



A theoretical first-principles study of detection of some gas molecules by adsorption on single layer pristine graphene

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Abstract

Graphene is highly recommended for nano-sized gas sensor applications. In this work, four gas molecules (CO, O₂, H₂, NO) have been adsorbed on the pristine graphene and some important factors such as adsorption energies E_{ad} have been calculated along with band structure and density of states, using the DFT method. The highest adsorption energy was for (CO) molecule (0.178 eV) the highest adsorption energy of the O₂ molecule was (0.285 eV). and the highest adsorption energy of the H₂ molecule was (0.441 eV) and the highest adsorption energy of the NO molecule was (0.277 eV). The H₂ molecule is more stable on the surface of graphene. From the alternations of the band structure and the density of states after adsorption compared to pure pristine graphene, it seems that there is a clear change for both of them, which indicates a modification in the electronic properties which implies measurable changes in electric conductance of graphene. Depending on this modification, sensors can be manufactured using graphene.

Keywords: Graphene, gas sensor, Adsorption, DFT.

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Introduction

Detection and monitoring of the presence and concentration of many flammable and toxic gas molecules are highly important in many interesting areas such as industry, energy saving, agriculture, military, medical diagnostic, public safety, environmental monitoring, and indoor air quality control [1]. Since there is no single ideal material that meets all sensing requirements, the search continues for new materials with properties that might be used in gas sensors. Many materials and technologies have been developed and the fundamental understanding of the mechanisms involved in the interaction of gases with the sensors and their surfaces has been continuously refined [2].

The most important criteria that researchers are seeking are; high sensitivity, good selectivity, and recovery time along with room temperature sensing capabilities. The gas sensors may be classified based on their sensing methods and divided into two groups: (a) methods based on variation in electrical properties and (b) methods based on variation in other properties [3]. One of the most important features of a material to be used for gas sensing is its high surface-to-volume ratio along with good thermal and chemical stabilities.

Generally, (2D) nanomaterials have a high surface-to-volume ratio hence are ideal for gas adsorption and their surfaces are highly reactive to the gases. Metal oxide



semiconductors are the most widely used gas sensing materials due to their high sensitivity, fast response time, and low cost [4,5]. However, the high operating temperatures (200 - 500 °C) [6], long recovery periods, and low selectivity [7] are restricted their applications in a rapidly changing environment. Polymers, on the other hand, have room temperature sensing capability but they are sensitive to humidity and therefore degrade quickly [8]. Graphene is one of the promising candidates for gas sensing [9]. Due to its exceptional properties many efforts have been made to implement it in optical [10], electrochemical [11], and mechanical [12] gas-sensor applications.

Graphene is a two-dimensional (2D), a single-layer sheet of sp^2 hybridized carbon atoms [13] that can be considered the origin of all graphitic forms of carbon nanostructures such as CNTs and fullerenes. [14] It is comprised of carbon atoms arranged in a honeycomb lattice with two atoms per primitive unit cell giving rise to important results for the transport properties of graphene. The π and π^* bands of a single layer of pristine graphene form Fermi cones which touch each other at a single point marking the presence of massless relativistic electrons [15] giving rise to unusual features that place it between conductors and semiconductors as a semimetal or a zero-gap semiconductor material [16].

Graphene has an enormous area per unit mass of $2600 \text{ m}^2 \text{ g}^{-1}$, in which the whole volume is exposed to the atmosphere. Moreover, graphene has high carrier density ($\sim 10^{12} \text{ cm}^{-2}$), high carrier mobility ($200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), and very low resistivity and noise at room temperature [17]. The high mobility of charge carriers and the ability to modify the electronic

properties in many ways such as doping, deformation, or interaction with different substrates place graphene among the most promising materials for future electronic devices [18]. Graphene-based gas sensors operate by adsorbing gas molecules on the graphene's surface, which act as donors or acceptors of electrons. The detection of gas molecules works by measuring alteration in the electrical conductivity of the material after the adsorption process. In this work, we discussed a computational investigation of conceivably graphene's sensitivity towards some gas molecules by observing the modifications on the energy band structure and density of states that are related directly to transport properties.

Method and calculation details

In the present study, the first principle DFT calculation has been performed using the Dmol3 program where Local density approximation (LDA) has been selected. The calculations were accomplished on a large unit cell ($4 \times 4 \times 1$) consisting of 32 carbon atoms. The lattice parameters (a, b, c) were such that ($a=b$) where their value was 9.838 \AA , and the value of (c), which represents the distance between graphene sheets, was selected ($c=30.00 \text{ \AA}$). Calculations start with geometry optimization of each sample and end with electronic structures calculations (band structures and density of states).

Results and discussion

Pristine graphene: To obtain sufficient information from the structures of the band, necessary we have to choose a path that covers all the important points of high symmetry for graphene. The path (G-M-K-G) was chosen at the Brillouin zone as shown in Figure (1) as it covers the important special points.



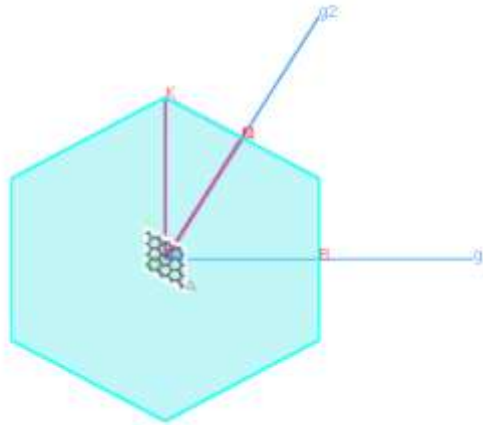


Figure (1) Brillion zones of graphene.

Figure (2) shows the band structures of pristine graphene where the energy band gap was (0.005eV) directly at the point (K), which is almost equal to zero. This result agrees with the practical results which define pristine graphene as a zero-gap semiconductor or a semimetal.

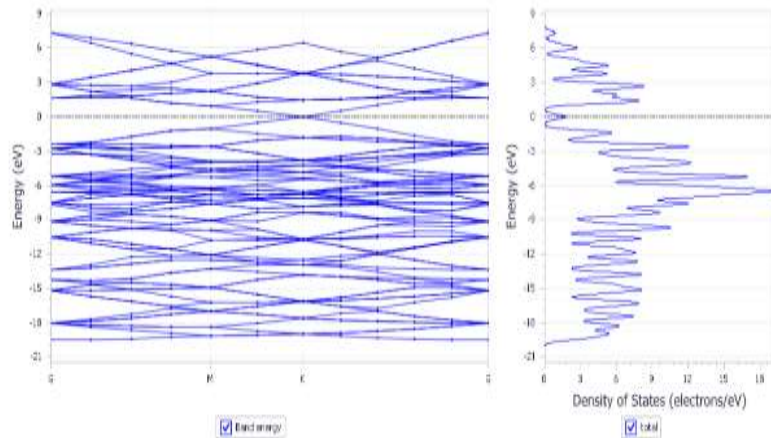


Figure (2) Electron structures (band structure and density of state) for pristine graphene.

The value of an energy gap is calculated as the difference between the two nearest points in the conduction band and the valence band and knowing if the gap is direct or indirect. If the gap values are on the same values of (k) then it is called a direct band gap while if it is located on different values of (k), then it is called an indirect band gap.

Graphene Adsorption: At this point, several gaseous molecules (CO, O₂, H₂, and NO) were attached as adsorbates to the surface of the graphene. Different adsorption sites have been tested to find out the most probable site. The adsorption energy (E_{ad}) of adsorbed molecules

on the surface of pristine graphene has been calculated as follows:

$$E_{ad} = E_{molecule+substrate} - E_{substrate} - E_{molecule} \dots\dots\dots (1)$$

$E_{molecule+substrate}$: the total energies of the pure molecule and graphene (PG), $E_{substrate}$: the total energy of the graphene sheet, $E_{molecule}$: The total energy of the adsorbed molecule (CO, O₂, or NO or H₂).

Three potential sites were selected for adsorption of gas molecules on the surface of graphene: 1- Site H is located above the center of the hexagonal graphene (Hole). 2- Site B is located between the two carbon atoms (Bridge). 3- Site T is located above the carbon atom (Top)



as shown in figure (3). To recognize the most probable site for gas molecules to adsorb on the surface of the graphene, we perform geometry optimization after adding gas molecules to the three sites and calculating the adsorption

energy in each case to find out the most probable site. The next step is to find out the adsorption impact on the electronic properties of graphene.



Figure (3) Adsorption three sites.

CO Adsorption: At this part, pristine graphene is adsorbed with a molecule of carbon monoxide to see how it affects the electronic structures and the energy bandgap. It was noted that the bond length (C-O) for a molecule of carbon monoxide is (1.139 Å), which is a value very close to the practically calculated bond length. This indicates that the CO was adsorbed as a molecule on the surface of the graphene. The value of binding energy that was calculated

(0.178 eV) indicates that the process is physical adsorption. The distance (l) between the carbon monoxide and the graphene sheet is equal to (3.366 Å), and the change in the length of the bond does not cause local distortions that affect the graphene where the binding energy decreases with increasing distance. The above results are agreeing with source [19] as shown in Figure (4).

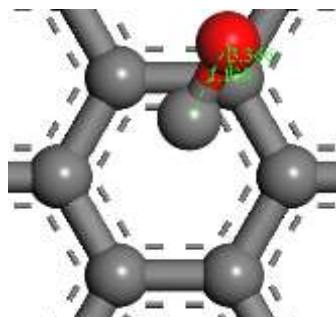


Figure (4) the graphene sheet adsorbed carbon monoxide with bond length and distance.

We notice from the results obtained in Figure (5) that the band structures do not show a definite change regarding Fermi level position and the energy gap. On the other hand, the band structure and the density of states displayed a significant change. The density of states in the conduction band extends to 12 eV, while in pristine graphene it is limited to 9 eV. Moreover, only two values appeared clearly after adsorption. The preferred site in which the

carbon monoxide molecule settled was (H) site and the adsorption energy calculated according to the equation is 0.178 eV. This energy shows that the adsorption is physical. The bond length (C-O) is equal to 1.139 Å after adsorption. It clearly shows that (C-O) does not dissociate and remains in the molecular state, and the value of the adsorption distance of the CO molecule from the graphene sheet is consistent with the



value of the adsorption energy and consistent with the published results.

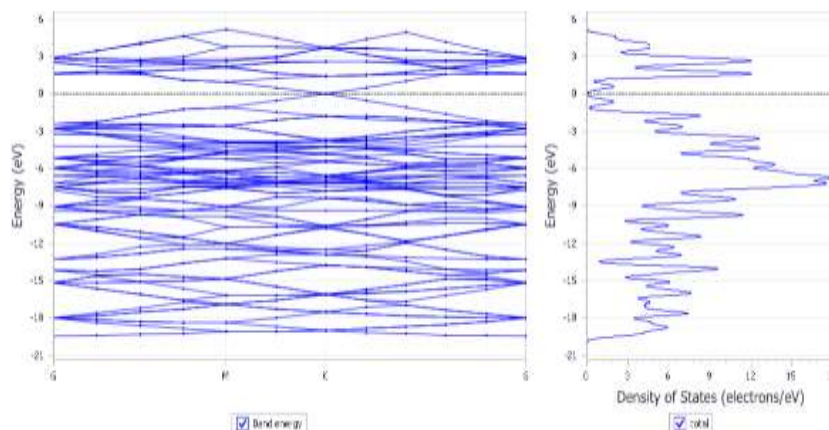


Figure (5) Electronic structures (band structure and density of state) of the graphene sheet adsorbed with a CO molecule.

Table (1) Shows the values of adsorption energy, bond length, and distance for different gas molecules.

gas molecule	Site of adsorption	l (Å ^o)	d (Å ^o)	E _{ad} (eV)
CO	H	3.366	1.139	0.178
O ₂	H	775.3	1.224	0.285
H ₂	H	3372.	0.768	0.441
NO	B	2694.	1.151	0.277

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Using Mullikan Analysis, the charges of the carbon atom and the carbon monoxide molecule were obtained as shown in Figure (6) for the (H) site.

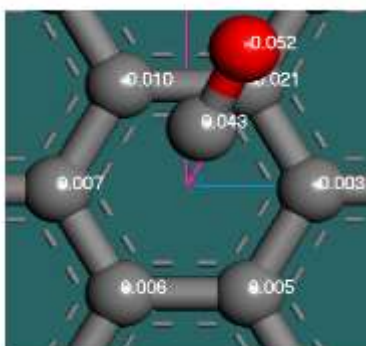


Figure (6) Distribution of charge values for the carbon monoxide molecule and the nearby carbon atoms.

The carbon monoxide molecule adsorbed on the surface of graphene with a positive charge (0.043 and -0.052) and the carbon atoms close

to it have negative charges ranging between (0.003-0.021) resulting in a transfer of electrons from the positive charge of the carbon



monoxide molecule to the negative charge On the surface of graphene, which leads to strengthening the bond between the carbon monoxide molecule and the graphene surface. Figure (6) shows a small partial transfer of charges between the graphene and the (CO) molecule, and this indicates that the bond is closer to (Vander Waals).

O₂ Adsorption:At this part, pristine graphene is adsorbed with an oxygen molecule to see how it affects the electronic structures and the bandgap energy. It was noted that the length of the bond (O-O) of the oxygen molecule is (1.224 Å), which is a value very close to the length of

the bond practically calculated for it. This indicates that the O₂ molecule was adsorbed on the surface of the graphene, especially that the small binding energy that was calculated from the relationship equals (0.285eV) indicates that the process is an adsorption process. As for the distance (l) between oxygen and other carbon atoms in the plate, it is equal to (3.775 Å) and the change in the length of the bond does not cause local distortions that affect the graphene if the binding energy decreases with increasing distance. The above results or the works are consistent with source [19] as it is illustrated in Figure (7).

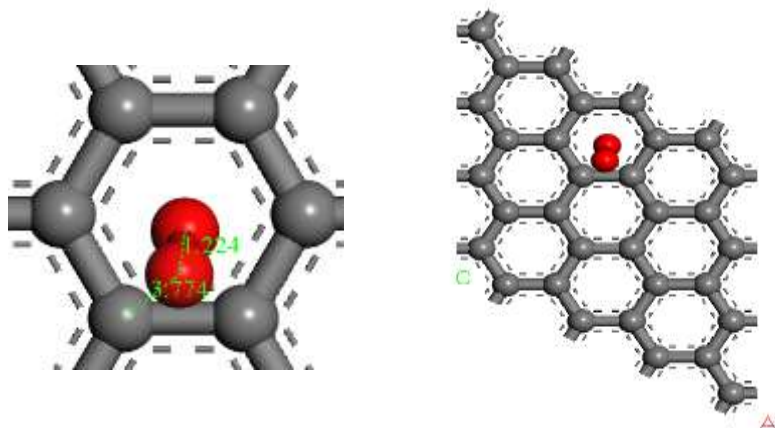


Figure (7) The graphene sheet adsorbed the oxygen molecule with the length of the bond and the distance.

We notice from the results obtained in Figure (8) that the band structures do not show a tangible change and the level remains in its position, as well as no change in the energy gap. As for the density of states, it shows a significant change, as the density pattern in the conduction band extends to 12 eV, while in pristine graphene it is limited to 9 eV. Moreover, only two values appeared clearly after adsorption. The preferred site in which the oxygen molecule settled is H and the adsorption

energy calculated according to the equation is 0.285 eV this energy shows that the adsorption is physical. The length of the bond (O-O) is equal to 1.224 Å. After adsorption, it clearly shows that (O-O) does not dissociate and remains in the molecular position, and the value of the adsorption distance of the O₂ molecule from the graphene sheet is consistent with the value of the adsorption energy and is consistent with the published research.



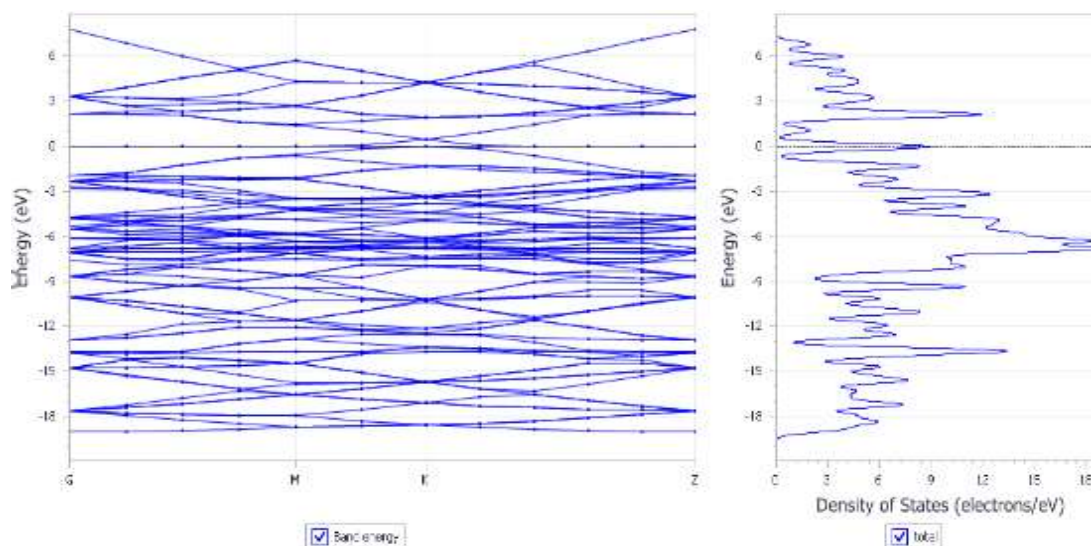


Figure (8) Electronic structures (band structure and density of state) of graphene sheets adsorbed with an (O_2) molecule.

Using Mullikan Analysis, the charges of the carbon atom and the carbon monoxide molecule were obtained as shown in Figure (9) for the (H) site.

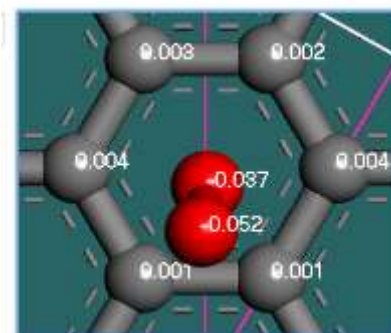


Figure (9) Distribution of charge values for the carbon monoxide molecule and the nearby carbon atoms.

The oxygen molecule adsorbed on the surface of graphene has a negative charge (-0.037) and (0.052) and the carbon atoms nearby have positive charges ranging between (0.001-0.004) this results in a transfer of electrons from the positive charge of the carbon atom to the negative charge on the surface of the graphene, which leads to strengthening the bond between the oxygen molecule and the surface of the graphene. Figure (9) shows a small molecular transfer of charges between the graphene and (O_2) molecule, and this indicates that the bond is closer to (Vander Waals).

H₂Adsorption:At this part, pristine graphene is adsorbed with a hydrogen molecule to see how it affects the electronic structures and the bandgap energy. It was noted that the bond length (H-H) for the hydrogen molecule is (0.768 Å), which is a value very close to the bond length practically calculated for it. This indicates that the H₂ molecule was adsorbed on the surface of the graphene, especially that the small binding energy that was calculated from the relationship equals (0.441eV) indicates that the process is an adsorption process. As for the distance (l) between hydrogen and other carbon atoms in the plate, it is equal to (3.372



Å°), and the change in the length of the bond does not cause local distortions affecting the graphene if the binding energy decreases with

increasing distance. The above results or works do not agree with previous studies as shown in Figure (10).

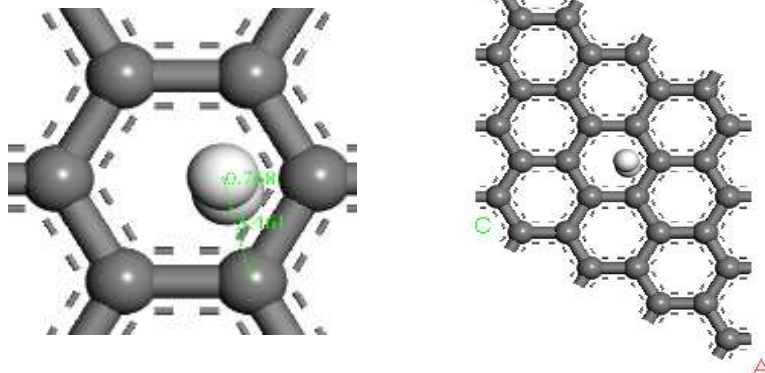


Figure (10) The Graphene sheet adsorbed hydrogen molecule with bond length and distance.

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We notice from the results obtained in Figure (11) that the band structures do not show a significant change and the level remains in its position, as well as no change in the energy gap. As for the density of states, it shows a significant change, as the density pattern in the conduction band extends to 12 eV, while in pristine graphene it was limited to 9 eV. In addition, only two values appeared clearly after adsorption. The preferred site in which the oxygen molecule settled is H and the adsorption

energy calculated according to the equation is 0.441 eV. This energy shows that the adsorption is physical. The bond length (H-H) is equal to 0.768 Å° after adsorption. It clearly shows that (H-H) does not dissociate and remains in the molecular position, and the value of the adsorption distance of the H_2 molecule from the graphene sheet is consistent with the value of the adsorption energy and is consistent with the published research.

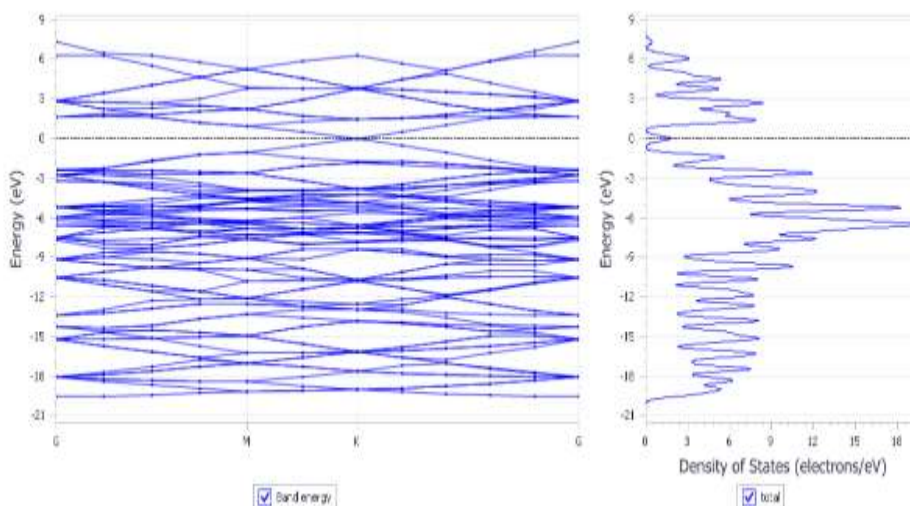


Figure (11) Electron structures (band structure and density of state) of H_2 adsorbed graphene sheets.

Using Mullikan Analysis, the charges of the carbon atom and the hydrogen atom were obtained as shown in Figure (12) for the (H) site.



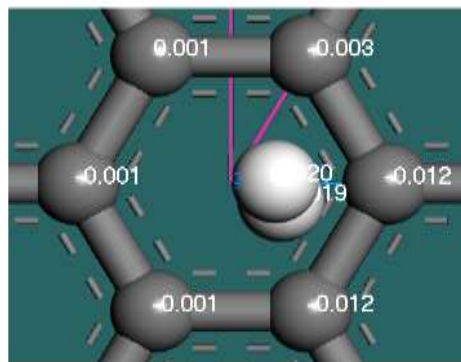


Figure (12) Distribution of charge values for hydrogen molecule and nearby carbon atoms.

The hydrogen atom adsorbed on the surface of graphene with a positive charge (0.019-0.020) and the carbon atoms nearby with negative charges ranging between (0.001-0.012) resulting in a large transfer of electrons from the positive charge of the hydrogen atom to the negative charge on the surface of the graphene, which leads to Strengthening the bond between the hydrogen molecule and the surface of the graphene. Figure (12) shows the small molecular transfer of charges between the graphene and the (H₂) molecule. This indicates that the bond is closer to (Vander Waals).

NO Adsorption: At this stage, pristine graphene is adsorbed with nitrogen monoxide molecules to see its effect on electronic structures and bandgap energy. It was noted that the bond

length (N-O) for the oxygen molecule is (1.151 Å), which is a value very close to the bond length practically calculated for it. This indicates that the NO molecule was adsorbed on the surface of the graphene, especially that the small binding energy that was calculated from the relationship equals (0.277 eV) indicates that the process is an adsorption process. As for the distance (l) between nitrogen and other carbon atoms in the plate, it is equal to (2.694 Å) and the change in the length of the bond does not cause local deformations that affect the graphene if the binding energy decreases with increasing distance. The above results or works are consistent with previous studies as shown in Figure (13).

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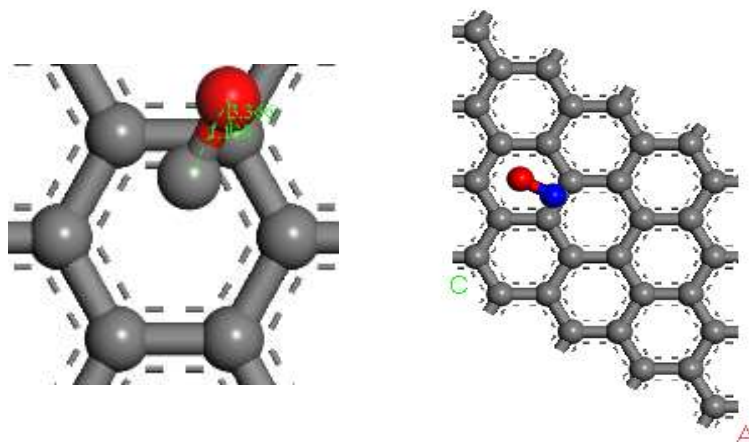


Figure (13) The graphene sheet adsorbed Nitrogen monoxide molecule with bond length and distance.

We notice from the results obtained in Figure (14) that the band structures do not show a tangible change and the level remains in its

position, as well as no change in the energy gap. As for the density of states, it shows a significant change, as the density pattern in the



conduction band extends to 12 eV while in pristine graphene it is limited to 9 eV. Moreover, only two values appeared clearly after adsorption. The preferred site in which the nitrogen monoxide molecule settled is B, and the adsorption energy calculated according to the equation is 0.277 eV and this energy shows that the adsorption is physical. The bond length

(N-O) is equal to 1.151 Å after adsorption. It clearly shows that (N-O) does not dissociate and remains in the molecular position, and the value of the adsorption distance of the NO molecule from the graphene sheet is consistent with the value of the adsorption energy and is consistent with the published research.

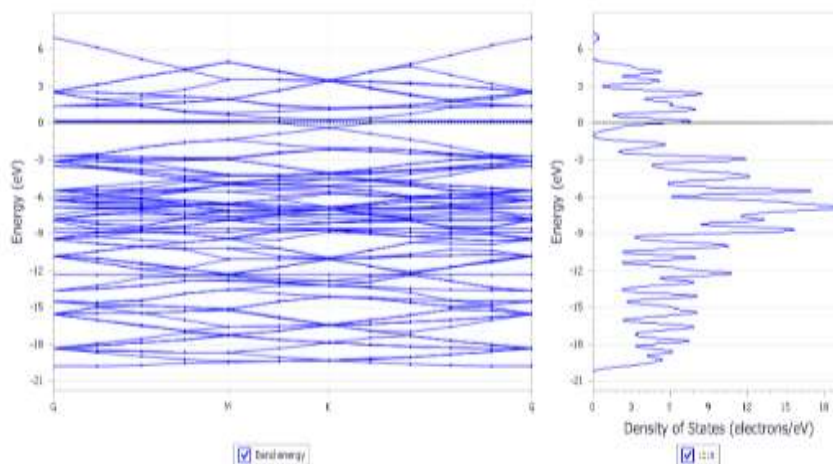


Figure (14) Electronic structures (band structure and density of state) of graphene sheet adsorbed with a molecule (NO).

Using Mulliken Analysis, the charges of the carbon atom and the nitrogen oxide molecule were obtained as shown in Figure (15) for the (B) site.

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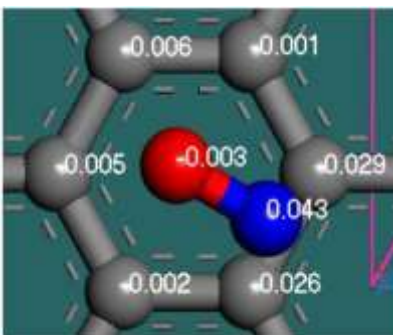


Figure (15) Distribution of charge values for the nitrogen monoxide molecule and the nearby carbon atoms.

The nitrogen monoxide molecule adsorbed on the surface of graphene has a positive charge (0.043) and a negative charge (0.003) and the carbon atoms nearby have negative charges ranging between (0.002-0.029) resulting in a large transfer of electrons from the positive charge of the nitrogen molecule to the negative charge on the surface of the graphene which leads to the strengthening of the bond between

the nitrogen monoxide molecule and the surface of graphene. Figure (15) shows a small molecular transfer of charges between graphene and (NO) molecule, and this indicates that the bond is closer to (Vander Waals).

Conclusions

The present work has demonstrated that it is possible to measure quantum scale changes in



electronic conduction within graphene after some gaseous molecules (CO, O₂, H₂, and NO). With this in mind, the possibility of pushing these sensors to their optimal level to detect single gas molecules seems reasonable. In this application, graphene gasps the benefit of being an extremely low-noise material. Because of this, even at the limit of no carriers and a few extra electrons, graphene's carrier concentration can change considerably. Additional to this benefit is the fact that graphene in this application enables the creation of four-probe devices on monocrystals. Graphene's sensitivity to gas molecules is mainly attributed to two factors: (1) graphene's π orbitals which interact with the adsorbates rooming on top via van der Waals interactions, and (2) graphene's high surface-to-volume ratio which is a benefit for all 2D materials.

The possibility of adsorption of (CO), (O₂), (H₂), and (NO) molecules on pristine graphene sheets and its evident influence on its electronic properties such as band structures and the density of states, are as follows:

- 1- pristine graphene (PG) might show appropriate sensitivity to CO molecules depending on the
- 2- noticed changes in the band structure and density of states.
- 3- Adsorption with O₂ molecule shows pulling the band structures to the higher Fermi level, PG appears more sensitive to O₂ molecule.
- 4- Upon adsorption of pristine graphene with H₂ molecule, the changes in the band structure formed at the Fermi level have shown high sensitivity to hydrogen.
- 5- When pristine graphene is adsorbed with a molecule of NO, we notice that the bands are pulled below the Fermi level and show sensitivity comparable to oxygen.
- 6- It was found that the highest CO adsorption energy on the graphene sheet is (0.178 eV), the highest O₂ adsorption energy on the graphene sheet is (0.285 eV), the highest H₂ adsorption energy on the graphene sheet is (0.441 eV) and the highest adsorption

energy is NO on The graphene sheet is equal to (0.277 eV). This means that all adsorptions are more likely physical type.

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