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Investigation of Interaction Hydrogen Sulfide with (5,0) and (5,5) Single-Wall Carbon Nanotubes by DFT Method

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In the present study the interaction of Hydrogen Sulfide with inside and outside single-wall carbon nanotube of (5,0) and (5,5) was investigated. This study was conducted using DFT at B3LYP/6-31G* level of theory. Computational calculations were performed in the gaseous phase in Gaussian 09. The geometry of all molecules under investigation was determined by optimizing all geometrical variables without any symmetry constraints. The harmonic frequencies were computed from analytical derivatives for all species in order to define the minimum-energy structures. The adsorption energies, the thermodynamic properties, HOMO-LUMO energy gaps and partial charges of the interacting atoms were also studied during two rotation kinds of H_2S molecules vertical and horizontal to the main axes of nanotube.

Keywords: Hydrogen Sulfide (H_2S), Single-Wall Carbon Nanotube (SWCNT), Adsorption Energy, Density Functional Theory (DFT).

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1. INTRODUCTION

Conceptually, a single-walled carbon nanotube (SWCNT) can be formed by rolling a grapheme sheet (hexagonal structure) into cylinder and a multi-walled nanotube (MWCNT) is composed of concentric grapheme cylinders with an interlayer spacing of 0.34 nm. Nanotube properties are highly structure/size dependent and are influenced by atomic arrangement (chirality), nanotube diameter and length, and morphology, or nanostructure. Wei et al. [1] demonstrated that multi-walled carbon nanotubes have extraordinarily high current carrying capacity, sutaining current densities greater than 10^9 A/cm^2. These novel electrical properties have generated substantial interest in utilizing carbon nanotubes in nanoelectronics [2].

The main feature of individual S-SWCNT sensors, besides their small sized, is that they operate at the room temperature with sensitivity as high as 10^3. An individual nanotube sensor can be used to detect different types of molecules. The selectivity is achieved by adjusting the electrical gate to set the S-SWCNT Sample in an initial conducting or insulating state. The fast response of a nanotube sensor can be attributed to the full exposure of the nanotube surface area to chemical environments [3].

Adsorption energy of NO_2 strongly relies on the electronic structure of nanotubes, NO_2 is adsorbed more strongly on metallic tubes than on semiconducting tubes. The diameter dependence of the adsorption energetics and kinetics in the chiral nonotubes are another interesting issue [4].

The adsorption of O_2 at defect zigzag and armchair edge sites of the graphite has been studied by means of density functional theory coupled with cluster models. The calculated adsorption energy 0.26 kcal/mol for O_2 physisorbed on the clean basal surface is in good agreement with the experimental value, suggesting that one-layer simple cluster model is an effective way to investigate the adsorption of molecular oxygen on the graphite surface. The local detailed carbon atoms arrangement can play an important effect on O_2 adsorption on zigzag and armchair edge sites respectively [5].

Humidity-assisted desorption of SO_2 and NO_2 was investigated on carbon nanotubes [6]. Carbon nanotube sensors can detect many much gases; for example O_2 [7], NH_3 [3, 8], NO_2 [9, 10] and SO_2 [11] and the change in electrical conductivity occurs after adsorption of molecules. These sensors have fast response time and high sensitivity to special gas molecules which is very favorable for certain applications [7].

In the present study the interaction of Hydrogen Sulfide with inside and outside single-wall carbon nanotube of (5,0) and (5,5) was investigated.

2. COMPUTATIONAL DETAILS

We considered single-wall zigzag (5,0) and armchair (5,5) carbon nanotubes. The diameters of the nanotubes are 4, 6.85 Å, and the length of the nanotubes are 8.5, 9.8 Å, respectively, and the average bond length is 1.42 Å. The (5,0) SWCNT containing 50 carbon atoms with 10 hydrogen atoms, and the (5,5) SWCNT containing 100 carbon atoms with 20 hydrogen atoms were selected for this purpose. Hydrogen sulfide in the vicinity of internal and external walls of the nanotubes were placed, and these structures optimized by Gaussian 09 software.

DFT is used to study the structural and electric properties of the tube-molecule systems during adsorption of H_2S molecule on the SWCNTs. In the cases, the calculations are carried out with the B3LYP/6-31G* level of theory [12]. Figure 1 shows the optimal structures.

The parameters calculated in this study are the energy interaction of H_2S with inside and outside wall of SWCNT, E_{ads}, through the following formula:

$$E_{ads} = En_{anotube\text{-}H2S} - (En_{anotube} + E_{H2S}) \qquad (1)$$

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where $E_{nanotube\text{-}H2S}$ is the total energy of the optimized nanotube-H_2S system, $E_{nanotube}$ is the total energy of the optimized nanotube and E_{H2S} is the total energy of the isolated H_2S molecule. By this explanation, $E_{ads} < 0$ corresponds to exothermic adsorption, which leads to a stable structure.

$$\Delta G_{tot} = \Delta G(H_2S - SWCNT) - [\Delta G(SWCNT) + \Delta G(H_2S)] \quad (2)$$

The total energy, zero point, the total internal energy and total enthalpy, are calculated to the formula same.

3. RESULTS AND DISCUTION

3.1 Thermodynamic Parameters

The results of the gaussian output files, thermodynamic parameters related to the electronic structure of (5,0) and (5,5) nanotubes in the presence of H_2S molecule, in the vicinity of internal and external walls have been listed in Table 1.

Tabel 1 – Thermodynamic parameters, the total zero-point energy, total internal energy, total enthalpy, total gibbs free energy, in the adsorption process of H_2S molecule on the internal and external walls of (5,0) and (5,5) nanotubes calculated by B3LYP/6-31G*

optimized systems	total zero point energy kcal/ mol	ΔUtot kcal/ mol	ΔHtot kcal/ mol	ΔGtot kcal/ mol
internal of (5,0)-H2S	335.0850	376.6882	333.7045	347.0703
external of (5,0)-H2S	-1.0040	0.1883	-0.3765	4.8947
internal of (5,5)-H2S	32.8810	33.5712	32.9437	41.7915
external of (5,5)-H2S	-0.3765	0.8158	0.3138	4.5180

Total Gibbs free energy of H_2S-SWCNT system were calculated for inside of (5,0) SWCNT, outside of (5,0) SWCNT, inside of (5,5) SWCNT and outside of (5,5) SWCNT, and they are 347.0703, 4.8947, 41.7915 and 4.5180 kcal/mol, respectively. Gibbs free energy, H_2S adsorption process is not thermodynamic favorable.

Lowest total zero point energy, the total internal energy and enthalpy in the process of H_2S adsorption on the external wall of (5,0) nanotubes has been observed and the lowest total Gibbs free energy is achieved when the interaction of H_2S on the external wall of (5,5) nanotubes.

3.2 Optical Parameters

According to the results, in Table 2, adsorption of H2S molecule on the external wall of the nanotube is more effective than the internal wall, and adsorption of H2S on the external wall of the (5,0) nanotube is more effective than external wall of the (5,5) nanotube. The adsorption of H2S on the internal wall of the (5,5) nanotube is more effective than internal wall of the (5,0) nanotube.

The lowest of energy gap is achieved in the process of H_2S adsorption on the external wall of (5,5) nanotube. After the interaction of H_2S on the inner wall of (5,5) is increased energy gap and after the interaction of H_2S on (5,0) carbon nanotube and the external wall of (5,5) nanotube is reduced energy gap.

The lowest of HOMO and LUMO energies is obtained in the process of H_2S adsorption on the external wall of nanotubes (5,0).

3.3 H_2S Rotation on the Nanotubes

H_2S molecule rotation in both the horizontal and the vertical rotation relative to the nanotubes have been shown in Fig. 2. Adsorption energy effect of H_2S molecule on the internal and external of SWCNTs has been studied when rotation of in two directions, vertical and horizontal respect to the nanotube axes at different angles. The origin of rotation angles for both type rotations of H_2S on the internal wall of nanotubes and horizontal rotation of H_2S on the external wall of nanotubes are 90 degrees, and the origin of the rotation angles for vertical rotation of H_2S on the external wall of nanotubes, is 0 degrees.

3.4 Base Set Superposition Error

The basis set superposition errors (BSSE) were estimated for the counterpoise correction [13] and effects on the energy changes have been used during the rotation of H2S molecule inside and outside nanotubes.

3.5 NBO Calculation

Gases absorption often changes the electronic properties of nanotubes. The environmental sensitivity can be useful in the detection of gas and making of gas sensors. Therefore, NBO calculations for all the rotations in order to calculate the charge differenc before and after adsorption of H2S molecule on nanotubes has been performed. Partial charge differences on the interaction of atoms, the (5,0) and (5,5) nanotubes in the presence of H2S molecule in the vicinity of internal and external walls for rotation were calculated.

Tabel 2 – Parameters, adsorption energy (E_{ads}), Corrected E_{ads}, BSSE, HOMO and LUMO energies (in Hartree), gap energy (in ev), dipole moment (in Debye), in the adsorption process of H_2S molecule on the internal and external walls of (5,0) and (5,5) nanotubes calculated by B3LYP/6-31G*

optimized systems	E_{ads}	Corrected E_{ads}	BSSE	HOMO	LUMO	E_{gap}	Dipole Moment
internal of (5,0)- H_2S	0.5336	0.5436	0.0100	-0.1667	-0.1034	1.7218	0.8725
external of (5,0)- H_2S	-0.0027	-0.0027	0.0000	-0.1781	-0.1149	1.7212	1.7648
internal of (5,5)- H_2S	0.0502	0.0442	-0.0060	-0.1596	-0.0965	1.7109	0.4002
external of (5,5)- H_2S	-0.0024	-0.0036	-0.0012	-0.1610	-0.0985	1.6997	1.8597

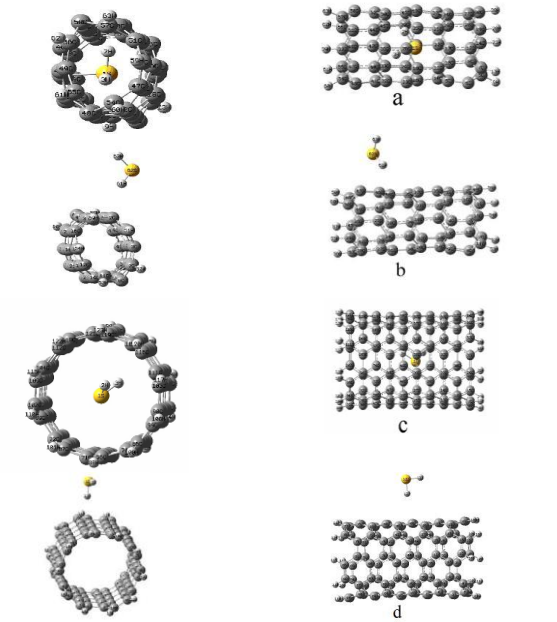

Fig. 1 – Molecular geometry and interaction between (5,0)SWCNT-SO2 (a, b) and (5,5)SWCNT-SO2 (c, d).

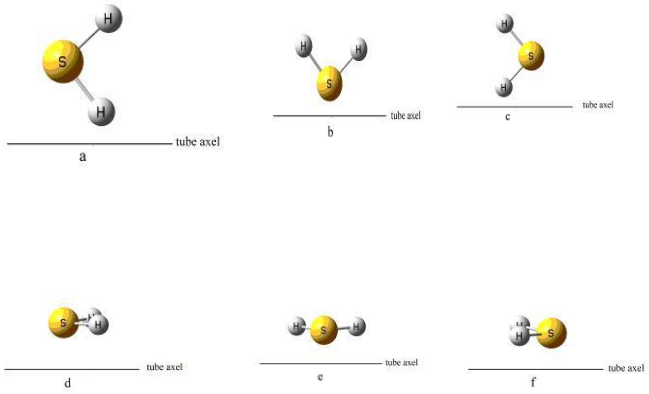

Fig. 2 – Vertical (a, b,c) and horizontal (d, e, f) rotations around the tube axle at 0o (a, d), 90o (b, e) and 180o (c, f) angles

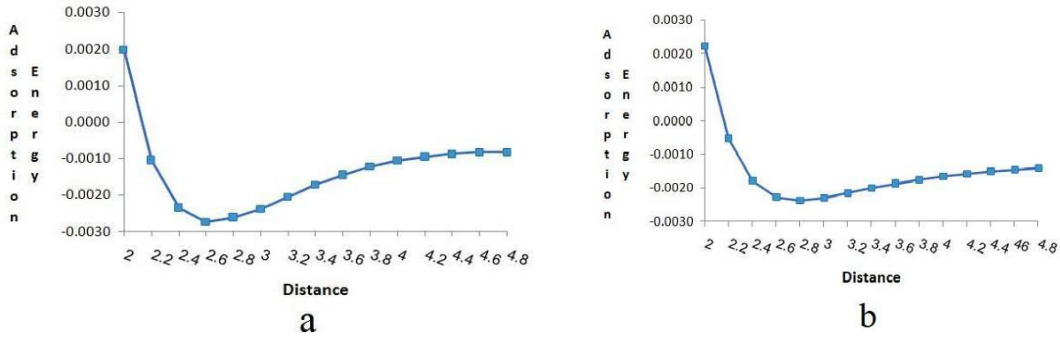

Fig. 3 – The effect H2S molecule distane on the adsorption energy from (5,0) SWCNT (a) and (5,5) SWCNT), by calculated B3LYP/6-31G*

4. CONCLUSION

H_2S molecule adsorption on the internal wall of (5,0) nanotube is chemical adsorption and absorption on the external wall of (5,0) nanotube and internal and external walls of (5,5) nanotube are the physical absorption.

Based on the calculations, the most adsorption situation of H_2S is at 90 degree parallel and vertical to main axes, and on the outside of SWCNTs is at 0 degree vertical to main axes and at 90 degree parallel to main axes. The most favorable adsorption distance between the molecule and external of (5,0) and (5,5) SWCNTs was 2.6 and 2.8 Å. H_2S molecule adsorption on the internal wall of (5,0) nanotube is chemical adsorption.

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