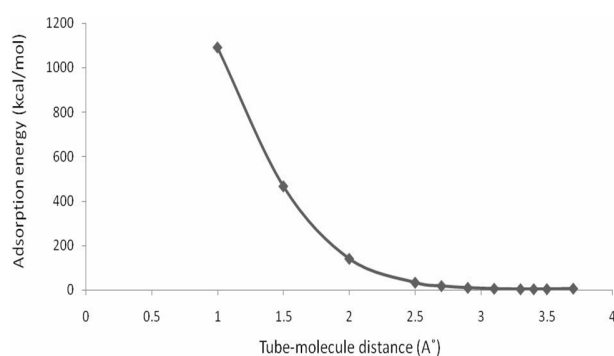

Fig. 5. Adsorption energy of CO_2 on internal of (5, 5) as a function of tube-molecule distance.

Experimental data yield a heat of adsorption of 0.024 eV for CO_2 on (9, 0), and the lower bound of computed binding energy is very similar (0.023 eV). This may have potential for greenhouse gas detection and bioremediation [10]. The experimental and simulated investigations on adsorbed gas on (9, 9) show the same qualitative behaviour, following the order $CO_2 > CO > N_2$ and $CH_4 > H_2$ of adsorption in SWNTs [11]. Therefore, it is predictable that (5, 0) and (5,

5) SWNTs have the potential to act as carbon dioxide sensors.

4. Conclusion

CO_2 adsorption on (5, 0) and (5, 5) SWNTs has been studied at various sites and tube-distances by DFT. The CO_2 molecule is weakly bound to nanotubes, and the tube-molecule interactions can be identified as physisorption. In the case of external walls, CO_2 adsorption is exothermicand is stronger for (5, 0) than for (5, 5), at -0.8884 and -0.0528 kcal/mol, respectively. The rotation energy barrier for (5, 5) is lower than for (5, 0) in all rotations, therefore (5, 5) is more activein these interactions. The energy gap changes significantly in the presence of carbon dioxide molecules on the inside surface of (5, 0) and conductivity is affected, but no remarkable change is observed in the electronic structure of (5, 5). It is predicted that CO_2 adsorption in bundle interstitial and groove sites may be stronger, and (5, 0) and (5, 5) SWNTs would be good sensors.

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