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A Theoretical Study of H_2S and CO_2 Interaction with the Single-Walled Nitrogen Doped Carbon Nanotubes

Mohsen Oftadeh[1], **Morteza Rezaeisadat**[2*], **Alimorad Rashidi**[3]

[1] *Ph.D., Chemistry Department, Payame Noor University, Tehran 19395-4697, I. R. of Iran*
[2] *M.Sc., Chemistry Department, Payame Noor University, Tehran 19395-4697, I. R. of Iran*
[3] *Ph.D., Nanotechnology Group, Research Center of Tehran Oil Technique, Tehran, Iran*

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ABSTRACT

The physical adsorption of hydrogen sulfide and carbon dioxide gases on the zigzag (5,0) carbon nanotubes doped with nitrogen was investigated through the application of B3LYP/6-31G* at the level of theory on Gaussian 03 software. A variety of stable and high abundance structures of nitrogen doped carbon nanotubes were considered in order to study the interaction between the mentioned gases in different situations by taking rotates of sour gas molecules in the inner and outer walls. Features such as correction of energy adsorption, energy gap, dipole moment, charge distribution, conductors and energy barrier as well as the main parameters such as the gas adsorption energy on the nanotubes were obtained. The results suggest that the nitrogen atom in the structure of carbon nanotubes causes to increase the adsorption of hydrogen sulfide and carbon dioxide gases. Adsorption of hydrogen sulfide on the nanotubes is more effective than carbon dioxide. Moreover, for both gases the adsorption processes are thermodynamically favorable. These nanotubes can be economically used to separate sour gases from natural gases and to recover the sulfur.

Keyword: Density functional theory; Energy adsorption; Single wall carbon nanotube doped with nitrogen; Hydrogen sulfide; Carbon dioxide.

1. INTRODUCTION

Today nanotechnology is a matter of concern for all people around the world. Great and unique specifications of these modern and new structures lead to a significant revolution in the industrial world [1]. One of the most commonly used structures, which is of a great importance in nanotechnology, is carbon nanotubes (CNT). Significant specifications of CNT are available from different sources [2]. These characteristics include thermal, chemical and structural properties [3-4]. Nanotube structures can be divided into three main groups namely, zigzag, armchair and chiral structures [5]. Because of its different structures and various applications, CNT is being increasingly applied in different industries and sciences [6-7]. One the most

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(*) Corresponding Author - e-mail: mory_rezaie@yahoo.com

important industries which has been paying so much attention to the applications of CNT are oil refinement and process industry. These structures are so noteworthy due to having high values of length to diameter ratios, low density, homologous porosity and relative high structural stability in adsorption and storage of gases [8-11]. Crude natural gas which is generally extracted from gas wells and crude oil wells consist large amounts of methane, ethane, propane, butane and small amounts of heavier hydrocarbons. In addition to the above mentioned compounds, some other impurities such as carbon dioxide and hydrogen sulfide are present in the natural gas [12]. Among these impurities, carbon dioxide and hydrogen sulfide are of a great importance. These are named acidic gases because they react with water and result in acidic compounds. Existence of the acidic gases in the gas pipeline will result in the corrosion and erosion of pipelines [13]. H_2S is one of the most harmful environmental pollutants. The crude natural gases are named sour gases due to having sulfur compounds specially H_2S [14-15]. The above mentioned issues show the significance of separating CO_2 from H_2S. The process in which CO_2 and H_2S impurities are separated from the crude natural gas is called sweetening of sour gas. The most common used methods of sweetening are amine and Klaus methods [16].

Common theoretical methods consist of process simulations, and have relatively lower costs in comparison to the experimental methods. Because nitrogenized compounds have a long history in the adsorption and sweetening of sour gases, the present study sought to analyze and study different structures of single wall nitrogen doped carbon nanotubes (NCNT) in terms of stability, synthesis feasibility and their abundances [17-21]. Having selected the proper structure, the interactions between H_2S and CO_2 gases adjacent to NCNT and the pathway of adsorption on the nanotubes were studied. Finally a comparison was done between the adsorption of acidic gases on NCNT and CNT [22].

2. COMPUTATIONAL METHOD

Due to the large number of constituent atoms, quantum calculations in nanotube structures could be time-consuming; therefore, in this research, qualitative surveys were considered in order to accelerate these calculations, an average base set is used in this study. Accordingly, B3LYP/6-31G* was used in order to optimize the structures, stability of wave function, frequency, Energy correction to the basis set superposition error (BSSE) and thermochemistry of calculations, for the purpose of these calculations, Gaussian 03 software for Linux operating system and a quad-core CPU equipped PC were used [23].

In this article, nitrogen-doped single wall zigzag nanotubes (5,0) were applied to the studies and analyses. The structure is drawn by HyperChem software. In order to prevent the effect of open end of single wall carbon nanotubes, both ends of the nanotubes were saturated by hydrogen atoms, to prevent any errors in complete optimization and frequency calculations [24]. Major calculations are about optimization of various CNT structures and the CNT adjacent to H_2S and CO_2 gases which lead to interactional energy calculations for adsorption. Adsorption energy calculations for each site, is defined as follows:

$$E_{ads} = E_{(gas-nanotube)} - E_{gas} - E_{nanotube} \tag{1}$$

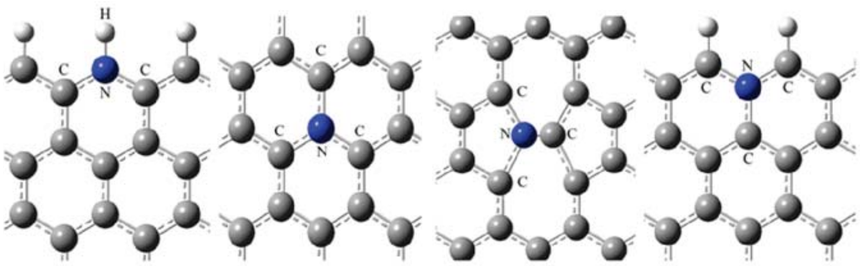
From among the calculations, electrical conductivity calculation can be mentioned. Energy gap can be a criteria and indicator of electrical conductivity, which is defined as:

$$\Delta E = E_{LUMO} - E_{HOMO} \tag{2}$$

A less energy gap leads to a more electrical property. The value of enthalpy changes in the physical surface adsorption is commonly in the range of -1 to -10 kcal/mol which is similar to the value of gas liquidity [25]. This quantity is defined as:

$$\Delta H^{\circ}_{298} = \sum_{Prod} \Delta H^{\circ}_{f} = \sum_{Reac} \Delta H^{\circ}_{f} \tag{3}$$

In summary, the structures of NCNT, formed by the substitution of one nitrogen atom with one of the carbon atoms in CNT, was analyzed. Then the interaction between acidic gases and NCNT was studied through selection of a proper structure.



(a) (b) (c) (d)

Figure 1: *a) (Structure 1): nitrogen is located in up-edge position; b) (Structure 2): nitrogen is substituted between carbon atoms inside the nanotube; c) (Structure 3): Stone-Wall (5-7-7-5) deficit [28]; d) (Structure 4): nitrogen is located in down-edge.*

3. RESULTS AND DISCUSSION

3.1. Evaluation of different structures for NCNT

With regard to different positions of carbon atoms on nanotube and also energy of nitrogen ions in substitution, six different structures were obtained for NCNT [26]. Among these structures, four main structures have been considered. These four structures are shown in Figure 1 for NCNT [27].

Structural optimization calculations are made for all the structures 1-4 in Figure 1. Then, the changed and transformed properties such as Energies of Structures were analyzed and evaluated. Table 1 presents a summary of some electron properties such as total energy, relative energy, energy gaps and dipoles moment for NCNT and their differences with CNT. Nitrogen is more electronegative than carbon (about 0.5), and because of this fact, some changes are found in bond length and bond angles in NCNT, and its structure is going to be changed from the initial structure. These changed and transformed structures, due to adding Nitrogen atom, are called Bamboo like structures, which are apparent especially in the structures of NCNT [27]. According to the definition of energy content, the lower the level of energy for a structure, the more stable is that structure, and it is considered as the main and optimum structure. According to Table 1, structure 1 has the lowest energy content, so it is the most stable structure. The highest level of energy and therefore the most unstable structure belongs to structure 3. In order to find the desired structure with the highest level of stability and synthesis feasibility, more detailed calculations are required. One of the most important and useful calculations in this field is the frequency and thermochemistry calculation. After calculation, there was no imaginary frequency, so these structures do not belong to transition states, and all of the structures are stable and feasible. In Table 2, a summary of results obtained from frequency calculations is provided. In empirical syntheses, obtained values for abundance of these structures shows that 80 percents of these structures relates to structure 2; structure 1 includes 15 percents; structure 4 consists of 4 percents, and about 1 percent belongs to other types of structure [28]. With

Table 1: *Summary of properties and specifications about NCNT structures and CNT.*

Structure	Total Energy (Hartree)	Relative Energy	Dipole Moment (Debye)	HOMO (Hartree)	LUMO (Hartree)	Energy Gap (eV)
Structure 1	-1926.858	0.855	1.52	-0.164	-0.108	1.512
Structure 2	-1926.815	0.852	3.31	-0.164	-0.111	1.433
Structure 3	-1926.779	0.850	2.16	-0.165	-0.124	1.117
Structure 4	-1926.797	0.851	0.96	-0.164	-0.105	1.596
CNT(5,0)	-1910.521	1.000	0.00	-0.194	-0.131	1.724

Table 2: *Summary of results obtained from frequency calculation.*

Structure	ΔU°_{tot}	ΔH°_{tot}	ΔG°_{tot}
Structure 1	-1926.4283	-1926.4274	-1926.4958
Structure 2	-1926.3818	-1926.3809	-1926.4509
Structure 3	-1926.3479	-1926.3469	-1926.4147
Structure 4	-1926.3615	-1926.3606	-1926.4288
Hydrogen Sulfide	-399.3379	-399.3370	-399.3604
Carbon Dioxide	-188.4868	-188.4859	-188.5104
NCNT & H_2S	-2325.7204	-2325.7194	-2325.8018
NCNT & CO_2	-2114.8687	-2114.8677	-2114.9502

regard to the high abundance of structure 2 and its low energy difference with structure 1, structure 2 is considered as the main and optimum structure in order to evaluate the interactions between acidic gases and this structure.

3.2. Different positions of gases adjacent to NCNT

Gas flow a completely accidental movement, so it is not possible to say exactly in what positions the gaseous molecules are located. Passing gases through internal or external wall of the CNTs, their accidental movements, as well as the existence of different atoms such as carbon, nitrogen, sulfur and oxygen will lead to different and various interactions between them [29]. So in order to have a detailed calculation all possible positions were considered. hydrogen sulfide gaseous molecules with C2v symmetry, which its main axis namely C2 axis is along with Z axis, will make three main positions for interaction with the main axis of nano tube which pass through the center of nano tube. Figure 2-a depicts these positions as well as the three main interactions between H_2S and NCNT in two visions [30]. Carbon dioxide gaseous molecule with D∞h symmetry is linear, so there are two main interaction positions as shown in Figure 2-b. With regard to the C2 axis, a 180° rotation around this

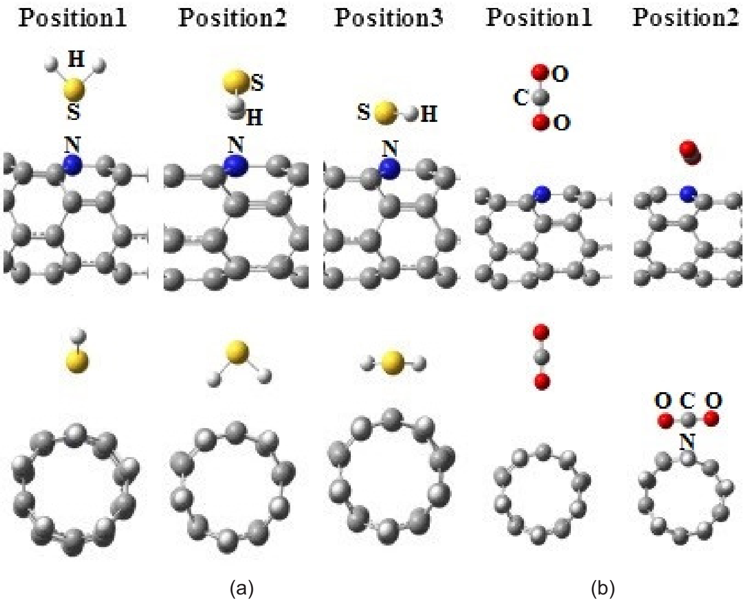


Figure 2: *a) Three main positions of interactions between H_2S and structure 2 of NCNT; b) Two main interaction positions between CO_2 and structure 2 of NCN.*

axis will lead to the formation of the initial structure of the molecule, so the rotation range should be defined between 0° and 180°. Therefore, the structures of the rotation angles of 20°, 40°, 60°, 80°, 100°, 120°, 140°, 160° and 180 ° were considered in this study. In order to evaluate the variously defined positions, it was necessary to do a complete optimization by a proper method in order to obtain the balanced distances of gaseous molecules from nanotubes. Then, in order to evaluate the rotations and consider different interaction positions, single point (SP) energy calculation was used which did not change the structure. Therefore, it was possible to rotate the gaseous molecule in proper directions and to calculate their related energies for their positions.

3.3. H_2S data analyses

Obtained data from the SP rotation energy calculations for different positions of hydrogen sulfide adjacent to NCNT are shown in Figure 3. The main parameter in this evaluation is the corrected adsorption energy, Figure 3-a. The corrected adsorption energy includes adsorption energy and correction of energy obtained from the superposition error of the basis set (BSSE). Positions 1 have positive adsorption values in all angles, so they are a little unstable. Position 2 in 40° to 140° have a good adsorption value and position 3 in 90° to 120° have stable levels of adsorption. Generally energy differences between different positions and energy barrier in rotations are low. Figure 3-d shows the values of energy gaps for adsorptions in different positions. Energy gaps are close in all the three positions, but in general the energy gaps for position 2 are less and the one for position 3 is more than other positions. So the electrical conductivity in position 2 is more than the other two positions. The changes in dipole moment has been shown in Figure 3-e. Generally the value of dipole momentum for position 2 is more than the other positions. Data obtained from the changes in the distance of H_2S gas from NCNT, is provided in Figure 3-f. The most stable energy belongs to a balanced distance equal to 4.6 Å which has about a 2.7 % difference from the obtained value for complete optimization; and if the points are considered with shorter distances then this error will decrease to 0.5 %. This Figure shows the potential energy curve used in the geometrical optimization of molecule. A useful comparison is conducted between adsorption energy of H_2S on CNT and NCNT, which is provided in Figure 3-c. Adsorption is more stable in NCNT than in CNT. Results obtained from the evaluation of adsorption from internal rotation of the gas molecule in NCNT are shown in Figure 3-b. Adsorption of H_2S in external wall of NCNT is more effective in comparison to its adsorption in internal wall.

3.4. CO_2 data analyses

Figure 4-a show the Data obtained from the corrected adsorption energy calculations for different positions of carbon dioxide adjacent to NCNT. The lowest level of adsorption energy belongs to position 2 which equals to 0.23 kcal/ mol. The trend of changes of the adsorption energy in position 1 is significant which is due to the change in the interaction of oxygen and nitrogen in different rotations. For both of the positions the most stable condition was obtained when there was an interaction between carbon and nitrogen. In the rotations of both positions, no negative stable adsorption was found. Figure 4-d presents the data obtained from the energy gaps. The lowest energy gap is in 120° and the highest energy gap is in 40° in position 1. The changes made in position1 are significant because of the interactions between oxygen and nitrogen atoms. According to Figure 4-e, dipole moments for all of angles in position 1 are more than dipole moments in position 2. Figure 4-b shows the data obtained from changes in the distances between CO_2 and NCNTs. the lowest energy found in the balanced distance equals to 3.4 Å which has about 0.3% error in comparison to the data obtained from complete optimization. Figure 4-c provides a comparison between adsorption energy on CO_2 on CNT as well as NCNTs. Adsorption of CO_2 is more stable in NCNTs than in CNT. According to Figure 4-f, adsorption of CO_2 inside the NCNTs is often neither effective nor useful.

3.5. Comparisons of H_2S and CO_2 adsorptions

Does NCNT as a separator catalyst show a better reaction to the separation of H_2S or that of CO_2 from sour gases in the sweetening process? The answer to this question is obtained from the analysis and evaluation of the comparison between adsorption energy of

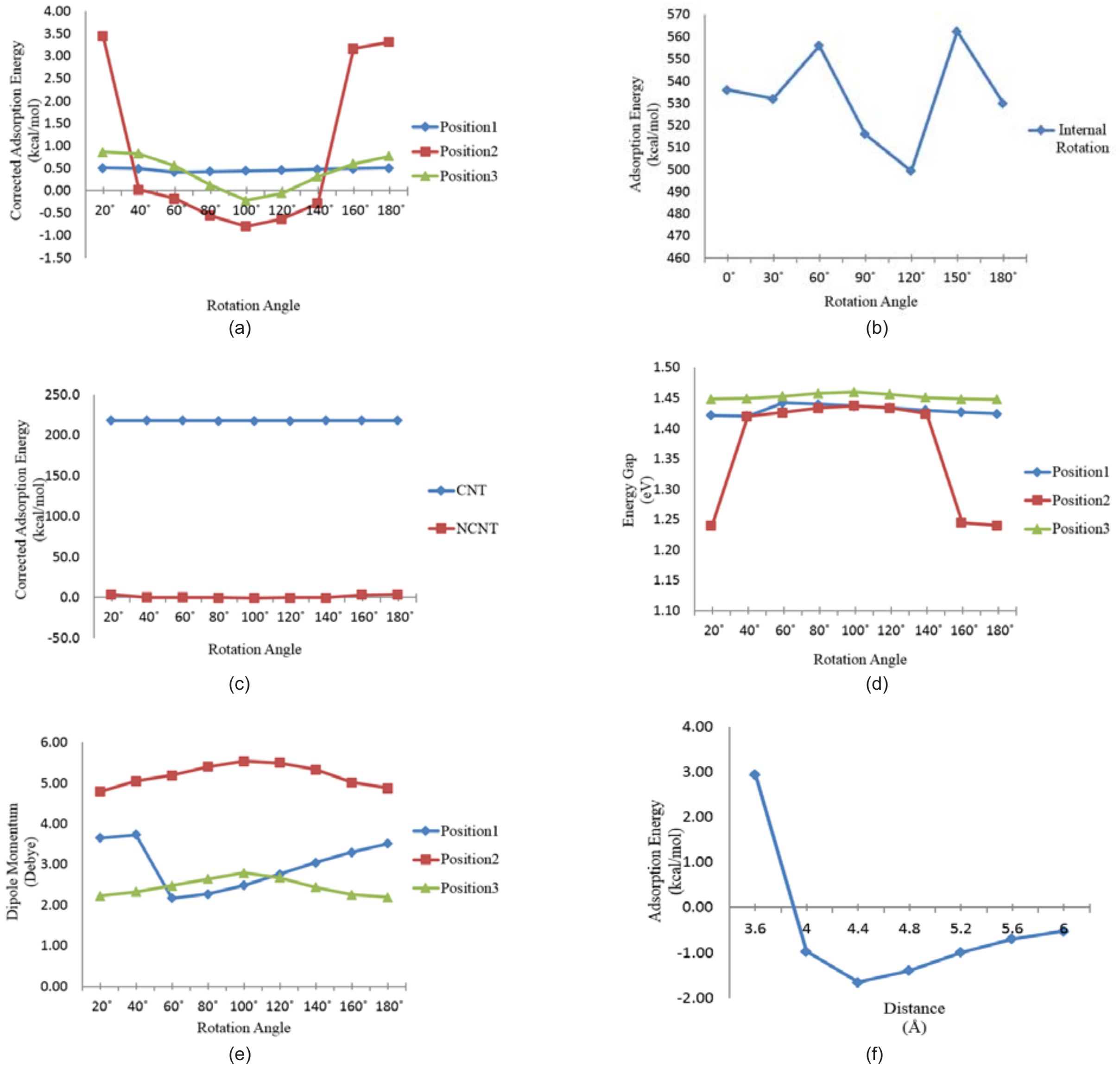
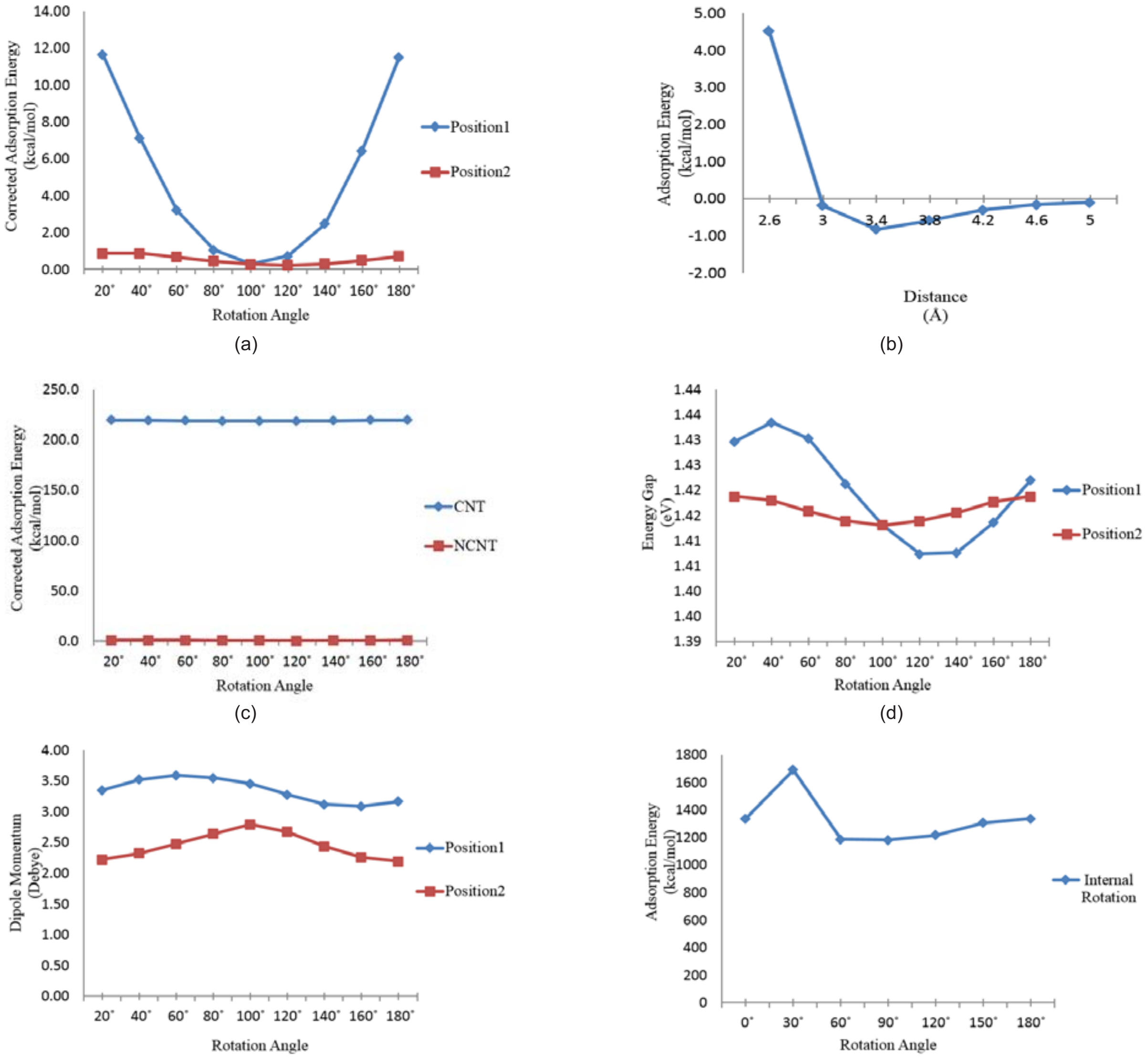


Figure 3: *The changes of corrected adsorption energy versus the rotations of H_2S at different positions on a) the external; b) the internal walls of the structure 2 of NCNT; c) The comparison between adsorption energies of H_2S on external wall of CNT and NCNT; the changes of d) energy gap; e) dipole moment versus the rotations of H_2S at different positions on the external walls of the structure 2 of NCNT and f) The changes of adsorption energy of H_2S vs. the distance of the molecule from NCNT.*

the desired gases. For H_2S and CO_2 the best adsorptions were found in position 2. In Figure 5-a indicates a comparison between the adsorption energy of both gaseous molecules on NCNTs resulting from the rotation. Generally, the adsorption of H_2S on NCNT is more effective than that of CO_2. There is a negligible 1 kcal/mol difference between the adsorption energies for both gases. A comparison between the adsorption energies of these two gaseous molecules on normal CNT is provided in Figure 5-b. Adsorptions of both gases on CNT are weak and unstable. Therefore, existence of nitrogen in the structure of CNT leads to an increase in the adsorption of H_2S and CO_2 gases. The value of ΔH298° for the adsorption of H_2S and CO_2 is -1.0 and -0.6 kcal/ mol, respectively. Adsorption process is thermodynamically desirable.

3.6. Electrostatic potential

Electrostatic potential or electric potential energy surface (EPES) indicates the electric charge distribution

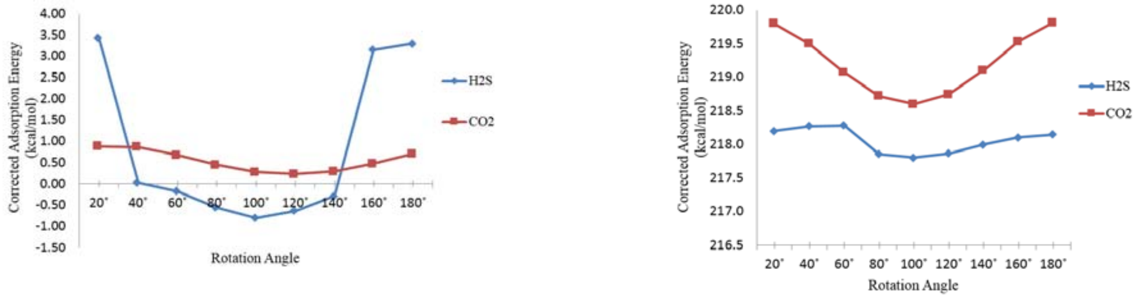


(a) (b)

(c) (d)

(e) (f)

Figure 4: *The changes of corrected adsorption energy versus the rotations of CO_2 at different positions on a) the external; b) the internal walls of the structure 2 of NCNT; c) The comparison between adsorption energies of CO_2 on external wall of CNT and NCNT; The changes of d) energy gap; e) dipole moment versus the rotations of CO_2 at different positions on the external walls of the structure 2 of NCNT and f) The changes of adsorption energy of CO_2 vs the distance of the molecule from NCNT.*



(a) (b)

Figure 5: *The Comparison between adsorption energies of H_2S and CO_2 on a) NCNT and b) CNT.*

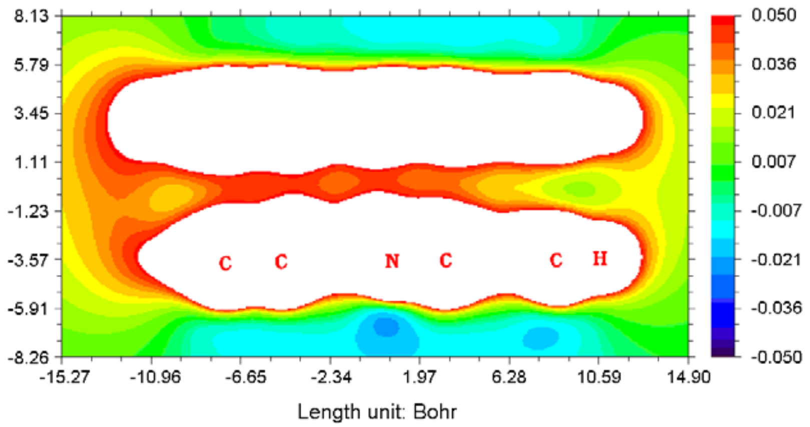


Figure 6: *A feature of the EPES for bare NCNT obtained from MultiWFN.*

around the system. This knowledge instruct to identify the probable positions for interaction or/and reaction. A feature of the EPES for bare NCNT has been depicted in Figure 6 which shows the positive electrostatic potential dominates around the tube and the minimum electrostatic potential presents on the nitrogen atom. So this area has more willing for interaction with the acidic gases from the positive electrostatic potentials zoon. This zoon is from the hydrogen atoms for H_2S and from the carbon atom for CO_2.

3.7. QTAIM analysis

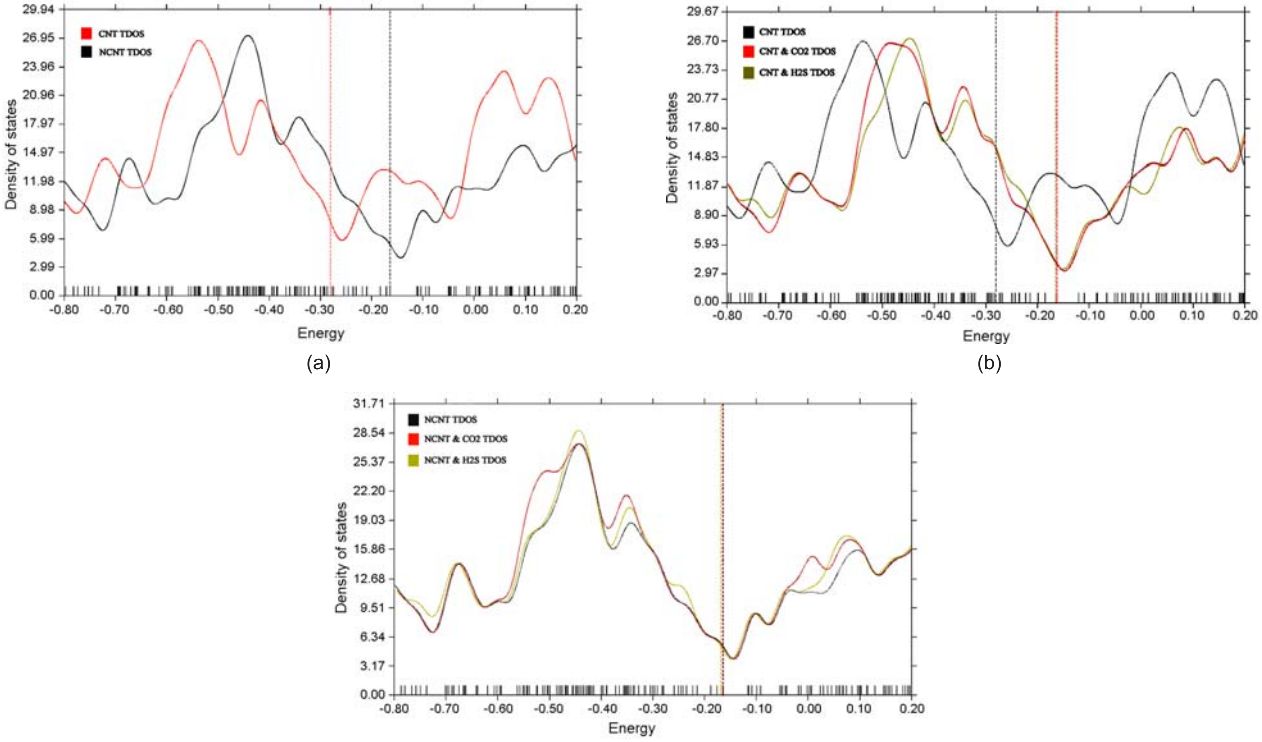
The obtained results about the identification of the critical points (CP) and bonding pathway through AIM2000 software including the type of critical point, electron density (ρ), Laplacian ($\Delta^2\rho$) and electron Hamilton (H) have been collected in Table 3 [31]. By paying attention to the positive values for the Laplacian it can be predicted the weak interactions between both H_2S and CO_2 gases with the NCNT. In other words because of low values for ρ and H for the two critical points of CO_2/NCNT the interaction is electrostatic, and about H_2S/NCNT because of more negative value for H in the BCP1 than CO_2/NCNT, the interaction is Vander Waals.

3.8. Density of states

The comparison of the density of states (DOS) for CNT and NCNT has been presented in Figure 7-a. This calculation is done by the MultiWFN software (Open source software on Linux). The Figure shows the DOS between the valance bond and conduction bond is not zero and states that both structures are semiconductors. The energy gap for the systems is 1.72 and 1.43 ev, respectively, which put on for the semiconductor ranges. In the present of nitrogen atom in the tube the energy gap decreases about 0.29 ev means more electric conductivity than CNT but no changes in the DOS in valance bond and more DOS in the conduction bond. So it is expected that NCNT has less electric conductivity than CNT. Fig 7-b shows that the present of the acidic gases on the CNT nanotubes causes to decrease the energy gap about 0.52 ev and change the DOS in the conduction bond. In addition the differences be-

Table 3: *Results of atoms in molecule (AIM) calculations about the critical points for H_2S/NCNT and CO_2/NCNT systems.*

System	AIM		CP		ρ	$\nabla^2\rho$	H
	NCNT	gas	type	name			
H_2S/NCNT	C	H	(3, -1)	BCP1	0.01015	0.0285	-0.00119
	C	H	(3, -1)	BCP2	0.00154	0.0048	-0.00029
CO_2/NCNT	N	C	(3, -1)	BCP1	0.00387	0.0156	-0.00088
	C	O	(3, -1)	BCP2	0.00324	0.0124	-0.00064



(a) (b)

(c)

Figure 7: *Density of states (DOS) for the CNT and NCNT bare and the adsorbed gases systems.*

tween the DOS for bare CNT and gas/CNT are high which leads to use the system for the identification of the gases. Because of the similar differences for the DOS of CO_2/CNT and H_2S/CNT they can't be used the tube for identification of the gas simultaneously. The calculated of DOS for bare NCNT and gas/NCNT has been shown in Figure 7-c which differs from the gas/CNT systems. All of the three systems have similar energy gap and the differences between them are infinitesimal (about 0.01 ev) but DOS for both valance and conduction bond is about similar. So it can't be used the NCNT for identification of the acidic gases. The performance of the CNT in the identification of the gases is higher than NCNT.

4. CONCLUSIONS

Adsorption of hydrogen sulfide and carbon dioxide gases on NCNT is more desirable in comparison to their adsorptions on CNT. Obtained results reveal that existence of Nitrogen in the structure of CNT leads to an increase in the adsorption of H_2S and CO_2. Adsorption of H_2S and CO_2 gases on the external wall of NCNT is better than their adsorptions on the internal wall. Adsorption of H_2S gas on the external wall of NCNT is a bit better than that of CO_2 on it. With regard to data obtained from natural bonding orbital (NBO) calculations, Adsorption of both gases are electrostatic, and there are no bonds between gaseous atoms and NCNT. Adsorption of both gases is desirable in terms of thermodynamic data. Corrections of energy are negligible based on the superposition error of basis set for both gases. It is suggested to consider correction values of energy for a better evaluation of adsorption energies. The frontier orbitals are similar in the CNT bare and CO_2-CNT; however, H_2S leads to a decrease in the HOMO orbital. Adsorption of the CO_2 and H_2S gases on the NCNT does not obviously affect the orbitals and DOS of the bare systems.

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