

Design Pollution Gas Sensor Using Graphene Ribbon: Density Function Theory (DFT)

Ruaa.S. Al-Hasnawy

Department of medical physics, Al-Mustaqbal University College, Babylon, Iraq

Ali S. Shaker

Iraqi Ministry of Health

Muntather H Albosaabar (✉ muntather84_iq@yahoo.com)

Iraq Ministry of Health <https://orcid.org/0000-0003-2054-9650>

Zahraa A. Al-Maamouri

Iraq Ministry of Health

Hamed A. Al-taee

Iraq Ministry of Health

Research Article

Keywords: Adsorption Energy, DFT, Energy Gap, HOMO, LUMO

Posted Date: July 19th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-484512/v1>

License:  This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Version of Record: A version of this preprint was published at Optical and Quantum Electronics on January 1st, 2022. See the published version at <https://doi.org/10.1007/s11082-021-03415-8>.

Design pollution gas sensor using graphene ribbon: Density Function Theory (DFT)

Ruaa.S.Al-Hasnawy¹, Ali S. Shaker², Muntather H. Albosaabar^{2,3}, Zahraa A. Al-Maamouri², Hamed A. Al-tae²

¹ Department of Medical Physics, Al-Mustaqbal University College, Babylon, Iraq,

² Iraqi Ministry of Health, Babil Health Directorate, Imam Sadiq Educational Hospital, Babylon, Iraq, ³ Department of Diagnostic Imaging & Radiotherapy, Faculty of Health Science, National University of Malaysia, Jalan Raja Muda Abdul Aziz, 50300, Kuala Lumpur, Malaysia

*Corresponding author: muntather84 iq@yahoo.com

Abstract

Density Function theory (DFT) calculation used to employed ground and excitation states for graphene ribbons, types of adsorption, energy gap, maximum wave length and optical band gap. Adsorption energy showed that CO₂ gas molecule have chemical adsorption in distance 1 and 1.5 Angstrom, distance 2 and 2.5 Angstrom appear physical adsorption, adsorption energy decreased when distance between surface and gas molecule increasing. Resulting from chemical adsorption energy gap change with distance 1 and 1.5 Angstrom because attract gas molecule with surface. Excitation energy for nano system in sample 1 and 4 shifted to low wavelength (blue shift) change from 1018 nm to 993 nm and 718 nm on series. Other sample have red shift and energy gap becoming open. Result showed that graphene ribbon sense carbon dioxide gas (CO₂).

Keywords: Adsorption Energy, DFT, Energy Gap, HOMO, LUMO.

1- Introduction

Graphene as a two dimensional material (2D) sp^2 hybrids for carbon atoms arranged like honeycomb lattice, graphene have exceptional characteristic such as superior surface to volume fraction, outstanding transport properties and few electrical noise[1]. Graphene a mono atomic layer of graphite considered to be an excellent sensor material[2]. 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 [3]. Graphene sensing applications are inspired by perfect flat structure which make all atom on surface exposed to the environment[4]. Electronic characteristic of pure graphene upon adsorption of different gas molecule on its surface is remembered as one of the essential subjects for improvements of graphene basis sensor [5]. Charge transfer between graphene sheet and the gas molecule relates to the direction of gas molecule with respect to graphene ribbon [6].

2- Simulation details

Optimization structure, electronic state, adsorption energy and transition energy calculations are computed using density function theory (DFT). Ground state calculation provide geometrical structure, molecular orbitals and adsorption energy. Excitation state computed by time depending-density function theory (TD-DFT). basis set using in present study is 6-31G and hybrid function B3LYP. Firstly, computed most geometrical structure between gas molecule and surface of graphene ribbon, change the distance between gas molecule ad surface of ribbon. Also determination type of adsorption between gas molecule and ribbon if it physical or chemical adsorption, finally computed ultra violet – visible spectra (UV-Visible).

3- Theoretical Background

The Schrödinger equation, which was proposed by Erwin Schrödinger in 1925, is central to the development of the theory of quantum mechanics. Any problem in the electronic structure of matter is covered by Schrödinger equation [7]:

$$\hat{H} \Psi = E \Psi \quad (1)$$

Where Ψ is the wave function, it expresses the mathematical form of the de Broglie wave associated with the particle, \hat{H} is the Hamiltonian operator, and E is the total energy of the system. Once the Schrödinger equation is solved, all electronic properties of the system can be calculated. The Hamiltonian operator, H , consists of two terms the kinetic energy of the electrons and the nuclei (T) and potential energy components (V) [8]:

$$\hat{H} = \hat{T} + \hat{V} \quad (2)$$

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{ne} + \hat{V}_{ee} + \hat{V}_{nn} \quad (3)$$

Where (\hat{T}_e) and (\hat{T}_n) are the kinetic energy operators of the electrons and nuclei, respectively. (\hat{V}_{ne}) the coulomb attraction between the nuclei and electrons, (\hat{V}_{ee}) the coulomb repulsion between electrons, (\hat{V}_{nn}) the coulomb repulsion between nuclei [9].

The kinetic energy operators are represented as:

$$\hat{T}_e = - \frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 \quad (4)$$

$$\hat{T}_n = - \frac{\hbar^2}{2 M_A} \sum_A \nabla_A^2 \quad (5)$$

Where: m_e and M_A are the electron and nuclear mass, respectively, ∇_i^2 is the laplacian operator of i electrons, which in Cartesian coordinates has the form:

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \quad (6)$$

The potential energy operators are represented as:

$$\hat{V}_{ne} = - \sum_A \sum_i Z_A \frac{e^2}{r_{Ai}} \quad (7)$$

$$\hat{V}_{ee} = \sum_{i<j} \frac{e^2}{r_{ij}} \quad (8)$$

$$\hat{V}_{nn} = \sum_{A<B} Z_A Z_B \frac{e^2}{R_{AB}} \quad (9)$$

Where $r_{ij} = |\vec{r}_i - \vec{r}_j|$ and Z_A is the charge of nuclei A, r_{Ai} is the distance between nucleus and electron, r_{ij} is the distance between i electron and j electron and R_{AB} is the distance between A nucleus and B nucleus [10].

The first major step in simplifying the general molecular problem in quantum mechanics is the Born-Oppenheimer approximation. This approximation is based on the fact that the nuclear masses are much greater than those of the electrons. Therefore, nuclei move much more slowly and they are nearly fixed compared with the electrons motion [11].

4- Result and discussion

We used equation (1) for calculation adsorption energy E_{ad} for system [12]:

$$E_{ad} = (E_{ribbon} + E_{gas}) - E_{gas+ribbon} \quad (10)$$

(E_{ribbon}) total energy for graphene ribbon before interaction, (E_{gas}) total energy for gas molecule and ($E_{isolated\ ribbon} + E_{gas}$) total energy for graphene ribbon and gas molecule during adsorption in electron volt unit (eV).

1- Relaxation Structure and Adsorption Energy

We calculated most relaxation between gas molecule in this case CO₂ gas, the most distance equal (3.64) Å with adsorption energy (3.003) eV, this value represents physical adsorption because distance between CO₂ gas molecule and surface of graphene ribbon is greater than covalent bond between carbon-carbon bond is equal (1.4600) Ang. Value calculated is modification in physical adsorption in study[12], that computed adsorption energy for most relaxation is -0.148 eV. After that study effect of distance on adsorption energies between gas molecule and ribbon the distance equal (1, 1.5, 2 and 2.5) ang., table 1 explain the adsorption energy for CO₂ as function of distance.

Table 1 explain the adsorption energy for CO₂ as function of distance between gas molecule and surface of graphene ribbon.

Distance (Å)	Adsorption Energy (eV)
1	-37.4804314
1.5	-29.1021645
2	-10.6014056
2.5	-3.0612375

From the table (1) we conclude that gas molecule in distance 1 and 1.5 have higher adsorption energy, the C-C length bond equal 1.43 (aromatic) for present study that agreement with[9], nearest gas molecule to graphene surface resulting high adsorption energy high interaction between gas and nano system. In distance 1 Å result show that high adsorption energy because the gas molecule is became close to graphene surface also oxygen atoms attract with carbon atom related to graphene ribbon. attract oxygen atom increasing adsorption energy and chemical interaction become very high. in this case chemical adsorption. For distance 1.5 Å, the gas

molecule distance reached approximately from C-C bond and the adsorption energy become (-29.1021) eV. This result show that gas molecule adsorption chemically. For distance 2 and 2.5 became grater from C-C covalent bonding and the energy decreased rabidly with increase distance between gas molecule and graphene ribbon surface. in other hand high adsorption distance low adsorption energy. Increasing in adsorption distance change case of interaction energy from high to low chemical adsorption. Graphene nano ribbon sense CO₂ gas molecule chemically[12].

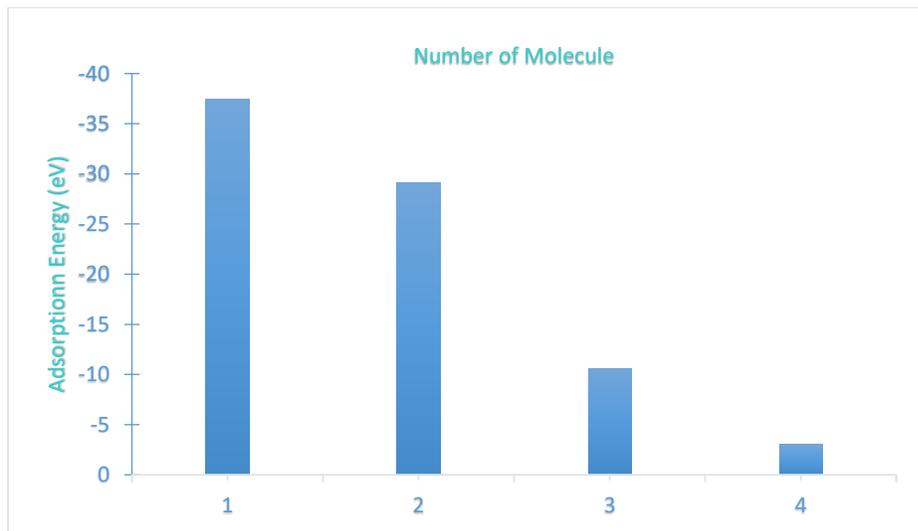


Fig (1) adsorption energy for molecule under study

2- Electronic State and Energy Gap

Molecular orbitals (HOMO) Higher Occupied Molecular Orbitals and (LUMO) Lowest Unoccupied Molecular Orbitals was show in figure (2), energy gap calculated from equation 2. It can be seen that molecular orbitals for pure graphene ribbon distribution around C-C bond for each HOMO and LUMO when gas molecule is absence. After gas molecule adsorption o surface of graphene ribbon, gas molecule attracted with surfaces and molecular orbitals localized around gas molecule for distance 1 and 1.5 Å. This disruption refer to high chemical adsorption between gas molecule and ribbon, also formation the

chemical bonding[13]. For distance 2 and 2.5 Å. The distribution of frontier molecular orbitals is becoming vanishes gradually and most molecular orbitals localized around graphene ribbon, few molecular orbitals distribution around gas molecule, result show that because low chemical adsorption between reacting system allow transfer small amount of charge but don't made any change in structure. Result of energy gap for pure graphene was 1.1 eV and this result agreement with[13]. Beginning interaction energy at distance near surface energy gap change because high chemical adsorption. Bonding that formed between gas molecule and atom related to graphene ribbon platy important role of electron transport between band. Increasing in adsorption distance the chemical adsorption energy decreased and band gap value fitted approximately to isolated graphene nano ribbon. Result show that at strong chemical adsorption band energy become very close and energy gap become opening. Table 2 listed HOMO, LUMO and Energy Gap (E_g) measuring in electron volt unit. Figure 2 graphene ribbon under study, Figure 3 HOMO and LUMO values, Figure 4 energy gap values and figure 5 molecular orbitals distribution.

$$E_g = (\text{LUMO} - \text{HOMO}) * 27.211 \text{ eV unit} [12] \quad (11)$$

Table 2: HOMO, LUMO and Energy Gap (E_g) measuring in electron volt unit

Molecule	Occ. eV	Vert. eV	E_g eV
1	-3.5529	-3.1036	0.449
2	-3.7102	-3.1725	0.537
3	-3.9616	-2.9883	0.973
4	-4.0636	-2.9842	1.079
5	-4.0979	-2.9926	1.105

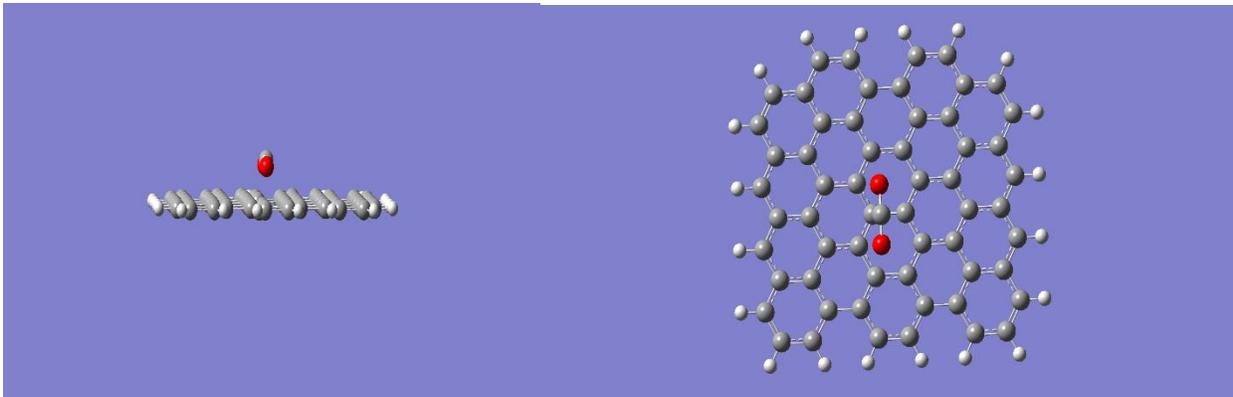
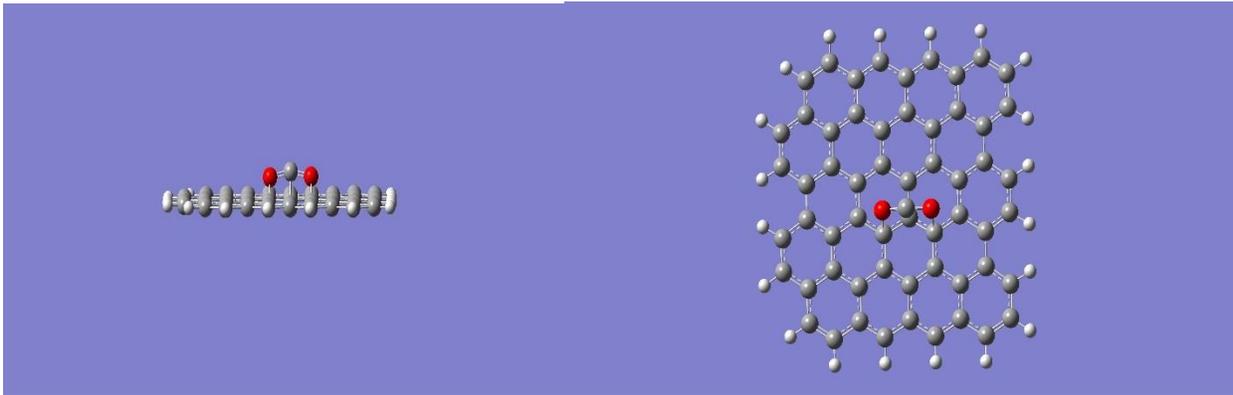
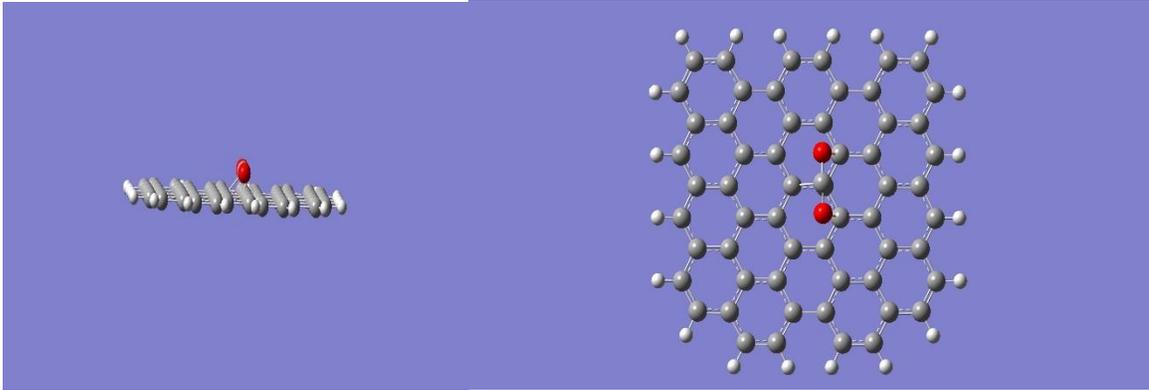




Figure 2: represent graphene nano ribbon under study that adsorption with gas molecule, adsorption distances was 1, 1.5, 2 and 2.5 on series. Red ball is Oxygen atom, Gray ball is Carbon atom and White ball is Hydrogen atom.

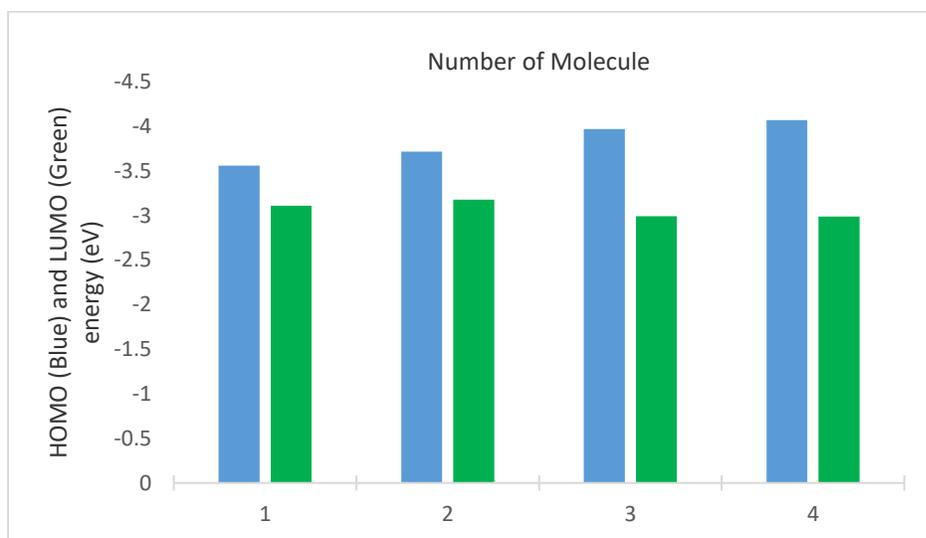


Figure 3 HOMO and LUMO values, Blue bar is HOMO energy and Green bar is LUMO energy measuring in eV unit.

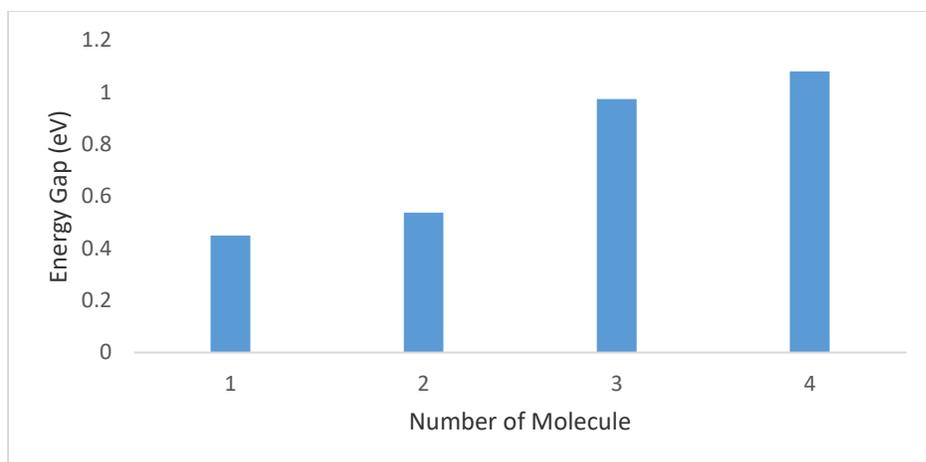
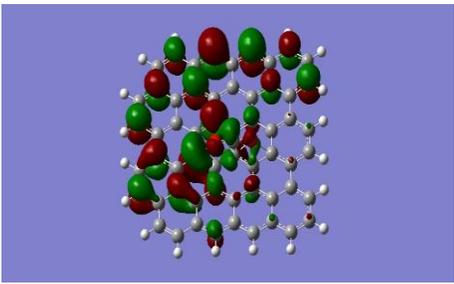
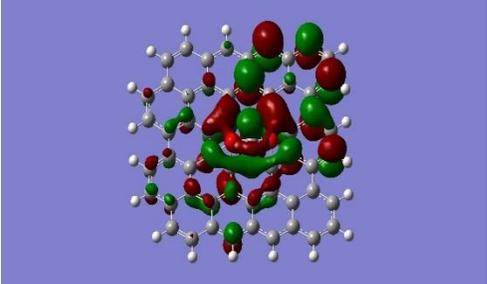
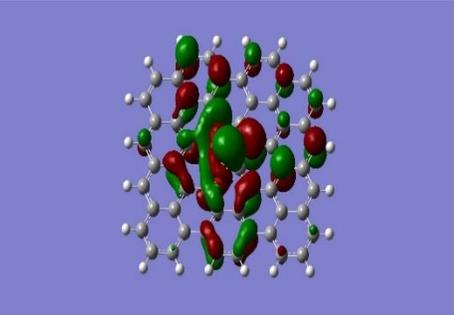
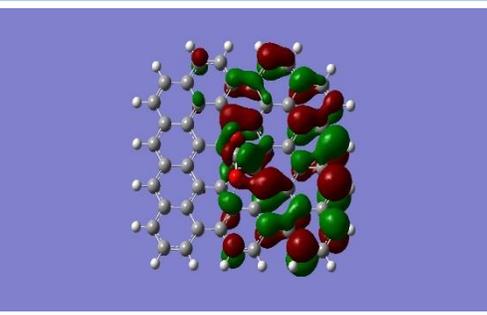


Figure 4: energy gap values Blue bar represent Energy gap values in eV unit.

D (Å)	HOMO	LUMO
1		
1.5		

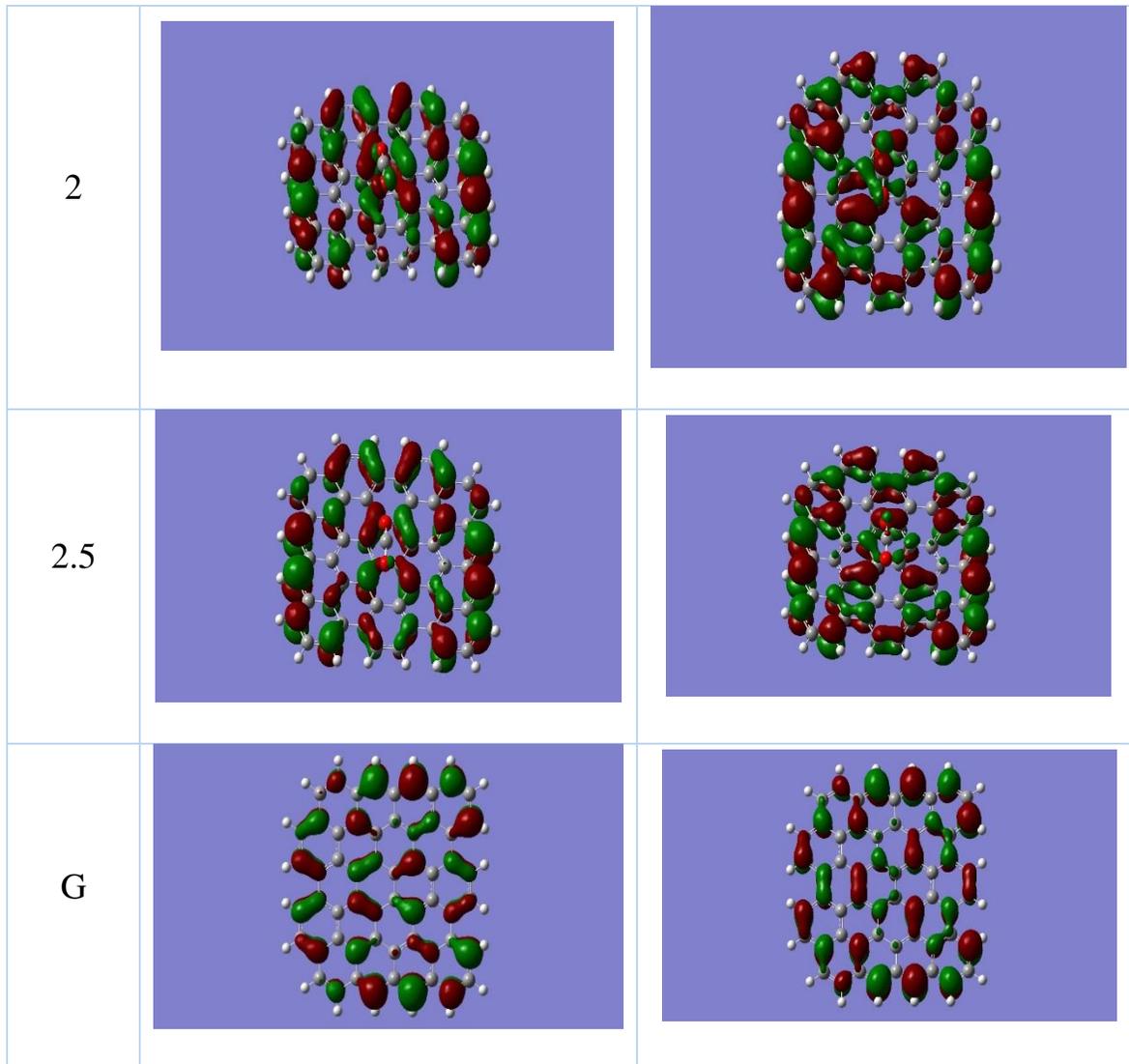


Figure 5: HOMO and LUMO distribution for graphene ribbon adsorbed with CO₂ gas molecule for distance 1, 1.5, 2 and 2.5. Green colour represent positive charge and red colour represent negative charge. Pictures listed HOMO and LUMO on series for all graphene ribbon

3- Optical proprieties

We used TD-DFT calculation to obtain UV-Visible properties improving basis set 6-31G hybrid function B3LYP, firstly for isolated system and change the distance between gas molecule and graphene ribbon. Finally calculated maximum wave length (λ_{\max}) and optical band gap, also shifting for UV-Visible spectrum.

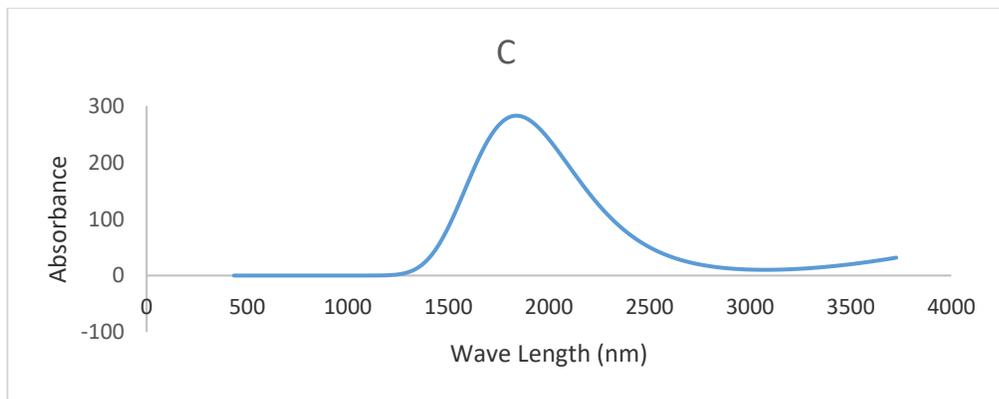
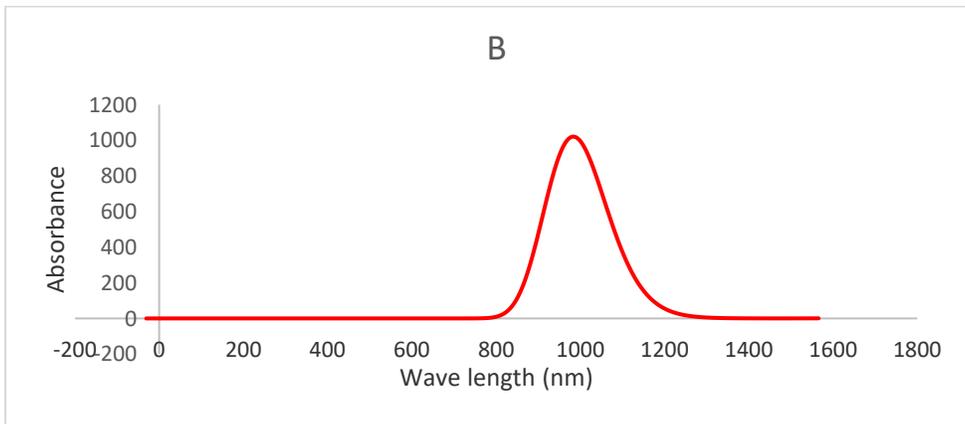
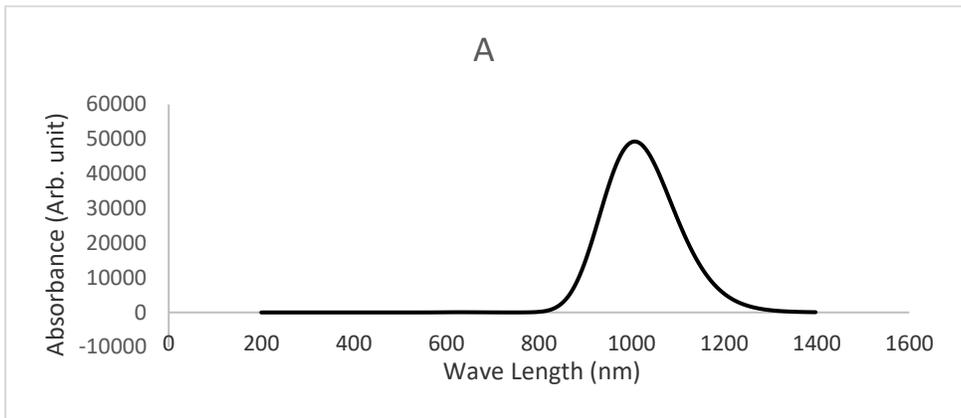
We can calculate optical band gap from equation 3 as follow[14]:

$$E_{g(\text{optical})} = 1240/\lambda_{\text{max}} \quad (12)$$

For Isolated graphene ribbon maximum wave length (λ_{max}) is equal 1018 nm with optical band gap 1.22 eV, absorbance wave length in infrared near from visible light. Distance 1 Å. Wave length shifted towered red region of electromagnetic radiation with 993 nm and optical band gap energy 1.24 eV[13]. Result show that increasing in excitation energy because the high chemical interaction between gas molecule and graphene ribbon. For 1.5 maximum wave length equal 1859 nm with optical band gap 0.67 eV, conclude that small excitation energy and UV-Visible shift towered long wave length. Distance 2 Å. appear three peak one is 750, 1118 and 1270 nm with optical band gap is 1.63, 1.11 and 0.97 eV, different in absorbance, optical spectrum shifted towered low wave length with high excitation energy. Finally, distance 2.5 we obtain max wave length 1048 nm and excitation energy 1.18 eV we conclude that because the physical adsorption the effect of gas molecule is vanished, max wave length reached approximately pure graphene ribbon, also peak in low absorption with wave length 718 nm with excitation energy 1.73 eV. The calculation that concluded have same behavior with study in[14].

Table 3 listed the maximum wave length (λ_{max}) and optical band gap

Molecule	Max. wave length (nm)	Optical Gap (eV)
A	and 1018	1.22
B	993	1.24
C	1859	0.67
D	750, 1118 and 1270	0.97
E	718 and 1048	1.18



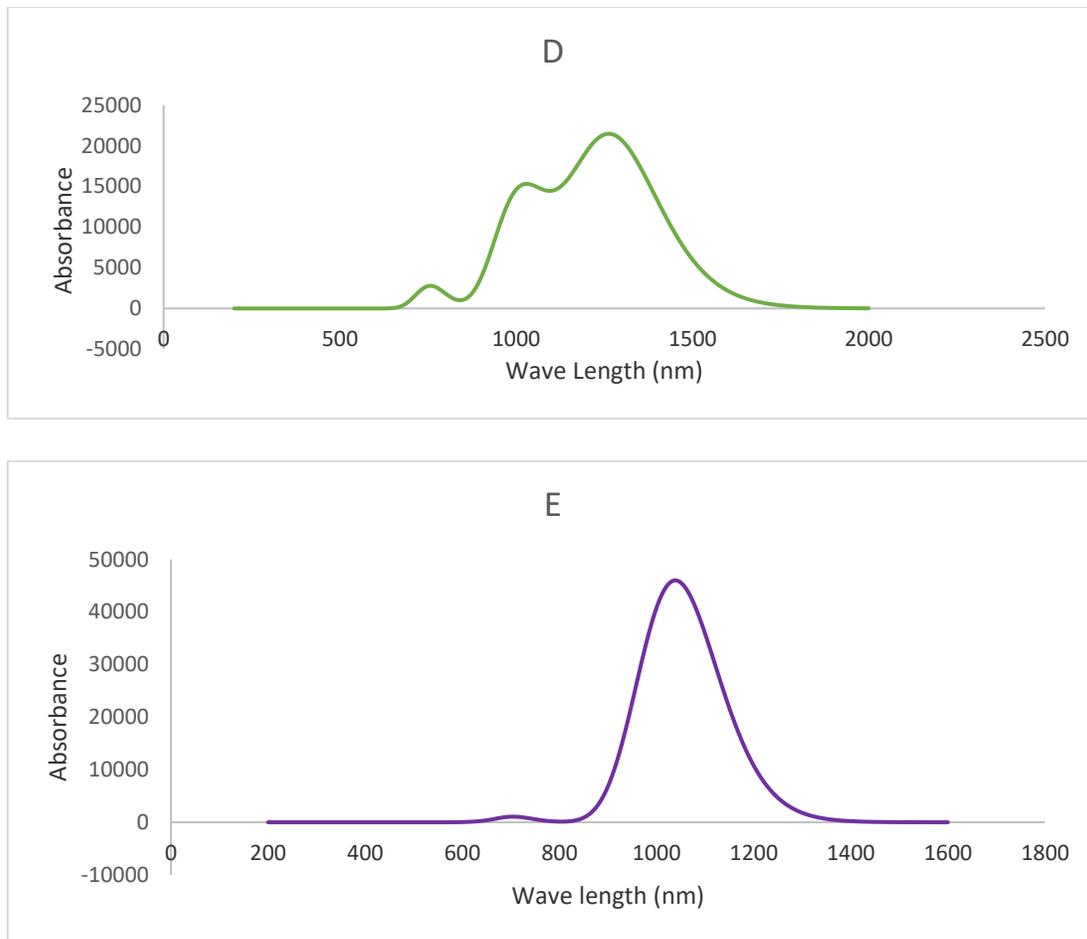


Figure 5 listed optical spectrums for graphene ribbon A for pure graphene, B for 1 Ang., C for 1.5 Ang., D for 2 Ang and E for 2.5 Ang.

4- Conclusions

- Result of geometrical. Electronic and optical proprieties of graphene material was agreement with experimental result.
- Chemical bond formed when gas molecule near the surface of graphene ribbon.
- Calculation of adsorption energy show that CO₂ gas molecule intract chemically with graphene nano ribbon.
- Increasing in adsorption distance the chemical interaction decreased.

- UV-Visible calculation shows that high interaction between gas molecule in surface, the spectrum shifted from red to blue region of electromagnetic radiation.

5- References

- 1- Harper, D.B. Nature 315, 55, (1985).
- 2- Ao. Z M, Jang J, Li S et al., **“Enhancement of CO detection in Al doped graphene”**, Chemical Physics Letter, 461(4), (2008).
- 3- Novikov S., Lebedeva N. et al., Sens. 2015, 108581, (2015).
- 4- Yu S., Wang X. et al **“Boron – Ntride based materials for removal of pollutants from aqueous solutions,”** a review. Chem. Eng. J., 333, p.p. 343-360, (2018).
- 5- Yavari F., Koratkar N., Physica B 427 (12), (2013).
- 6- Leenerarts O., Partoens B., et al **“Adsorpton of H₂O, NH₃, CO, NO₂ and NO₂ on graphene: A first principle study”**, Physical Review B : 77(12), 125416, (2008).
- 7- Tang, C. L. **“Fundamentals of Quantum Mechanics for Solid State Electronics and Optics”**, NY publishes, Ithaca, (2004).
- 8- Hameka H. F. **“Quantum Mechanics: A Conceptual Approach”**, Leiden University, John Wiley & Sons, Inc., (2004).
- 9- Cox. A. **“Introduction to Quantum Theory and Atomic Structure”, Lecture in Organic Chemistry”**, University of Oxford, (1995).
- 10- FITTS D. D. *“ Principles of Quantum Mechanics: as Applied to Chemistry and Chemical Physics”*, Cambridge University Press, New York, (2002).

- 11- Cox P. A. *"introduction to Quantum Theory and Atomic Structure"*, Oxford University Press Inc., New York, (1996).
- 12- Ali Shokuhi Rad, **"Al-doped graphene as a new nanostructure adsorbent for some halomethane compound: DFT calculations"**, Surface Science 645 p.p. 6-12, (2016).
- 13- Batzill M., and Diebold U., Phys. Chem. Chem. Phys. 9 2307, (2007).
- 14- Raeyani D., Shojaei S., Ahmadi-Kandjani S., **"Optical Graphene Quantum Dots Gas Sensors: Theoretical Study"**, Super Lattices and microstructure, p.p. 3, (2017).