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Adsorption calculations for CH_4 and HCN molecular gas on graphene nano-ribbons: DFT and TD-DFT study

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ABSTRACT

Density function theory calculations used to investigate the ability of graphene nano ribbon to use as gas sensor applications. Relaxation structure, molecular orbitals, energy gap and adsorption energy are calculated by used at basis set 6-31G and hybrid function B3YLP. From the results conclude that graphene nano-ribbon good sensing for toxic gas molecule but in various ratios, for two adsorption types physical and chemical adsorption graphene nano-ribbon sensing two gases but it sensing for Hydro Cyanide (HCN) gas greater than Methane (CH_4) gas. Energy gap change in chemo adsorption mechanism for stander graphene nano-ribbon, change 2.5 eV to (1.17-2.23) eV for HCN gas, (2.08-2.47) eV for CH4 gas with respect to adsorption distance (1, 1.5, …, 4.5) (Å) angstrom, respectively. From these results conclude the effect of chemo adsorption decreasing when adsorption distance increasing. From optical calculation obtains that only in chemical adsorption appear optical shift (red or blue shift), in physical adsorption no any shifting appears. These results show that the graphene nano-ribbon can be used as a gas sensing in atmospheric.

Key words : Energy gap (E_g), Adsorption energy (E_{ad}), Ionization potential, Electron affinity (EA).

1. INTRODUCTION

The discovery of graphene, a single layer of carbon atoms has added a new class of materials to the material family, that of one-atom thickness, two-dimensional materials[1]. Graphene was discovered in 2004 when Geim and co-workers at Manchester University refused single - layer samples from graphite[2]. The electronic, mechanical and thermal properties of graphene are very sensitive to lattice imperfections; therefore, the study of changing in this material is critically important. Furthermore, the other graphene allotropes such as carbon nanotubes (armchair, zigzag and chiral) and fullerenes are investigating enormously[3]. Ideal graphene is a semimetal contains a vanishing density of states at the Fermi energy with remarkably high carrier mobility at room temperature, therefore, single-layer graphene can be considered as a semiconductor with zero energy gap or behave as semi-metallic material[4]. Because of graphene as a two-dimensional material (2D) so that it has sp2 hybrids for carbon atoms arranged like honeycomb lattice. Also, it has an exceptional characteristic such as superior surface to volume fraction, outstanding transport properties and few electrical noises[5]. Graphene a mono atomic layer of graphite considered to be an excellent sensor material[6]. The ability of adsorption and fraction surface to volume of graphene make it an ideal gas sensing material, different atmospheric gases adsorbed on graphene has been investigated simulation and applications[7]. Graphene sensing applications are inspired by the perfect flat structure which makes all atom on the surface exposed to the environment [8]. Electronic characteristic of pure graphene upon adsorption of the different gas molecules on its surface is remembered as one of the essential subjects for improvements of the graphene basis sensor[9]. Charge transfer between the graphene sheet and the gas molecule relates to the direction of the gas molecule with respect to the graphene ribbon[10].

2- SIMULATION TOOL

Optimization structure, electronic state, adsorption energy and transition energy calculations are computed using density functional theory (DFT) for the ground state and for excitation state use time depending – density function theory (TD-DFT), Gaussian package 09, basis set at level 6-31G hybrid function B3LYP. Firstly, computed most geometrical structure between the gas molecule and surface of the graphene ribbon, change the distance between the gas molecule and surface of the ribbon. Also, determination type of adsorption between a gas molecule and ribbon if it physical or chemical adsorption. Finally, calculate UV-Visible properties for graphene nano-ribbon with an adsorbed gas molecule.

3- THEORETICAL BACKGROUND

First density functional theory was published by Thomas[11] and Fermi[12] in the 1920s. In the idea of this approach was the density of electrons n(r) that measured instead of the position of electrons. It was not accurate enough as it neglects

the quantum corrections to the Coulomb potential which will later introduce as exchange and correlation. It proposed an expected value of the kinetic term in the H operator that depends solely on the density. This approach is acceptable only in high electron density metals where the quantum corrections to the Coulomb potential can be neglected. In the 1960s complete the new formalism which proposed by Kohn and Sham[13] that sparked a new era in physics. It provides many results that are in accordance to results from experiments in various fields such as crystals, biophysics, molecular physics and many more. Hohenberg and Kohn in 1964 showed that the ground state of a many electron system can be determined by the ground state electron density ρ(r) [14]. (DFT) is built on two fundamental theorems [15].

Theorem I: The ground state energy of a many-electron system is a unique, universal functional of ground state electron density ρ(r).

Theorem II: The functional of ground state energy is minimized by the ground state electron density ρ(r) for a many-electron system.

The ground state energy functional E_V can be described as [16]:

$$E_V[\rho] = \int \rho(\vec{r}) V_{ext}(\vec{r}) d\vec{r} + F_{HK}[\rho] \quad (1)$$

The external potential $\hat{V}_{ext}$ is uniquely defined by the electron density ρ($\vec{r}$). The total energy can be written as[17]:

$$E_o = T[\rho_o] + \int V_{ext}(r)\rho_o(r)dr + J[\rho_o] + E_{NC}[\rho_o] \quad (2)$$

Where T[ρ_o] is the kinetic energy, E_{NC}[ρ_o] is the non-classical electron–electron interaction energy and J[ρ_o] is the classical coulomb energy defined as:

$$J[\rho_o] = \frac{1}{2} \frac{\rho_o(r1)\rho_o(r2)}{|r1-r2|} dr1dr2 \quad (3)$$

V_{ext} directly depends on the system and it is simply the coulomb potential of the nuclei. Therefore, the total energy can be written as:

$$E_o = \int V_{ext}(r)\rho_o(r)\, dr + F_{HK}[\rho_o] \quad (4)$$

Where F_{HK} is a universal functional of the electron density:

$F_{HK}[\rho] = T[\rho]+J[\rho]+E_{NC}[\rho]$

Hohenberg-Kohn theorem assumes that F_{HK} exists, but the actual form of F_{HK} is unknown and must be approximated.

adsorption energy.

$$E_{ad}=(E_{gas} + E_{ribbon})-E_{gas\text{-}ribbon} \quad (5)$$

Where E_{ad} adsorption energy, ($E_{gas+}E_{ribbon}$) total energy for adsorption system, E_{gas} total energy of molecular gas and E_{ribbon} total energy of ribbon measured in electron volt unit (eV). From this equation it can be express the type of adsorption if it chemical or physical adsorption[16,19].

Relaxation distance between gas molecule and graphene nano ribbon surface was computed by (DFT) with basis set 6-31G and hybrid function is B3YLP. Relaxation adsorption distance for CH4 gas molecule is 3.55 Å and the adsorption energy is 0.0027 eV. HCN relaxation distance is 3.86 Å and the adsorption energy is -0.0299 eV. The result shows that sensitivity on these distance is very weak, in the other hand graphene nano ribbon capture gas molecules in different ratios [18].

To investigate the sensitivity of graphene nono ribbon for a gas molecule by change adsorption distance between two reaction system the adsorption energy will be. Table 1 listed the energy of adsorption with respect to the distance. Explain that the adsorption process becomes more negative value when decreasing distance from 4.5 to 1 Å with split step is 0.5. So that the CH_4 has chemical adsorption in distance less than 1.5 Ang where the stander bond length between the carbon and hydrogen atom is 1.008 Å[17] and for HCN the distance less than 2 Å where the stander bond length between the carbon and Nitrogen atom is 1.45 Å[17]. The result shows the adsorption process from the computed result for relaxation adsorption distance. Also, the result proves the adsorption mechanism is physical. Physical adsorption appears because the distance between gases molecule and graphene nano ribbon are grater than a length between C-H and C-N in CH_4 and HCN gases respectively[20]. A condition of chemical adsorption is the distance between gas molecule and graphene nano ribbon (d) is equal or less bond length of atom in the gas molecule[20]. Chemical adsorption occurs where the distance between gases molecule and graphene decreased between 1 and 1.5 Å. The result shows that HCN gas molecule chemical adsorption at 1 and 1.5an and CH4 only in 1 ang. HCN chemically adsorption greater than CH4 shows in table 1. it sensitivity for HCN gas molecule more than CH_4 gas molecule in two types of adsorption mechanism. A negative number means charge transfer from graphene to gas molecules[14]. Results show that the graphene nano ribbon sensing for the two gases but in difference ratio as shown in Figure 1.

More negative adsorption energy gave high adsorption of gas molecule on graphene nano ribbon[19].

Table 1: listed the values of adsorption energy measured in eV unit.

	Adsorption energy (eV)	
Distance (Å)	CH_4	HCN
1	-7.3088	-19.2980
1.5	-2.1496	-5.9456
2	-0.5278	-1.8585
2.5	-0.1034	-0.4000
3	-0.0136	-0.07891
3.5	0.0015	-0.03265
4	0.0027	-0.02993
4.5	0.0006	-0.02993

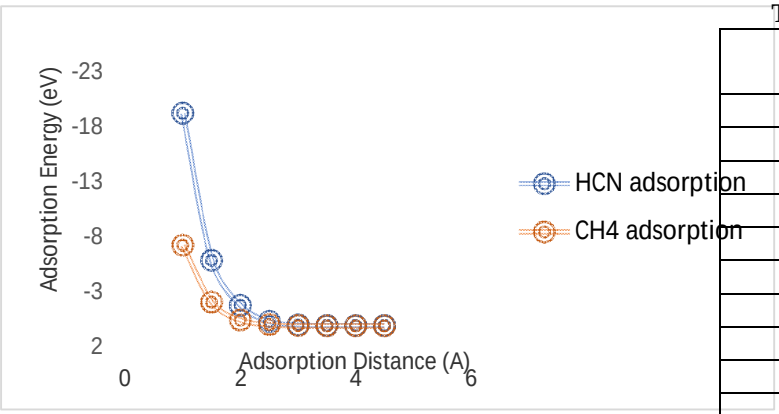

Figure 1: represent adsorption energy as function of distance for HCN and CH_4 molecular gases

4. MOLECULAR ORBITALS AND ENERGY GAP

Tables 2 and 3 listed the frontier orbitals Higher Occupied Molecular Orbitals (HOMO) and Lower Unoccupied Molecular Orbitals (LUMO) and energy gap (Eg) without and with gases molecule. For pure graphene nono ribbon, the molecular orbitals (HOMO and LUMO) localized a round C-C bond. After adding gas molecules, the distribution of molecular orbitals changed. Figures 2 and 3 show curves of molecular orbitals energy and energy gap respectively for the system under study. Figure (4) show the distribution of HOMO and LUMO orbitals for HCN and CH4 for different distance respectively (in appendix). The energy gap calculates from equation 7[17]. Results indicate the energy gap becomes smaller when gas molecules adsorbed chemically also LUMO is increasing and HOMO decreased. Physical adsorption shows that molecular orbital distribution only around graphene nano ribbon. Molecular orbitals energy at physical adsorption has energy approximately equal for pure graphene nano ribbon.

E_g= LUMO-HOMO (7)

Table 2: listed values of HOMO and LUMO.

	HOMO (eV)		LUMO (eV)	
D. (Å)	CH4	HCN	CH4	HCN
1	-4.376	-3.653	-2.289	-2.481
1.5	-4.767	-4.188	-2.290	-1.950
2	-4.793	-4.660	-2.269	-2.091
2.5	-4.791	-4.652	-2.257	-2.111
3	-4.787	-4.654	-2.253	-2.119
3.5	-4.785	-4.662	-2.251	-2.128
4	-4.768	-4.671	-2.234	-2.136
4.5	-4.783	-4.677	-2.249	-2.144
Pure G	-4.781		-2.247	

Table 3: listed values of energy gap for nano-system.

	Energy Gap (eV)	
D. (Å)	CH4	HCN
1	2.086	1.172
1.5	2.477	2.238
2	2.524	2.568
2.5	2.532	2.540
3	2.533	2.534
3.5	2.533	2.533
4	2.533	2.533
4.5	2.533	2.533
Pure G	2.533	

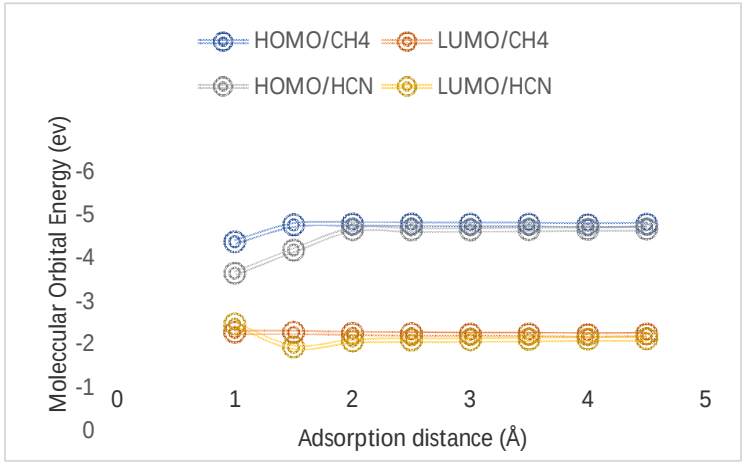

Figure 2: represent curves of molecular orbitals energy.

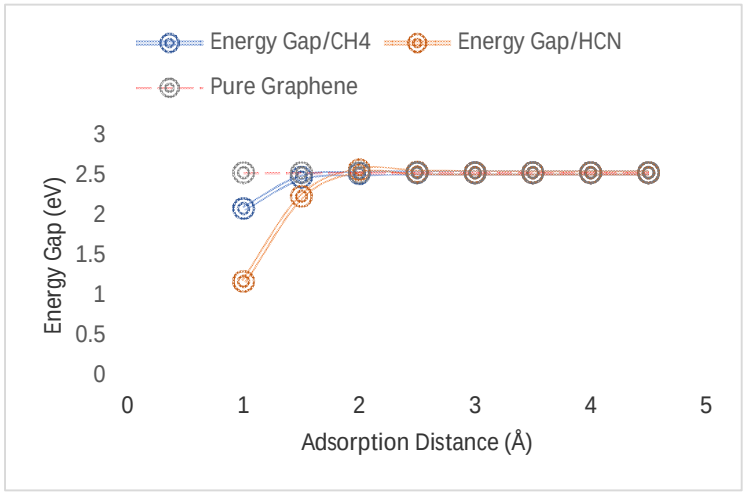

Figure 3: energy gap curves for adsorbed system.

5- OPTICAL PROPRIETIES

One of the important characteristics of optical proprieties is known as the shift that occurs in UV-Visible spectra. To determine the adsorption if it chemical or physical type. The change in adsorption height between a gas molecule and graphene nano ribbon cause shift in UV-Visible spectra.

Figures 5 and 6 represent UV spectra for two gases adsorbed on the graphene nano ribbon surface. Figures show that the HCN gas molecule has a red shift and CH_4 has a blue shift resulting from chemical adsorption. Physical adsorption for gases shows there are no shift and UV spectra computed fixed on the value of pure graphene nano ribbon[21][22].

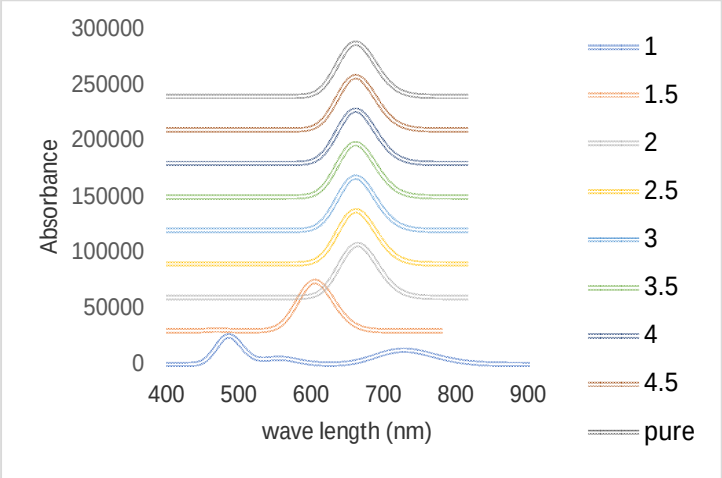

Figure 5: represent UV spectra for CH_4 gas molecule adsorbed on graphene nano ribbon.

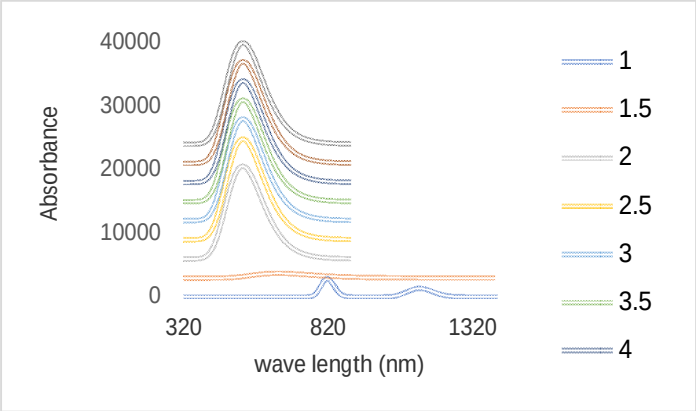

Figure 6: represent UV spectra of HCN gas molecule adsorbed on graphene nano ribbon.

6- CONCLUSIONS

1 Geometrical structure for pure graphene is agreement with experimental study.
2 Orientation of gas molecule agreement with past study.
3 Chemical adsorption obtains that HCN gas molecule is strongest than CH_4, also in physical adsorption.
4 Only in chemical adsorption appearing a shift in UV spectra for two studied gases.
5 Graphene nano ribbon has a good sensitive for the two studied gases.

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Appendix

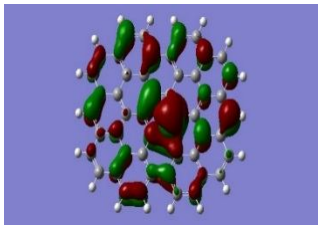
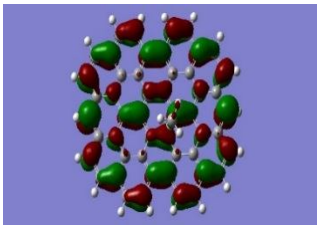
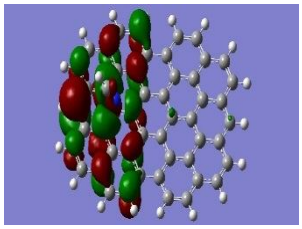
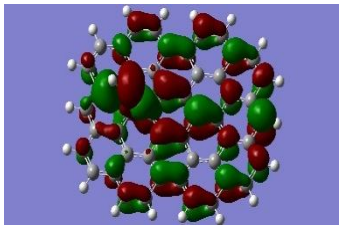
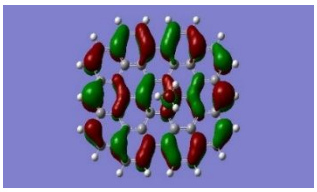
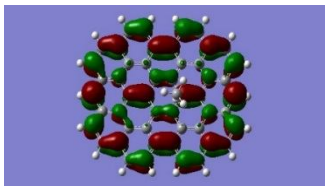
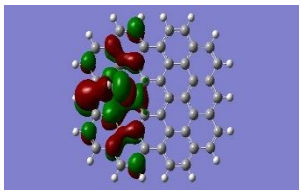
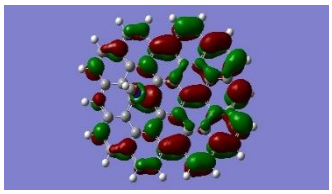
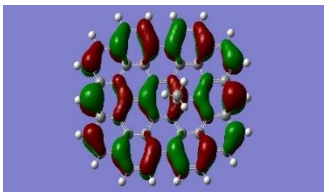
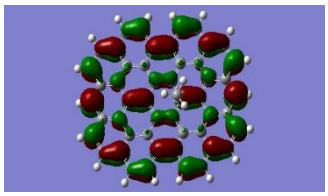
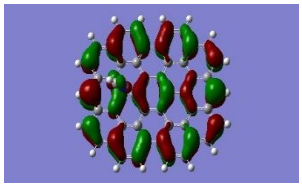
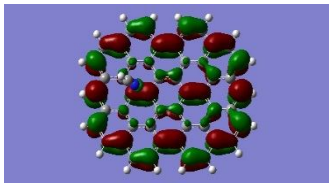
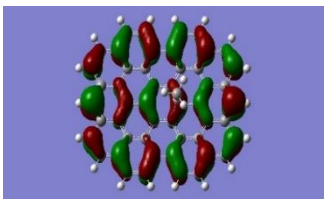
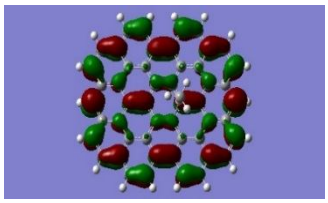
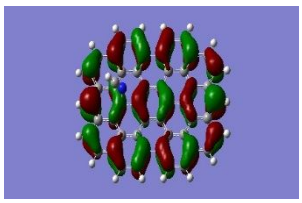
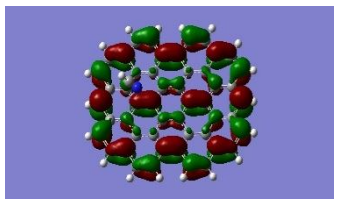
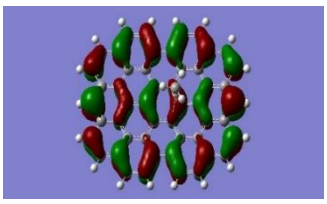
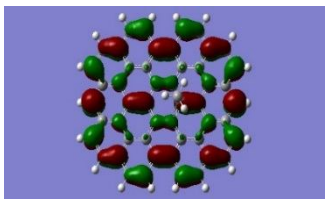
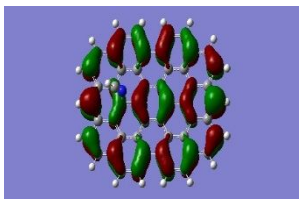
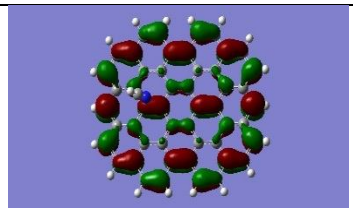
Disc.	Molecular Orbital for CH_4 Adsorption		Molecular Orbital for HCN Adsorption	
D (Å)	HOMO	LUMO	HOMO	LUMO
1				
1.5				
2				
2.5				
3				

Figure 4*:* HOMO & LUMO distribution