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Comparative Adsorption Calculations for Carbon Mono-Oxide and Hydro Cyanide Gas Molecules Interaction with Graphene Material Using Density Function Theory

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Abstract

Density Function Theory (DFT) tool was used to evaluate ground and excitations proprieties for the graphene nano-ribbon and also, computed geometry orientation between the gas molecule and the surface of the nano-system. The ground state calculations are providing relaxation structure, molecular orbital energy, and adsorption energy. Excitation properties are providing UV-Visible proprieties. In the pure state, the bond length for graphene nano-ribbon was in agreement with theoretical calculation and experimental. During the adsorption mechanism especially in the chemical interaction, all proprieties of the system will be changed. Molecular orbital distribution in chemical interaction overlaps gas molecules and some atoms related to graphene nano-ribbon in the distance near the surface. The UV-Visible calculation indicates that only the chemical adsorption appears shifting in the spectrum. Two gases under study have red shifting in electromagnetic radiation. Finally, graphene nano-ribbon was more acceptable to detect CO gas molecules than HCN, and also the ability to use this system in the environmental field.

Keywords: Adsorption energy, Energy gap, Chemical adsorption, Haydro cyanide, Graphene nano-ribbon.

1. Introduction

Graphene as a two-dimensional connected carbon sheet is an excellent material that has exceptional properties such as superior surface to volume fraction, little electrical noise and outstanding transport properties[1]. Graphene has more superior efficiency in addition to its unique two-dimensional structure and has unique chemical properties such as outstanding electrical, optical and mechanical properties. Due to its excellent properties, graphene has been commonly used in a number of ways, such as energy generation, spintronics and field effects transistor (FET)[2]. Graphene has also been proven to have possible uses in detection molecules, both experimental and theoretical. Graphene may be chosen as a novel material for adsorption and desorption due to its low dimensions and wide surface area process[3]. Graphene is a zero band gap semiconductor with its valence and conduction bands touching in corner of the Brillion zone in called Dirac points[4]. Graphene is a crystalline allotrope of carbon with two-dimensional properties. Its atom are densely packed in regular atomic scale in hexagonal pattern, each atom has four bonds, one σ-bond with each of its three neighbor and one π-bond that is oriented out of plane, bond length between carbon-carbon atom is 1.42 Å a part[5]. The aim of a present study were been investigated ability of graphene nano material to

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detection toxic gases in nature. DFT and TD-DFT method was used to describe ground and excited state, also interaction between gases molecule and the surface of graphene nano materials.

2. *Graphene* doped *metallic atoms*

A major limitation of its future application in gas-based sensor because pure graphene is rather chemically inert due to sp2 bonding between carbons atom in graphene plane sheet[6]. Because high specific area of it allows transfer charge with external gas molecule adsorbed[7]. However many theoretical and experimental studies show that graphene has weak physical adsorption of most gas molecule[7]. Therefore, to solve this problem researchers used many mechanisms such as defect vacancy and doped graphene by metal atom[8]. Graphene doped by metal atom led to significant structural and electronic properties, also electrical conductivity and chemical reactivity during adsorption process to detection small gas molecule[9]. Worthy notice that doped graphene by metallic atom creates modifications process without damaged one atom thick of it[10]. Many studies show that introduction of defect or doped metallic atom in graphene will modified charge transfer strength between it and gas molecule adsorbed, also enhance sensitivity and selectivity of gas-based sensor[11]. Gas sensing was important environmental issue for hazard toxic gases molecule. One of these gases was mono oxide (CO) molecule, it widely studied by researcher because it is harmful human body and it is the main cause of air pollution. CO adsorption on surface of nano tubes such as boron-nitride, aluminum- nitride and aluminum-phosphide, also other structure of III-V group of element table[12].

3. *Adsorption in graphene nano materials*

Adsorption mechanism is considered one of the important kinds of surface science, it is defined as process when molecule and ions called adsorbate stick on surface of a solid called adsorbent[13]. The transition of the adsorbent from the liquid phase to the solid phase continues until the balance between the amount of adsorbent contained in the adsorbent and the amount of adsorbent remaining in the solution is achieved[14]. In general it is classified to chemical and physical adsorption mechanism[15]. In chemical adsorption high amount of electron transport between two reaction system, high energy rises during this process it ranged from 40-800 kJ/mol, and this process was irreversibly. All of these result back to presence chemical bond between adsorbent and adsorbate[16]. In physical adsorption weak van der Waals interaction appear, no electron exchanges between them. Small amount of energy rises it ranged from 5-40 kJ/mol.

4. *Theoretical base and details*

Over the last 35 years Density Functional Theory (DFT) has become one of the standard

methods for calculations in several branches of physics and chemistry. Among all the other methods to electronic structure calculations, like e.g. Configuration Interaction (CI), Coupled Cluster (CC) and Møller-Plesset (MP) Perturbation Theory[17]. The rather special place of DFT becomes directly clear from the fundaments, as it was first formulated in1964 by Hohenberg and Kohn.

Density functional theory (DFT) is a widely used quantum mechanical method in physics and chemistry to investigate many-electron systems' electronic structure. Today it is one of the most important tools used to evaluate the ground-state properties of metals, semiconductors and insulators. DFT is one of the most widely used and useful methods in physics and chemistry computational[18].

The starting point for the theory of density was the Thomas-Fermi model; in 1927, Thomas and Fermi defined the energy of an atom by representing its kinetic energy as a function of electron density, combining this with the classic expressions for interactions among nuclear-electron and electron-electron, which can also be defined in terms of electron density[19]. The DFT focuses on the much simpler electron density $\rho(r)$. In general, the electron density is the number of electrons N per unit volume for a given state. It is dependent only on three coordinates independently of the number of electrons of the system[20]

Nanotube modular software was used to build input sample in protein data base form (.pdb). Send saved structure to gaussian (5.0) version to computed possible properties. Density Function Theory (DFT) method was used to computed geometrical proprieties include bond length and angle between atoms[21]. Electronic proprieties include molecular orbitals energy and adsorption energy. Optical characteristic involves ultraviolet-visible spectrum computed by Time Depending-Density Function Theory (TD-DFT). 6-31G* basis set was used in present at hybrid function B3LYP for ground and excitation state.

5. Result and discussion

5.1. Geometrical proprieties

In the present section, will investigate geometrical proprieties for pure graphene nano- ribbons and determine the relaxation distance between gas molecules and the surface of the nano-system. Figure (1) list the geometry structure for pure graphene nano-ribbon. The bonds length for C-C (single), C=C (double), C=C (aromatic) and C-H are (1.4555), (1.3661), (1.4305), and (1.0859) Å values of bond length are agreements with past study in[22]. Angles between atoms listed for (C--C--C) and (C=C-H) are 120.232 and 119.922 degree.

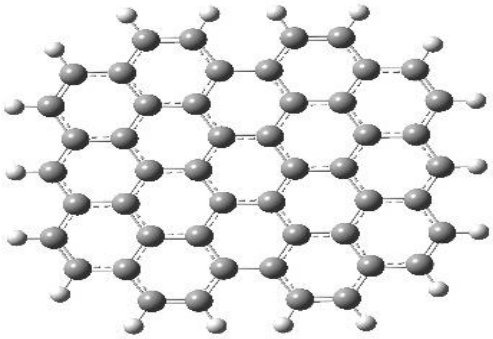


Figure (1): Represents graphene nano-ribbon, white ball is hydrogen and gray ball is carbon.

5.2. Adsorption energy

This section will be discussing the effect of changing adsorption distance between gas molecules and the surface of nano-ribbon and also, determine the limits of physical and chemical interaction between them. Table (1) listed adsorption energy as a function for interaction distance between gas molecule and the surface of nanosystem and split-step equal 0.5 Å. For CO gas molecule, Adsorption energy can be calculated according to equation (1)[23]. The results indicate that graphene is sensitive to gas molecules but in a small amount of energy transfer between them this is clear for distances 3.5 to 2. Distance from 2 to 1 Å adsorption energy increases and the nanosystem began sense to a gas molecule. Increasing adsorption energy led to the formed chemical bond between the C atom belonging to the graphene ribbon and the C atom in a gas molecule. Bonding led to chemical adsorption that rising high adsorption energy. Energy absolute value increased from 3.9809 to 34.0385 eV. HCN gas molecule in the same distance indicates that in physical interaction rises small energy resulting from adsorption mechanism and this appears in distance 4 to 2 Å. Suddenly adsorption energy increasing reaches an absolute energy value equal to 19.298 eV, this value is smaller than CO adsorption energy in a chemical process. The increase in adsorption energy because loan pair formed between C in graphene ribbon and N related to a gas molecule. A higher negative energy refer to more stable system[24]. Results show that CO gas molecules have high adsorption energy because of of the strong difference in the electronegativity of C and O atoms[25]. Figure 2 represent adsorption energy curves for interaction gas molecule. The final result shows that HCN gas molecule adsorption has higher physical adsorption compared with CO. But, in the chemical adsorption CO gas molecule was have high interaction energy compared with HCN

$$\mathbf{E_{ad} = (E_{gas}+E_{ribbon})-E_{complex}} \qquad \mathbf{1}$$

E_{ad} was adsorption energy

E_{gas} total energy for gas molecule

E_{ribbon} total energy for graphene nanomaterial

$E_{complex}$ total energy for interaction system (gas molecule and surface of graphene nanomaterial)

Table: (1) lists of computed adsorption energy in electron volt unit (eV).

D (Å.)	CO	HCN
1	-34.0385	-19.2980
1.5	-22.3212	-5.9456
2	-3.9809	-1.8585
2.5	-0.9224	-0.4000
3	-0.1659	-0.07891
3.5	-0.0163	-0.03265
4	-0.00216	-0.02993

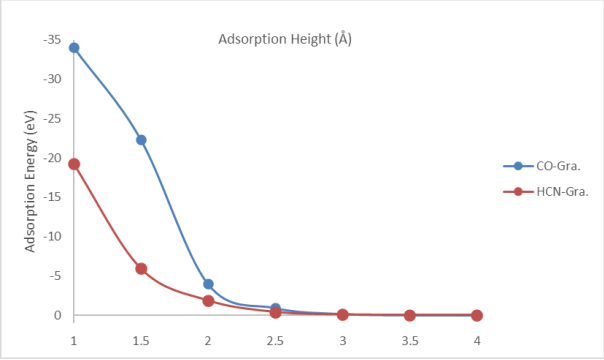
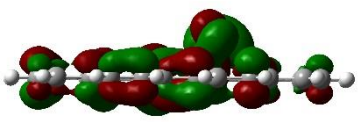
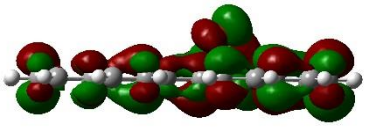
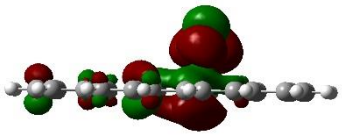
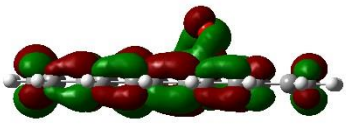
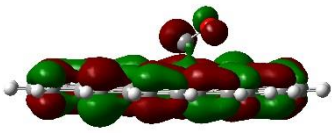
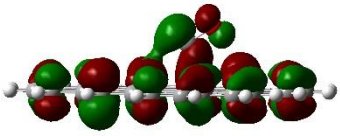
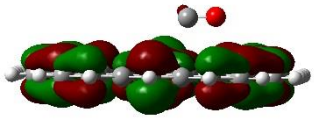
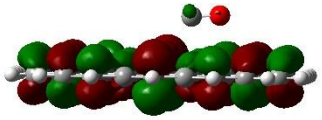
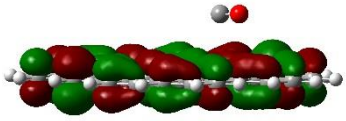
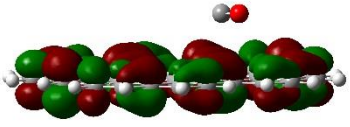
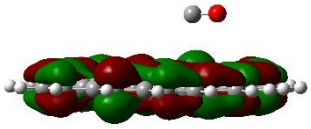
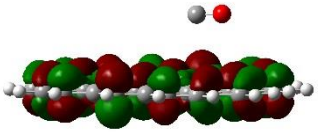
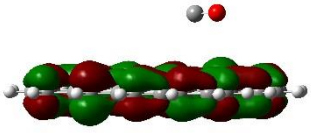
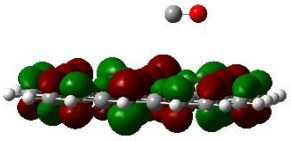


Figure 2: represent adsorption energy curves for interaction gas molecule.

5.3. Molecular orbital energy and energy gap

Higher Occupation Molecular Orbitals (HOMO), Lower Unoccuption Molecular Orbitals (LUMO), and energy gap (Eg) were important parameters to

determine the ability of electrons to transition and the type of materials classification (Conductor, Semiconductor, and Insulator)[26]. For pure graphene nano-ribbon, HOMO and LUMO were distributed around C-C bonding. The distribution of molecular orbital of it was symmetry[22]. The HOMO is more essential orbital on the charge transfer consequently always to graphene. Because mainly it is located on the atom of a gas molecule, the charge transfer is largest when the atom of gas is closed to the surface. Results indicate that for distance near-surface of graphene nano-ribbon molecular orbitals increases because high adsorption mechanism, on the other hand, a high amount of electrons transfer from graphene nano-ribbon to gas molecule. Also increasing the distance between them all molecular orbitals energy is fixed on the pure state of graphene nano-ribbon. distribution of HOMO and LUMO for these distances remain at pristine graphene nano-ribbon this means no hybridizing also weak interaction between them. Figure 3 represent molecular orbital distributions for pure and interaction state. Results in Table (2) show that the energy gap decreased when interaction increases when gas molecules near-surface and Van der Waals occur. Also, the result indicates when the energy gap decreased in distance near the surface the graphene nano-ribbon has high stability[27]. The result shows that also for distance far from surface energy gap for adsorbed systems remain at pristine graphene nano-ribbon energy gap, in other hand increasing in energy gap ability to sense for gases decreased[28].

D (Å)	CO-HOMO	CO-LUMO
1		
1.5		
2		
2.5		
3		
3.5		
4		

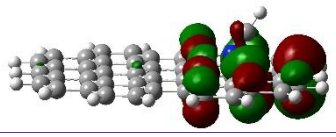
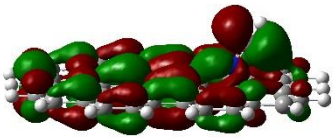
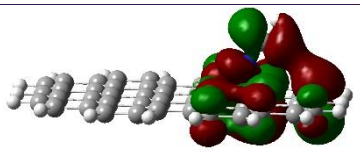
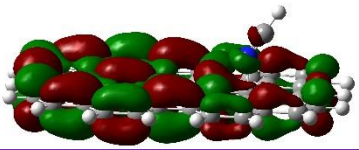
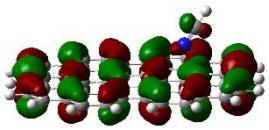
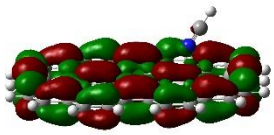
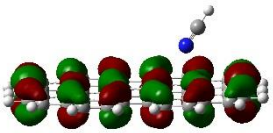
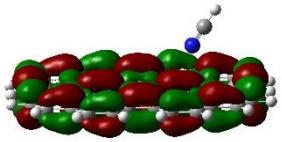
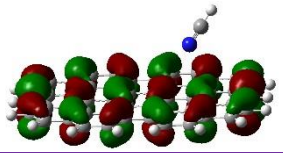
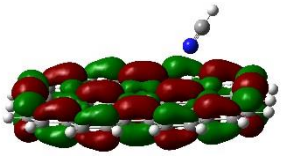
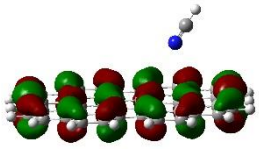
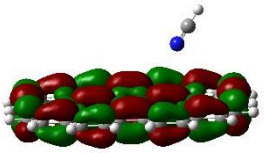
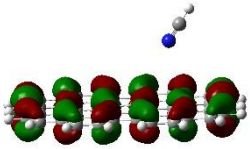
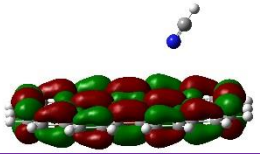
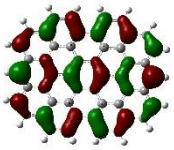
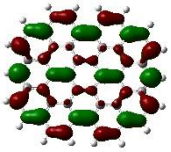
D (Å)	HCN-HOMO	HCN-LUMO
1		
1.5		
2		
2.5		
3		
3.5		
4		
Isolated state		

Figure (3): represent molecular orbital distributions for pure and interaction state.

Table (2): Represent energy gap values for adsorbed molecular system in eV unit.

D (Å)	CO	Transition ratio	HCN	Transition ratio
1	1.588	HOMO->LUMO (95%)	1.172	HOMO->LUMO (95%)
1.5	1.555	HOMO->LUMO (94%)	2.238	HOMO->LUMO (91%)
2	2.505	HOMO->LUMO (92%)	2.568	HOMO->LUMO (95%)
2.5	2.530	HOMO->LUMO (95%)	2.540	HOMO->LUMO (95%)
3	2.532	HOMO->LUMO (95%)	2.534	HOMO->LUMO (95%)
3.5	2.533	HOMO->LUMO (95%)	2.533	HOMO->LUMO (95%)
4	2.533	HOMO->LUMO (95%)	2.533	HOMO->LUMO (95%)

5.4. ***Ultraviolet-visible spectroscopic***

In this part, will be investigating the effect of the gas molecule on optical properties for graphene nano-ribbon, and also determine the type of shifting blue or red. The optical calculation is an important part to determine the type of shifting for adsorption gases on the surface of graphene ribbon[29]. TD-DFT method will be used to compute UV-Visible properties at basis set 6-31G with hybrid function B3LYP. This section used B3LYP because it is a good tool to descried aromatic systems. For pure graphene ribbon maximum absorbed wavelength is equal (525.2) nm. Figure (4) represents UV-Visible spectra for an adsorbed gas molecule on the surface of graphene nano-ribbon are (CO and HCN). The result indicates that all UV-Visible spectra have a redshift. Some gases in the chemical adsorption mechanism appear in a 2 and 3 transition state and this is clear at distances 1 and 1.5 Å. Also, results demonstrate when adsorption distance increases the ability of interaction between the gas molecule and surface decreases. The wavelength of absorption decreased until fit on pure graphene nano-ribbon from this result indicates that interaction strength become vanshing[30].

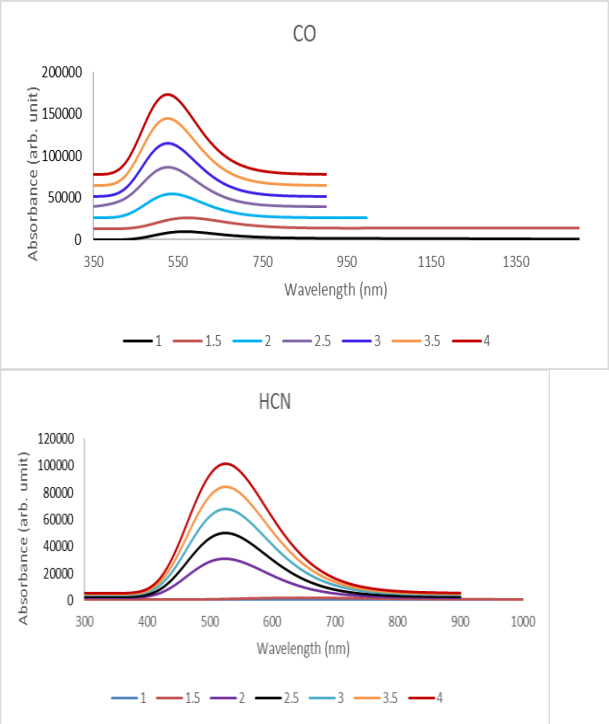


Figure (4): represents UV-Visible spectra for adsorbed gas molecule on surface of graphene nano-ribbon are (CO and HCN).

6. *Conclusions*

In the present study, the DFT method has been used to explain the interaction between toxic gases molecules and the surface of graphene nano-ribbon.

Calculation of adsorption energy shows that graphene nano-ribbon has been sensing for CO gas molecule in chemical interaction more than HCN also, in physical adsorption.

Chemical adsorption effect on molecular orbital energy and it clear in charge distribution around the surface.

As a result of chemical adsorption UV-Visible spectra have been shifted to the red region of electromagnetic radiation, and it gives a base for the design of optical sensors applied in the environmental field.

7. *References*

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