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ORIGINAL ARTICLE

DFT Investigations for sensing capability of a single-walled Carbon nanotube for adsorptions H_2, N_2, O_2 and CO molecules

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Abstract

Single-walled carbon nanotubes (SWCNTs) have a great deal of attention due to their unique properties. These properties of SWCNTs can be used in various devices such as nanosensors. SWCNTs nanosensors have fast response time and high sensitivity to special gas molecules which is very favorable for important applications. Recently, gas adsorption over outer surface of SWCNTs nanosensors was arguably a very interesting theoretical study. Here, the sensing capability of (6, 0) SWCNTs for adsorption H_2, N_2, O_2 and CO molecules are studied. The geometry optimization, electronic, thermodynamic, and vibrational properties have been investigated. All the calculations are based on the density functional theory (DFT) at the B3LYP/6-31G level through the Gaussian 09W program package. It is found that, adding these molecules to SWCNT causing a small increase in the bond lengths, and an increase in the total energy. In IR spectra, it is observed increasing the vibration modes and higher stretching vibration wave numbers of SWCNT with the studies molecules. This work confirms that (6, 0) SWCNT can be used as nanosensor, and using DFT investigations, it is possible to obtain much more data to apply in medical science and industrial technologies.

Keywords: *Adsorption energy; DFT; IR spectra; Sensing capability; SWCNT.*

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INTRODUCTION

Since the discovery of carbon nanotubes (CNTs) in 1991 [1], there great deal of attention due to their unique structural, electrical, thermal, optical, and mechanical properties[2, 3]. Numerous CNT-based devices, such asfieldeffect transistors, nonvolatile random access memories, sensors,fieldemission displays, and organic solar cells, have been developed [4, 5]. CNTs in two principal forms, single-walled carbon nanotubes (SWCNTs) and multi-walled (MWCNTs) [5, 6].

A SWCNTs are portentous material for potential components of future devices in many fields [2, 7]. Because of their small size, large surface area, and the this property of SWCNT, it can be used in various applications such as productive gas storage components and nanosensors [5]. A SWCNTs have been exponentially enquiry for the detection of gas molecules, so that the nanosensors devices based on SWCNTs have the ability to specify very weak physical exciters in nanoscale [8].

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In recent years, gas adsorption over outer surface of CNTs (such as CO and CO_2) was arguably a very interesting theoretical study [9-15]. CNTs nanosensors can detect many much gases, and the change in the electrical conductivity occurs after adsorption of molecules [16]. These sensors have fast response time and high sensitivity to special gas molecules which is very favorable for important applications.

There are many experiments studied, which explain the effect of gas adsorption on the geometrical, electronic and thermodynamic properties of SWCNTs. But these effects are not yet well understood due to the absence of a reliable theoretical model. The density functional theory (DFT) computations have been reported to be the high potential tool to study the previous properties [17-19].

In this work, the sensing capability of (6, 0) SWCNT system for adsorption H_2, N_2, O_2 and CO molecules are investigated. Based on

DFT calculations, the geometry, electronic, thermodynamic, and vibrational properties are studied and compared.

COMPUTATIONAL DETAILS

Here, adsorption behaviors of H_2, N_2, O_2 and CO molecules on the SWCNT surface are taken into consideration. It has been chosen (6,0) SWCNT system, which consist of from 36 carbon atoms with length and diameter (6 Å and 4.82 Å), respectively. Due to the absence of periodic boundary conditions in molecular calculations, it is necessary to saturate the carbon dangling bonds with 12 hydrogen atoms. All quantum calculations were carried out all-electron level using the Gaussian 98 suite of programs [20] and these calculations are based on the relations mentioned in the references [21-23]. It has been established that DFT is able to accurately treat such systems due to incorporation of the exchange-correlation effects [24, 25].

RESULTS AND DISCUSSIONS

In the following sections, the result will discuss the geometrical, electronic and thermodynamic properties of (6, 0) SWCNT with and without various molecules.

Molecular geometries and bond lengths

Before proceeding to the physical properties calculation, it is necessary to find out the geometry optimization of (6, 0) SWCNT and the gas molecules under study, as displayed in Fig. 1, for SWCNT-H_2 (see Fig. 1a), SWCNT-N_2 (see Fig. 1b), SWCNT-O_2 (see Fig. 1c), and SWCNT-CO (see Fig. 1d). The equilibrium geometries for all studied molecules were fully optimized at the DFT level of theory using a B3LYP functional together with the standard 6-31G basis set in gaseous phase.

Table 1 showed variations in bond length after H_2, N_2, O_2 and CO molecules adsorption on the SWCNT surface, where X_1 represents the first atom H_1, N_1, O_1 and C, while X_2 represents the second atom H_2, N_2, O_2 and O, respectively. The result can interpret that C-C bond length after adding the adsorption of H_2, N_2, O_2 and CO molecules to (6, 0) SWCNT, is due to the fact that these molecules are more electronegative than the carbon. This property, amid arrangement of C-H, C-N and C-O bond, cause halfway positive charge on both carbon particles and subsequently make electrostatic repugnance between this two carbon molecule which results in expanding C-C bond length.

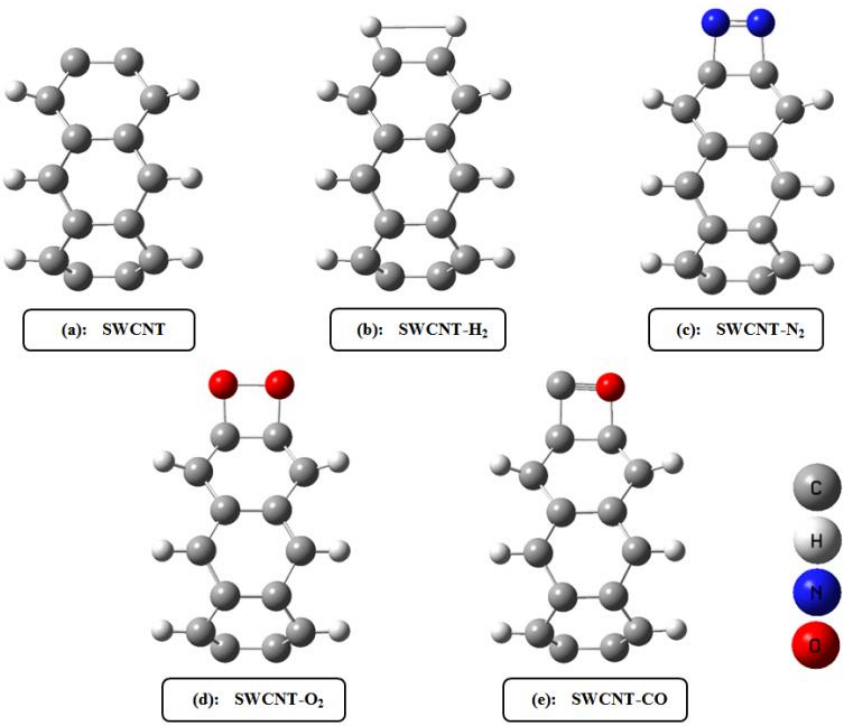

Fig. 1: Optimized molecular geometries of SWCNT with the adsorbed H_2 , N_2 , O_2 and CO molecules.

As shown in Table 1, the changes in length of the bonds are much small. This fact shows that the physical adsorption of H_2, N_2, O_2 and CO molecules over SWCNT surface is very difficult. It may be clear that sometimes there is no any adsorption which can lead to apparent changes of the length and the diameter of SWCNT.

Molecular electronic properties

From Table 2 and Fig. 2a it is clear that the total energy increases as the number of atoms increases which is due to adding H_2, N_2, O_2 and CO molecules. The difference between the total energy for SWCNT and SWCNT-X it caused due to emerges between non-bonding orbitals of SWCNT and H_2, N_2, O_2 and CO molecules. These results agree with the results of the molecular physics.

The highest occupied and the lowest unoccupied molecular orbital (HOMO and LUMO) for these structures were calculated by the DFT with B3LYP/6-31G. The energy of HOMO is often associated with the electron donating ability of the molecules, whereas the energy of LUMO is associated with the electron accepting ability of the molecules. Therefore, the high value of HOMO indicates a high tendency to donate electrons to appropriate acceptor molecule with low empty molecular orbital energy. Likewise, low value of LUMO indicates a high tendency to accept electrons from the metal surface. The results presented in Table 2 show that the SWCNT-CO has the higher energy of HOMO. The gap between the HOMO and LUMO energy levels of the molecules is another important descriptor that should be studied. Large values of the energy gap imply high electronic stability and then low reactivity, when low values imply that it will be easier to remove an electron from the HOMO orbital to LOMO which can be a good result in reactivity. The results in Table 2 show that adding adsorbed H_2, N_2, O_2 and CO molecules to SWCNT lead to increase the energy gap. The energy gap is a parameter relying on HOMO and LUMO. The presence of the adsorbed molecules modifies energy levels of SWCNT. Therefore, the conductivity and also the reactivity of SWCNT are reduced. This effect was the largest in SWCNT-O_2, it has the highest energy gap (2.657 eV) due to the oxygen element is oxidizing agent.

The electric dipole moment which represents a generalized measure of bond properties and charge densities in the molecules being studied are listed in Table 2. It is clear that the SWCNT-CO has a higher dipole moment (3.833 Debye), see Fig. 2b. This means the charge of distribution and

Table 1: The bond length (r in Å unit) of (6, 0) SWCNT with the adsorbed molecules H_2 , N_2 , O_2 and CO. Here X_1 represents the first atom (H_1, N_1, O_1 and C) and X_2 represent the second atom (H_2, N_2, O_2 and O), respectively.

Structure	r (X_1-C)	r (X_2-C)	r (C-C)
(6,0) SWCNT	-	-	1.4555
(6,0) SWCNT-H_2	1.0853	1.0853	1.5049
(6,0) SWCNT-N_2	1.5027	1.5067	1.4980
(6,0) SWCNT-O_2	1.4789	1.4789	1.4801
(6,0)SWCNT-CO	1.5307	1.4962	1.4906

Table 2: The electronic properties of (6, 0) SWCNT with the adsorbed H_2, N_2, O_2 and CO molecules.

Structure	Total Energy (a.u.)	Electronic States (a.u.)		Energy Gap (eV)	Dipole Moment (Debye)	Adsorption Energy (eV)
		HOMO	LUMO			
(6,0) SWCNT	-921.229	-0.141	-0.098	1.182	0.000	-
(6,0) SWCNT-H_2	-922.481	-0.158	-0.064	2.573	2.222	-2.095
(6,0) SWCNT-N_2	-1030.619	-0.175	-0.078	2.650	3.591	2.204
(6,0) SWCNT-O_2	-1071.525	-0.175	-0.077	2.657	3.335	-2.421
(6,0) SWCNT-CO	-1034.412	-0.176	-0.078	2.650	3.833	2.068

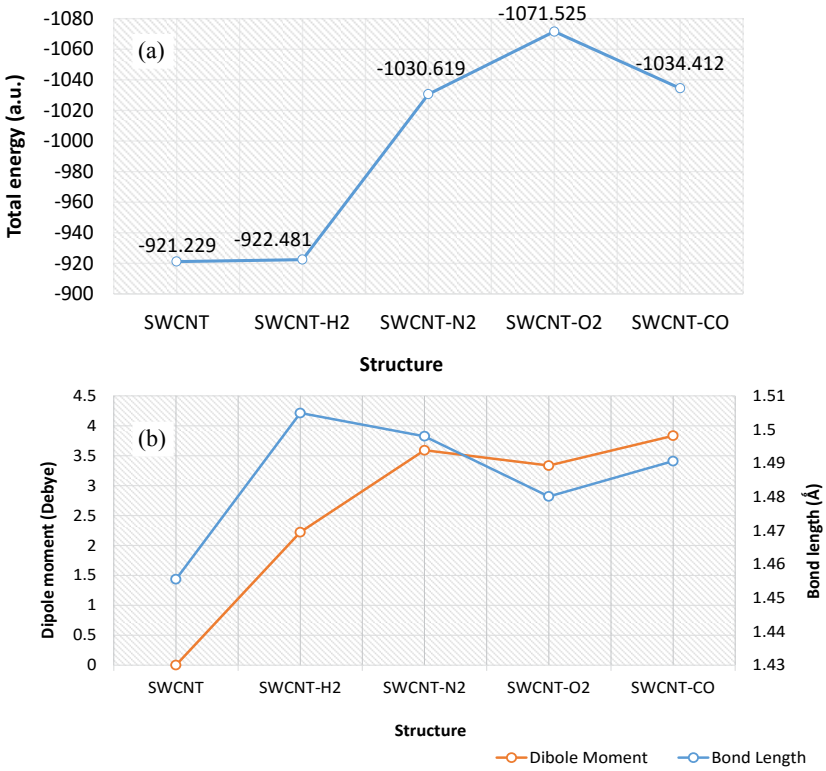

Fig. 2: a) The total energy, b) The dipole moment and the bond lengths of SWCNT with the adsorbed H_2, N_2, O_2 and CO molecules.

increasing of the average distance bonds is better.

The effects of adsorption of molecules on adsorption energies in the SWCNT are related to their electronic structure. When the molecules were adsorbed on the SWCNT, their interaction became very weak. Therefore, significant changes in the band gap were not observed. The result results appear that adsorption of H_2 and O_2 molecules on the SWCNT is more effective than N_2 and CO (as shown in Table 2). The difference in adsorption energy between these molecules caused interactions over the surface. The reducing characteristic of adsorbed molecules and the transmission of its non-binding pairs of electrons to neighbor carbon molecules over carbon rings on SWCNT surface, caused resistance rising and also an increase in SWCNT diameter. The result also can interpret this fact as follows: the big dipole moment depends to the big distance between electron clouds, then, as the distance becomes bigger the absolute value of adsorption energy will become higher.

Molecular thermodynamic properties

The thermochemistry properties such as the total zero point energy, the internal energy, the enthalpy change, and the Gibbs free energy change were calculated from the structure being studied and listed in Table 3. By adding these molecules on the (6, 0) SWCNT, the result observed that all thermochemistry functions are increasing due to increasing vibrational intensities as shown in Table 3.

Vibrational properties

In IR spectra, when the bonds of the same atoms vibrate in the same phase, the symmetric stretching happens, while the asymmetric stretching is happening when the bonds vibrate in different phases. The number of vibrational frequency modes was calculated by the relation, *3N-6* where *N* is the number of atoms in the structure [26].

Particularly, the vibration frequencies of C-H stretching in the region 2900-3100 cm^{-1} is for symmetric stretching and 3100-3250 cm^{-1} for asymmetric stretching, see Fig. 3a. While the vibration frequencies of C-H bending (680-860 cm^{-1} see Fig. 3b), C-O bending (1000-1300 cm^{-1} see Fig. 3c), C=C bending (1475-1700 cm^{-1} see Fig. 3d), and C≡N stretching (2220-2260 cm^{-1} see Fig. 3e). These calculations are having a good agreement with the experimental data [27, 28].

Table 3: The thermochemistry properties in kcal/mol unit of SWCNT with the adsorbed H_2, N_2, O_2 and CO molecules.

Structure	Total zero point energy	Internal energy	Enthalpy change	Gibbs free energy change
SWCNT	173.190	181.975	1.4555	149.345
SWCNT-H_2	190.535	198.614	1.5049	167.102
SWCNT-N_2	181.041	189.954	1.4980	156.766
SWCNT-O_2	179.842	188.949	1.4801	155.370
SWCNT-CO	180.292	189.283	1.4906	155.962

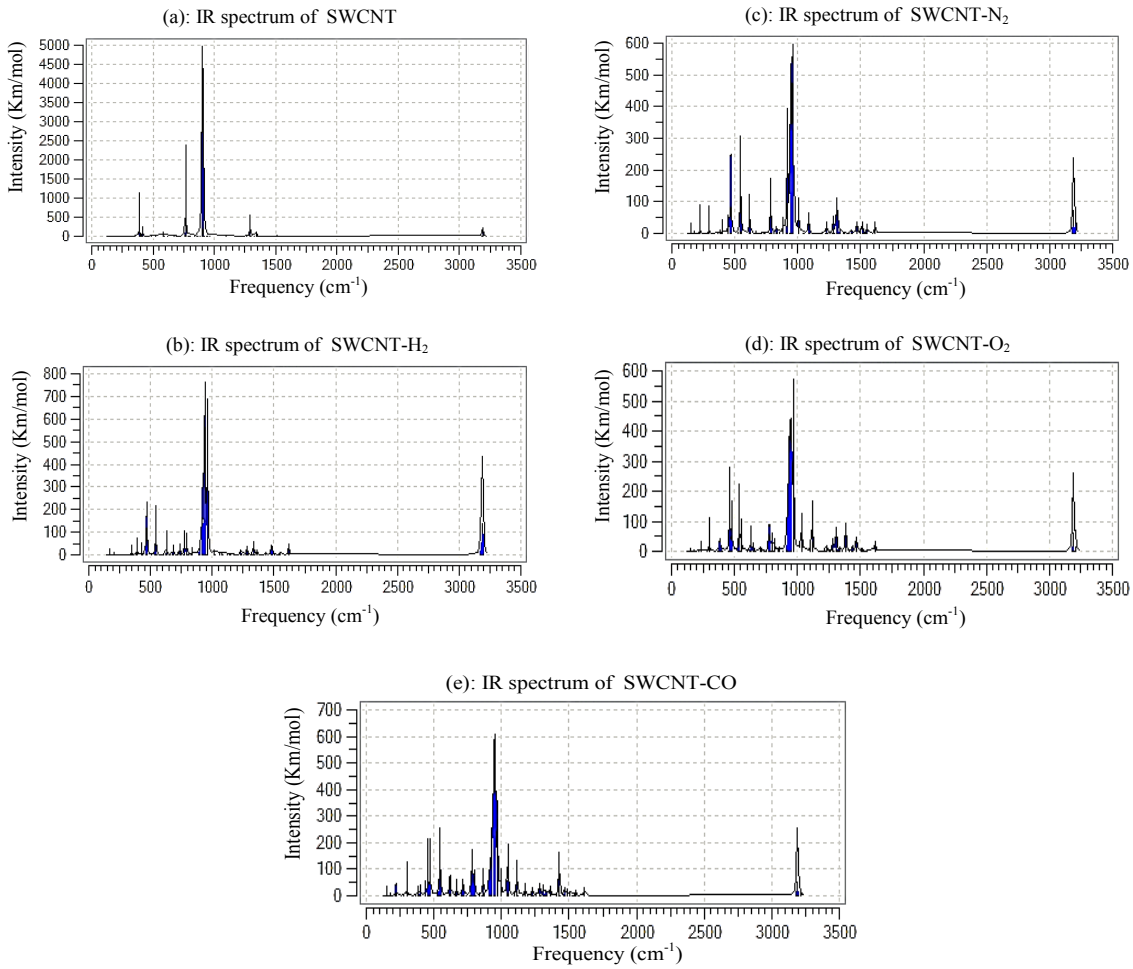

Fig. 3: The IR spectra of SWCNT with the adsorbed H_2, N_2, O_2 and CO molecules.

CONCLUSION

In summary, the sensing capability of (6,0) SWCNT system for adsorption H_2, N_2, O_2 and CO molecules is investigated. Based on DFT calculations, the following points are noteworthy: the geometry optimization of SWCNT has been found in a good agreement with experimental data. Adding H_2, N_2, O_2 and CO molecules to SWCNT causing an increase in the bond lengths, but this change are much small. These molecules also cause increase the total energy of SWCNT. The SWCNT-CO has a higher dipole moment. Adsorption energies in the SWCNT are related to their electronic structure. When the molecules were

adsorbed on the SWCNT, their interaction became very weak. Therefore, significant changes in the band gap were not observed. All thermochemistry functions of SWCNT are increased with adsorbed molecules. These molecules lead to an increase in the vibration modes and higher stretching vibration wave numbers of SWCNT. Finally, this study showed that (6, 0) SWCNT can be used as nanosensor for many applications.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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