Journal of University of Babylon for Pure and Applied Sciences, Vol. (27), No. (3): 2019

Investigate of the Energy Gap, Ionic Charge and Infrared Spectra (IR) Of Ge Nanocrystals

Hussein Fadhal Hussein

Directorate of Education Babylon
husseinaashuor@gmail.com

ARTICLE INFO
Submission date: 1 / 4 /2017
Acceptance date: 24 /4/ 2017
Publication date: 1 /6/ 2019

Abstract

Density functional theory (DFT) has been used in this work at the B3LYP level with (6-31G**) basis set to find out Energy Gap, Ionic Charge and Infrared Spectra (IR) of Ge Nanocrystals for crystal 8, 16 , 54 , 64 and 128 atoms, the study shows that the energy gap decrease with increasing of the number of atoms in crystal which have the same lattice constant approximately .

While the atomic charge is studied for two states, the 8 and 64 atoms oxygenated surfaces, the results show that there is a gradient of net charge from the oxygen atoms on the surface toward the Ge atoms at the center of each crystal,

According to Infrared spectra there are two types of stretching vibration, symmetric and asymmetric, the symmetric stretching happens when the bonds of the same atoms vibrate in the same phase which appear as peak point, and the asymmetric stretching happens when the bonds vibrate in different phases which appear as bottom point.

Key words: Ge, Energy Gap, Ionic Charge, Infrared Spectra

Introduction

The most semiconductors important is germanium which has a small band gap, allowing it to efficiently respond to infrared light [1]. It is therefore used in infrared spectroscopes and other optical equipments which require extremely sensitive infrared detectors [2]. Its oxide's index of refraction and dispersion properties make germanium useful in wide-angle camera lenses and in microscope objective lenses [3]. Germanium is a highly important infrared optical material and can be readily cut and polished into lenses and windows [4]. It is used particularly as the front optic in thermal imaging cameras working in the (8 – 14 nm) wavelength range for passive thermal imaging and for hot-spot detection in military and fire fighting applications [5]. The material has a very high refractive index (4.0) and so needs to be anti-reflection coated [6].

In order to reduce computational efforts, and separate surface and core properties, germanium nanocrystals are represented by a heterojunction between the surface and the core. The surface represents the outer most four layers and the core by the rest of the internal region of nanocrystal [7].

Atoms in many semiconductors such as Ge are periodically arranged in a crystal lattice, the unit cell is defined as the smallest atomic arrangement which can be repeatedly used to generate the entire crystal lattice [8]. Germanium has a diamond lattice, which can be regarded as two interpenetrating fccsublattices with one sublattice displaced from the other by one quarter of the distance along a diagonal of the cube [9]. The lattice constant (a) is defined as the distance between two nearest neighbors in the simple cubic part of the unit cell [10]. In a diamond lattice, all atoms are surrounded by four equidistant nearest neighbors that lie at the corner of a tetrahedron [11,12].

Theory

Density functional theory (DFT) has been used in this work at the B3LYP level with (3-21G**) basis set. The results have been carried out by Gaussian 03 program. (DFT) is one of the useful methods to calculate the all electronic structure of atoms, molecules and solids [12,13].

This method uses the electron density, which based on the Thomas – Fermi and Thomas – Fermi – Dirac models in which the models proved to be of little use because they cannot yield a lower total energy for a molecule than for separated atoms. Hohenberg –Kohn crossed this problem by presenting two fundamental results [14]. First, the ground state electron density uniquely determines the Hamiltonian and, therefore, the ground state electronic wave function and all properties of the system. Second, the true density functional of the electronic energy assumes its minimum for the correct ground state density [15].

Hohenberg-Kohn results reduced the problem of solving the many body Schrödinger equations to the problem of minimizing a density functional. Kohn – Sham approach is the famous work that was more embraced in many purposes [16].

In quantum theory calculations, it is necessary to find the geometry optimization of the system studied. Quantum mechanics programs, such as, Gaussian, represent the geometry input in a special form called z-matrix. The z-matrix specifies the positions of atom (i) by three geometric parameters [17]:

$r(i , j)$, $\theta (i , j , k)$ and $\Phi (i, j, k,\ell)$

Where

$0 \leq r (i , j) \leq \infty$, $0\leq \theta (i , j , k) \leq 180^o$, $-180^o \leq \Phi (i , j , k , \ell) \leq 180^o$

r is the distance (bond length) between two atoms.

θ is the bond angle at (j) between lines (j-i) and (j-k)

Φ is the dihedral angle between the two planes defined by (i-j-k) and (j-k-ℓ) meeting at the line (j-k).

This scheme, which was originally suggested by Eyring [R.O.Jones, 2006, P. A. Kollman and K. M. Merz, 2007].

The z-matrix has advantages over coordinates when it comes to geometry optimization. If the three geometric coordinates for a point are given three surfaces on which the point where the three surfaces intersect.

The Cartesian coordinates must be calculated and then finding a non-linear system of equations:

$$\rho_{\alpha\lambda}(\mathrm{r} ; \mathrm{c}_\lambda) = 0 \quad ; \quad \lambda = 1, 2, 3 \text{ and } \quad \alpha_\lambda \in \{1, 2, 3, 4, 5\} \ldots\ldots(1)$$

Where C_λ stands for the collection of constants that determine the shape, size, position and orientation of the surface.

Essen finds that the most stable and accurate way to solve this system by the minimal of the sum of the squares to the three surface functions [R.O.Jones, 2006, H. Dorsett and A. White, 2000]:

$$F(r)=\sum_{\lambda=1}^{3} f_{\alpha\lambda}(r;C_{\lambda})\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

A minimum of this function, F(r), is easily found by searching for a zero of its gradient by means of Newton–Raphson method.

DFT calculations have been performed by Gaussian 03 program, the Gaussian 03 program proved height efficacy to perform several calculations and compute many of molecular properties, DFT calculations are useful for large radical systems and antiaromatic molecules[18,19]. DFT will be able to describe both the nondynamical and dynamical correlation effects in a balanced way at lower computational costs, DFT method is more reliable than abinito function based method, DFT method has been successfully applied to the prediction of activation barriers of chemical reactions, magnetic properties and electronic states[19,20]

The exchange–correlation energy for a non-interacting system is exactly defined and known as the Hartree-Fock exchange energy [21]. While the exchange-correlation energy for fully interacting system is not well defined, and it should be approximated with a common density functional. The weighted sum of these two results is known as the functional of B3–LYP [22]:

$$E_{xc}^{B3LYP}=E_{xc}^{LDA}+a_0\left(E_x^{HF}-E_x^{LDA}\right)+a_x\left(E_x^{GGA}-E_x^{LDA}\right)+a_c\left(E_c^{GGA}-E_c^{LDA}\right)\ldots\ldots..(3)$$

Where a_o , a_x and a_c are three empirical parameters and the best value of these parameters had been found as follow (a_o=0.20, a_x=0.72 and a_c=0.81) [23].

The forbidden energy gap is calculated for all structure by the following formula[24]:

$$E_{GAP}=E_{LUMO}-E_{HOMO}\quad\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

Where E_{GAP} is the forbidden energy gap.

E_{LUMO} is the energy of the lowest unoccupied molecular orbital.

E_{HOMO} is the energy of the highest occupied molecular orbital.

Calculations

Table (1):- the energy gap with Lattice constant for Ge nanocrystale

Parameter	**Present work**						
	Ge Core					**Ge core +surface**	
	8 atoms	**16 atoms**	**54 atoms**	**64 atoms**	**128 atoms**	**8 atoms**	**64 atoms**
Energy gap(eV)	2.55	2.50	2.41	2.40	2.26	0.19	0.28
Lattice constant(nm)	0.515	0.517	0.518	0.519	0.510	0.529	0.539

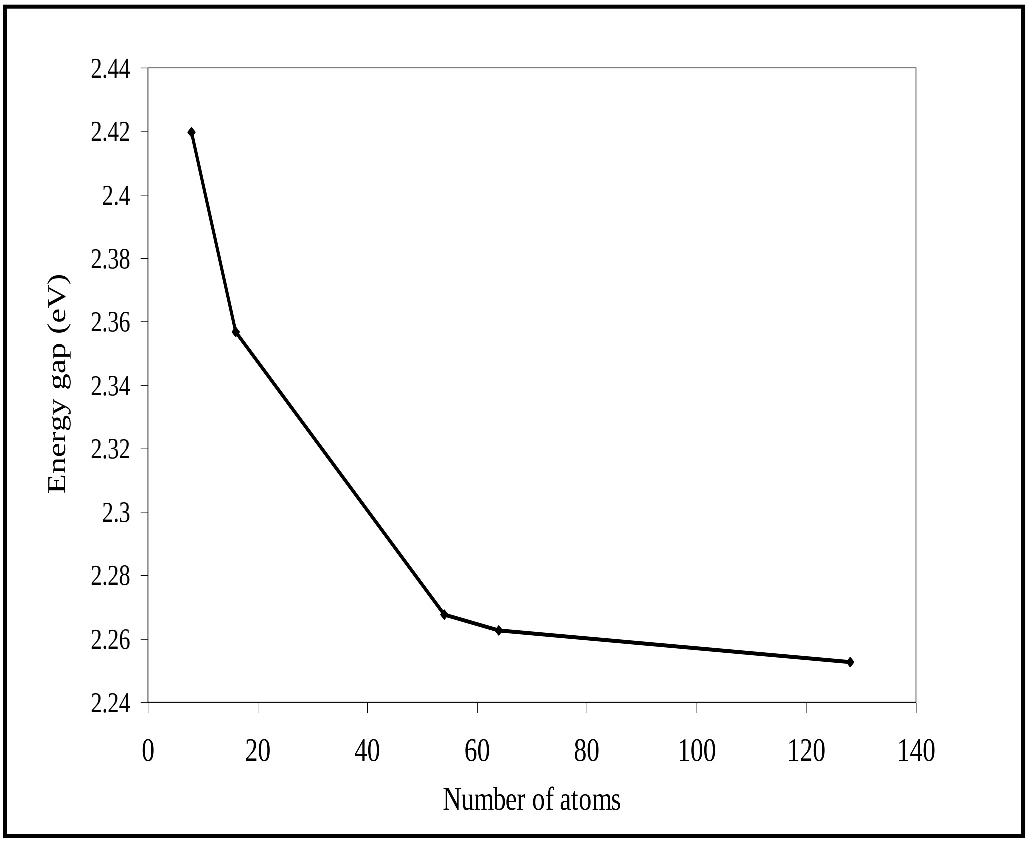


Fig. (1) The energy gap of germanium core nanocrystals as a function of number of atoms.

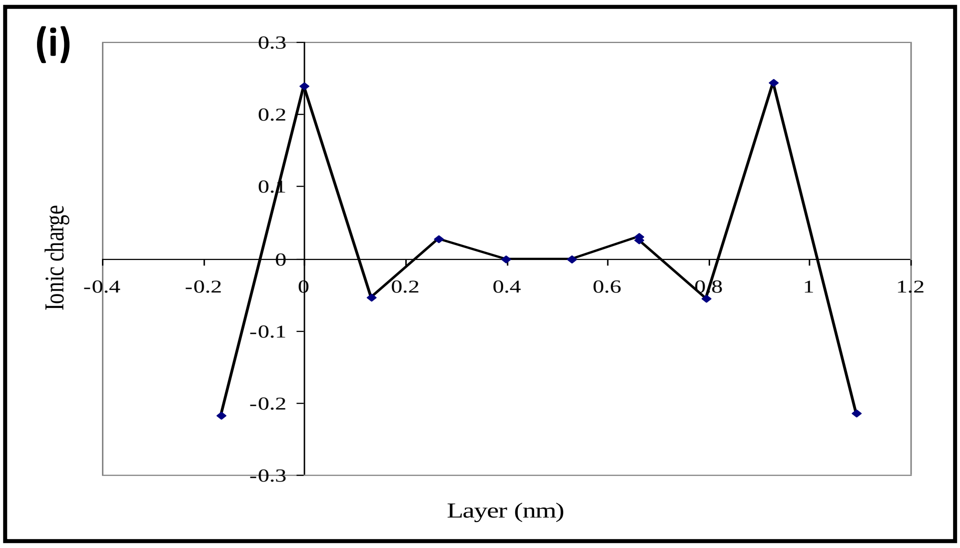
It's clear from figure (1) that the energy gap decrease with increasing of the number of atoms in crystal, the 128 atoms state is a multiple of the cubic primitive cell has smaller energy gap value. The energy gap of 128 atoms (2.26) eV is in good agreement with the resultant value of 2.21 eV reported by the reference [25] for Ge .

When we compare the value of energy gap between the case of 64 atoms and 128 atoms then shows that the size of the cell has no pronounced effect on the electronic structure of the core of nanocrystals in the case of large number of atoms, whereas the effect of size is more pronounced in the case of a small size (8, 16, and 54 atoms).

Whoever, a small energy gap means small excitation energies to the manifold of excited states. Therefore, soft molecules with small energy gaps, their electron density change more easily than a hard molecule, and due to that, soft molecules will be more reactive than hard molecules[26].

The Ionic Charge

In this work the atomic charge is studied for two states, the 8 and 64 atoms oxygenated surfaces as shown in Figure (2) (i) and (ii) .



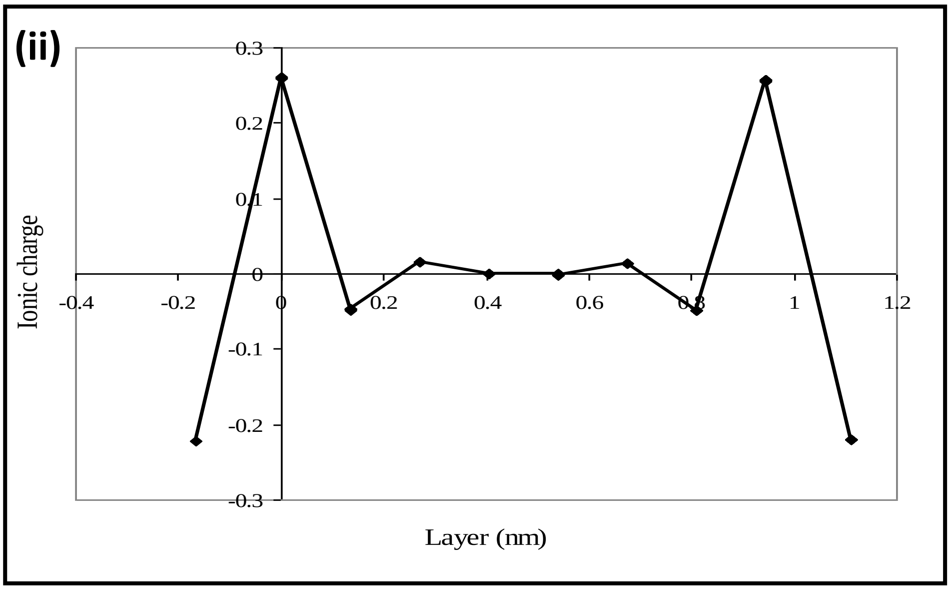


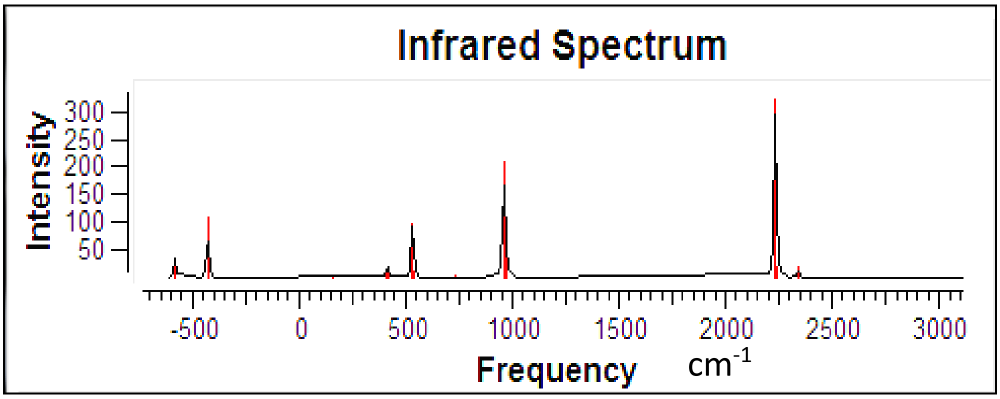
Fig.(2) the Ionic charge for the two oxygenated surface [(a) a^2 (b) $4a^2$] area .

From Figure (2) as the size of the nanoparticles increases, the number of Ge atoms in comparison with the number of oxygen atoms or the germanium-oxygen atom ratio increases. The results show that there is a gradient of net charge from the oxygen atoms on the surface toward the Ge atoms at the center of each crystals, the same gradient is found in Ge nanofilms [32].

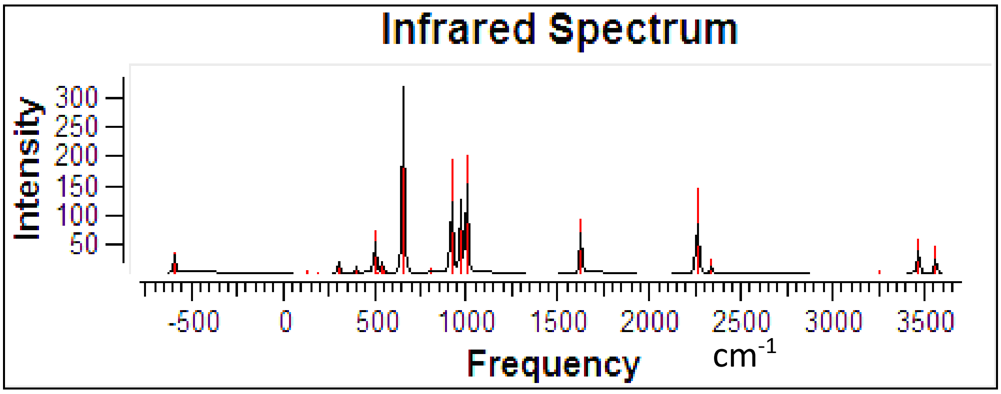
Infrared spectra

Molecular frequencies depend on the second derivative of the energy with respect to the nuclear positions [28]. Frequency calculations are valid only at stationary points on the potential energy surface. Thus, frequency calculations must be performed on optimized structure [29]. The complexity of IR spectrum is typical of most infrared spectra, and illustrates their use in identifying substances, socialized medicine, ability to use information from infrared and mass spectrometry to identify an unknown compound, night vision and control devices [30].

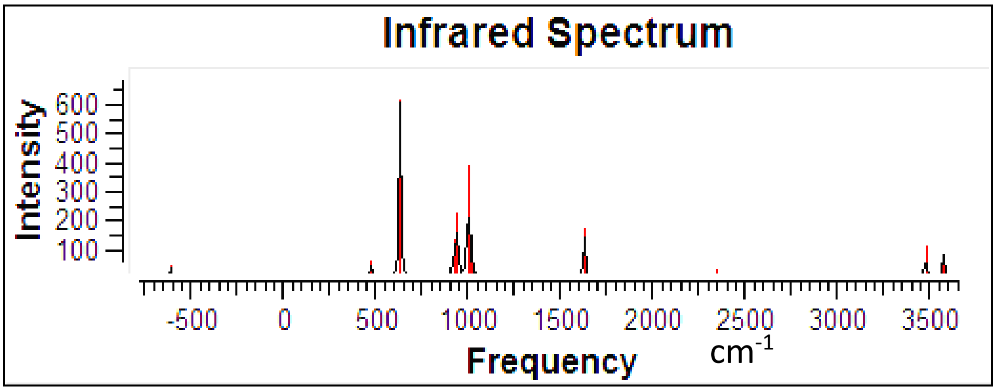
Vibrational modes are often given descriptive names, such as stretching, bending, scissoring, rocking and twisting.



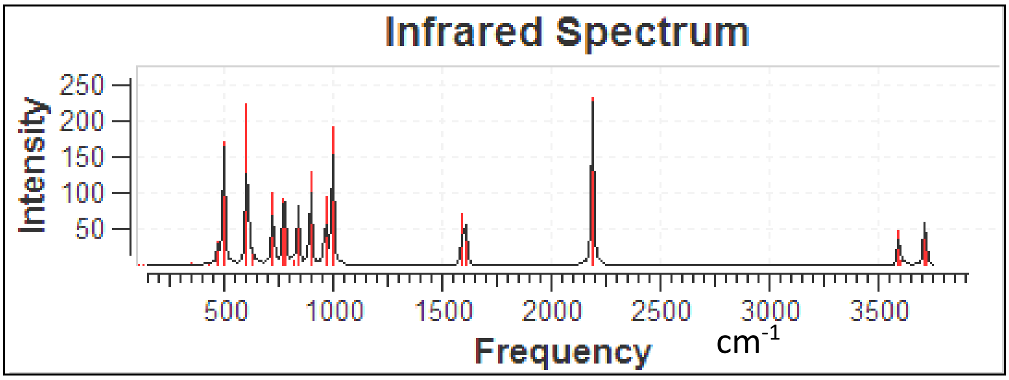
Figure(3-1): IR spectrum for 8 atoms (core)



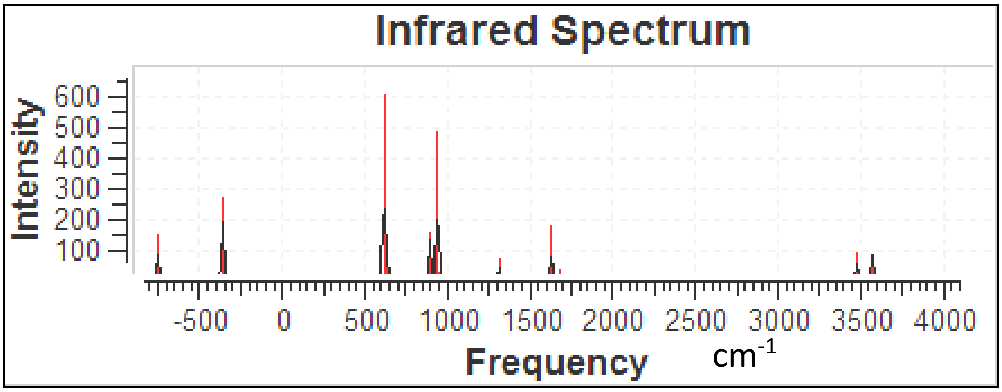
Figure(3-2): IR spectrum for 16 atoms (core)



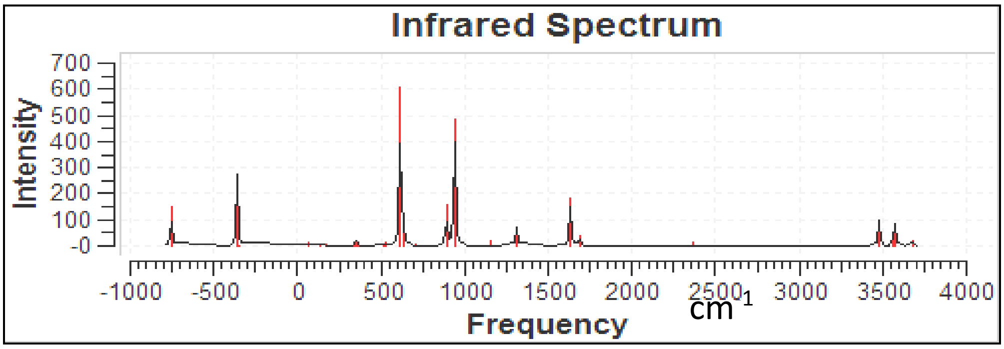
Figure(3-3): IR spectrum for 54 atoms (core)



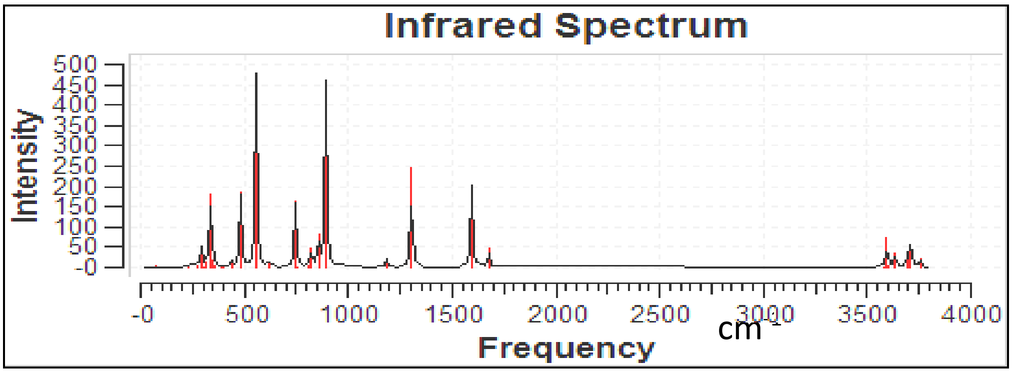
Figure(3-4): IR spectrum for 64 atoms (core)



Figure(3-5): IR spectrum for 128 atoms (core)



Figure(3-6): IR spectrum for 8 atoms (core & surface)



Figure(3-7): IR spectrum for 64 atoms (core & surface)

There are two types of stretching vibration symmetric and asymmetric, the symmetric stretching happens when the bonds of the same atoms vibrate in the same phase, and the asymmetric stretching happens when the bonds vibrate in different phases, most of the absorptions cited are associated with stretch vibrations[31-33].

Conclusions

1- Density functional theory (DFT) with B3LYP functional level is an efficient for studying the properties of these crystals. DFT is more accurate, but its take much more time to outcomes than others.
2- The energy gaps for all Ge nanocrystal decrease with increasing of the number of atoms in a crystal , a small energy gap means small excitation energies of the manifold of excited states.
3- Ionic Charge and Infrared Spectra depend on the type of atoms in a crystal and the bond between these atoms.

CONFLICT OF INTERESTS.
There are non-conflicts of interest .

References

1. L. Van Dao, X. M. Wen, M. T. T. Do, P. Hannaford, E. C. Cho, Y. H. Cho, and Y. D. Huang, "Time-Resolved and Time-Integrated Photoluminescence Analysis of State Filling and Quantum Confinement of Silicon Quantum Dots," Journal of Applied Physics, Vol. 97, 013501 (5 pages), (2005).
2. M. Grundmann, R. Heitz, N. Ledentsov, O. Stier, D. Bimberg, V. M. Ustinov, P. S. Kopev, Z.I. Alferov, S. S. Ruvimov, P. Werner, U. Gosele, and J. Heydenreich, "Electronic Structure andEnergy Relaxation in Strained InAs/GaAs Quantum Pyramids," Superlattices andMicrostructures, Vol. 19, pp. 81-95, (1996 **).**
3. A. H. Harker and F.P. Larkins, "A Large Unit Cell Semiempirical Molecular Orbital Approach to The Properties of Solid II. Covalent Materials: Diamond and Silicon" J. Phys. C, V 12 P 2497 (1979).
4. P. Huang and E. A. Carter, "Advance in Correlated Electronic Structure Methods for Solids, Surface, and Nanostructures", Rev. Phys. Chem., 59 (361), (2008).
5. W. Hehre, L. Random, P. Schleyer, and J. Pople, "Ab-initio Molecular Orbital Theory ", John Wiley and Sons (1986).
6. L. C. Kimerling, L. D. Negro, M. Stolif, J.H.Yi, J. Michel, X. Duan, E. H. Sargent, T. W. Chang, V. Sukhovatkin, J. Haavisto, and J.Leblanc, "Si-Rich Dielectrics for Active Photonic Devices", Boston University, (2009).
7. L. Pavesi, and R. Turan, "Si nanocrystals", Wiley-Vch, (2010).
8. C. Delerue, M. Lannoo, and G. Allan, Phys. Stat. Sol. (b), 1(115), (2001).
9. L. Khriachtchev, "Silicon Nanophotonics", University of Helsinki, Finland, (2009).
10. M. Fujii, Y. Yamaguchi, Y. Takase, K. Ninomiya, and S. Hayashi, Applied Physics Letters, 85(7), (2004).

11. A. R. Wilkinson, "The Optical Properties of Silicon Nanocrystals and the Role of Hydrogen Passivation", Ph.D. Thesis, The Australian National University, (2006).
12. D. A. Neamen, "Semiconductor Physics and Devices", University of New Mexico, (2003).
13. S. M. Sze and K. K. Ng, Physics of semiconductor devices, 3rd edition, Wiley (2007).
14. G.E.Scuseria and V.N. Staroverov ; "Progress in the Development of Exchange Correlation Functional", Elsevier, Amsterdam , (2005).
15. J. Hutter; "Lecture notes in Computational Chemistry: Electronic Structure Theory", Physical Chemistry Institute , University of Zurich, Winter thurerstrasse 190, 8057 Zurich, Switzerland , (2005) , Hutter@ pci.unizh.ch.
16. E.F. Valeev and C.Sherrill; "The Diagonal Born-Oppenheimer Correction beyond the Hartree-Fock Approximation", Journal of Chemical Physics, 118 , 9, (2003).
17. A. K. B. Bender;"Structure Modeling of Aluminosil-Sesquioxanes", Ph.D. Thesis, Berlin, Germany,(2000).
18. V.N.Glushkov ; "Alternative Techniques in open-shell SCF Theory", International Journal of Quantum Chemistry , 99 , pp.236-246 , (2004).
19. H. I. Aboud and A. J. Najim; "Theoretical Study of Structures, Energies, Dipole Moment, and IR Spectra for Amino Benzene Group Molecules Using Density Functional Theory", Journal of Babylon University, (2011).
20. R.O.Jones ; "Introduction to Density Functional Theory and Exchange-Correlation Energy Functional",Computationalnanoscience , NIC series , John Von Neumann institute for Computing , Julich , 31 , IS BN 3-00-017350-1,45-70 , (2006).
21. P. A. Kollman and K. M. Merz; " Computer modeling of the interactions of complex molecules ", Acc. Chem. Res. 23, 246, (2007).
22. H. Dorsett and A. White ; "Overview of Molecular and Ab initio Molecular Orbital Methods Suitable for use with Energetic Materials", Aeronautical and maritime research laboratory, Australia , (2000).
23. Johannes Grotenderst; "High Performance Computing, in Chemistry", John Von Neumann institute for computing ,Julich , NIC series ,25,(2004).
24. G. Robert , Parr, Yang and Weitao ; "Density Functional Theory of Atom and Molecules", Oxford University Press, Oxford ,(1994).
25. Pina Romaniello; "Time Dependent Current Density Functional Theory for Molecules", Ph.D. Thesis, Materials Science Center, University of Groningeen, Netherlands, (2006).
26. R. G. Pearson; "Chemical Hardness and Density Functional Theory", J. Chem. Sci. 117, 5, 369, (2005).
27. J. Simons; "An introduction to theoretical chemistry", Cambridge University Press, (2003).
28. Michael Muller; "Fundamentals of Quantum Chemistry, Molecular Spectroscopy and Modern Electronic Structure Computational", Rose Hull man Institute of Technology, Terre Haute, Indiana, (2002).

29. J. W. Ochterski; "Vibrational Analysis in Gaussian", Gaussian incorporation, Wallingford CT, help@gaussian.com, (1999).
30. Thomas L. Floyd; "Electronic Devices", 7th Edition, Pearson Prentice Hall, (2005).
31. Young D. Hugh , Freedman A. Roger and Ford A. Lewis, University Physics with Modern Physics, 13th Edition Pearson, (2012).

32. P. Gori, M. Marsili, V. Garbuio, and O. Pulci, "Ab Initio Calculations of Electronic Properties of 2-Dimensional Materials" University of Rome Tor Vergata and INFM-CNR-SMC, Rome, Italy and ETSF, (2010).
33. V. Kumara and Y. Kawazoe," Metal-Encapsulated Icosahedral Superatoms of Germanium and Tin with Large Gaps" Institute for Materials Research, Tohoku University, App. Phys. Lett. Vol. 80, No. 54, 566 (2001).

الخلاصة

استخدمت طريقة دالة الكثافة ذات المستوى B3LYP في هذا البحث لايجاد فجوة الطاقة و الشحنة الايونية و كذلك طيف الاشعة تحت الحمراء لبلورة جرمانيوم نانوية في حالة 8 ذرات و 16 ذرة و 54 ذرة و 64 ذرة و 128 ذرة , و قد اظهرت الدراسة بان فجوة الطاقة لتلك البلورة تتناقص مع زيادة عدد الذرات في البلورة والتي تمتلك تقريبا نفس ثابت الشبيكة.

بينما تم دراسة الشحنة الذرية للسطح المؤكسد للحالتين 8 ذرات و 64 ذرة و قد اوضحت الدراسة بان الشحنة الكلية لذرات الاوكسجين عند السطح المؤكسد تتجه نحو ذرات الجرمانيوم الموجودة في مركز البلورة و هذه النتيجة تنطبق على جميع البلورات .

بالاعتماد على ترددات طيف الاشعة تحت الحمراء فان هنالك نوعين من الاهتزازات هما الاهتزاز المتماثل و الاهتزاز اللامتماثل , يحدث التردد المتماثل عندما تهتز الاواصر في نفس الذرات بنفس الطور فيظهر هذا النوع من التردد على شكل قمة , بينما يحدث التردد الغير متماثل اذا اهتزت هذه الذرات بطور مختلف و الذي يظهر على شكل قعر.

الكلمات الدالة:– جرمانيوم , فجوة الطاقة , الشحنة الايونية , طيف الاشعة تحت الحمراء .