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A Theoretical Study on the Effect of Intercalating Sulfur Atom and Doping Boron Atom on the Adsorption of Hydrogen Molecule on (10,0) Single-Walled Carbon Nanotubes

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Adsorption of molecular hydrogen on single-walled carbon nanotube (SWCNT), sulfur-intercalated SWCNT (S-SWCNT), and boron-doped SWCNT (BSWCNT), have been studied by means of density functional theory (DFT). Two methods KMLYP and local density approximation (LDA) were used to calculate the binding energies. The most stable configuration of H_2 on the surface of pristine SWCNT was found to be on the top of a hexagonal at a distance of 3.54 Å in good agreement with the value of 3.44 Å reported by Han and Lee (Carbon, 2004, 42, 2169). KMLYP binding energies for the most stable configurations in cases of pristine SWCNT, S-SWCNT, and BSWCNT were found to be -2.2 kJ mol^{-1}, -3.5 kJ mol^{-1}, and -3.5 kJ mol^{-1}, respectively, while LDA binding energies were found to be -8.8 kJ mol^{-1}, -9.7 kJ mol^{-1}, and -4.1 kJ mol^{-1}, respectively. Increasing the polarizability of hydrogen molecule due to the presence of sulfur in sulfur intercalated SWCNT caused changes in the character of its bonding to sulfur atom and affected the binding energy. In H_2-BSWCNT system, stronger charge transfer caused stronger interaction between H_2 and BSWCNT to result a higher binding energy relative to the binding energy for H_2-SWCNT .

Keywords: Hydrogen adsorption, Binding energy, SWCNT, Boron-doped SWCNT, Sulfur-intercalated SWCNT

INTRODUCTION

The main goal of many researches in the area of energy is finding new hydrogen storage medium [1]. The major advantage of using hydrogen as a source of energy in fuel cells is because it is clean where its product is heat and H_2O. Therefore, development of a safe, effective, and cheap hydrogen storage and transportation technologies is extremely important for hydrogen/air fuel cells or hydrogen-driven combustion engines [2,1(d)]. Metal hydride system using Zr, Mg, Ti, and La alloys were tested for storage tanks but even though they have sufficient storage capacity, they are expensive and heavy for commercial production focused on mobile applications [2,1(b)]. Discovery of carbon nanotubes (CNTs) in 1991 by Iijima [3] has stimulated researches on preparation and determination of physical properties of the nanotubes. CNTs and other nanostructure carbon materials have attracted considerable interest in materials of energy storage due to their unique properties [4].

There has been a good deal of interest in the past several years in the possibility of storing hydrogen on single-walled carbon nanotubes (SWCNTs). The hope is that these novel carbon materials have such highly uniform pore sizes, high surface areas, and attractive surface potentials that hydrogen can be adsorbed at high enough density to reach the Department of Energy (DOE) targets for vehicular fuel cells [5,1(c)] and releases easily, which means the adsorption should be physically.

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Various studies on hydrogen storage of the carbon nanotubes and graphite nanofibers (GNFs) or carbon nanofibers (CNFs) have been reported [5]. Firlej et al. [1(d)] from a numerical simulation deduced a value of about 5 kJ mol^{-1} for the binding energy of molecular hydrogen on the carbon based materials. Volpe and Cleri [6] reported molecular hydrogen is physisorbed at graphite like surfaces at a distance of about 3 ± 0.3 Å with a binding energy in the range 1.9-7.7 kJ mol^{-1}. Carbon nanotubes can be doped with electron donors and acceptors with resulting charge transfer to the SWCNTs [7]. Simonyan et al. [1(a)] suggested that charging of SWCNTs can significantly improve adsorbent performance of nanotubes, because the electrostatic interactions between the hydrogen quadrupole and induced dipole with a charge tube may be as strong as dispersion interactions in an uncharged system.

Cabria et al. [8] have theoretically studied the physisoption biding energy of hydrogen molecule on the carbon nanotube (8,2) that has a quasi-metallic properties. They reported a value of 8.5 kJ mol^{-1} for binding energy by using Local Density Approximation method, while Rangel et al. [9] reported a value of 7.4 kJ mol^{-1} for binding energy of hydrogen adsorption on pristine SWCNT. Durgun et al. [10] have suggested values between 2.4 kJ mol^{-1} to 5.9 kJ mol^{-1} for the binding energy of hydrogen molecule on the surface of CNT.

Chen et al. [11] reported that doping alkali metals like lithium and potassium into carbon nanotubes structure increases the capacity of hydrogen adsorption by 14 to 20 weight percent between 298 K to 673 K. Many experimental works has been performed trying to investigate the hydrogen adsorption in single-walled nanotubes and to improve the storage capacity of the tubes by doping and intercalating the other elements [12]. Despite of some extensive efforts in this area, there are still some questions that have to be answered regarding the effect of the method of calculations and also effect of the kind of doped- and intercalated atoms into the SWCNTs [13].

Wang et al. [14] investigated the ability of boron-doped single-walled (8,0) carbon nanotube as a novel sensor to detect the presence of formaldehyde. They reported the high sensitivity of boron-doped SWCNT is attributed to the strongly chemical interaction between the electron-rich oxygen atom of formaldehyde and the electron-scarce boron atom of the doped SWCNT. Zhou et al. [15] have theoretically studied the effect of doping boron and nitrogen into the SWCNT on hydrogen adsorption by means of a plane-wave pseudopotential CASTEP code. They reported that molecular hydrogen adsorption energies in the B and N-doped SWCNT in all configurations are much smaller than those in the pristine SWCNT. Their results are in contrast with the reported results by Sankaran and Viswanathan [16]. They reported that presence of heteroatoms in the SWCNT activate hydrogen molecule and leads to adsorption of hydrogen on the carbon sites in nanotube. They studied the chemisorption of hydrogen on the surface of SWCNT. Durgun et al. [10] reported a value of 2.4 kJ mol^{-1} for the binding energy (E_b) of hydrogen molecule on the surface of boron doped SWCNT and a value of 5.9 kJ mol^{-1} using local density approximation (LDA). They concluded that B substitution does not enhance H_2-SWCNT interaction. Zhao et al. [17] calculated E_b=-2.9 kJ mol^{-1} for B substituted fullerene (C_{36}) and obtained bonding state with E_b=37.6 kJ mol^{-1} using LDA.

Guo et al. [18] have studied the binding energy of SH_2 on the surface of CNT and reported a value of 46.8 kJ mol^{-1} for the binding energy and conclude the adsorption is still physisorption.

The objective of the present study was the investigation of the effect of doping boron or intercalating sulfur atom on the SWCNT on the binding energy of molecular hydrogen physisorption on these systems. To the best of our knowledge, no theoretical or experimental study is reported on the adsorption of molecular hydrogen on the surface of sulfur-intercalated SWCNT to date. Also we were interested to study how much binding energies are dependent on the calculation methods.

Computational Methods

Geometries of the stationary points are optimized by means of Gaussian03 program [19]. The semi-empirical method, AM1 [20], was used to find the initial optimized geometries. Two different theoretical methods were used to calculate the binding energy of hydrogen molecule on the surface of nanotube. The first method was DFT method of KMLYP method [21] which uses a combination of the HF exchange functional and the Slater exchange functional [22].

The correlation is a combination of the LYP [23] functional and the 1980 correlation functional of Vosko, Wilk, and Nusair (VWN) [24]. The second method to calculate the binding energy was the DFT calculations using the local spin density approximation (LDA) [25]. The NBO calculations have been performed to study the qualification of possible charge transfers. In this article, the reported charge transfers are the net transferred charges.

DFT methods like LDA and generalized gradient approximation (GGA) result in symmetrical densities for many systems that should not be symmetrical. However, the hybrid functional of KMLYP include HF exchange and can describe the asymmetry properly [26]. This problem is even less of a concern for KMLYP than for B3LYP since the new method includes a relatively large amount of HF exchange.

Although, the binding energies for the systems being investigated in this article are assumed to be small and causing the basis set superposition error (BSSE) to be important, we were not able to do the BSSE calculations for such large systems by our computational facilities.

RESULTS AND DISCUSSION

Adsorption of H_2 on SWCNT

The geometry of optimized (10,0) SWCNT consisting of 80 carbon atom and 20 ending hydrogen atom $C_{80}H_{20}$ is shown in Figure 1. Hydrogen atoms were put at both ends of the tube to saturate the dangling bonds. Several relative position of the hydrogen molecule approaching to the exterior wall of SWCNT is examined to find the best position. To investigate the interaction of hydrogen molecule with the exterior wall of the SWCNT, three configurations were selected, Figure 2. H_2 molecular axis is perpendicular to the nanotube wall and the molecule is on the top of a carbon atom, case A in Figure 2. H_2 molecular axis is perpendicular to the nanotube wall and the molecule is on the top of the center of a hexagon, case B in Figure 2. H_2 molecular axis is parallel to the nanotube wall and the molecule is on the top of the center of a hexagon, case C in Figure 2. For all these configurations a geometry optimization was carried out and binding energy (E_b) was calculated by means of equation (1).

$$E_b = E_{CNT-Molecule} - E_{CNT} - E_{Molecule} \quad (1)$$

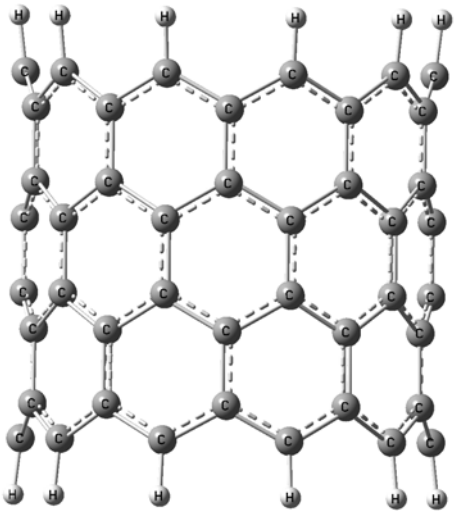


Fig. 1. Optimized structure of single-walled carbon nanotube [$C_{80}H_{20}$].

where $E_{CNT\text{-}Molecule}$ is the energy of hydrogen molecule adsorbed on nanotube, E_{CNT} and $E_{Molecule}$ are the energies of CNT and molecule, respectively. Our calculations indicated that the most stable position of hydrogen molecule is the configuration shown in Figure 2 as case B, that the hydrogen atom is on the top of a hexagon in SWCNT in accordance with the reported results by Han and Lee [27] and the axis of H_2 molecule is 44^o relative to the axis perpendicular to the surface of nanotube. The configuration that is shown in Figure 3 (that is case B after geometry optimization) is the most stable form of H_2 on SWCNT. As shown in Table 1, the distance of hydrogen molecule from the SWCNT was found to be 3.5 Å and its binding energy was calculated to be -2.2 kJ mol^{-1}. According to LDA calculations E_b was found to be 8.8 kJ mol^{-1}. Table 1 compares our results with the reported data in the literature. The charge transfer analysis from NBO calculations on H_2-SWCNT system indicated that only 0.002|e| charge is transferred from the nanotube into the hydrogen molecule orbitals. According to our calculations, no charge is transferred from hydrogen molecule towards CNT. The calculated low binding energy -2.2 kJ mol^{-1} indicates a weak van der Waals interaction between hydrogen and SWCNT.

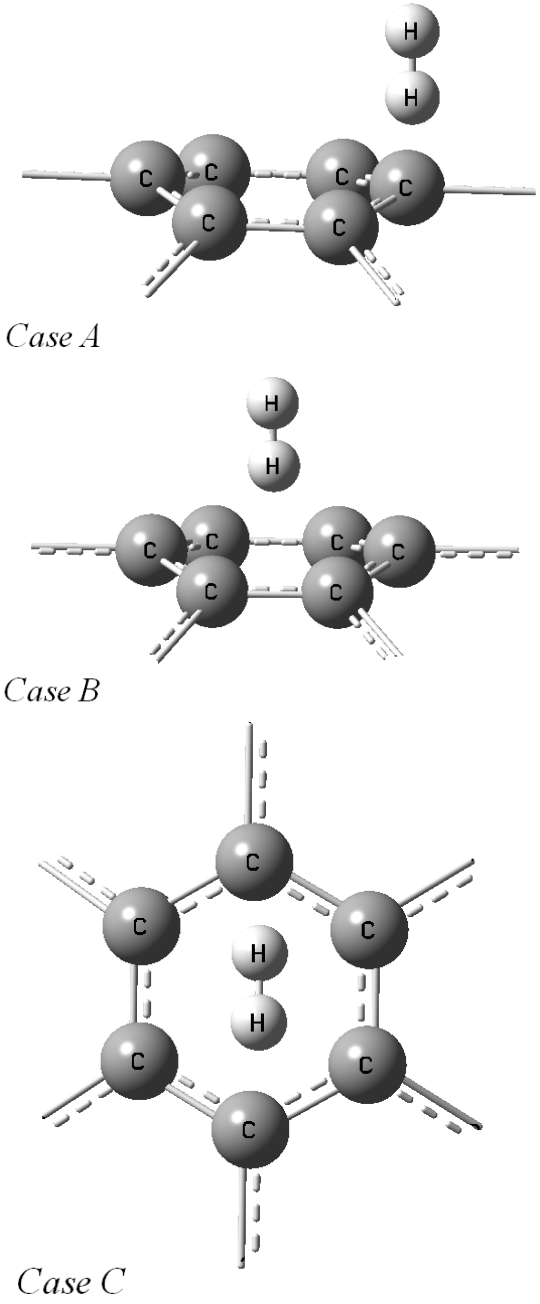


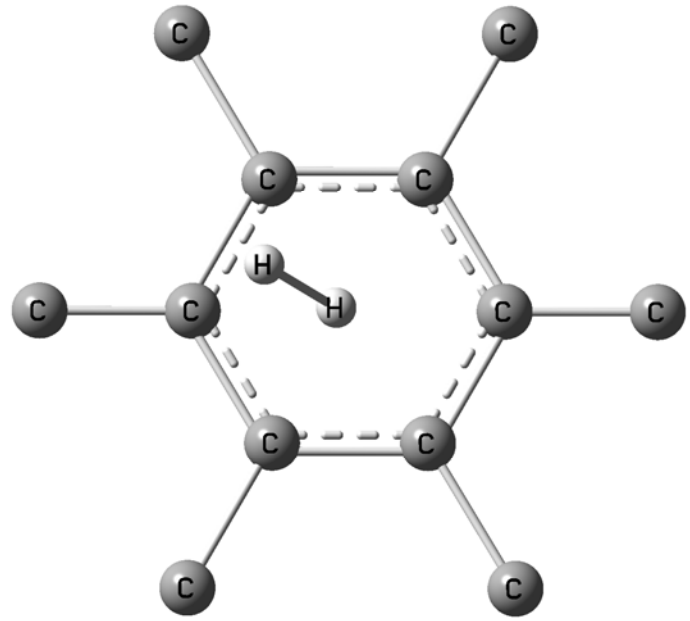
Fig. 2. Atomistic configurations of H_2 physisorption with the H_2 axis perpendicular to the (10,0) SWCNT wall, above a carbon atom (A), above a hexagon (B), and the H_2 axis parallel to the (10,0) SWCNT wall above a hexagon surface (C).

Wang et al. [14] are believe that LDA calculations can accurately describe the properties of SWCNTs and their interactions with gaseous molecules, which means value of -8.8 kJ mol^{-1} from our LDA calculation for E_b should be more reliable. Unfortunately, no experimental value is reported for E_b to date.

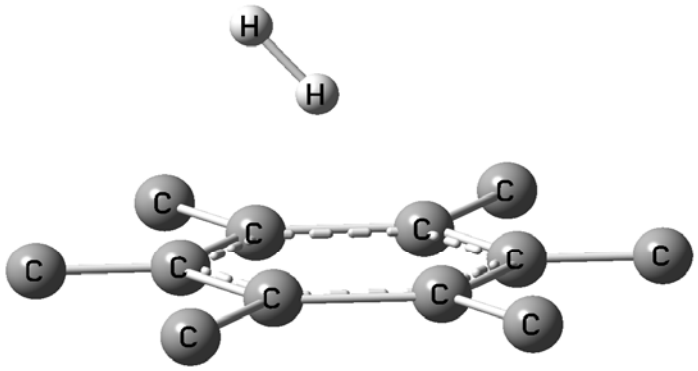
Sulfur-Intercalated SWCNT

To study the effect of presence of the other elements on the surface of CNTs or doping of them into the CNTs some efforts have been made by different groups. We were interested to study the effect of presence of sulfur atom on the surface of nanotube. Sulfur is one of the materials that exist as H_2S contaminant in natural oil and gas, which is relatively cheap and could be used as intercalated element on the surface of carbon nanotube to increase the binding energy of molecular hydrogen with the surface of SWCNTs. Various positions of sulfur atom on the exterior wall of the SWCNT were examined to find the most favorable site as shown in Figure 4, in which sulfur is placed on the top of a carbon atom, case D, on the top of the middle of a C-C bond, case E, and on the top of the center of a hexagon, case F.

The potential energy surfaces for these three cases D, E and F were scanned and plotted in Figure 5, which shows the best position should be case D. Unfortunately, we were not able to find the best position by optimization processes because the system was heavy. Our calculations indicated the best position of sulfur was at a distance of 2.13 Å on the top of carbon atom in SWCNT, Case D in Figure 4, that is due to maximum overlap between the orbitals of sulfur and carbon atom in this case. The binding energy (E_b) for sulfur atom on the surface of SWCNT was found to bo -124.0 kJ mol^{-1} as listed in Table 1. Natural Bond Orbital (NBO) analysis showed that there is a strong interaction between p orbitals of sulfur and carbon atom. The NBO calculations indicated the charge transfer occurs in both sides, from carbon and carbon-carbon bonds to sulfur orbitals and vice versa. But sulfur was found to be more electron acceptor and the net charge transfer is about -0.21|e| towards sulfur atom. This kind of interaction was the reason for such a high binding energy of -124.0 kJ mol^{-1} and so sulfur undergoes almost chemisorption process on the surface of the exterior wall of the SWCNT.



(a)



(b)

Fig. 3. Configuration of optimized structure of adsorbed H_2 on the surface of SWCNT, (a) top view (b) side view.

Table 1. Binding Energy (kJ mol^{-1}) and Distance (Å) of Hydrogen Molecule from the Surface of SWCNT for Different Cases.

	Our results		From literature
	E_b (kJ mol^{-1})	Distance (Å)	E_b (kJ mol^{-1}) / Distance (Å)
Pristine SWCNT			
Case A	-1.9	3.09	-8.5[d]
Case B	-2.2, (-8.8)[a]	3.54	[-3.3 / 3.44][b], [-3.7 / 3.27][e], -9.7[d], [25.4 / 6.105][d], 7.4[f]
Case C	-1.1	3.12	-9.0[d]
S intercalated SWCNT			
S-SWCNT	-124.0	2.13	
H_2-S-SWCNT	-3.5, (-9.7)[a]	3.00	
B doped SWCNT			
Case G	-2.7	3.11	-3.6[d]
Case H	-3.5, (-4.1)[a]	2.90	
Case I	-2.5	2.81	-0.7[d]
Case J	-2.3	2.90	-1.2[d]

[a] numbers in parenthesis are from our LDA results, [b] data from ref. 26, [c] data from ref. 1(e), [d] LDA results from ref. 15, [e] from ref. 4(c), [f] from ref. 9.

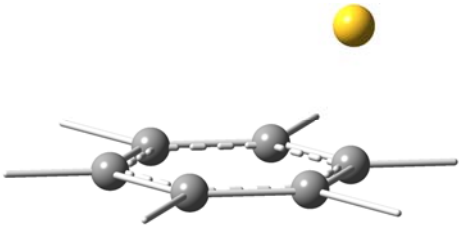
Adsorption of H_2 on Sulfur-Intercalated SWCNT

Geometry optimization was performed to study the effect of intercalating sulfur atom on the adsorption of hydrogen molecule on the surface of SWCNT. To determine the most favorable configuration and binding energy (E_b) of H_2 molecule on the S-SWCNT different position for hydrogen molecule were selected as initial gauss. The distance and orientation of hydrogen molecule relative to the S-SWCNT were optimized while the structure of S-SWCNT was set to be fixed.

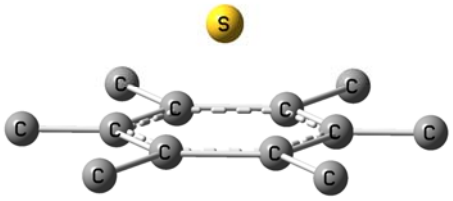
The optimized position of hydrogen molecule on S-SWCNT is shown in Figure 6. Hydrogen molecule is placed on the top of center of a hexagon on the surface of SWCNT and its distance was found to be 3.0 Å from the surface, and also the distance of hydrogen from the sulfur was found to be 3.1 Å. Intercalating sulfur atom on the surface of SWCNT causes the hydrogen molecules aggregate around the sulfur atom on the surface of nanotube. The binding energy of hydrogen adsorbed on the sulfur-intercalated SWCNT was found to be -3.5 kJ mol^{-1} at the KMLYP level, a higher value than what calculated for H_2-SWCNT system. LDA calculations gave a value of -9.7 kJ mol^{-1} for the binding energy of H_2 on the surface of S-SWCNT. On the basis NBO population analysis, charged sulfur caused polarization in hydrogen molecule that didn't exist in H_2 adsorbed on SWCNT, where affected the character of bonding on S-SWCNT, resulting in stronger interaction, and increased binding energy. NBO results, indicated charge transferring occurs from carbon orbitals and carbon-carbon bonding orbitals towards sulfur atom orbitals and vice versa. There was also charge transfer from sulfur atom towards hydrogen molecule orbitals, but no charge transfer was found from hydrogen molecule towards sulfur atom. Our calculations indicated the net transferred charge on sulfur atom and hydrogen molecule was found to be -0.22|e| and -0.003|e|, respectively. The results of our calculations on the binding energies are listed in Table 1.

Structure of Boron-doped SWCNT

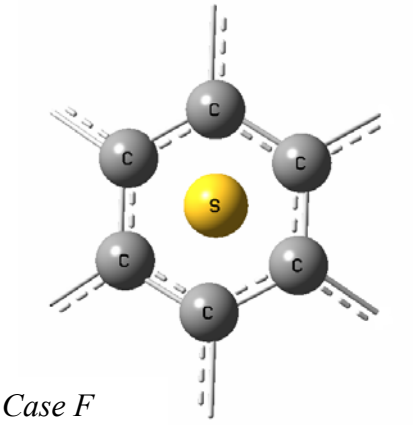
In the present study, we were also interested to study the effect of doping boron atoms into the structure of carbon nanotube to study the effect of calculation method on the binding energy. To study the effect of doping other elements in to the carbon nanotubes structure, different attempts have been made by researches to date. As discussed in the Introduction Section, some researchers reported doping of



Case D



Case E



Case F

Fig. 4. Atomistic configurations of intercalated sulfur atom above a carbon atom (D), above a C-C bond (E), and above a hexagon (F) on the (10,0) SWCNT.

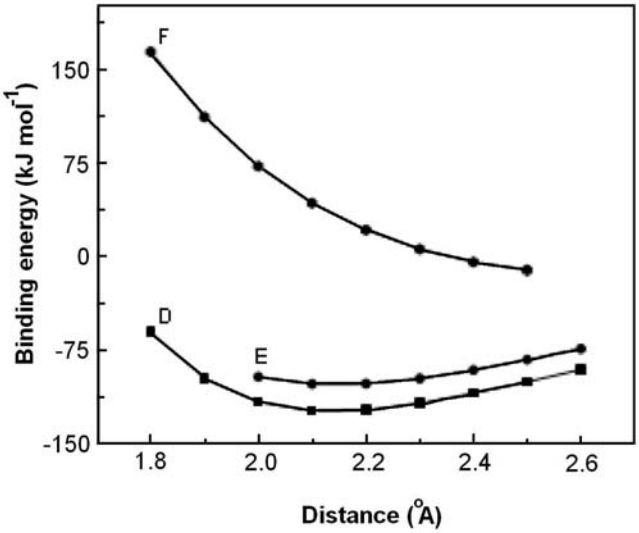


Fig. 5. Potential energy surfaces for different configurations of sulfur (cases D, E and F) at the exterior wall of the SWCNT.

boron increases the binding energy of H_2, which is in contradiction of the other reports in the literature. A structure of 20 boron atoms doped in 60 carbon atom nanotube was selected for our Boron-doped SWCNT (BSWCNT) system. In most of previous studies, only one or two boron atom is doped into the CNTs. The NBO calculations indicated the net charge transfer from boron atoms towards carbon atoms in BSWCNT system. In the following section the geometry and binding energy of hydrogen molecule on the surface of $C_{60}B_{20}H_{10}$ nanotube is reported.

Adsorption of H_2 on $C_{60}B_{20}H_{10}$

To investigate the structure and binding energy of hydrogen molecule adsorbed on the BSWCNT, several configurations for different orientations of H_2 molecule on the external wall of BSWCNT were selected initially. As shown in Figure 7, in configuration G, the H_2 molecular axis is perpendicular to the nanotube wall and the hydrogen molecule is on the top of a boron atom. In configuration H, the H_2 molecular axis is perpendicular to the nanotube wall and the molecule is on the top of a carbon atom. In configuration I, the H_2 molecular axis is perpendicular to the nanotube wall and the molecule is on the top of the center of a hexagon. In

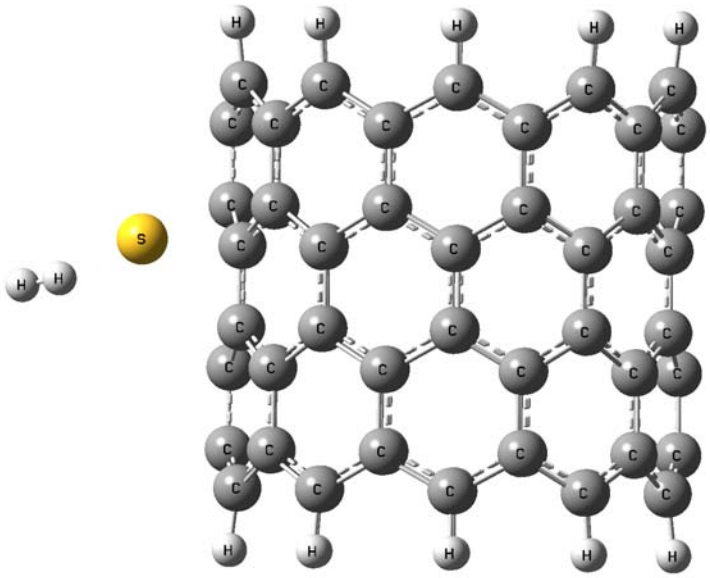


Fig. 6. Optimized configuration of adsorbed hydrogen molecule on the sulfur-intercalated SWCNT.

configuration J, where H_2 molecular axis is parallel to the nanotube wall and the molecule is on the top of the center of a hexagon.

Geometry optimizations were performed to find the best geometry and its binding energies. The most stable configuration of the H_2 molecule on the surface of BSWCNT was found to be case H in Figure 7, at which hydrogen axis is perpendicular to the nanotube wall and H_2 molecule is placed on the top of a carbon atom. The optimized structure of H_2-BSWCNT is shown in Figure 8. The distance of H_2 and its binding energy was found to be 2.9 Å and -3.5 kJ mol^{-1}, respectively, Table 1. LDA calculations gave a value of -4.1 kJ mol^{-1} for the binding energy of H_2 on the surface of BSWCN.

Our NBO population analysis showed that boron doped SWCNT system transfers 0.003|e| charge on the hydrogen molecule, which means stronger interaction between H_2 and BSWCNT relative to H_2-SWCNT, so binding energy in H_2-BSWCNT system is higher than that calculated for H_2 adsorption on the surface of pristine SWCNT at the KMLYP level, the same as what was observed for H_2-sulfur intercalated SWCNT system.

Therefore, our results showed that intercalating of sulfur or doping of boron changes the electronic properties of SWCNT and increase the binding energy of adsorbed hydrogen molecule on the surface of SWCNT. But LDA results gave a different scheme for the binding energy. According to LDA calculations the binding energy in H_2-BSWCNT is less than that for H_2-SWCNT.

CONCLUSION

Effect of intercalating of sulfur atom on the external surface of SWCNT and doping boron atom in the structure of SWCNT on the binding energy of molecular hydrogen are investigated. The binding energy of hydrogen molecule to the surface of (10,0) SWCNT was found to be in the range of the reported values in the literature (see Table 1). To use of SWCNT as storage medium for molecular hydrogen two main properties should be considered, high capacity of the medium and physically adsorption of hydrogen molecule. Pristine CNT may not be used as a hydrogen storage medium as long as hydrogen is physisorbed on the exterior walls of the CNT because of the very low binding energy as suggested in the

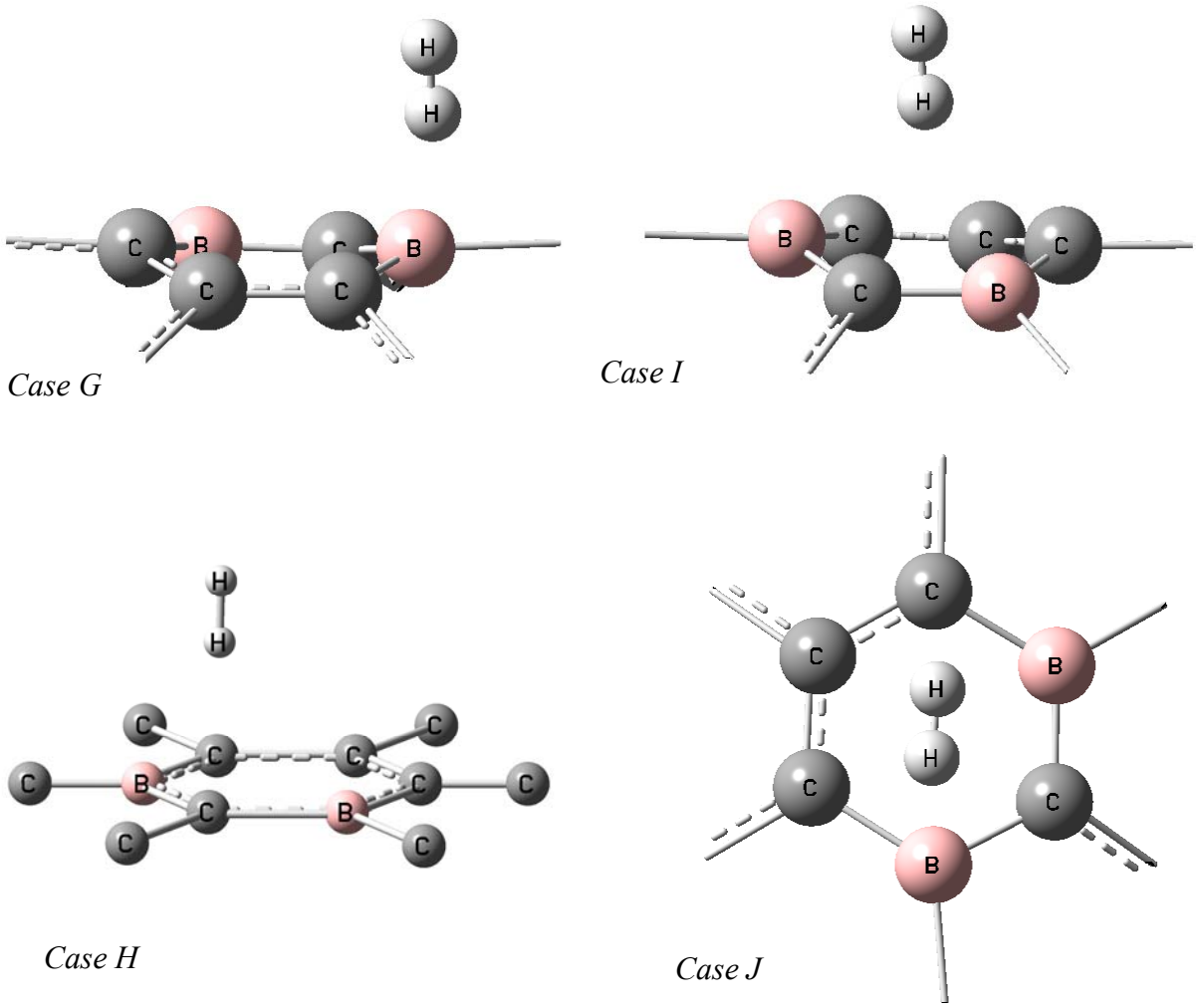


Fig. 7. Atomistic configurations of H_2 physisorption with the H_2 axis perpendicular to the SWCNT wall, above a boron atom (G), above a carbon atom (H), above a hexagon (I), and H_2 axis parallel to the SWCNT wall above a hexagon (J).

literature. There are two possible way to increase the binding energy of hydrogen into the surface of CNT, chemisorptions of hydrogen atom on the surface of CNT or doping the other elements into the structure of CNT or intercalating of some elements on the surface of CNT. Dissociation energy of hydrogen molecule is very high (about 440 kJ mol^{-1}) that means it is not a suitable method for hydrogen storage on the CNT. Therefore, the other two methods seem more feasible if we could find the right choice. Our results indicated the presence of intercalated sulfur on the external surface of SWCNT causes an increase in partial polarization of incoming hydrogen molecule that increases a stronger interaction between hydrogen molecule and SWCNT. The same effect observed for doping boron atom into the structure of CNT. But the binding energies in both cases are still so weak to be used as hydrogen storage media. Increasing the number of sulfur

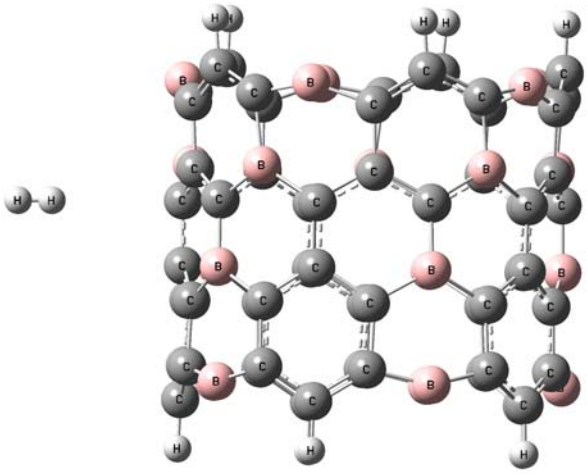


Fig. 8. Optimized configuration of adsorbed H_2 in B-doped SWCNT.

atoms might increase the binding energy of H_2 that should be investigated. Our study indicated that CNT is a god absorbent for sulfur atoms.

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