Egypt. J. Chem. **Vol. 64,** No. 5 pp. 2607 - 2612 (2021)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Studying the adsorption energy of CO gas molecule in different nano-systems using density function theory

Mohammed A. Al-Seady[a*], Eman Ahmed[b], Hayder M. Abduljalil[c] and Ahmed Abdlridha Ekhewish[a]

[a]*University of Babylon-Environmental Research and Studied Centre-Babylon-Iraq*

[b]*Al-Mostaqbal University Collage-Medical Physics Department-Babylon-Iraq*

[c]*University of Babylon-Collage of Science-Physics Department-Babylon-Iraq*

Abstract

In this report density function theory calculations were used to computed ground state properties for pure and Aluminum doped nano-system (graphene/boron-nitride). Ground state calculation provide relaxation structure, molecular orbital energy, adsorption process and charge transfer. Hybrid function used in this study was (B3LYP) and basis set 6-31G*. bond length calculation for pure and doped nano-system was agreements with experimental measurements. Adsorption energy calculations show low energy raising during interaction between gas molecule and surface of nano-systems. Also, result show that type of adsorption was physical. Molecular orbital energy doesn't effect during interaction process. Charge transfer calculation show that CO gas molecule act as donor in system pure graphene, boron-nitride and Al-graphene and act as acceptor in Al-boron-nitride.

Keyword: Adsorption energy, Energy gap, Physical adsorption, Charge transfer, Molecular orbitals.

1. Introduction

Graphene is the name given to a single layer of graphite, made up of sp2 hybrids carbon atoms arranged in honeycomb lattice, consist of two interpenetrating triangular sub-lattice and is a basic building block for carbon allotropes of other dimensionalities similar to fullerenes and carbon nanotubes[1]. Graphene is a zero band gap semiconductor with its valence and conduction bands touching in corner of the Brillion zone in called Dirac points[2]. Development of graphene based electronics depends on ability to open a tunable band gap, various approaches have been developed to fabricate high-performance graphene device by engineering their band gaps so as to improve their semiconducting properties[3]. Boron-Nitride (BN) was one of the like graphene (G) form as a two-dimensional materials (2D). BN was a chemical compound formed from equal number from Boron (B) and Nitrogen (N) atoms[4]. The BN have one layer of graphitic structure which it has applied as one of the promises of dielectric parts[5]. BN is a polar materials because have equal number from positive charge of (B) and negative charge of (N) atom[5]. The atoms formed structure have sp2 hybridization and strong sigma bond formed at this process[6]. BN has high gap between HOMO and LUMO and bang gap energy equal 6 eV[7]. The advantage of BN nano materials has applied at physical and chemical sensors, hydrogen storage and catalysis and contaminant removal in very harsh environments[8]. The aim of present study investigation adsorption energy of carbon mono-oxide in pure and doped nano-ribbon (graphene and boron-nitride). In doped mechanism used aluminium atom.

2. Doped process.

Because the high specific area of it allows transfer charge with external gas molecule adsorbed[9]. However, many theoretical and experimental studies show that graphene has weak physical adsorption of most gas molecule[9]. Therefore, to solve this

*Corresponding author e-mail: wellmsc@gmail.com

Receive Date: 27 December 2020, Revise Date: 19 February 2021, Accept Date: 04 March 2021

DOI: 10.21608/EJCHEM.2021.55434.3169

problem, researchers used many mechanisms such as defect vacancy and doped graphene by metal atom[10]. 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[11]. 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[12]. Gas sensing was an 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 the surface of nanotubes such as boron-nitride, aluminum- nitride and aluminum-phosphide, also other structure of III-V group of element table[13].

3. Tools and material in present study.

Density function theory was used to computed electronic, structural, molecular orbital energy, adsorption process and charge transport for systems under study. All nano structure was built used nanotube modular software. Al atom used in doped mechanism for modify some physical properties for nano systems. CO gas molecule was interacted with the surface and checked ability of adsorption strength in different distance. In present study hybrid function (B3LYP) was used to describe system and a Basis set was 6-31G*.

4. Previous study.

Alireza Saffarzadeh studied in (2010) modelling of gas molecule in graphene nano-ribbon using DFT calculation. Result show that amount of charge transfer depends on orientation of gas molecule and length of ribbon. The highest occupied molecular orbital in CO molecule is located on the C atom[14]. Khadije Imani, et al., studied in (2012) adsorption energy of some toxic gases. DFT calculation show that CO gas molecule contributed localized in centre of original band gap. CO gas molecule adsorption act as acceptor[15]. S. M. Aghaei, et al., in (2017) studied behave of adsorption energy for gases molecule (CO, NO, NO2 and NH3). First principle calculation was used to estimate most stable adsorption configurations, adsorption energies, binding distances, charge transfers, electronic band structures. Result showed adsorption energy for CO gas molecule was less than -1 eV. indicating that the BC3-based sensor has a low and moderate sensitivity to CO[16].

5. Theoretical Background

One of the key quantum mechanical methods used in physics and chemistry to investigate the electronic structure of many-electron systems is density functional theory (DFT), in particular molecules based on a strategy of modeling electron correlation via general functional of the electron density [17]. DFT is among the most popular and versatile methods available in computational physics and computational chemistry [18]. Today DFT is one of the most important tools for calculating ground state properties of metals, semiconductors and insulators.

The functional predecessor to density theory was the Thomas-Fermi model, developed by Thomas and Fermi in 1927. They calculated the energy of an atom by representing its kinetic energy as a functional of the electron density, combining this with the classical expressions for the nuclear-electron and electron-electron interactions, which can both also be represented in terms of the electron density [19].

In DFT the main focus is not only on the N-electron wavefunction $\Psi=(\vec{x}1,\vec{x}2,\ldots\vec{x}N)$ and the associated Schrödinger equation, but instead on the much simpler electron density ρ(r). The electron density is the number of electrons per unit volume for a given state. It is dependent only on 3 coordinates independently of the number of electrons of the system.

Thus it can be as this follows [20].

$$N=\int\rho(r)dr \qquad 1$$

The fundamental concepts of DFT rely on the ground state energy and all other ground state electronic properties are uniquely determined by the electron density. Furthermore, the exact ground state of the system corresponds to the electronic density for minimal total energy. The Hamilton operator of n-electron system within the Born-Oppenheimer approximation can be described by [17].

$$\hat{H}=\hat{T}+V_{ext}+V_{ee}$$

The external potential V ext is uniquely defined by the electron density ρ(r). The total energy can be written as:

$$E_o=T[\rho_o]+\int V_{ext}(r)\,\rho_o(r)\,dr+J[\rho_o]+ENC[\rho_o]$$

Where T[ρo] is the kinetic energy, ENC[ρo] is the non-classical electron–electron interaction energy and J[ρo] is the classical coulomb energy defined as :

$$J[\rho_o]=1/2((\rho_o)(r1)\,\rho_o(r2))/(|r1-r2|)\,dr1dr2$$

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

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

Where FHK is a universal functional of the electron density:

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

Hohenberg–Kohn theorem assumes that FHK exists, but the actual form of FHK is unknown and must be approximated.

6. **Results and discussion: geometrical proprieties.** Geometrical characteristics summarized on bond length and angle between atoms computed for graphene nano-ribbon when toxic gas molecule absence. Bond length for C-C, C=C, 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[21]. The result shows that agreement with a previous study[22]. In doped nano systems Bond length for Al atom surrounded by three neighbors carbon atom are (1.74183-1.76034) Å. Bond length between three neighbor nitrogen atom varies (1.7214-1.7224) Å. Starching in bond length back to Al atom heavier than B atom. Figure (1) lists the geometry structure for pure and doped nano-ribbon (graphene and boron-nitride). Results for doped nano-ribbon show approximately agreements with experimental measurements.

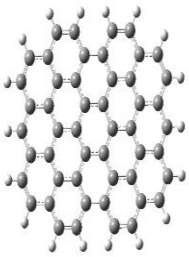
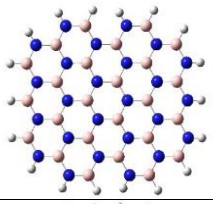
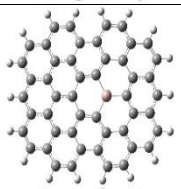
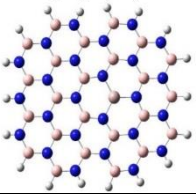
Sample	Geometrical structure
Pure graphene	
Pure boron-nitride	
Doped graphene	
Doped boron-nitride	

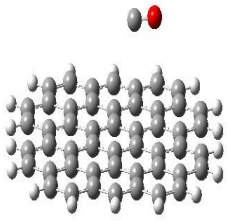
Figure (1): represent geometrical structure for systems under study.

7. Adsorption energy discussion

In this section placed gas molecule in random phase across the surface of nano system. By using density function theory calculation, obtain relaxation adsorption distance and minimum energy that transport between gas molecule and nano system. Table 1 listed adsorption energy measured in eV unit and relaxation distance in Å unit. For pure nano system result show that CO gas molecule have negative adsorption energy, but in boron nitride system it positive values. This result indicates that CO gas molecule sensitive in pure graphene nano-ribbon but in low adsorption energy. This result obeys the condition of physical adsorption limitation. More negative adsorption energy means more binding system[23]. For doped nano-ribbons in Al atom adsorption relaxation distance in graphene increasing compared with pure system, because starching in skelton of graphene the surface during adsorption process. In doped boron-nitride relaxation distance similar to pure system, because gas molecule snacked with the surface of doped nano-ribbon[24]. All adsorption energy in doped nano-ribbon was positive, this mean at relaxation distance these systems cannot sense CO gas molecule[16]. Only pure graphene nano-ribbon can sense CO gas molecule. Positive adsorption energy mean interaction absence between gas molecule and the surface of nano-ribbon. Figure (2) represent relaxation adsorption distance between two reactors.

Table 1: listed adsorption energy measured in eV unit and relaxation distance in Å unit.

System	E_{ad} (eV)	Relaxation distance (Å)
Pure graphene	-0.051	3.88
Pure boron-nitride	0.058	3.34
Al-graphene doped	1.125	4.05
Al-boron-nitride doped	0.340	3.34

	structure
CO-pure graphene	

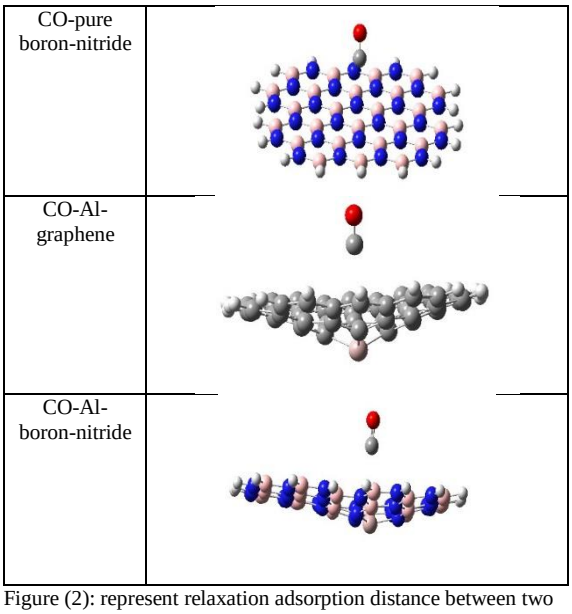


Figure (2): represent relaxation adsorption distance between two reactors.

8. Molecular orbital energy analysis.

In this section discussion a state of molecular orbital distribution for nano-system and explain the change on it, also energy gap. table (2) represent molecular orbital energy for isolated and interacted systems. In case of interaction of gas molecule with the surface of graphene and it doped by aluminium atoms. Result shows that small amount of electron transport between molecular orbital resulting from low physical adsorption energy raised during interaction. For boron-nitride and it derivative result show that have small electrons transfer across band energy. Also, tight of electron transfer resulting from low energy raised from physical adsorption between gas molecule and boron-nitride and it derivative[25-28].

Table (2): represent molecular orbitals energy in eV unit.

System	HOMO	LUMO
Pure graphene	-4.780	-2.247
Co-graphene	-4.789	-2.256
Graphene-doped Al	8.035	-6.479
Co-Al-doped graphene	-7.977	-6.481
Pure boron-nitride	-6.431	-0.131
Co-boron-nitride	6.434	-1.139
Boron-nitride doped Al	-6.428	-0.218
Co-Al-doped boron-nitride	6.403	-1.381

9. Charge transfer.

Charge transfer consider on of an important tool to determine amount of electron transport between reactor systems. Track of charge depending on sign of charges transport. If charge transport has positive value it means transport from gas molecule to nano-system. If it negative charge transport from nano-system to gas molecule[29]. Table 3 represent values of charge transport between reactors system measured in e unit. Result show that the charge transfer in pure graphene was very small. Doped by aluminum atom charge transfer modified. Truck of charge transfer from nano-system to gas molecule. Mean typed of gas molecule was acceptor. In case of boron-nitride, pure case small amount of charge transfers due to low adsorption energy. Result show that charge transfer from gas molecule to nano-system. So, gas molecule act as donor. Doped boron-nitride case of charge transfer change, amount of charge transfer increasing. Also doped by aluminum atom change gas molecule state from donor to acceptor[30-33].

Table (3): represent charge transfer between reactors systems.

System	Charge transport (e)
CO-Pure graphene	-0.0032
CO-Al-Graphene	-0.1307
CO-Pure boron-nitride	0.0163
CO-Al-boron-nitride	-2.1370

10. Conflict of interest.

There are no conflicts to declare.

11. Formatting of funding sources

There are no funding sources.

12. Acknowledgments

I acknowledgment Prof. Dr. Mohammed R. Mahran and Assist. Prof Ewies F. Ewies for their help to complete this work.

References

1- Novoselov K. S., Geim A. K., Morozov S. V., D. Jiang, Zhang Y., Dubonos S. V., Grigorieva I. V., and Firsov A. A., Electric field effect in atomically thin carbon films. science, vol. 306, no. 5696, pp. 666-669, 2004.

2- Wallace P. R., The band theory of graphite. Physical review, vol. 71, no. 9, p. 622-634, 1947.

3- Kumar S., Anija M., Kamaraju N., Vasu K., Subrahmanyam K., Sood A., and Rao C., Femtosecond carrier dynamics and saturable absorption in graphene suspensions. Applied physics letters, vol. 95, no. 19, p. 191911, 2009.

4- Hu R., Wang X., Dai S., Shao D., Hayat T., and Alsaedi A., Application of graphitic carbon nitride for the removal of Pb (II) and aniline from aqueous solutions. Chemical Engineering Journal, vol. 260, pp. 469-477, 2015.

5- Song L., Ci L., Lu H., Sorokin P. B., Jin C., Ni J., Kvashnin A. G., Kvashnin D. G., Lou J., and Yakobson B. I., Large scale growth and characterization of atomic hexagonal boron nitride layers. Nano letters, vol. 10, no. 8, pp. 3209-3215, 2010.

6- Lee C., Li Q., Kalb W., Liu X. Z., Berger H., Carpick R. W., and J. Hone, Frictional characteristics of atomically thin sheets. science, vol. 328, no. 5974, pp. 76-80, 2010.

7- Ravichandran J., Manoj A., Liu J., Manna I., and Carroll D., A novel polymer nanotube composite for photovoltaic packaging applications. Nanotechnology, vol. 19, no. 8, p. 085712, 2008.

8- Sukhorukova I. V., Zhitnyak I. Y., Kovalskii A. M., Matveev A. T., Lebedev O. I., Li X., Gloushankova N. A., Golberg D., and Shtansky V. D., Boron nitride nanoparticles with a petal-like surface as anticancer drug-delivery systems. ACS applied materials & interfaces, vol. 7, no. 31, pp. 17214-17225, 2015.

9- Song H. Q., Liu Z., and Zhang D. B., Interlayer vibration of twisted bilayer graphene: A first-principles study. Physics Letters A, vol. 383, no. 22, pp. 2628-2632, 2019.

10- Hu X., Liu M., Liu X., Ma Y., Nan H., Bi D., Qiao L., and Li Y., Sensing and absorbing of sulfur mustard using Pt-decorated graphene from first-principles calculations. Physica E: Low-dimensional Systems and Nanostructures, vol. 114, p. 113634, 2019.

11- Beheshtian J., Kamfiroozi M., Bagheri Z., and Ahmadi A., Computational study of CO and NO adsorption on magnesium oxide nanotubes. Physica E: Low-dimensional Systems and Nanostructures, vol. 44, no. 3, pp. 546-549, 2011.

12- Zhang X., Yu L., Gui Y., and Hu W., First-principles study of SF6 decomposed gas adsorbed on Au-decorated graphene. Applied Surface Science, vol. 367, pp. 259-269, 2016.

13- Beheshtian J., Baei M. T., and Peyghan A. A., Theoretical study of CO adsorption on the surface of BN, AlN, BP and AlP nanotubes. *Surface Science*, vol. 606, no. 11-12, pp. 981-985, 2012.

14- Saffarzadeh A., Modeling of gas adsorption on graphene nanoribbons. *Journal of Applied Physics*, vol. 107, no. 11, pp. 114309-114320, 2010

15- Imani K., Jafari G., and Abolhasani M. R., Electronic Structure Calculation of Adsorbate Gas Molecules on an Armchair Graphene Nanoribbon. *ISRN Condensed Matter Physics*, vol. 2012, pp. 1-12, 2012.

16- Aghaei S., Monshi M., Torres I., and Calizo I., Adsorption and Dissociation of Toxic Gas Molecules on Graphene-like BC_3: A Search for Highly Sensitive Molecular Sensors and Catalysts. *arXiv preprint* arXiv:1706.00774, 2017.

17- Sahni V., Quantal Density Functional Theory II: Approximation Methods and Applications. *Springer-Verlag, Berlin Heidelberg*, 2010.

18- Lipkowitz K., Larter R., Cundari T. and Boyd B., Reviews in Computational Chemistry. Vol. 21, *John Wiley & Sons*, Inc., Hoboken, New Jersey, 2005.

19- Cramer J., Essentials of Computational Chemistry: Theories and Model. *John Wiley & Sons Ltd*., the Atrium, Southern Gate, Chichester, England, 2nd Edition, 2004.

20- Dorsett H. and White A.; Overview of Molecular and Ab initio Molecular Orbital Methods Suitable for use with Energetic Materials. *Aeronautical and maritime research laboratory*, Australia, 2002.

21- R. Majidi R., Karami , Rahmani K., and A. M. Khairogli A. M., Electronic properties of hydrogenated porous Graphene based nanoribbons: A density functional theory study. *International Journal of Nano Dimension*, vol. 11, no. 2, pp. 112-119, 2020.

22- Kadhim B. B. and Muhsen H. O., Infrared Absorption and Raman Spectra of BNNT-Fluorouracil: A Density Functional Theory Study. *International Journal of Science and Research (IJSR)*, vol. 6, no. 8, pp. 1690-1695, 2017.

23- Ao Z., Yang J., Li S., and Jiang Q., Enhancement of CO detection in Al doped graphene. Chemical Physics Letters, vol. 461, no. 4-6, pp. 276-279, 2008.

24- Mohammed A. Al-Seady and Hayder M. Abduljalil, Study of Some Environmental Applications of Graphene and Boron-Nitride Nano-Ribbons Using Density Function Theory. *Master thesis, university of Babylon*, 2020.

25- Leenaerts O., Partoens B., and Peeters F., Adsorption of H_2O, NH_3, CO, NO_2, and NO on graphene: A first-principles study. *Physical Review B*, vol. 77, no. 12, p. 125416, 2008.

26- Rad A. S. and Ayub K., Adsorption of thiophene on the surfaces of $X_{12}Y_{12}$ (X= Al, B, and Y= N, P) nanoclusters; A DFT study. *Journal of Molecular Liquids*, vol. 238, no. 210, pp. 303-309, 2017.

27- Anithaa V., Shankar R., and Vijayakumar S., Adsorption of Mn atom on pristine and defected graphene: a density functional theory study. *Journal of molecular modeling*, vol. 23, no. 4, p. 132, 2017.

28- Rad A. S. and Foukolaei V. P., Density functional study of Al-doped graphene nanostructure towards adsorption of CO, CO_2 and H_2O. *Synthetic Metals*, vol. 210, no. 75, pp. 171-178, 2015.

29- Chandiramouli R., Srivastava A., and Nagarajan V., NO adsorption studies on silicene nanosheet: DFT investigation. *Applied Surface Science*, vol. 351, no. 2 pp. 662-672, 2015.

30- Sakina S., Johari Z., Auzar Z., Alias N. E, Abidin M., and Yusoff M. F. M., Improving graphene nanoribbon gas sensing behavior through warping. *Materials Research Express*, vol. 4, no. 1, p. 015003, 2017.

31- Omidvar A. and Mohajeri A., Edge-functionalized graphene nanoflakes as selective gas sensors. *Sensors and Actuators B: Chemical*, vol. 202, no. 68 pp. 622-630, 2014.

32- Ammar H. Y. and Badran H., Effect of CO adsorption on properties of transition metal doped porphyrin: A DFT and TD-DFT study**.** *Heliyon*, vol. 5, no. 10, p. 02545, 2019.

33- Samadizadeh M., Peyghan A. A., and Rastegar S. F., Sensing behavior of BN nanosheet toward nitrous oxide: a DFT study. *Chinese Chemical Letters*, vol. 26, no. 8, pp. 1042-1045, 2015.

دراسة طاقة الامتزاز لجزيئة غاز اول أوكسيد الكربون في أنظمة نانوية مختلفة بأستخدام نظرية دالة الكثافة

محمد اياد السعدي[a*] ايمان احمد[b] حيدر محمد عبد الجليل[c] احمد عبد الرضا اكحيوش[a]

[a]جامعة بابل- رئاسة جامعة بابل-مركز البحوث والراسات البيئية-بابل-العراق
[b]كلية المستقبل الجامعة-قسم تقيات الفيزياء الطبية-بابل-العراق
[c]جامعة بابل-كلية العلوم-قسم الفيزياء-بابل-العراق

الخلاصة

في هذا التقرير ، تم استخدام حسابات نظرية دالة الكثافة لحساب خصائص الحالة الأرضية لنظام النانو النقي والألمونيوم المشبع (الجرافين / نيتريد البورون). يوفر حساب الحالة الأرضية بنية الاسترخاء والطاقة المدارية الجزيئية وعملية الامتزاز ونقل الشحنة. استخدمت الدالة الوظيفة الهجينة (B3LYP) ومجموعة الأساس 6-31G. حسابات اطوال الرابطة لنظام النانو النقي والمطعم متفق تقريبا مع القياسات التجريبية. تظهر حسابات طاقة الامتزاز ابعاث منخفضًا للطاقة أثناء التفاعل بين جزيء الغاز وسطح أنظمة النانو. أيضا ، تظهر النتيجة أن نوع الامتزاز كان فيزياويا". لم تتأثر الطاقة المدارية الجزيئية أثناء عملية التفاعل. يُظهر حساب نقل الشحنة أن جزيء غاز ثاني أكسيد الكربون يعمل كمانح في نظام الجرافين النقي ، اما أنظمة الكرافيين المطعم بالالمنيوم ونتريد البورن النقي والمطعم فان جزيء الغاز يعمل كمستقبل.