طاقة الامتزاز لجزيء اول اوكسيد الكاربون في اشرطة الكرافين/بورون نترايد بواسطة مبدأ الطاقة الاولي

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Adsorption energy for CO gas molecule in graphene/boron-nitride nano-ribbon using first principle study

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Abstract:

In this paper density function theory (DFT) and time-depending (TD-DFT) utilizing to compute ground state and excitation proprieties for graphene/boron-nitride nano-ribbon. Ground state calculation explains all bonded length for relaxation system are agreement with an experimental study. Energy gap for two nano system in a range of semiconductor devices that able use at the sensor of gas. Adsorption energy for system Graphene/CO is more stable from system B-N/CO system, this result appear for distances more than 1.5 Angstrom some of adsorption energy reached 0 eV and take positive value. Reverse from system Graphene/CO began from 15.5 eV and steady on 2.2 eV. Optical proprieties showed the nearest distance between two reactant 1 and 1.5 Angstrom graphene/CO system shifted towered infrared spectrum region and back to the stable state when distance increasing between graphene nano-ribbon, B-N/CO system by interaction with gas molecule shifted towered blue-shifted also when gas molecule go far from ribbon UV_Visible shifted to violet spectrum. FTIR spectrum proved chemical adsorption by appearing peak of CO gas molecule.

Keywords: Energy Gap, Boron-Nitride, Graphene, Adsorption Energy and Excitation Energy.

الملخص:

تم في هذه الورقه البحثيه استخدام نظريه الداله الوظيفية لحسابات الحاله الارضيه والحالة المتهيجة باستخدام الداله المعتمده علي الزمن. حسابات الحالة الارضيه بينت ان جميع اطوال الاواصر متفقه مع الحسابات العملية. فجوات الطاقة المحسوبه ضمن مدى النبائط التي تعمل كواشف للغاز. غاز احاي أوكسيد الكاربون مستقر اكثر في الكرافيين قياسا بالبورون نترايد. ظهرت بعض القيم الموجبه لعملية الامتزاز وكذلك تلاشي الطاقه بقيمه صفر الكترون فولط. حسابات الاشعه فوق البنفسجيه بينت ان الطيف يزاح الي المنطقه تحت الحمراء في امتزاز الكرافيين وللمنطقه البنفسجية في البورون–نترايد. حسابات الاشعه تحت الحمراء اثبتت اليه التفاعل الكيميائي باظهار قمه غاز احادي أوكسيد الكاربون ضمن التراكيب.

الكلمات المفتاحية: فجوة الطاقة ، البورون – نيتريد ، الجرافين ، طاقة الامتزاز وطاقة الإثارة.

1. Introduction

Graphene two-dimensional materials arranged carbon sheet is an excellent material that has ideal proprieties such as the fraction of volume to the surface, few electric noises and high electronic transport[1]. The development of semiconductor materials for gas sesnor applications is more active in present-day by discovery graphene (2D) materials, which have various technical applications including sensors[1]. The flat structure of it makes all atoms on the surface exposed to the environmental application, the report showed that graphene has capable of detecting various guest molecules with atomic precision[2]. Graphene calcification in to two types are armchair graphene nano ribbon (AGNR) and zigzag graphene nano-ribbon (ZGNR), AGNR have semiconductor proprieties with no magnetism[3], ZGNR show semi-metal proprieties with stable antiferromagnetic, which supply a potential nano-device application for ZGNR[4]. Simulation study and laboratory study have obtained the electronic proprieties of graphene nano-ribbon can be regulated by edge modification[4],

adsorption atoms[5] and impurities for a type n or p semiconductors impurities[6]. Graphene has several composites like Boron-Nitride (BN), Aluminum-Nitride (AlN), Boron-Phosphate (BP) and other composites from III-V and II-V group, which have wide application for sensing nano-device[7]. Hexagonal Boron-Nitride (h-BN) has a wide band gap, high thermal conductivity and low dielectric constant, other nitride composite like (GaN) and (AlP) have the same proprieties[8]. White graphene or (2D h-BN) in the form of few-layer crystals or a single layer of (h-BN), has been appeared of as a fundamental building blocked of van der Waals heterostructures[9]. (h-BN) have an indirect band-gap at 5.955 eV and optical proprieties of it determined by phonon-assisted transitions[10].

2. Computational details

Density Function Theory (DFT) calculation has been used to compute optimization structure, Higher Occupied Molecular Orbitals (HOMO), Lowest Unoccupied Molecular Orbitals (LUMO), Energy Gap (Eg), and Adsorption Energy (Ead) carried out with basis set 6-31G with hybrid function (B3LYP) in ground state calculation for graphene/boron-nitride nano-ribbon. Time Depending-Density Function Theory (TD-DFT) calculation has been used to estimate optical proprieties for graphene/boron-nitride nano-ribbon with the same basis set and hybrid function in ground state calculation. First calculation geometry relaxation for stander ribbon, the most distance between gas molecule and graphene/boron-nitride nano-ribbon, calculate adsorption energy to determine types of reaction and finally calculate the absorbance spectrum (UV-Visible). Finally calculated FTIR spectroscopy.

3. Theoretical background

Fermi and Thomas used the expression for the kinetic, exchange and correlation energies of the homogeneous electron gas[11]. Density functional theory is one of the most popular and successful quantum mechanical approaches to matter [12]. Density function theory is a quantum mechanical method used in physics and chemistry to investigate the electronic structure of many-electron systems, in particular molecules based up on a strategy of modeling electron correlation via general functionals of the electron density[13]. (DFT) derives properties of a many-particle system as a function of electron density $\rho(r)$. (DFT), depending on one spin and three spatial coordinates for every electron (assuming fixed nuclear positions), is not, in and of itself, particularly intuitive for systems of more than one electron [14]. The electron density is defined as the probability of finding an electron(s) in a specific place and tends to zero as the distance between the electron and nucleus tends to infinity. The wave function approaches become significantly more complicated mathematically as the number of electrons increases[15].

4. Result Analysis

4.1.Geometry Relaxation and Adsorption Energy

Figure (1) listed the geometry structure for pure graphene/boron-nitride ribbon, bond length for C-C, C=C, C=C (aromatic) and C-H are (1.4555), (1.3661), (1.4305) and (1.0859) Angstrom values of bond length are agreements with the past study[16]. For the boron-nitride ribbon the bond length between B-N, (N-H) and (B-H) are (1.4539), (1.0121) and (1.1909) Angstrom agreements with previous a study[17] this result when the gas molecule is absence. The white ball is Hydrogen atom, Blue ball is Nitrogen atom and the Gray ball is Boron atom.

Firstly, compute the most possible distance between ribbon and gas molecule we get, for graphene ribbon most distance is equal (3.88) Angstrom with energy (-0.0462) eV and for boron-nitride ribbon most distance is (3.34) Angstrom with energy (0.0952) eV. In the results showed for graphene ribbon in the most distance there is physical adsorption with the amount of charge is a transfer. Boron-nitride in the most distance no charge transfers no mechanism of adsorption, we modification adsorption ability by change distance between two-reactor systems, CO molecule act as donor[18]. Adsorption energy computed from equation 1[3]

Ead=E(gas+ribbon)- Egas-Eribbon   1

Now study the effect of the gas molecule on stability of structure by interaction gas molecule with surface by different distance between two reactors. From (1-3.5) Angstrom (step is 0.5) and calculation adsorption energy to determine types of adsorption mechanism, for graphene ribbon the adsorption for distance 1 and 1.5 Ang is chemo adsorption because the adsorption high is agreement approximately with C-C bonding is equal (1.4554) Ang, far from this value is began physical adsorption, the value of adsorption for first two high of adsorption is (-15.5048 and -6.62316) eV, these high value back to strong chemical interaction between Carbon atom in graphene ribbon with Oxygen atom in gas molecule, add to gas molecule sharing with the structure of ribbon, other distance from (2-3.5) gas molecule go far from the surface of graphene ribbon effect of gas molecule is reduce, charge transport is minimized and adsorption energy varies (-3.401- -2.236) eV and we obtain the adsorption process decreased and finally steady at -2.236 eV.

For boron-nitride ribbon for same distance used in graphene ribbon we obtain that, distance 1 and 1.5 also chemo adsorption because the distance between two reactor equal B-N bond length approximately. Adsorption energy for these distance are (-16.4408 and -3.3333) eV high energy back to high chemical interaction, from distance (2-3.5) the adsorption energy began decreased rapidly from (-1.099 – (0.005) and the positive sign refer to no interaction between gas molecule and boron-nitride ribbon. From this result conclude from distance 3 -3.5 gas molecule isolated from boron-nitride ribbon, there no any charge transfer between them.
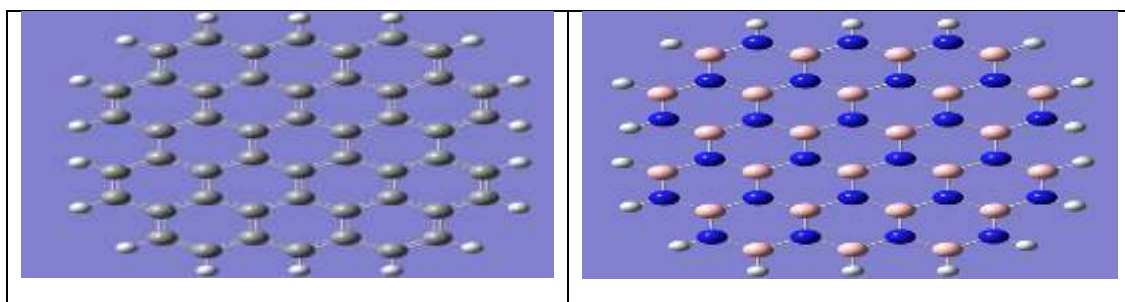

Figure 1: represent graphene/boron-nitride ribbon, the Black ball is Carbon atom, the White ball is Hydrogen atom, the Blue ball is Nitrogen atom and the Gray ball is Boron atom.

Table (1) listed adsorption energy for graphene/boron nitride ribbon measured in eV unit

Discerption	Adsorption Energy (eV)	
Adsorption High	Graphene ribbon	Boron-Nitride ribbon
1	-34.5048	-16.4409
1.5	-23.62316	-3.33335
2	-5.40138	-1.09932
2.5	-1.41906	-0.21769
3	-0.25547	0.032653
3.5	-0.20586	0.051701

from table 1 we conclude that the CO gas molecule is active on graphene ribbon greater than boron-nitride ribbon, and mines sign refer to charge transfer between gas molecule and ribbon.
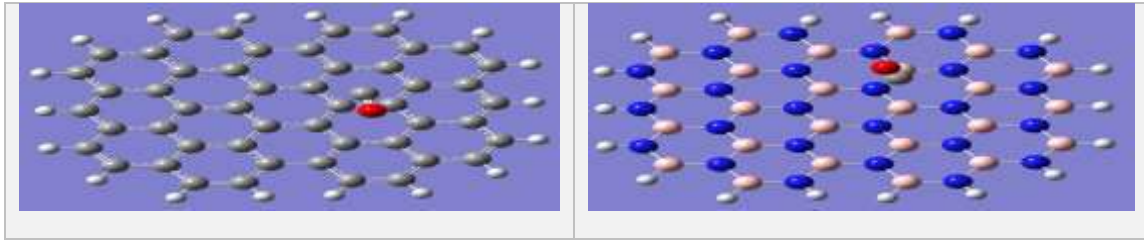
Figure 2: show the most relaxation structure between gas molecule and graphene/boron-nitride ribbon and Red ball represent Oxygen atom.
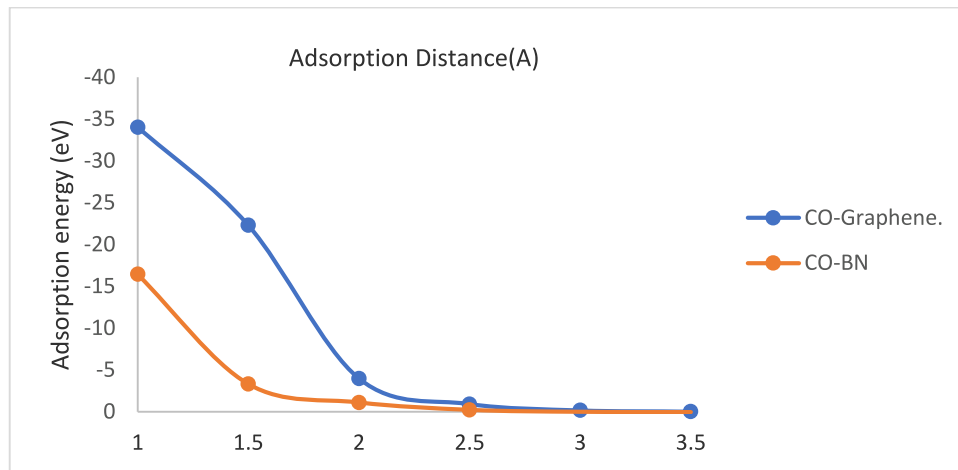

Figure (3): represent adsorption energy for CO gas molecule adsorbed on Graphene/ Boron-nitride measured in eV unit.
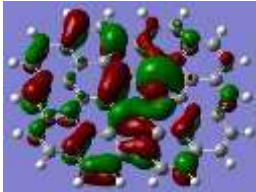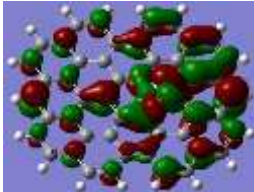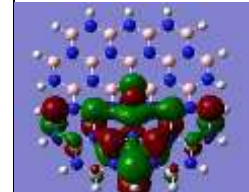
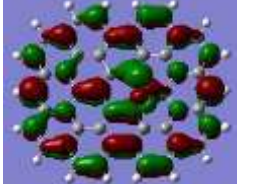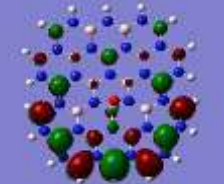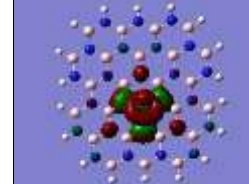## 4-2. Electronic states and Energy Gap
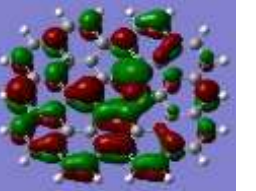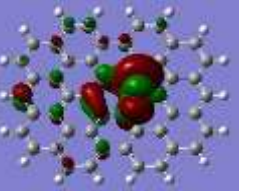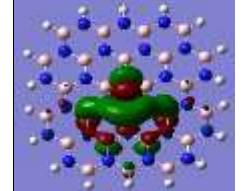
Higher Occupation Molecular Orbitals (HOMO), Lower Unoccuption Molecular Orbitals (LUMO) and Energy Gap (E_g) are important parameters to determine ability of electrons transition and type of materials classification (Conductor, Semiconductor and Insulator). First energy gap for stander ribbon without gas interaction on the surface, energy gap for graphene ribbon is 2.55 eV is semiconductor materials and boron-nitride ribbon band gap energy is 6.20 eV insulator materials classified, these two values are agreements with[17][3]. Molecular Orbitals for graphene ribbon surrounding C-C bonding and for boron-nitride surround B-N, B-H and N-H bonding. Second study presence gas molecule (CO) effect on electronic state and energy gap, for graphene ribbon for distance (1-3.5) Angstrom, the disruptions of (MO) overlap gas molecule because chemical adsorption between two reactor and high charge transfer, changer in value of energy gap energy from (1.7-2.4) eV, chemical adsorption varied in adsorption high is 1 and 1.5 angstrom, above these distance is physical adsorption, mechanism of occupation s become decreased gas molecule and graphene ribbon become two isolated system. For boron-nitride ribbon for the same distance and same gas molecule, (MO) distribution overlap gas molecule and decreased occupation around B-N bonding, chemical adsorption active in distance 1 and 1.5 Angstrom, for distance (2-3.5) same case in graphene ribbon occupation is decreased and gas molecule become system refused from boron-nitride ribbon. The energy gap varies from (4.60-5.45) eV, in other case chemical adsorption change in energy gap values and physical adsorption change in band gap value but stay on insulator materials. Table (2) represent values of HOMO, LUMO energies and Energy Gap in the eV unit, Energy Gap calculated from equation [11]. Figure 4 represent HOMO and LUMO disruptions for all ribbon under study, figure 5 represents values of HOMO and LUMO energies and figure 6 bang gap energy.

$E_g = E_{LUMO} - E_{HOMO}$ 2

Table (2) represent values of HOMO, LUMO energies and Energy Gap in eV unit

Discerption	Graphene ribbon			Boron-Nitride ribbon		
distance	HOMO	LUMO	E_g	HOMO	LUMO	E_g
1	-4.3972	-2.6261	1.77	-5.3583	-0.3205	5.03
1.5	-4.0672	-2.7787	1.28	-5.6024	-1.0005	4.60
2	-4.9224	-2.5257	2.39	-6.4492	-0.9899	5.45
2.5	-4.8732	-2.4394	2.43	-6.4432	-1.0808	5.36
3	-4.8348	-2.6288	2.20	-6.4332	-1.1450	5.28
3.5	-4.8168	-2.8345	1.982321	-6.4299	-1.1298	5.30

Disc.	Graphene ribbon/CO		Boron-Nitride ribbon/CO	
D	HOMO	LUMO	HOMO	LUMO
1				
1.5				
2				

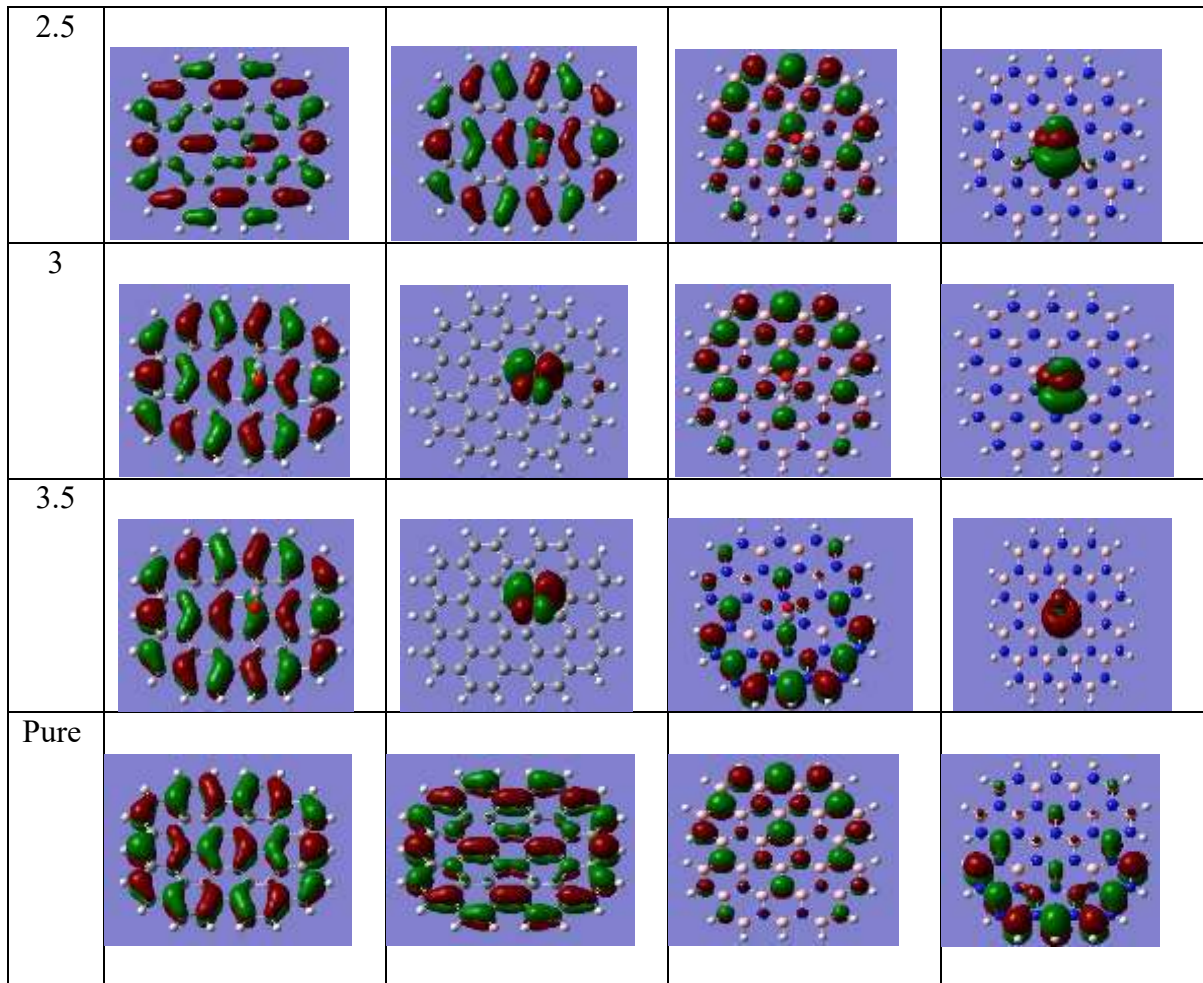|				
2.5				
3				
3.5				
Pure				

Figure 4: represent HOMO and LUMO disruptions for all ribbon under study, Green colour represent positive charge and red colour represent negative charge.
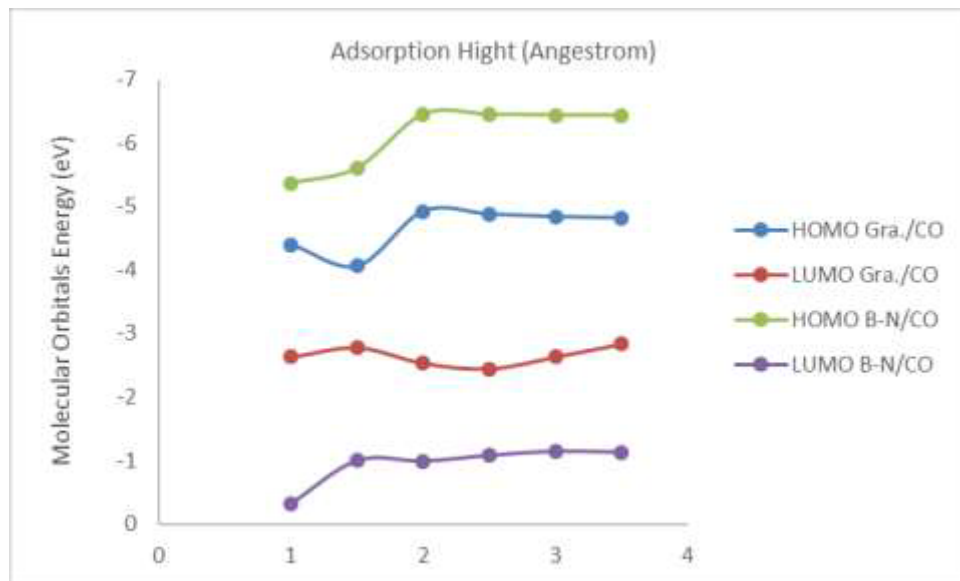

figure 5: represent values of HOMO and LUMO energies for graphene/boron-nitride ribbon that interaction with gas molecule.
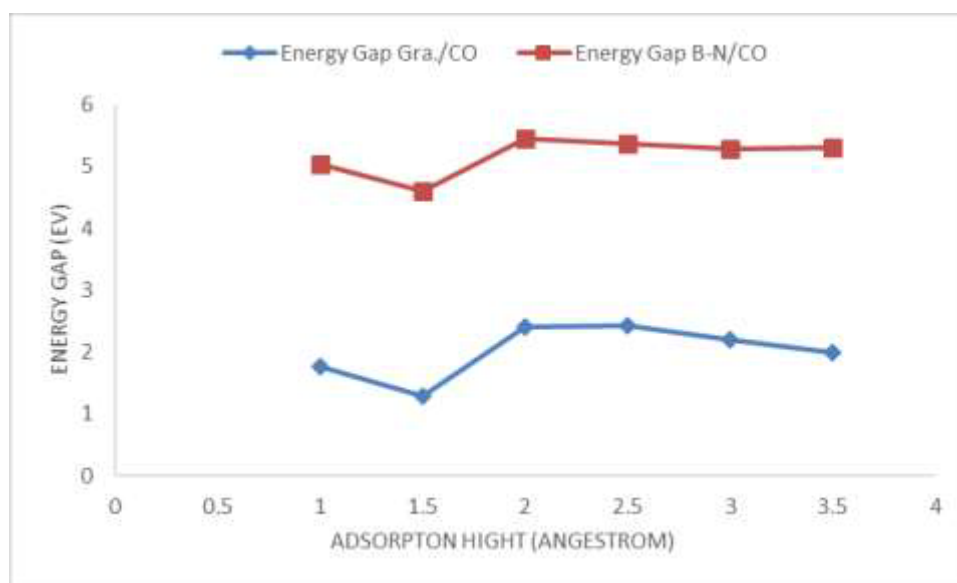
figure 6: bang gap energy for graphene/boron-nitride ribbon that interaction with gas molecule

5. Optical Proprieties
5.1 UV-Visible calculation
In this part study effect of the gas molecule on optical proprieties for graphene/boron-nitride ribbon, determine a type of shifting blue or red and compute excitation energy. Firstly, for pure graphene ribbon maximum absorbed wave length is equal (525.2) nm with excitation energy equal (2.36) eV, for boron-nitride ribbon maximum wave length equal (213.24) nm with exaction energy (5.82) eV[20][10], obtain that boron-nitride has high excitation energy compared with graphene ribbon. The secondary study effect of mono carbon oxide on optical proprieties with different distance began from 1-3.5 angstrom. Graphene adsorbed with CO gas molecule for distance 1 and 1.5 Angstrom that represent chemical adsorption, the maximum wave length is 1765.29 nm with exaction energy 0.70 eV and 1046.78 nm combine energy 1.18 eV, concluded from that chemical adsorption shifted towered to mid and near infrared spectrum. For physical adsorption represented by distance 2 to 3.5 Angstrom, high absorbed appear on (568, 550, 696 and 820) nm and exaction energy are (2.18, 2.25, 1.78 and 1.51) eV respectively we can conclude physical interaction between gas molecule and graphene ribbon led to red shifted. For boron-nitride ribbon for same distance and same behaviour, distance 1 and 1.5 Angstrom high absorbance appear on (306.76 and 337.69) nm exaction energy is (4.04 and 3.67) eV for chemical adsorption led to blue shifting combine high energy and this true because of the high gap between valance and conduction band. Physical adsorption began from distance (2-3.5) Angstrom maximum wave length are (265.53, 252.28, 254.29 and 251.22) nm excitation energy are (4.66, 4.91, 4.88 and 4.94) eV, an interaction between the gas molecule and boron-nitride ribbon stay in same region of stander ribbon, Violet spectrum with high energy and short wave length back to the high gap between two bands (valance and conduction), in other discuses electron need high energy to transition from valance band to conduction band resulting from pi-pi interaction[20]. figure 7 and 8 represent UV-Visible spectrum for adsorbed graphene ribbon.
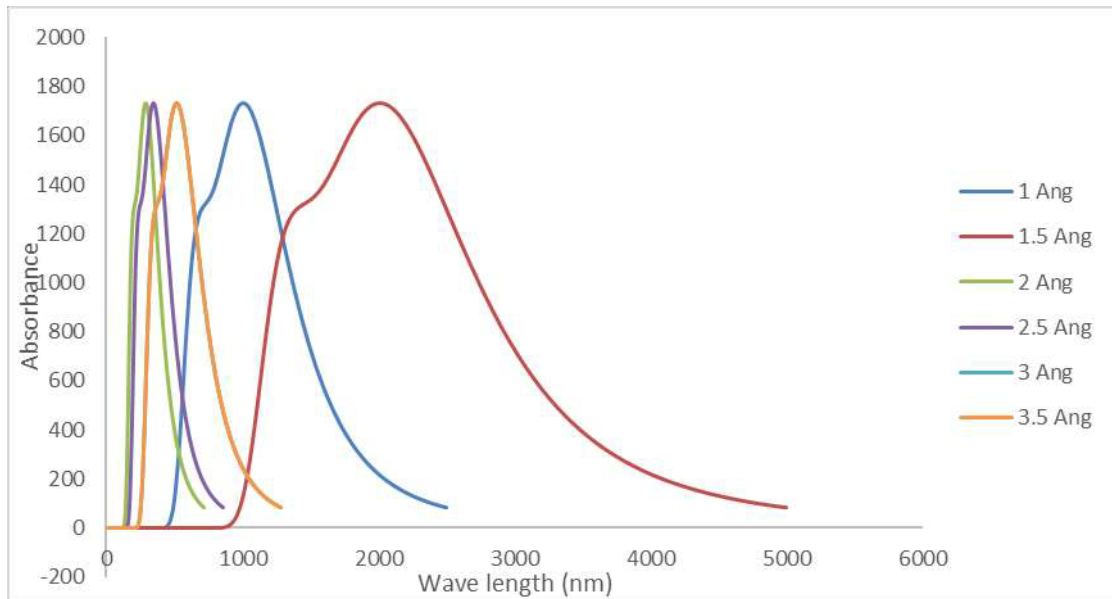
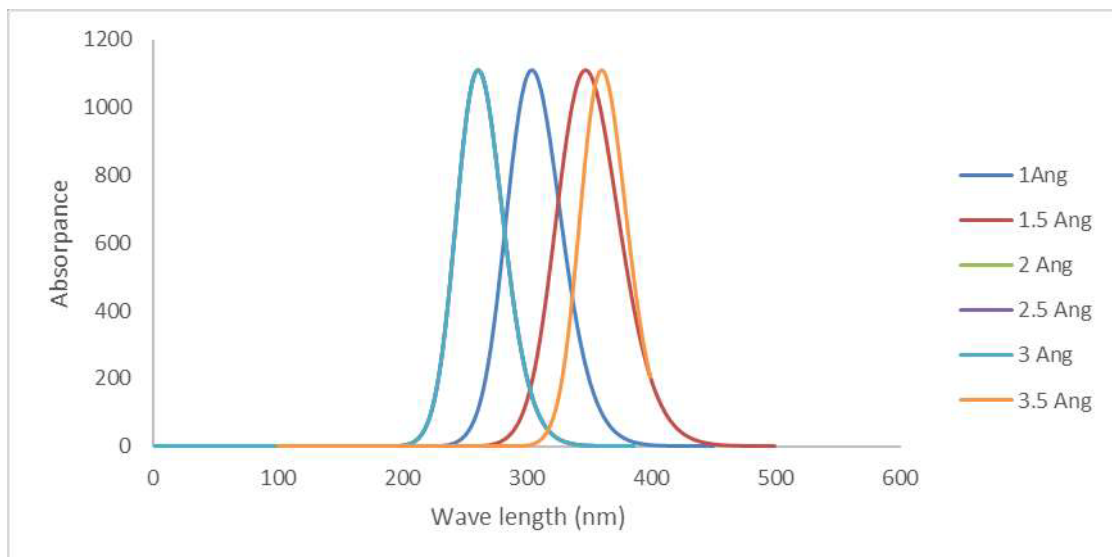Figure 7: UV-Visible for Graphene adsorbed with mono carbon oxide gas molecule

Figure 8: UV-Visible for Boron-Nitride adsorbed with mono carbon oxide gas molecule

5.2 Fourier Transformation-Infrared Radiation (FT-IR).

In this section study (FT-IR) spectroscopic to determine functional group for graphene and boron-nitride before and after adsorption with CO gas molecule, also this property used to prove chemical adsorption process. For pure graphene and boron-nitride nano ribbon resulted showed, a functional group of (C-C) appear on (1600.18) medium, (=C-H) appear on (3186) represent sp^2 hybrid for the aromatic ring, (C-H) sharp appear on (928) bending with alkene group[19]. Spectroscopic characteristics for the boron-nitride ribbon are listed on stretching mode for B-N appear on 1498 and bending mode appear on 1422, for B-H and N-H functional group appear on 3594.53 and 2691.84 for stretching mode 872.42 and 791.41 for bending mode respectively and these result agreements approximately with[20]. After adding CO molecule on the surface and for successful chemical interaction calculated FTIR proprieties to appointment wave number of mono carbon oxide if it shares in chemical interaction, for graphene/CO system we conclude, C-O group appear in region 1568 cm^{-1} near approximately from computed a value equal 1655 cm^{-1}. For B-N/CO

174

system the wave number of C-O appears in position 2151 cm-1 approximately for computed value equal (1700-2125) cm-1[19]. Figure 9 and 10 FTIR spectra for pure graphene and CO adsorbed molecule and pure B-N and CO adsorbed molecule respectively.
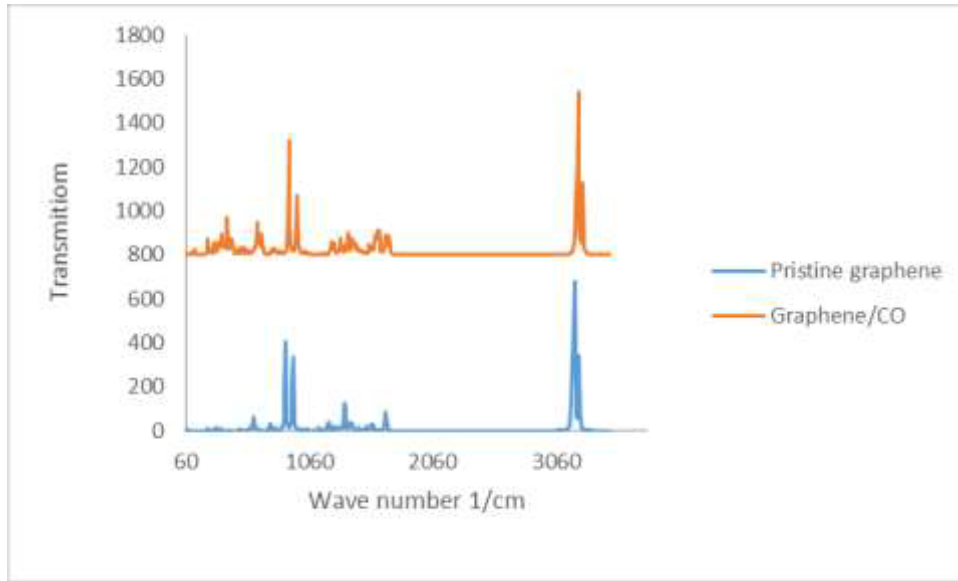

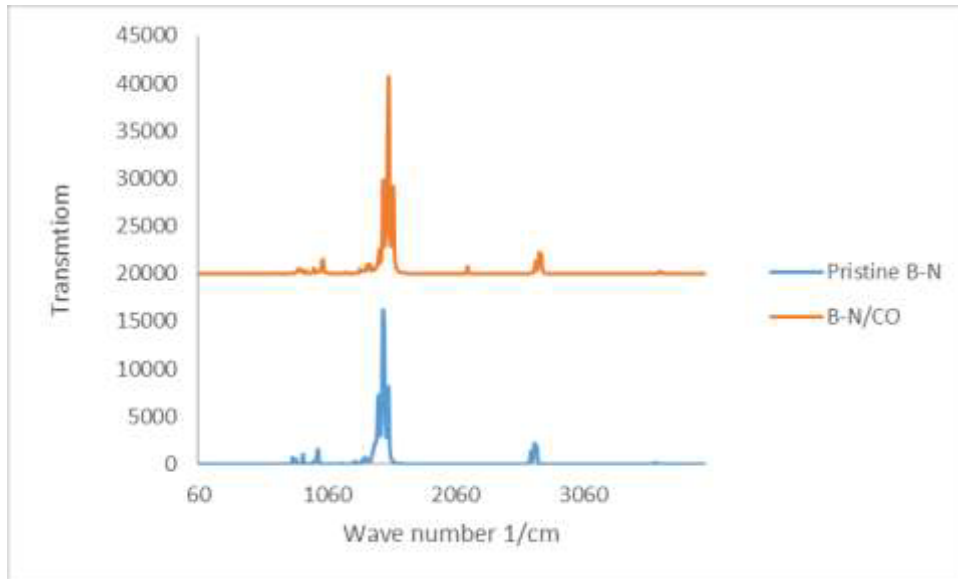Figure 9: FTIR spectra for pure graphene and CO adsorbed molecule

Figure 10: FTIR spectra for pure B-N and CO adsorbed molecule

6. Conclusions

1- Adsorption energy showed that graphene nano-ribbon good sensing for CO gas.
2- For distance greater than 1.5 Angstrom gas molecule in graphene ribbon sensing in two types of adsorption (chemical and physical), B-N sensing only in chemical adsorption.
3- Chemical adsorption proved by FTIR by appearing CO gas molecule peak in spectrum
4- Optical properties, in chemical adsorption shifted to IR region for graphene nano-ribbon and shifted to blue region for B-N nano-ribbon, physical adsorption nano system back to stable state.

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