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Investigation Adsorption Strength of Toxic Gases Molecule Interaction with boron-Nitride Copper Decorate Using First Principle Study

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

Mohammed A. Al-Seady, Sura Ali Hamza
University of Babylon-Environmental Research and Studied Centre-
Babylon-Iraq

Noor AL-Huda Salih
Babylon Government-
Third Nader-Babylon-Iraq

Hasanein Ameer Hamza
Al-Mustaqbal University College,Department of Medical Physics, Hilla, Babil, Iraq

Abstract:- In present study, density function theory was used to computed adsorption strength of toxic gases across surface of boron-nitride copper decorate nano-ribbon. Gases under study was carbon mono-oxide (CO), hydro cyanide (HCN) and methane (CH4). Copper atoms has clear effect on structural and electronic properties of boron-nitride nano-ribbon especially energy gap property, it is change from insulator to semiconductor material in other hand, modify electrical conductivity. Adsorption calculation shows that methane gas molecule has more binding energy compared with other gases and this clear in distance 1 and 1.5Å from surface. HCN and CO gases molecule have chemical interaction only and this clear in distance near surface. CH4 gas molecule has more binding energy in chemical and physical interaction for distance between it and surface.

I. INTRODUCTION

Boron-Nitride (BN) is one of the like graphene (G) form as a two-dimensional materials (2D). BN is a chemical compound formed from equal number from Boron (B) and Nitrogen (N) atoms[1]. The BN have one layer of graphitic structure which it has applied as one of the promises of dielectric parts[2]. BN is a polar material because have equal number From positive (B) and negative (N) atomic charges. The atoms form structure have sp2 hybridization and strong sigma bond formed at this process[3]. BN has high gap between HOMO (Higher Occupied Molecular Orbitals) and LUMO (lower Unoccupied Molecular Orbitals) and band gap energy equal 6 eV[4]. It have many important properties like high specific volume area, electrical insulation, high thermal stability, ultraviolet photoluminescence. The advantage of BN nano materials is that it can be applicated in physical and chemical sensors, hydrogen storage and catalysis and contaminant removal in very harsh environments[4]. First theoretical study of BN nano material in 1994 and it was prepared successfully at 1995. Many of technical method has use to prepare BN nano material like arc discharge, chemical vapour deposition (CVD), substitution reaction, pulse laser ablation (PLD) and low temperature method. Figure (1) family structure of boron-nitride allotrope.

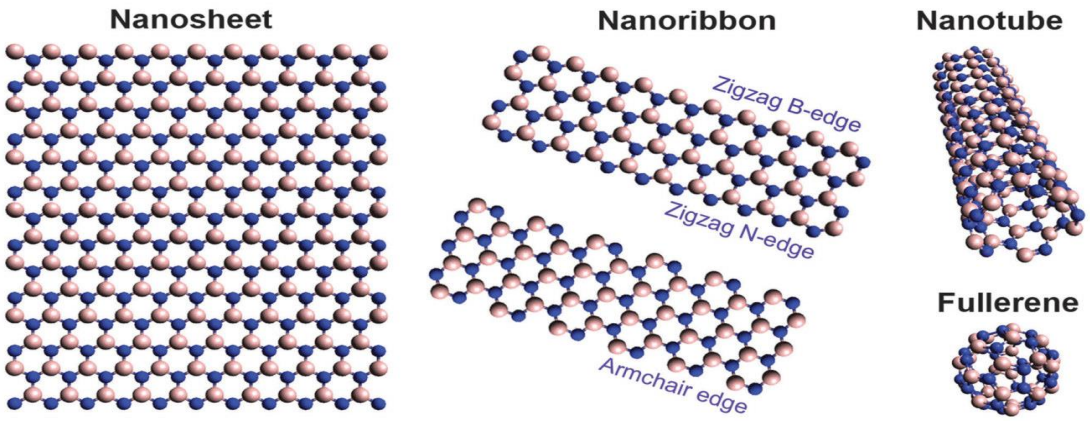

Fig. 1: Shows family of BN nano structure nano sheet, nano-ribbon, nano tube and fullerene[5].

II. ADSORPTION AND ITS TYPES

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[6]. Adsorbate attached on adsorbent surface, consequently the degree of freedom and limited surface free energy decreases because unbalanced forces between two reactors[6]. The transition of the adsorbent from the liquid phase to the solid phase continues until the

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balance between the amount of adsorbent contained in the adsorbent and the amount of adsorbent remaining in the solution is achieved[7]. In general it is classified to chemical and physical adsorption mechanism[8]. 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[9]. 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. One important factor of reducing energy is absence chemical bonding. Finally, physical adsorption was more acceptable on multi-layer system[10].

III. ADSORPTION ENERGY

The formation of a bond between a molecule and a metal surface is an important phenomenon in a number of processes including heterogeneous catalysis, contact formation in molecular electronics[11], and anchoring of biomolecules to solids for sensors and other biomedical applications[12]. The adsorption energy is a key quantity describing the strength of the interaction of molecules with the surface. The adsorption energy can be measured by advanced surface science techniques[13]. Alternatively, density functional theory (DFT) offers the possibility of calculating adsorption energies with reasonable accuracy. The theoretical model that describe adsorption energy following this equation[14]:

$$E_{Ad}=E_{(Gas+Rib.)}-(E_{(Gas)}+E_{(Rib.)}) \quad (2.21)$$

Where E_{Ad} represent adsorption energy, $E_{(Gas+Rib.)}$, $E_{(Gas)}$ and $E_{E(Rib.)}$ are total energy for mixture adsorption, gas molecule and isolated nano-ribbon, respectively.

IV. SIMULATION STEPS

Nano tube modular is used in this study to generate graphene nano-ribbon structure n=m=3 and tube length 1 nm. Export structure to Gaussian 5.0 version for display system. Then exporting the input data to Gaussian 09, this is to compute geometrical and electronical proprieties, also adsorption energy. DFT method was used to compute the ground state properties depending on electron density. Molecular orbital energy provides a Higher Occupied Molecular Orbital (HOMO) and Lower Unoccupied Molecular Orbitals (LUMO), Energy gap and Relaxation structure were computed by DFT method. UV-Visible properties are computed by the time depending-density function theory. Basis set used in present study was 6-31G and hybrid function B3LYP[15,16].

V. GEOMETRICAL PROPERTIES OF BORON-NITRIDE COPPER DECORATE

This section deals with the effect of Cu atom on structural, electronic and optical Properties of doped system. Figure 2 represents geometrical structure of BN-Cu nano-ribbon. Bond length for B-N, B-H and N-H agree with result in chapter (3 and 4). New types of bond formed between Cu and three N atoms. Bond length between Cu-N varies between (1.7712- 1.7957) Å[17]. Also, noted structure of B-N nano-ribbon stretching because atomic radius of Cu greater than B atom. Also, bond angles between B-N, B-H, B-N agreement with past section in chapter (3 and 4). The bond angle between Cu and neighbor N atoms are (103.9269-131.5891) degree[17]. Table (1) listed values of electronic Properties of BN-Cu system compared with BN nano-ribbon. Result indicate that clear effect of Cu atom on electronic Properties. Total energy decreased due to the effect of doped metal atom. Also, molecular orbital energy decreased and this clear in LUMO orbital. Energy gap modified also, BN nano-ribbon because doping mechanism changed from insulator to semiconductor material. On the other hand Cu atom modify conductivity of BN nano materials. Figure (3) represent UV-Visible spectra for BN-Cu nano-ribbon computed by TD-DFT. From a figure appear clear effect of Cu atom on optical characteristic. Results showed spectra have two absorbance peaks one in red region of electromagnetic radiation and the other in near IR region[18]. This result proved that Cu atom make shifting for UV-Visible spectra from blue to red region of electromagnetic radiation.

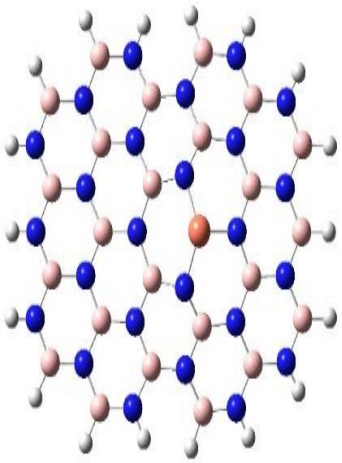

Fig. 2: represent geometrical structure of BN-Cu nano-ribbon.

Property	Pristine B-N[19]	BN-Cu (present study)
E_T	-2003.2414	-3618.45
HOMO	-6.4313	-6.1344
LUMO	-0.1317	-4.0251
E_g	6.2996	2.1093
IP	6.4313	6.1344
EA	0.1317	4.0251

Table 1: listed values of electronic Properties of BN-Cu system compared with BN nano-ribbon.

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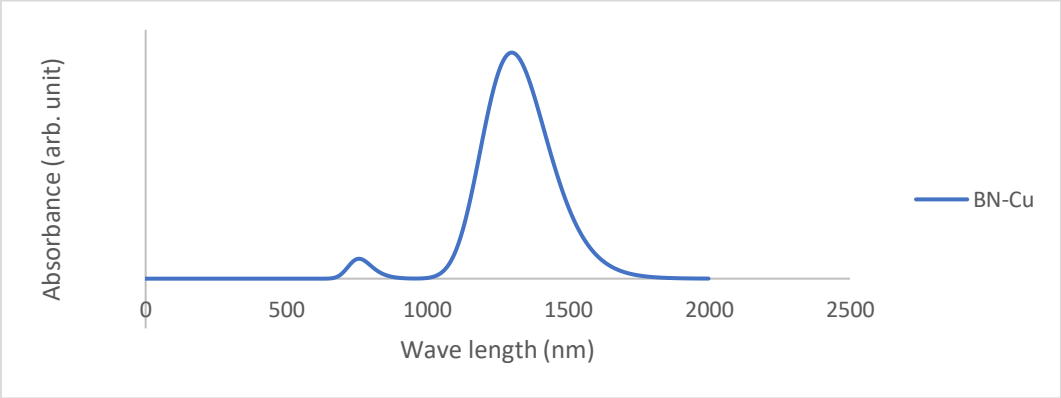

Fig. 3: represent UV-Visible spectra for BN-Cu nano-ribbon

VI. ADSORPTION ENERGY

In this section study mechanism of interaction between gas molecule and surface of BN-Cu nano ribbon. First step placed gas molecule in randomly phase and compute relaxation distance between gas molecule and surface of BN-Cu. Table (2) listed the values of relaxation distance and minimum adsorption energy. Results showed that relaxation distance for CO and HCN were nearest to surface compared with pure graphene nano-ribbon. The binding energy for two gases were smaller than pure system. For CH4 relaxation distance was greater than pure ribbon but more binding energy. Figure (4) explain most possible orientation for gas molecule around surface.

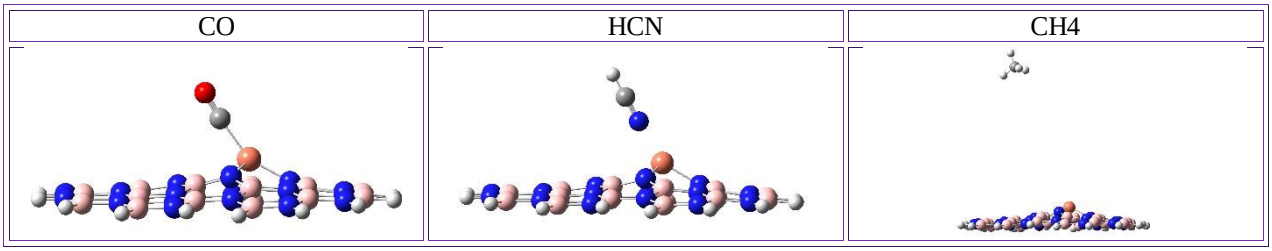

Fig. 4: explain most possible orientation for gas molecule around surface

Gases	E_{ad}	D (A)
CO	0.5331	1.93
HCN	0.0214	1.99
CH4	-0.0022	11.70

Table (2): listed the values of relaxation distance and minimum adsorption energy.

Table (3) listed values of adsorption energy as function of distance. Results indicated that effect of Cu atom on adsorption process clear, for CO adsorption notice that increasing in chemical adsorption and modified it only in distance near surface. HCN adsorption mechanism also modify chemical adsorption, in 1 A distance was greater than pure BN nano-ribbon after that all adsorption process decreased and system separation. In CH4 adsorption mechanism of doped have high effect in present process. Cu let BN nano-ribbon more sensitive for methane gas molecule compared with pure system. BN-Cu system was more favorite for CH4 gas compared with other gases. Figure (5) represents geometrical structure for adsorbent systems.

D (Å)	CO	HCN	CH4
1	-29.4992	-34.5494	-50.3974
1.5	-1.1953	-1.5197	-8.8104
2	0.5206	0.5825	-1.8480
2.5	0.2295	0.3516	-0.3610
3	0.0428	0.1279	-0.0265
3.5	0.0478	0.0083	-0.0319
4	0.1012	0.0651	-0.0300

Table 3: listed values of adsorption energy as function of distance

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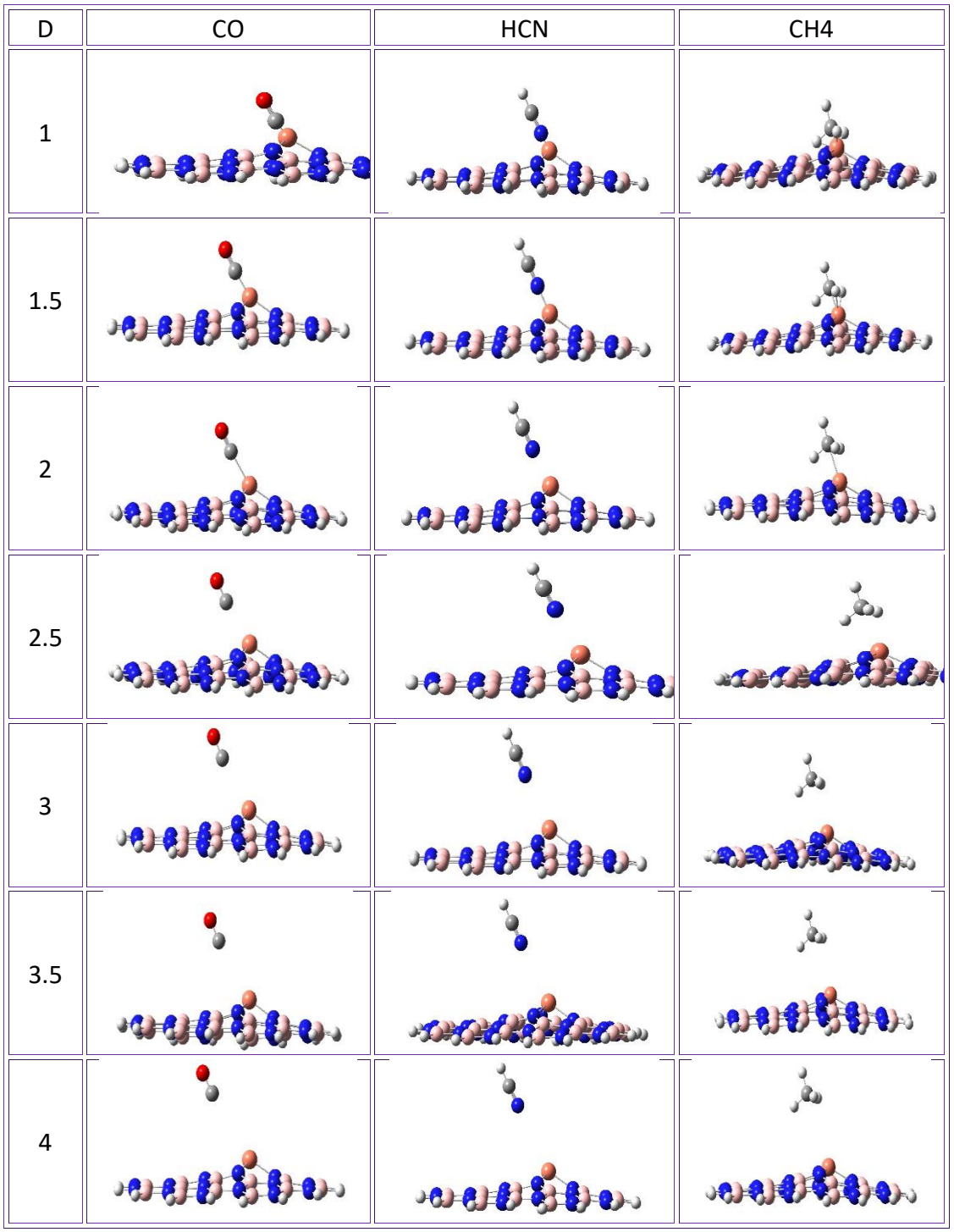

Fig. 5: represents geometrical structure for adsorbent systems.

VII. MOLECULAR ORBITALS AND ENERGY GAP

In this section study effect of interaction between gas molecule and surface on molecular orbital distribution and energy gap. Energy gap important factor that explain nature of interaction. Molecular orbital distribution shows a charge distribution between gas molecule and BN-Cu nano-ribbon.Results indicated that HOMO energy for CO and HCN were grater than BN-Cu, that mean decreased in energy level. For CH_4 adsorption effect of gas molecule on HOMO level was clear. It decreasing rapidly with increasing adsorption distance. LUMO level was more stable compared with HOMO. It clear when occur chemical adsorption LUMO energy decreased compared with isolated BN-Cu nano-ribbon. By increasing adsorption distance LUMO energy also decreased. CH_4 adsorption was more stable compared with CO and HCN molecule. Figure (6) represent curve of molecular orbital energy.

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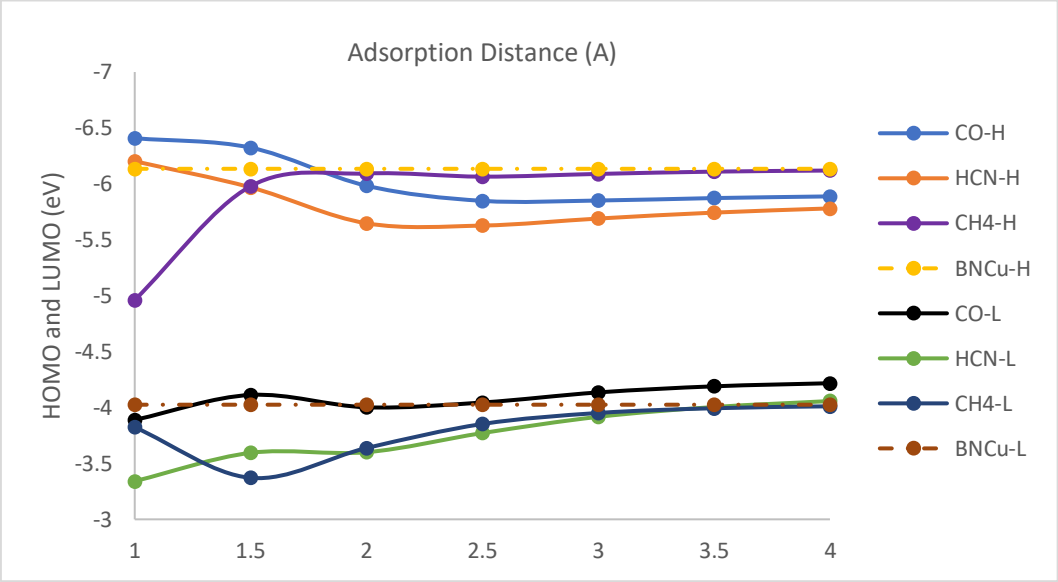

Fig. 6: represent curve of molecular orbital energy

Results showed that during chemical adsorption the band gap for CO and HCN increasing, but for CH_4 it smaller than two gases. On other hand band gap for CH4 adsorption become opening and let high amount of electron transport across band energy. Optimum track for band gap appears in CH_4 adsorption because by increasing adsorption distance energy gap value fitted on stander BN-Cu gap. Figure (7) represents curves of energy gap values measured in eV unit.

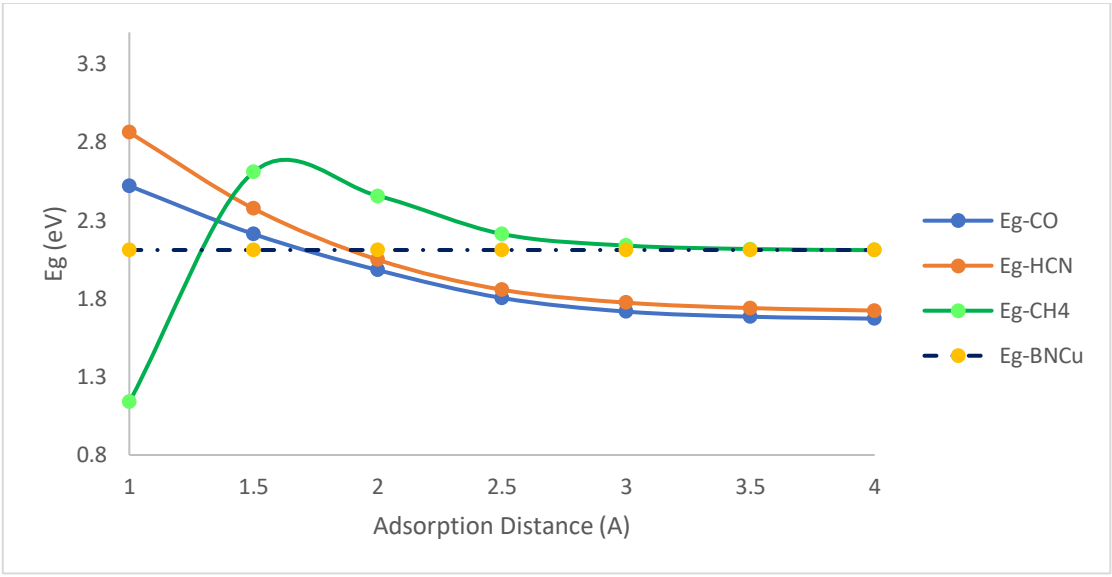

Fig. 7: represent curves of energy gap values measured in eV unit.

VIII. UV-VISIBLE SPECTROSCOPY

In this part study effect of gas adsorption on optical shifting toward red or blue region of electromagnetic radiation. For BN-Cu nano ribbon in past section notice it has two absorption peaks one in red region of electromagnetic radiation and other peak in near FT-IR. Red region consider fundamental band of absorption and other was secondary band appear in sub energy level and it useless. For CO/BN-Cu adsorption we noticed that absorption peak appears in (704.55 and 763.22) nm in distance 1 and 1.5 A. UV-Visible spectra shifted toward blue shifted of electromagnetic radiation. For distance (2, 2.5…, 4) spectrum have randomly wave length of absorption, and systems become unstable and this clear in adsorption calculation for system under study. For HCN/BN-Cu system absorption wave length for distance 1 and 1.5 are (534.8 and 670) nm. These computed wave lengths explain chemical adsorption shifted UV-Visible spectra towered high energy region of electromagnetic radiation (short wave length) and band energy become narrow compared with isolated nano system. Also, for distance 2 to 4 A interaction between gas molecule and BN-Cu nano-ribbon under gas randomly phase and wave length of absorption was unstable. CH_4/BN-Cu absorbance wave length in chemical and physical adsorption was stable. In distance 1 to 2.5 A many of absorbance peak appear are (710, 1530, 2600, 735, 1014 and 2349) nm. These absorbance wave lengths indicate that CH4 molecule gas

can be sensitive by BN-Cu in different absorbance wave length of electromagnetic radiation. distance from 3 to 4 A wave length of absorbance fitted on isolated BN-Cu nano-ribbon.

IX. CONCLUSIONS

- Copper metal atom enhance electrical conductivity of boron-nitride nano-ribbon
- Carbon mono-oxide and hydro cyanide have chemical interaction between them and surface of Cu-boron-nitride other distancedoesn'tappear any interaction.
- Methane gas was more and more reactive with surface of Cu-boron-nitride nano-ribbon in term of physical and chemical adsorption.

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