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Research Article

Electronic and vibrational spectroscopic properties of GaAs diamondoids using Density Functional Theory

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Abstract

In the present work we study the electronic structure, FTIR and Raman spectra of GaAs diamondoids structure as a function of particle size and shape by using density functional theory at the generalized gradient approximation level of Perdew, Burke and Emzhof (PBE), through Gaussian 09 program with 3-21G basis states. The frequencies in the vibrational spectrum are analyzed against reduced masses, force constants and intensities of vibration. The results show that both total energy and energy gap decrease in their value as the nanocrystals cluster grow in size. Diamondoids structure molecule used to vary the nanoparticals size being of standard shape and size. Diamondoids have the least surface effects so the trends can point towards bulk properties. Results showed that GaAs bond lengths generally decrease as the number of cages increases with remarkable dependence on the shape of the diamondoids molecules. Tetrahedral angles and bond lengths are used to compare different sizes of GaAs diamondoids molecules.

Keywords: *GaAs, diamondoids structures, DFT , infrared spectroscopy.*

Introduction

GaAs is III-V compound semiconductor bulk or nanocrystals are excellent material in many electronic devices (S. M. Sze and K. K. Ng. 2007; J. Perriere *et. al.* 2001; J. Jiang *et. al.* 2009; S. Okamoto *et. al.* 1998). The direct band gap of GaAs gives it superiority in light emitting devices. Nanocrystals of GaAs are manufactured in different methods that range from laser ablation (J. Perriere *et. al.* 2001) to chemical implantation (S. Okamoto *et. al.* 1998). These nanocrystals give us the ability to maneuver many physical properties such as energy gap and lattice constant to fulfill the range of requirements of electronic devices.

In the present work we shall investigate some properties of GaAs diamondoids structure using Ab- initio density functional theory method. This method is the usual cluster full geometrical optimization in connection with Hartree-Fock method (HF) which is one of the most accurate methods to simulate electronic structure and optical properties of nanocrystals. This method is also the most computationally expansive both in time and resources (J. B. Foresman *et. al.* 1996).

The cluster full geometrical optimization calculation are available to run with DFT in Gaussian 09 program (J. B. Foresman *et. al.* 1996; M. J. Frisch *et. al.* 2003) which is used in the present work. The theoretical calculation of vibrational infrared frequency and Raman lines of GaAs nanocrystal cluster and the variation of these vibrations from molecular to bulk size is investigated. Several previous calculations from other authors assigned different origins for some of the well observed lines, such as the experimental (0 -300 cm^{-1}) GaAs bulk lines (S. M. Sze and K. K. Ng. 2007; N.N.Greenwood1996) .

Theory

Ab-initio density functional theory at level of the generalized gradient approximation of Perdew Burke and Emzerhof (PBE) is used in the present work to determine stable optimized positions of atoms in the nanocrystal (J. B. Foresman *et. al.* 1996). 3-21G basis function is chosen to perform the above calculations so that all vibrational analysis is performed with the same level of theory, which is feasible within our computer system in terms of memory and time.

The present method starts from molecular size building up structures to reach the nanoscale region (bottom-up method). There is essentially solid state method reapplied to nanoscale sizes (top – down methods). Diamondoids are perfectly size and shape selectable, hydrogen passivated, and *sp*3-hybridized carbon nanostructures. Of particular interest in nanoparticals is the size-dependence of their electronic structure, often referred to in recent literature as quantum confinement (QC) effects. As they are perfectly size-selectable, diamondoids enjoy great popularity in the investigation of such effects (Tobias Z. *et. al.* 2013). The recently discovered higher diamondoids have thus generated much excitement in regards to their potential versatility as nanoscale devices. Despite this excitement,

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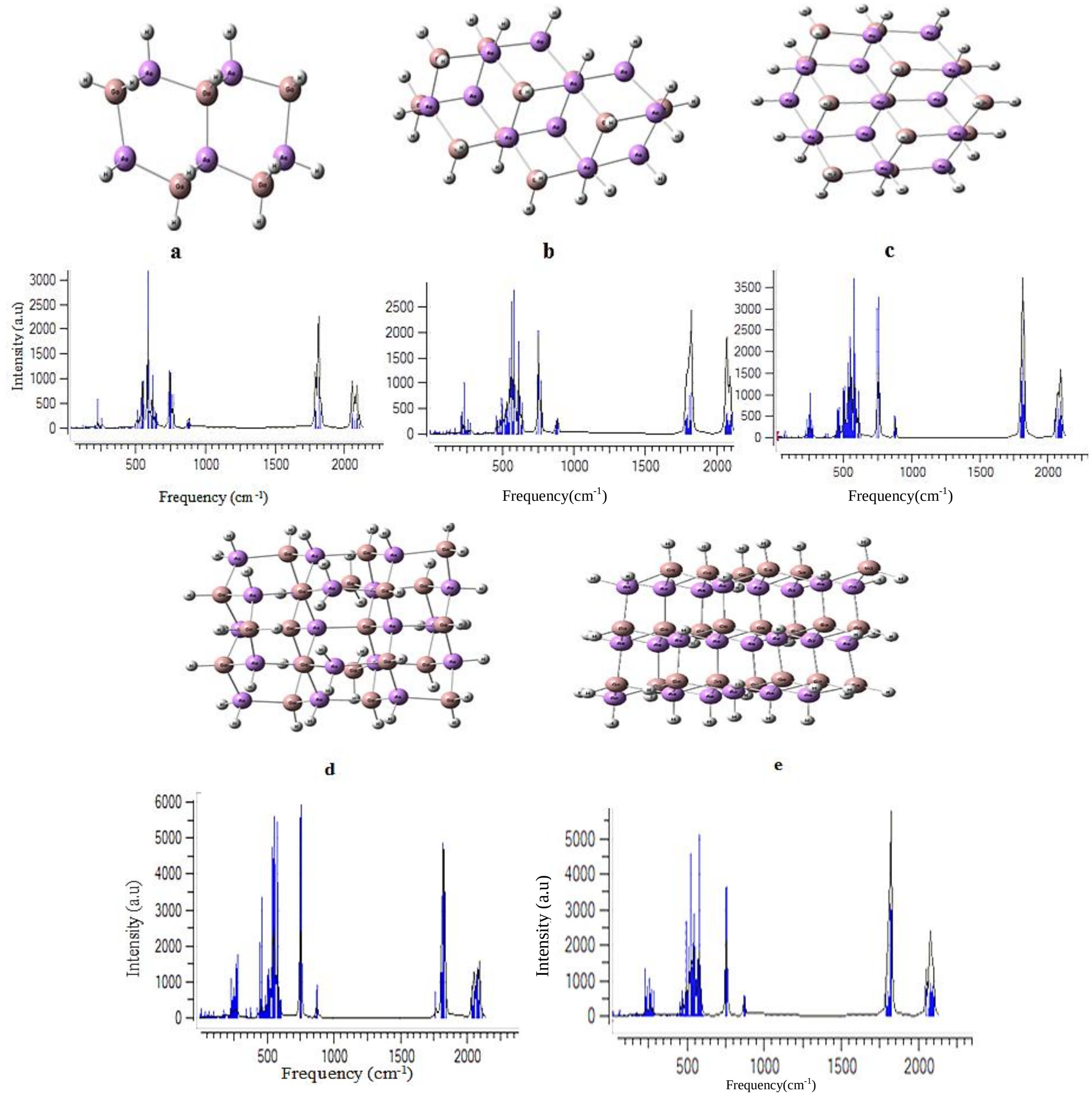

Fig 1: Shape of geometrically optimized and I.R spectra of GaAs- diamondoids as a function of frequency of a-diamantane $Ga_7As_7H_{20}$ b-tetramantane $Ga_{11}As_{11}H_{28}$ c-hexamantane $Ga_{13}As_{13}H_{30}$ d- octamantane $Ga_{20}As_{20}H_{42}$ e-decamantane $Ga_{22}As_{22}H_{42}$

however, very little is known about the properties of isolated diamondoids on metal surfaces, a very relevant system for molecular electronics (Y. Wang *et. al.* 2008).

Results and discussion

The program Gaussian 09 is used to optimize the geometries and calculate the vibrational spectra of GaAs diamondoids nanocrystals (diamantane, tetramantane, hexamantane, octamantane and decamantane). The calculated frequency error that results from ab-initio calculation (Tobias Z. *et. al.* 2013).

The previous estimation of this scale factor for PBE theory by using 3-21G basis is 0.991 (Lakard B., *et. al.* 2003) . Note that different author use different scale factors for the same basis at the same level of calculations (Lakard B., *et. al.* 2003). The present scale factor is one of the nearest scale factors to be un scaled data (very close to 1) and will be used without modification for all spectra. In Fig (1) shows geometrical optimization method is used in the present work to obtain the electronic structure of GaAs molecules as while as infrared spectrum as a function of frequency. These include cage like molecules as following diamantane $Ga_7As_7H_{20}$, tetramantane $Ga_{11}As_{11}H_{28}$, hexamantane $Ga_{13}As_{13}H_{30}$**,** octamantane $As_{20}Ga_{20}H_{42}$ and decamantane $As_{22}Ga_{22}H_{42}$.

Bulk GaAs is identified by its IR absorption at approximately 0-300 cm^{-1} vibrational mode peak (S. M. Sze and K. K. Ng. 2007; J. Perriere *et. al.* 2001; J. Jiang *et. al.* 2009; S. Okamoto *et. al.* 1998; J. B. Foresman *et. al.*

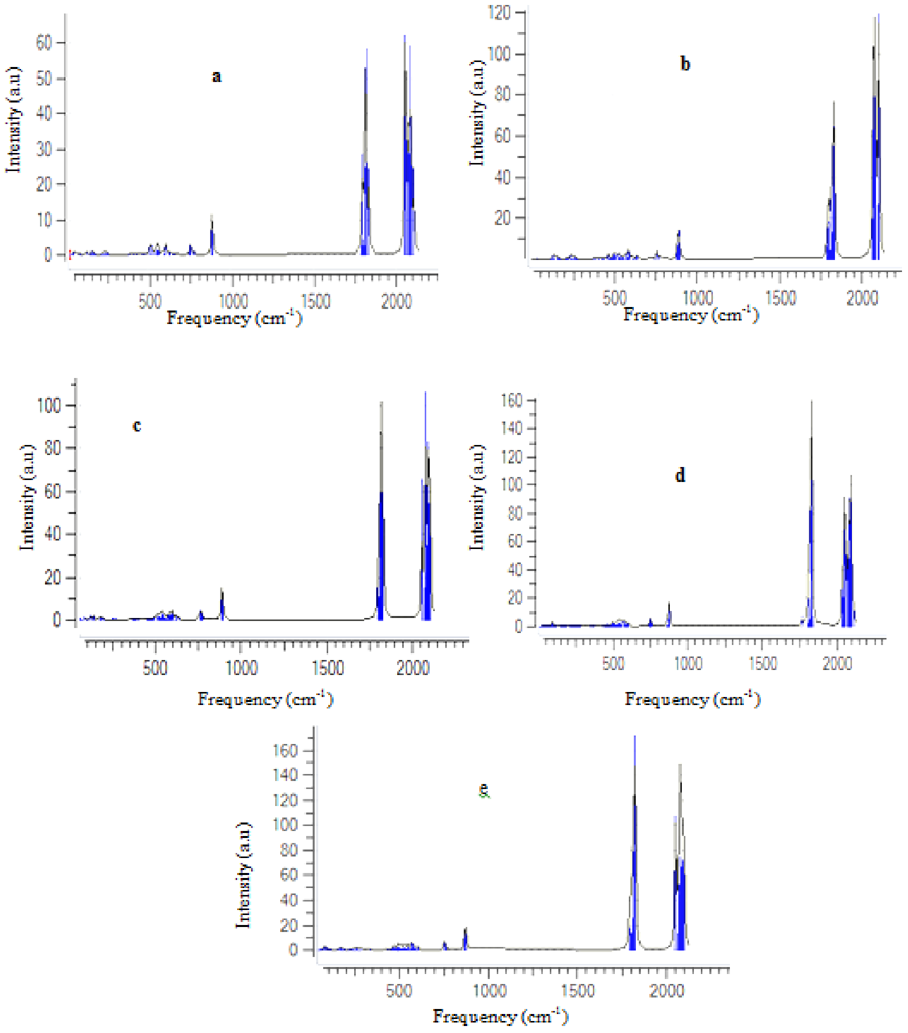

Fig. 2: Raman intensities of GaAs-diamondoids of infrared spectrum as a function of frequency of a- diamantane $Ga_7As_7H_{20}$ b- tetramantane $Ga_{11}As_{11}H_{28}$ c- hexamantane $Ga_{13}As_{13}H_{30}$ d- octamantane $Ga_{20}As_{20}H_{42}$ e- decamantane $Ga_{22}As_{22}H_{42}$

1996; M. J. Frisch *et. al.* 2003; N.N.Greenwood1996; Siegfried Wartewig 2003). However, the highest intensity line in the presently calculated Fig. 1 for GaAs diamondoids is at 599 cm^{-1} while decamantane is 1818 cm^{-1}. We notice a shift in the intensity maxima toward right side of the infrared vibrational frequencies. This includes the 950–2450 cm^{-1} modes in the Ga-H and As-H vibrational region. The region around the broad peak at 599 cm^{-1} has Ga–As.

The highest intensity line in the presently calculated Fig.2 for GaAs diamantane is at 2052 cm^{-1}, tetramantane is at 2102 cm^{-1} and hexamantane is at 2076 cm^{-1} while octamantane and decamantane is around 1830 cm^{-1}.The shift in the intensity maxima of about 2000 cm^{-1} of the Raman vibrational frequencies. This includes the 990–2500 cm^{-1} modes in the Ga-H and As-H vibrational region.

Using the formula (1) that relates frequency of vibration to the force constant and reduced mass:

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

The reduced mass μ of two particles of masses m_a and m_b is given by:

$$\frac{1}{\mu} = \frac{1}{m_a} + \frac{1}{m_b} \qquad (2)$$

Although the above equation is for diatomic molecules, it can be used for the understanding of vibrational modes of other larger molecules (Blakemore J. S. 1982). Fig (3) that represents the reduced masses of GaAs-diamondoids vibrations, the left parts of Ga-As vibrations are larger than right parts of H vibrations and the right part is nearly equal to 1.The high reduced mass mode (HRMM) of decamantane Fig (3-e) is larger than of the other diamondoids.

Fig (4) shows GaAs-diamondoids force constants as a function of vibration frequency. A part from the statistical difference between the numbers of vibration frequencies of all GaAs-diamondoids, all shapes in the Fig (4) are nearly similar in shape. The shapes in Fig (4) begin from approximately 0 cm^{-1} of Ga-As vibrations and ends at less than 300 cm^{-1}, whereas right parts of H vibrations starts at approximately 375 cm^{-1} and ends at nearly 2200 cm^{-1}.

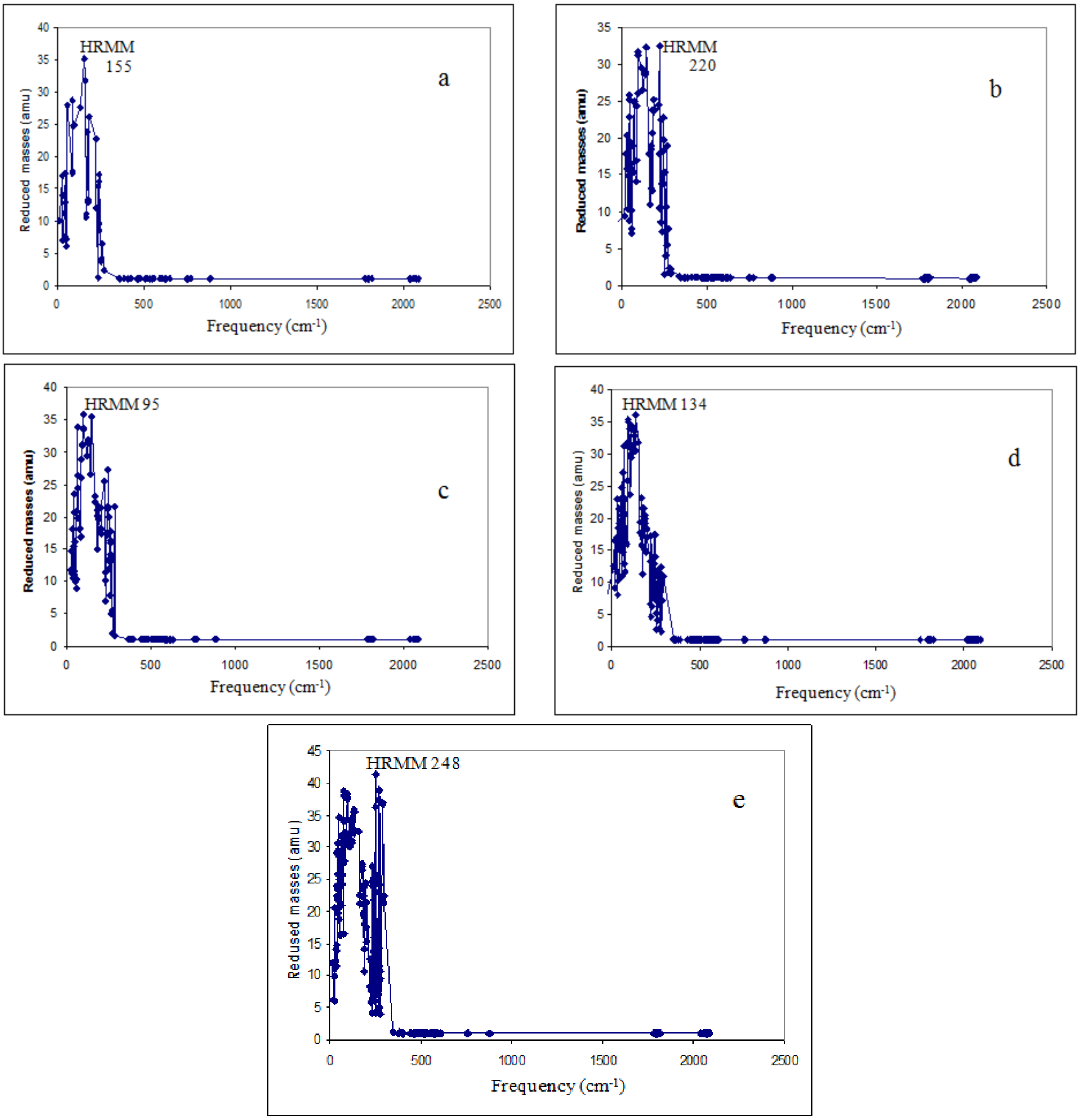

Fig. 3: GaAs-diamondoids reduced mass as a function of vibration frequency of a- diamantane $Ga_7As_7H_{20}$, b- tetramantane $Ga_{11}As_{11}H_{28}$, c- hexamantane $Ga_{13}As_{13}H_{30}$, d- octamantane $Ga_{20}As_{20}H_{42}$, e- decamantane $Ga_{22}As_{22}H_{42}$

The GaAs diamondoids bond lengths generally decrease as the number of cages increases with remarkable dependence on the size of the diamondoids molecules, as shown in Fig (5).

Fig 6 illustrates GaAs decamantane bond lengths against number layers starting from arsenide hydrogenated surface until we reach the gallium hydrogenated surface layer at the opposite face of the nanocrystal. The experimental bulk GaAs bond lengths 2.45A˚ is inside this distribution range. The two equal Ga–As bonds that are near the surface are mediated by a smaller Ga–As bond. H– Ga and H– As bonds are nearly constant through all the molecules and are equal to 1.53A˚-1.57A˚ .This is expected since these bonds are localized only at the surface.

Fig.7 shows the tetrahedral angle as a function of number of layers for GaAs decamantane using the same path of Fig(6). The variation of tetrahedral angle between atoms starting from gallium hydrogenated surface layer (H-Ga-As angle) until we reach the arsenide hydrogenated surface layer (Ga-As-H angle) at the opposite face of the nanocrystal. The tetrahedral angles range from 114.12A˚ to 108.81A˚ is compared with the ideal diamond and zincblende structure tetrahedral angle of 109.47º (Blakemore J. S. 1982). Tetrahedral angles approach the value of bulk as we go to higher diamondoids. The value of this angle decreases slightly starting from gallium terminated surface and ending at the arsenide terminated surface. The tetrahedral angle of decamantane is much closer to the ideal value 109.47º than that of diamantane.

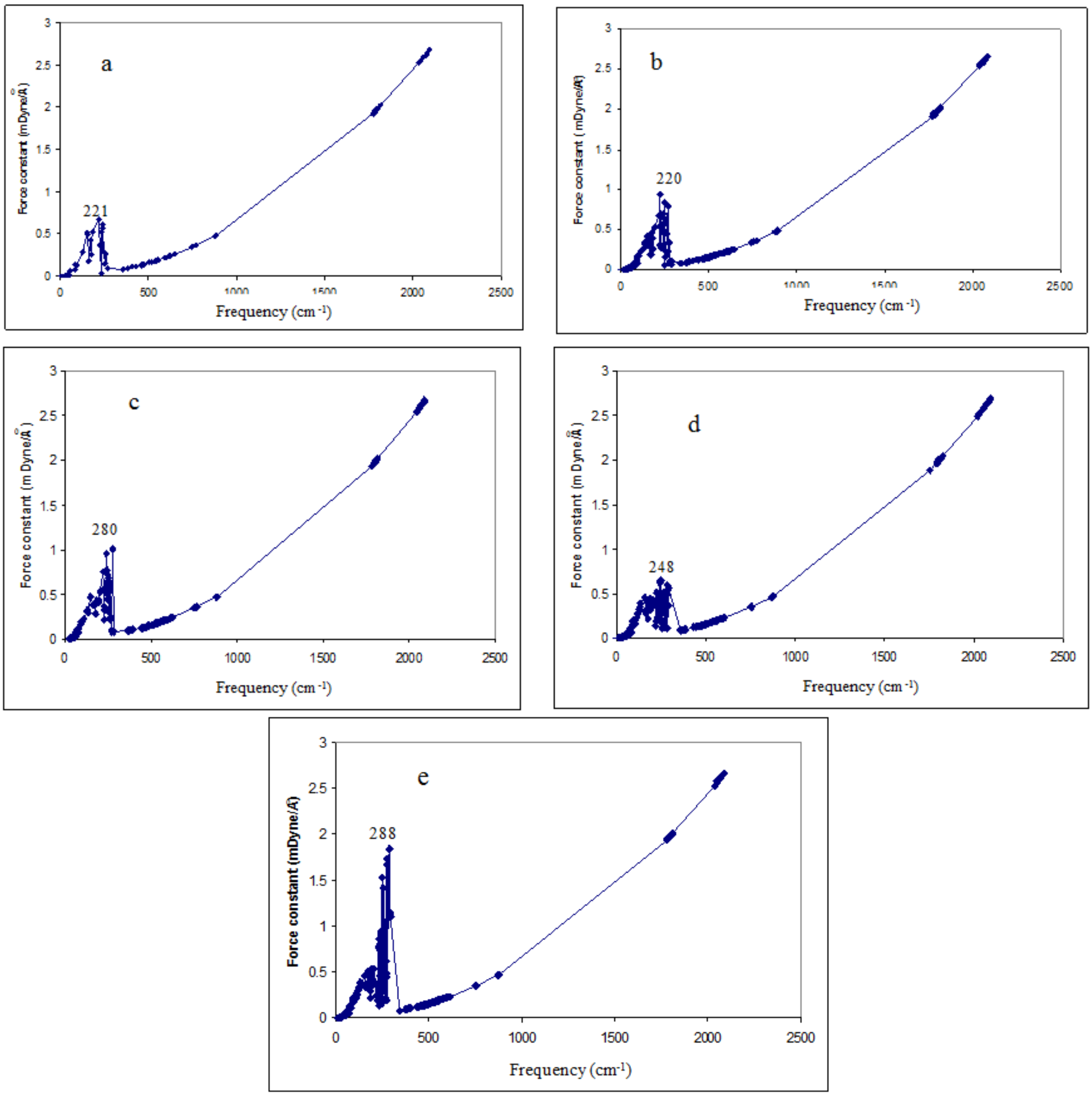

Fig 4: Force constant of GaAs- diamondoids as a function of frequency of a- diamantane $Ga_7As_7H_{20}$ b- tetramantane $Ga_{11}As_{11}H_{28}$ c- hexamantane $Ga_{13}As_{13}H_{30}$ d- octamantane $Ga_{20}As_{20}H_{42}$ e- decamantane $Ga_{22}As_{22}H_{42}$

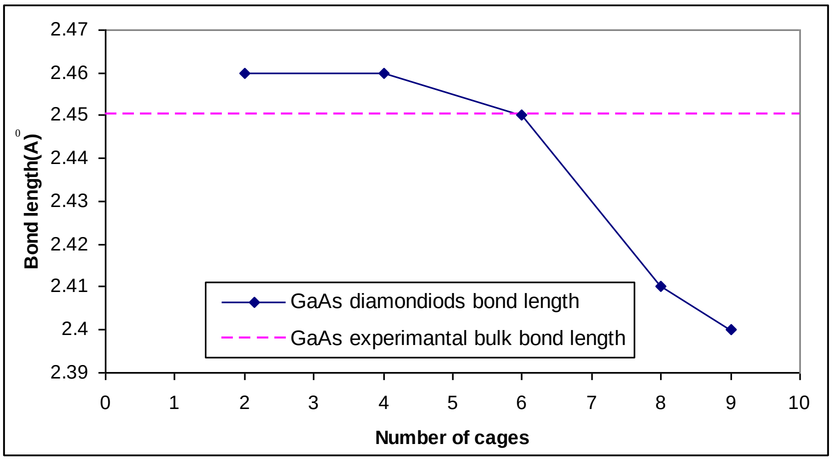

Fig. 5: Bond lengths of GaAs diamondoids .PBE/3-21G theory is used for the calculations of this figure. The dashed line represents the experimental bulk value of Ga-As bond length

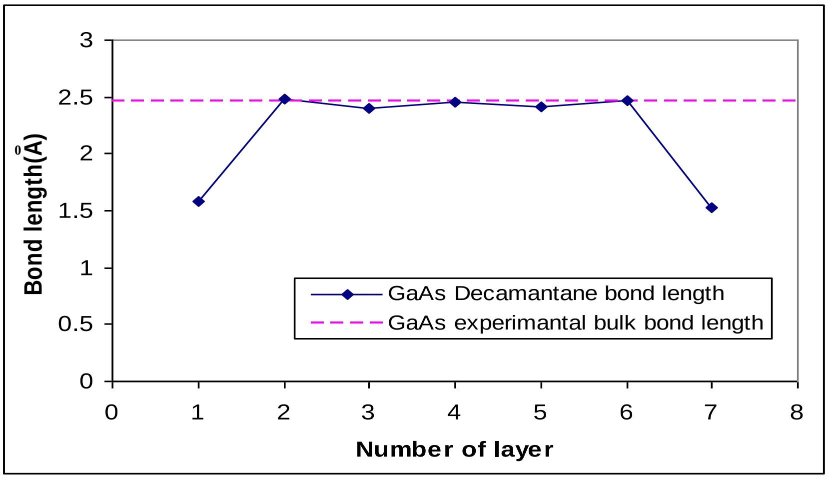

Fig. 6: Bond lengths of GaAs-decamantan.PBE/3-21G theory is used for the calculations of this figure. The dashed line represents the experimental bulk value of Ga-As bond length.

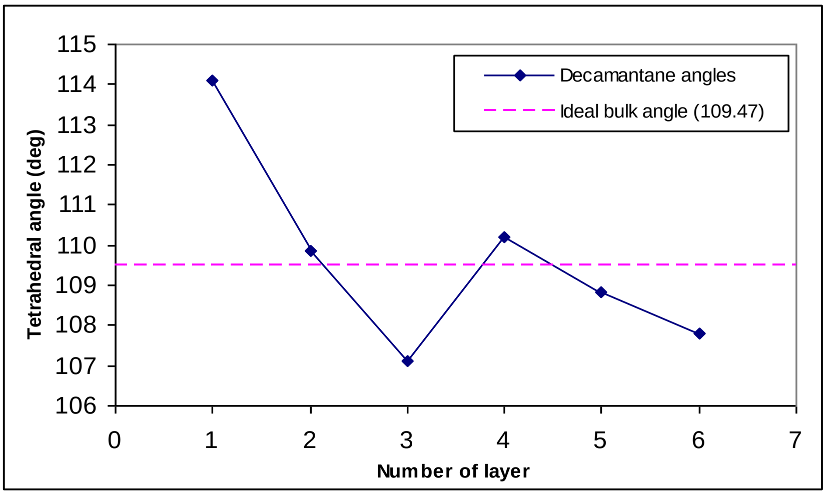

Fig. 7: The variation of tetrahedral angle between molecules starting from the gallium terminated layer (H-Ga-As angle) until we reach the arsenide terminated layer (Ga-As-H angle) at the opposite side of the diamondoids (solid line). This angle is compared with the ideal diamond and zincblende structure tetrahedral angle of 109.47^o (broken line) (Blakemore J. S. 1982)

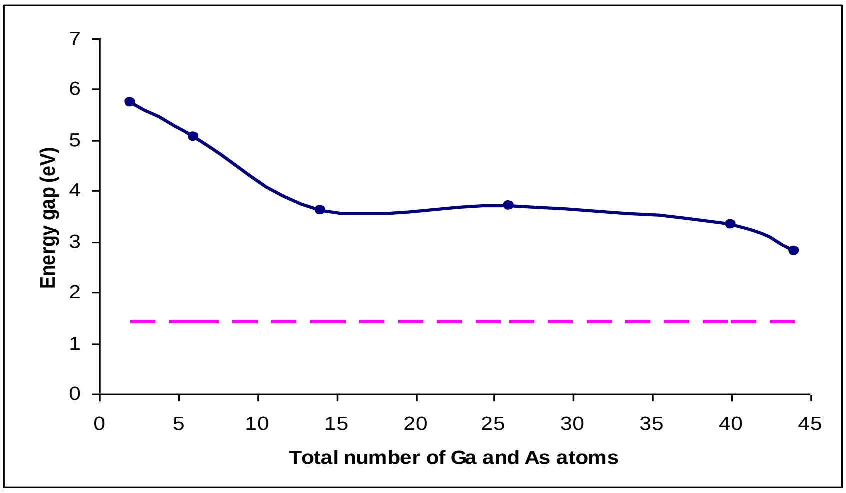

Fig. 8: Energy gap as a function of total number of Ga and As atoms in GaAs diamondoids. The dashed line represents the experimental value of bulk GaAs gap at 1.42 eV (S. M. Sze and K. K. Ng. 2007)

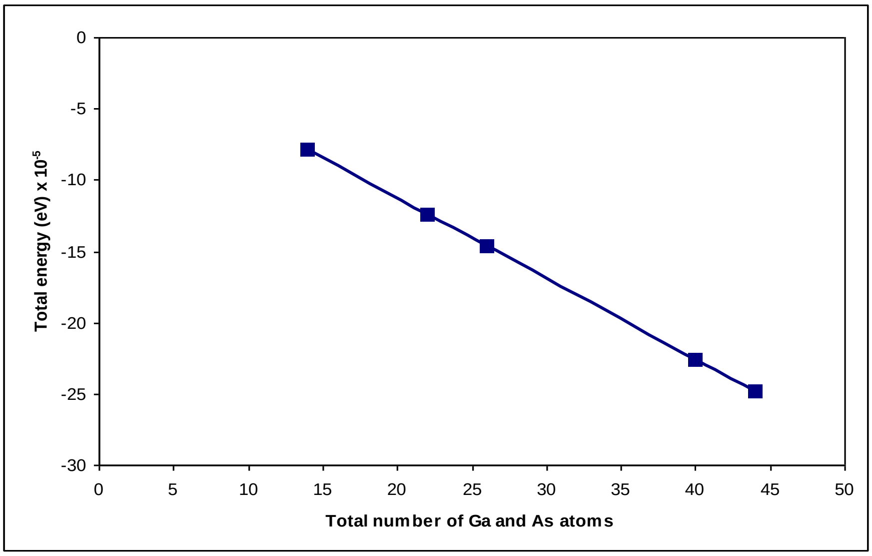

Fig. 9: Total energy as a function of total number of Ga and As atoms in GaAs diamondoids.

This is due to the effect of surface reconstruction that has an effect on all the atoms in GaAs-diamantane (all the atoms are bonded to surface hydrogen atoms) while it has an effect on some of the atoms in GaAs-decamantane.

The energy gap reduces from 3.62 eV in GaAs-diamantane to 2.8 eV in GaAs-decamantane. This reduction is in compliance with confinement effects that require size reduction of the energy gap as manifested in Fig (8). The value 2.8 eV for GaAs-decamantane is half the way towards the bulk value at 1.42 eV(S. M. Sze and K. K. Ng. 2007).

Fig. (9) Shows the variation of the total energy with the variation of the number of GaAs atoms, it is shown that the total energy decreases with increasing the number of Ga and As atoms. On the scale shown in this figure, the size dependence of the energy is linear.

Conclusion

As concluding remarks, we can note that the present theory can adequately reproduce many of the experimental data of infrared vibrational frequencies. This includes the 950–2450 cm^{-1} modes in the Ga-H and As-H vibrational region. The region of Ga-As mode of vibration is between 0 – 595 cm^{-1}. The present theory reproduce adequately various Ga-H and As-H vibrations, which include symmetric, asymmetric, wagging, scissor, rocking and twisting modes. It also reproduce the movement of the highest reduced mass Ga-As of nanocrystals grow in size.

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