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Study the Effect of Oxygen on Coronene Electronic and Spectroscopic Properties via the Density Functional Theory (DFT)

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Abstract

The electronic properties (such as energy gap HOMO levels. LUMO levels, density of state and density of bonds in addition to spectroscopic properties like IR spectra, Raman spectra, force constant and reduced masses as a function of frequency) of coronene C_{24} and reduced graphene oxide $C_{24}O_X$, where x=1-5, were studied.. The methodology employed was Density Functional Theory (DFT) with Hybrid function B3LYP and 6-311G** basis sets. The energy gap was calculated for C_{24} to be 3.5 eV and for $C_{24}O_x$ was from 0.89 to 1.6862 eV for x=1-5 ,respectively. These energy gaps values are comparable to the measured gap of Graphene (1-2.2 eV). The spectroscopic properties were compared with experimental measurements, specifically the longitudinal optical modes which agreed well.

Keywords: graphene, graphene oxide, DFT.

دراسة تأثير الأوكسجين على خواص الكرونين الألكترونية و الطيفية بواسطة نظرية دالية الكثافة

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الخلاصة

تمت دراسة الخواص الإلكترونية (مثل فجوه الطاقه والمستويات المشغوله HOMO والمستويات الفارغه LUMO, كثافه الحاله وكثافه الاصره . بالإضافة إلى الخصائص الطيفية مثل أطياف الأشعة تحت الحمراء وأطياف رامان ، ثابت القوة والكتلة المختزلة كدالة للتردد) للكرونين C_{24} وأوكسيد الجرافين المختزل $C_{24}Ox$ حيث x=1−5 . تستخدم المنهجية الحالية نظرية دالية الكثافة DFT مع الداله الهجينهB3LYP و مجموعه الأساس 6−311G** . تم حساب فجوة الطاقة لتراكيب C_{24} وكانت 3.5 فولت بينما بالنسبة $C_{24}O_x$ حيث x = 1−5 فقد اختلفت من (0.89 إلى 1.6862) اليكترون قولت حسب قيمة x . قيم فجوات الطاقة هذه مقاربة للقيم المقاسة لأكسيد الجرافين (1−2.2 فولت). تمت مقارنة الخواص الطيفية بالقياسات التجريبية وتحديداً الأنماط البصرية الطولية التي اتفقت بشكل جيد.

1. Introduction

Graphene is made from carbon atoms fused together in a (2D) hexagonal lattice construction [1]. It has the ability to change into multiple shapes with different dimensions

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and structures, so it is a new doorway to technical research and materials science. Figure 1 illustrates the different forms of graphene. Because of its flexibility, graphene can be rolled and twisted and can accumulate in (0D) fullerenes, (1D) carbon nanotubes, (2D) graphene and (3D) graphite, as shown in Figure 1 [2] [3]. Nevertheless, graphene properties, such as high conductivity, single atom thickness, large electrochemical window, and large surface area, with a two-dimensional carbon sheet remains unchanged [4].

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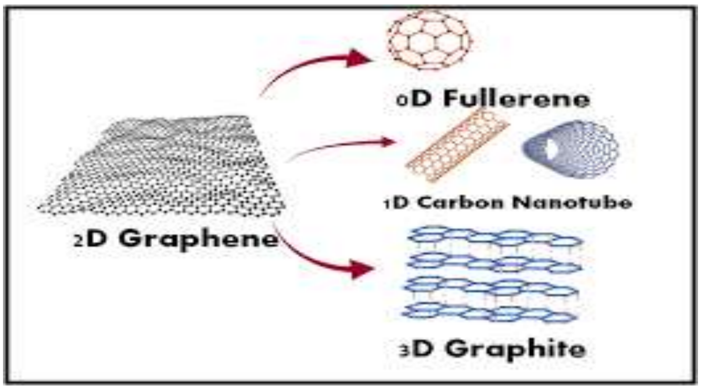


Figure 1: The graphene structure and shape

In 2004, Andre Geim and Kostya Novoselov, described, for the first time, mono crystalline graphitic films [1] Six later, they were awarded the 2010 Nobel Prize in Physics "for ground breaking experiments regarding the two-dimensional material graphene". Fourteen years later the first report of single-layer graphene was published [5].Interest in graphene-based magical formulations has continued to flourish.

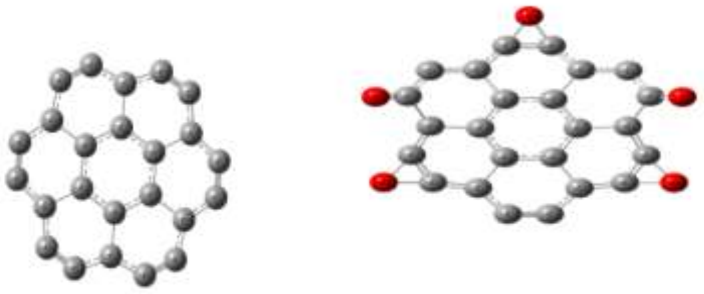
From Figure 1, To overcome such limitations of graphene, it can be transformed into distinctive forms, such as quantum dots (QDs), nano ribbons, foams, and hydrogels according to suitability [6,7,8].Many techniques have been developed to create graphite tinny films and a few graphene layers. Experimental indication for two-dimension crystals appeared in 2004 [1] and 2005 [9] while tinny films of graphene and extra materials were exfoliated from molybdenum disulphide, niobium disulphide and hexagonal boron nitride for the first time as of their bulk equivalents (Figure 1). Through mechanical exfoliation, using a Scotch tape , slight fragments of the order of numerous microns were obtained which were called graphene [10] [11]. Although this method gives the highest quality graphene but for mass production, fabrication method is needed that can synthesize wafer scale graphene. In recent years, various techniques have been established for graphene synthesis. However, mechanical cleaving (exfoliation). Techniques for preparing graphene have evolved in recent years [1] [12].

The aim of this research is to study the effect of oxygen vacancy posts (OVs) on C_{24} that dictate the chemical and physical properties of metal oxides, and play a key role in energy storage, sensors, catalyst etc. [13], [14].

2. Theory

The electronic and spectroscopic characteristics of Coronene C_{24} and reduced graphene oxide $C_{24}O_x$ (where x=1-5) single-layer nanostructures were investigated using the theoretical approximations method. In this study Density Functional Theory (DFT) with hybrid function B3LYP and 6-311G** basis sets were used. To adjust for vibration frequencies, scaling factors (0.967) were utilized [15].

All computations were performed using Gaussian 09 software [16]. In this study, the electronic properties and spectroscopic features of C_{24} single layer nanostructures as a function of the number of oxygen atoms $C_{24}O_x$ with geometrical optimization were studied (as shown in Figure 2).



(a) **(b)**

Figure 2: The geometrical optimization structure of (a) C_{24} and (b)$C_{24}O_5$

3. Results and Discussion

3.1 Electronic Properties

3.1.1 Energy Gap

The energy difference between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) is termed the energy gap:

$$E_g = |LUMO - HOMO| \quad (1)$$

Figure 3 shows the HOMO and LUMO energy levels of C_{24} and $C_{24}O_X$ where x=1-5. The energy gap was compared with that of the bulk graphene (G) and with graphene oxide (GO) which were equal to 1.4 eV for G [17] and (1– 2.2 eV) for GO [18][19]as shown in Figure 4. The energy gap was calculated for coronene C_{24} nanostructures to be 3.5eV . Because of the high symmetry of coronene structure without levels inside the energy gap and the effect of Coulomb interaction and quantum confinement geometry which greatly influence the quasi-particle band gap [20].

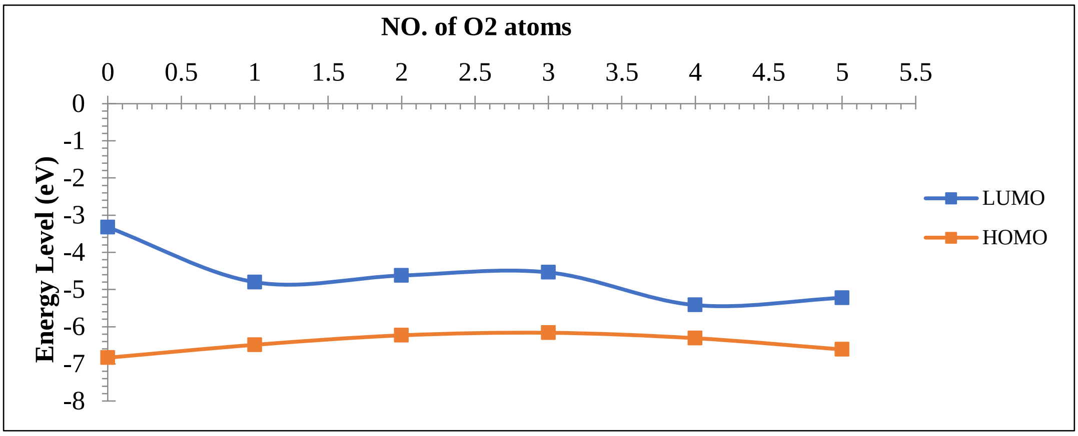


Figure 3: Energy Levels of Coronene (HOMO and LUMO) as a Function of a number of oxygen atoms.

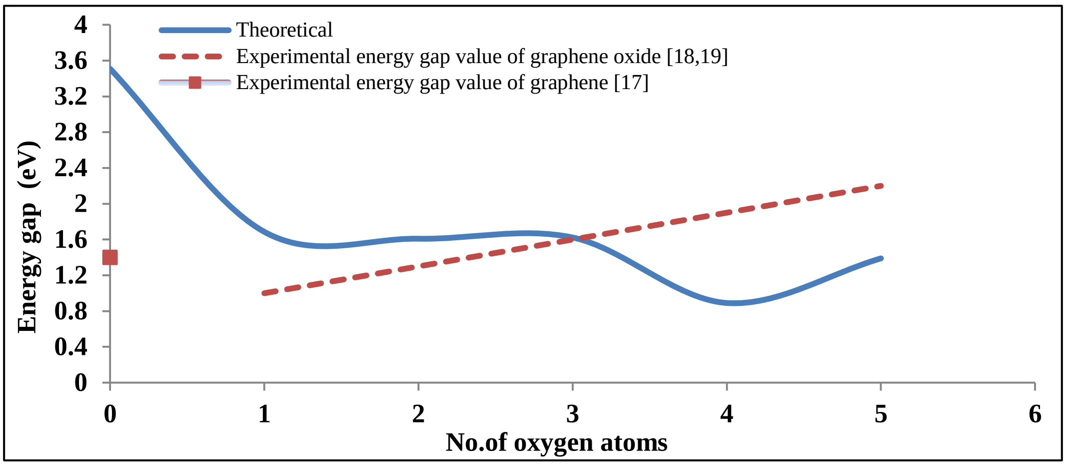
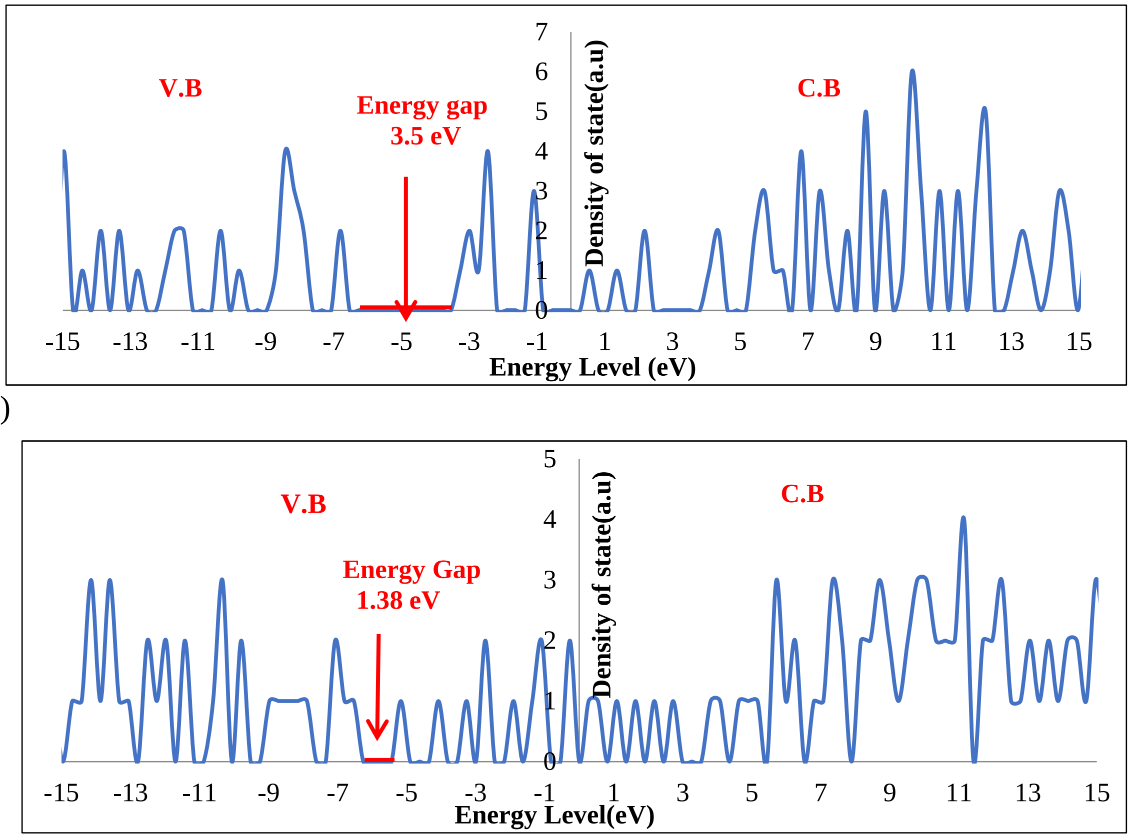


Figure 4: Energy band gap of reduced graphene oxide $C_{24}O_X$ as a function of oxygen atoms

The energy gap of reduced graphene oxide (rGO) decreased with the increase of the degree of reduction of graphene oxide (because of the broken symmetry of C_{24} and the addition of levels inside the energy gap) and it begins to increase, approaching the practical value, when the fifth oxygen atom was added.

3.1.2 Density of states

Figure 5 shows density of state of C_{24} and $C_{24}O_5$ as a function of the energy levels. The energy band gap between the filled (Valence Band)and the high molecular low orbital (Conduction Band) was calculated, (and) which were 3.5eV and 1.38eV ,respectively.

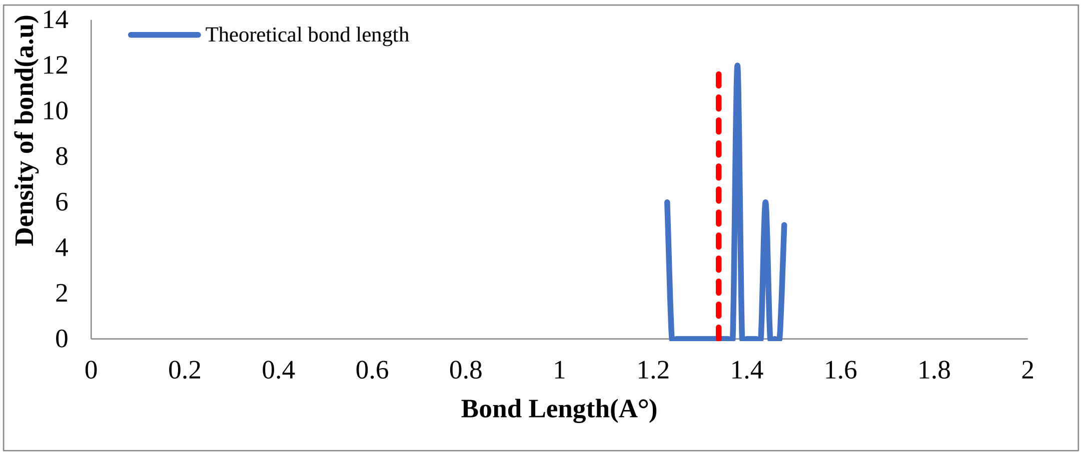


(a)

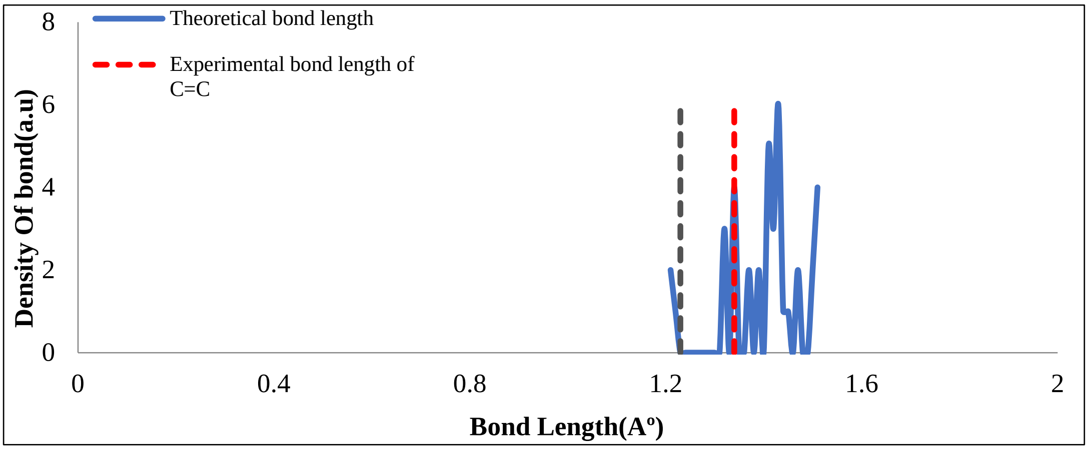
(b) **Figure 5:** Density of states for (a) C_{24} and (b) $C_{24}O_5$ a function of energy levels

3.1.3 Density of Bonds

Figure 6 illustrates theoretically the density of bonds for C_{24} and $C_{24}O_5$,(1.38 and 1.22) °A respectively as compared with the experimental values of bonds (1.34A° for the C=C bond , 1.23A° for the C=O)[21].



(a)



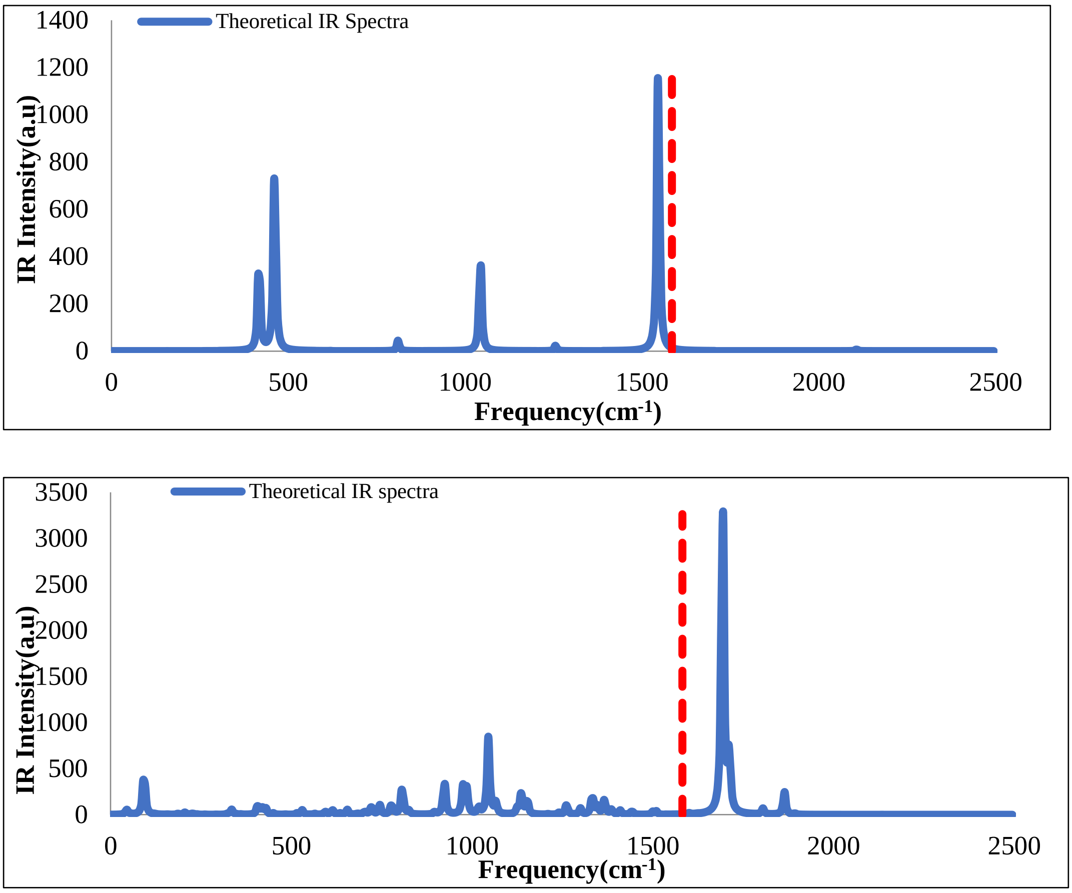
(b)

Figure 6: The density of bonds of (a) C_{24} and (b) $C_{24}O_5$

3.2 Spectroscopic properties

3.2.1 IR and Raman Spectrum

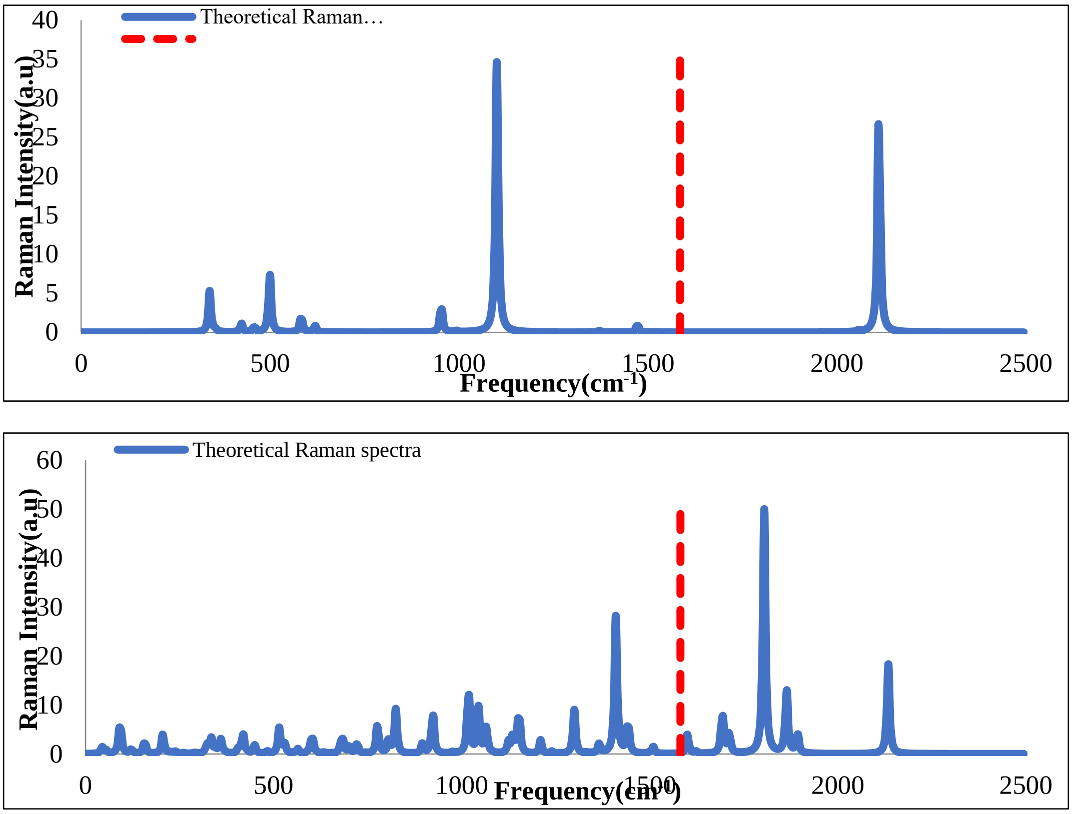
Figure 7 illustrates the intensity of IR of C_{24} and $C_{24}O_5$ as a function of frequency. A maximum intensity at frequencies (1545 and 1696) cm^{-1} was noted . These results were compared with experimental values of longitudinal optical (LO) mode of G bulk and GO at (1582 and 1585 cm^{-1}) [22] [23]. It was found that the intensity of IR increases as the number of oxygen increases. Whereas, lower peak intensities of G and GO of Raman spectra were noted, as illustrated in Figure 8. Maximum intensity was observed at frequencies (1100 and 1805) cm^{-1}, respectively.



(a)

(b)

Figure 7: IR spectra for (a) graphene C_{24} and (b) graphene oxide $C_{24}O_5$.



(a)

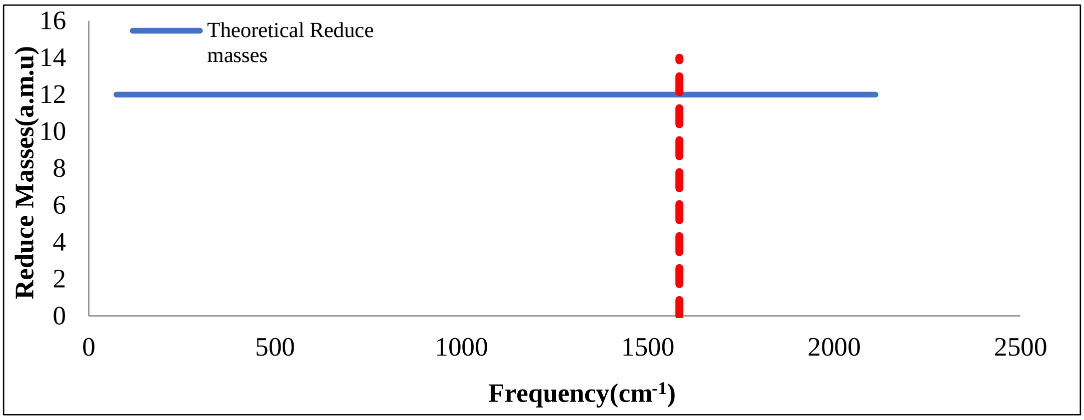
(b)

Figure 8: Raman spectra of (a) graphene C_{24} and (b) graphene oxide $C_{24}O_5$.

3.2.2 Reduced masses and Force constant

Figures 9 and 10 show the reduced mass and the force constant of C_{24} and $C_{24}O_5$ as a function of frequency and compared with the experimental values of the longitudinal optical (LO)mode of vibrational frequency of the G and GO [22] [23]. The longitudinal optical represents the last point in the reduced mass. It can be noticed that the force constant(k) is directly proportional to frequency(ν) while the reduced mass(μ) of molecules is inversely proportional to the frequency, as in Equation 2:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad (2)$$



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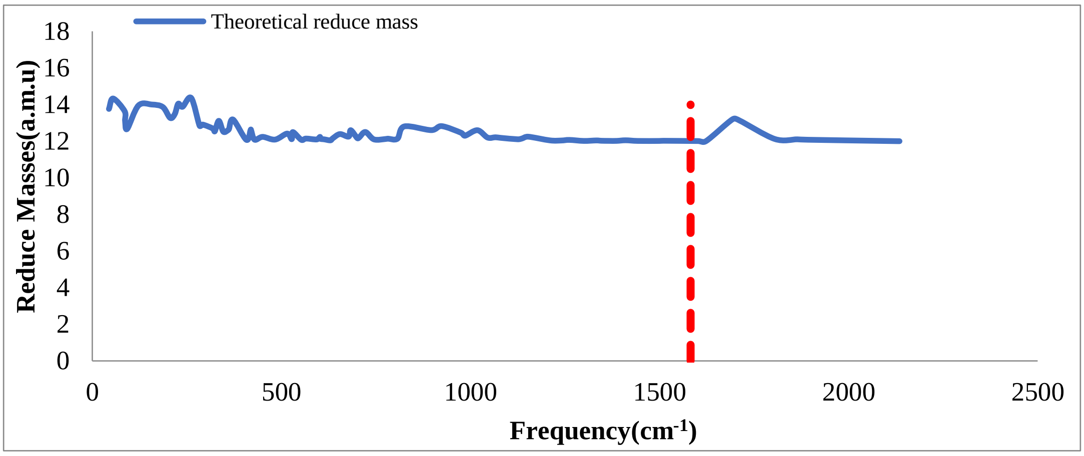
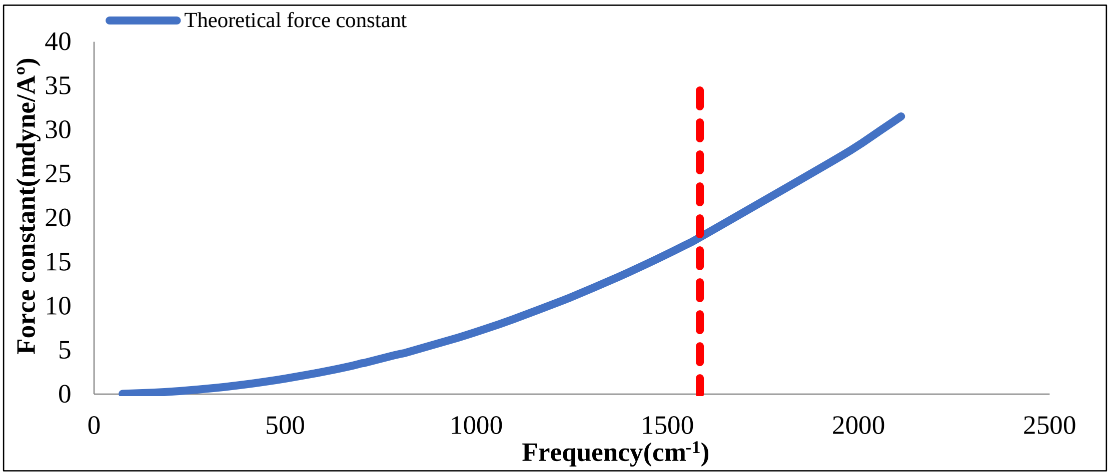


(b)

Figure 9: Reduced mass of (a) C_{24} and (b) $C_{24}O_5$.



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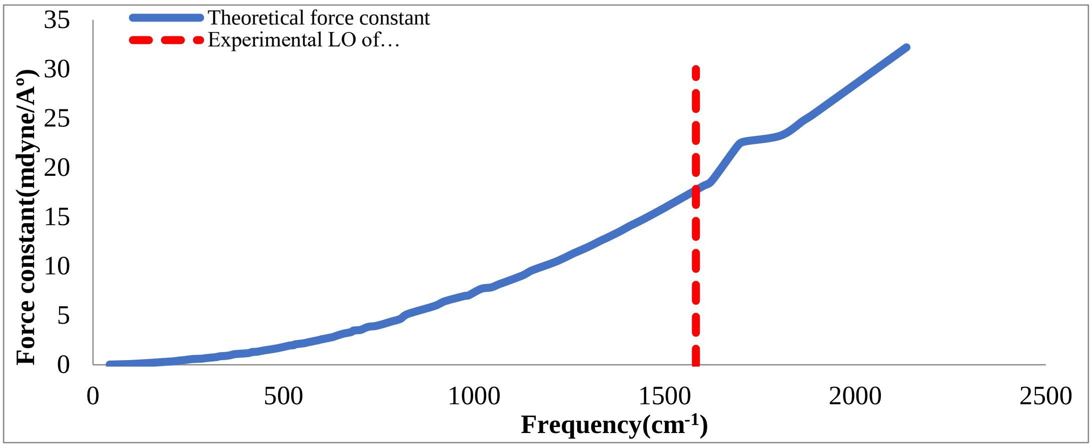

(b)

Figure 10: Force constant of (a) C_{24} and (b) $C_{24}O_5$

4. Conclusions

The electronic and spectroscopic properties of coronene C_{24} and reduced graphene oxide $C_{24}O_x$ where x=1-5 were studied via Density Functional Theory (DFT). The energy gap with wide range was calculated for coronene C_{24} nanostructures because of the high symmetry of coronene structure without levels inside the energy gap and the effect of Coulomb interaction and quantum confinement geometry greatly influence the quasi-particle energy gap. The energy gap of the reduced graphene oxide decreased with the increase of the number of oxygen atoms because of broken symmetry of C_{24} and add level inside the gap . The spectroscopic properties agreed well with the experimental values.

References

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

[2] Anindya Nag, Arkadeep Mitra, Subhas Chandra Mukhopadhyay" ,,Graphene and its sensor-based applications: A review," *Sensors and Actuators A: Physical*, vol. 270, pp. 177-194, 2018.

[3] Lakshmi Prasanna Lingamdinne, Janardhan Reddy Koduru, Rama Rao Karri,, "A comprehensive review of applications of magnetic graphene oxide based nanocomposites for sustainable water purification," *Journal of environmental management*, vol. 231, pp. 622-634, 2019.

[4] Tapas Kuilla, Bhadra, S., Yao, D., Kim, N. H., Bose, S., & Lee, J. H" ,.Recent advances in graphene based polymer composites," *Progress in polymer science*, vol. 35, no. 11, pp. 1350-1375, 2010.

[5] Dimitrios G.Papageorgiou, Ian A.Kinloch, and Robert J.Young" ,Mechanical properties of graphene and graphene-based nanocomposites," *Progress in Materials Science*, vol. 90, pp. 75-127, 2017.

[6] A.R.Marlinda, N.Yusoff, SureshSagadevan, and M.R.Johan, "Recent developments in reduced graphene oxide nanocomposites for photoelectrochemical water-splitting applications," *International Journal of Hydrogen Energy*, vol. 45, no. 21, pp. 11976-11994, 2020.

[7] Sagadevan S., Chowdhury, Z. Z., Johan, M. R. B., & Rafique, R. F" , .A facile one-step hydrothermal synthesis of HfO2/graphene nanocomposite and its physio-chemical properties," *Materials Research Express*, vol. 5, no. 3, p. 035014, 2018.

[8] Xu Y., Sheng, K., Li, C., & Shi, G" , .Self-assembled graphene hydrogel via a one-step hydrothermal process," *ACS Nano*, vol. 4, no. 7, pp. 4324-4330, 2010.

[9] K. S. Novoselov, Jiang, D., Schedin, F., Booth, T. J., Khotkevich, V. V., Morozov, S. V., & Geim, A. K" ,Two-dimensional atomic crystals," *Proceedings of the National Academy of Sciences*, vol. 102, no. 30, pp. 10451-10453, 2005.

[10] A.A. Balandin, S.Ghosh, W.Bao, I. Calizo, D.Teweldebrhan, F.Miao, and C.N.Lau, "Superior thermal conductivity of single-layer graphene," *Nano letters*, vol. 8, no. 3, pp. 902-907, 2008.

[11] H. P. Boehm, R. Setton and E. Stumpp" ,Nomenclature and terminology of graphite intercalation compounds (IUPAC Recommendations 1994)," *Pure and Applied Chemistry*, vol. 66, no. 9, pp. 1893-1901, 1994.

[12] S. C .Ray, "Application and uses of graphene oxide and reduced graphene oxide," *Applications of graphene and graphene-oxide based nanomaterials*, vol. 1, 2015.

[13] Y.Liu, Xiao, C., Li, Z., & Xie, Y" ,.Vacancy engineering for tuning electron and phonon structures of two-dimensional materials," *Advanced Energy Materials*, vol. 6, no. 23, p. 1600436, 2016.

[14] M.Ma, Zhang, K., Li, P., Jung, M. S., Jeong, M. J., & Park, J. H" ,.Dual oxygen and tungsten vacancies on a WO3 photoanode for enhanced water oxidation," *Angewandte Chemie*, vol. 55, no. 39, pp. 11819-11823, 2016.

[15] M. T. HUSSEIN, T. A. FAYAD , M. A. ABDULSATTAR,, "Concentration effects on electronic and spectroscopic properties of ZnCdS wurtzoids: a density functional theory study," *Chalcogenide Letters*, vol. 16, no. 11, pp. 557-563, 2019.

[16] Mohammed T. Hussein, and Hanan A. Thjeel Al-Ogaili,"Vibration properties of ZnS nanostructure Wurtzoids: ADFT study," *In Journal of Physics: Conference Series*, vol. 1178, no. 1, p. 012015, February 2019.

[17] Tian, H.,Yang, Y., Xie, D., Cui, Y. L., Mi, W. T., Zhang, Y., & Ren, T. L. , "Wafer-scale integration of graphene-based electronic, optoelectronic and electroacoustic devices," *Scientific reports*, vol. 4, no. 3598, pp. 1-9, 2014.

[18] Mattson, E. C., Johns, J. E., Pande, K., Bosch, R. A., Cui, S., Gajdardziska-Josifovska, M., , J H Chen, M. ,Hersam, M. C. , and Hirschmugl, C. J."Vibrational excitations and low-energy electronic structure of epoxide-decorated graphene," *journal of physical chemistry lettes*, vol. 5, no. 1, pp. 212-219, 2014.

[19] Liang, H" , .Mid-infrared response of reduced graphene oxide and its high-temperature coefficient of resistance," *Aip Advances*, vol. 4, pp. 107131- 107136, 2014.

[20] Li Yang, Cheol-Hwan Park, Young-Woo Son, Marvin L. Cohen, and Steven G. Louie, "Quasiparticle energies and band gaps in graphene nanoribbons," *Physical Review Letters*, vol. 99, no. 18, p. 186801, 2007.

[21] Marjorie C. Caserio John D. Roberts, *BASIC Priciples of Organic Chemistry/SECOND EDITION.: W. A. Benjamin, Inc.* , 1977.

[22] A .Jorio, "Raman spectroscopy in graphene-based systems: prototypes for nanoscience and nanometrology," *International Scholarly Research Notices*, vol. 2012,article ID 234216, 2012.

[23] Yan Shen, Songbo Yang, Peng Zhou, Qingqing Sun, Pengfei Wang, Li Wan, Jing Li, Liangyao Chen, Xianbao Wang, Shijin Ding, David Wei Zhang, "Evolution of the band-gap and optical properties of graphene oxide with controllable reduction level," *Carbon*, vol. 62, pp. 157-164, 2013.