

Study IR- Raman Spectra properties of Aluminium Phosphide Diamondoids Nanostructures via DFT

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ABSTRACT

Density Functional Theory has been utilized to investigate the electronic and structural characteristics of Aluminium phosphide (AIP). The exchange-correlation potential was calculated using the Generalized Gradient Approximation. The structural, electronic and vibrational features of AIP diamondoids and nanocrystals were investigated using Density Functional Theory at the PBE/6-31(d) level, which included polarization functions. Vibrational modes have been optimized concerning IR intensity, force constants, and lowered masses. In this study there are two components to the vibrational force constant for AIP diamondoids. The first one is distinguished by a reduced mass that is greater than 1 amu and consists primarily of Al-P vibrations that are positioned roughly between 0 and 231 cm^{-1} . The second component has a decreased mass very near to 1 amu and is in the 1228–2400 cm^{-1} range. It is entirely made up of hydrogen vibrational modes. AIP diamondoids were evaluated with the results of experimental bulk in terms of molecular size-related changes in allocated vibrational frequencies.

KEYWORDS: DFT; AIP; diamondoids nanostructures; IR-Raman spectral.

الخلاصة

استخدمت نظرية دالية الكثافة لدراسة الخصائص البنيوية والالكترونية لفوسفيد الألمنيوم. وتم استخدام تقريب الميل المعمم للجهد الارتباطي التبادلي. تم حساب الخواص الالكترونية والطيفية للتركييب البلورية لمويسات فوسفيد الألمنيوم باستخدام نظرية دالية الكثافة ضمن المستوى PBE/6-31(d) المتضمن لدالة الاستقطاب (d). وكذلك تم تعيين الأنماط الاهتزازية المتمثلة بثوابت القوة وشدة IR والكتل المختزلة. في هذه الدراسة هناك جزئين ثابتين للقوة لمويسات فوسفيد الألمنيوم تميز الجزء الاول بقيمة للكتلة المختزلة أكبر من (1amu) والتي تتكون أساساً من اهتزازات Al-P التي يتم وضعها تقريباً بين (0 cm^{-1} and 231). اما الجزء الثاني له كتلة مختزلة قريبة جداً من (1 amu) ويقع في مدى (1228–2400 cm^{-1}) وهي ضمن انماط اهتزاز الهيدروجين. وتمت مقارنة التغيير المرتبط بالحجم للترددات الاهتزازية المعينة لمويسات فوسفيد الألمنيوم مع القيم التجريبية للأحجام الكبيرة.

INTRODUCTION

At 300 K, AIP can be defined as one of the compound semiconductors with a lattice constant of 0.545 nm. AIP is a semi-conductor with a large indirect band gap. AIP crystallizes in the zinc-blende (zb) structure under normal conditions [1]. It's employed as active material in LEDs and optoelectronic devices, among other things; it's also important in optoelectronic applications in the range of the short wavelength, also for high power, high temperature, and high frequency [2, 3].

Diamondoids are considered nanoscale hydrogen terminated carbon cages [4]. Carbon-based functional nanostructures also referred to as diamondoids, have gotten much attention.

Diamondoids are a class of nanoscale diamond-like carbon nanoclusters that are terminated via hydrogen atoms and are thermodynamically extremely stable [5]. The gap energy, IR spectra, and Raman spectrum of AIP diamondoids have all been investigated by H. Jawad [6]. The research revealed the advantages of using diamantine as an insulating substance to connect drugs to our bodies without interfering with other medications while still delivering medicine to the affected areas. Using the Gauss View and Gaussian 09 software package [7], which refers to an Ab-initio electronic structure program, the optimized structure and vibrational spectra were calculated. The year 09 was used to denote 2009. Many researchers regard Gaussian, a piece of commercial quantum

chemistry software from Gaussian Incorporated, as the industry standard for molecular modeling and computational chemistry. All of the key approaches to molecular modeling, including molecular mechanics, ab-initio, semiempirical, and density functional theory (DFT), can be carried out using Gaussian [8]. The ab-initio density functional theory approach, which utilized cluster full geometrical optimization with the complementary Hartree-Fock approach for simulating the optical characteristics and electronic structure of nanocrystals, is a technique of high importance. In addition, this approach is the most resource and time intensive [9].

MATERIALS AND METHODS

Density Functional Theory (DFT) was utilized to perform within Generalized Gradient Approximation (GGA) utilizing Perdew-Burke-Ernzerhof (PBE) exchange-correlation function [10-12]. This study used an even number

of cages with almost equiaxed dimensions, as well as two more small compounds, Al₃P₃H₁₂ and AlP₆H₆, that are not diamondoids, to demonstrate size effects.

The initial step is to do a geometrical optimization, which is succeeded by vibrational and frequency study. Frequencies are multiplied by a suitable scaling factor (0.986) for assigning the frequencies to the current approach and basis set (PBE/6-31(d)), which must lessen statistical mismatching between the theoretical and the experimental data [13]. This may have compelled us to eliminate a few of the heavier diamondoids because employing larger basis sets causes computational challenges, which are explained in this paper. In the current work include the geometrically optimized of AIP-tetramantane (Al₁₁P₁₁H₂₈) and AIP-octamantane (Al₂₀P₂₀H₄₂) diamondoids structure molecules as shown in Figure 1a and Figure 1b.

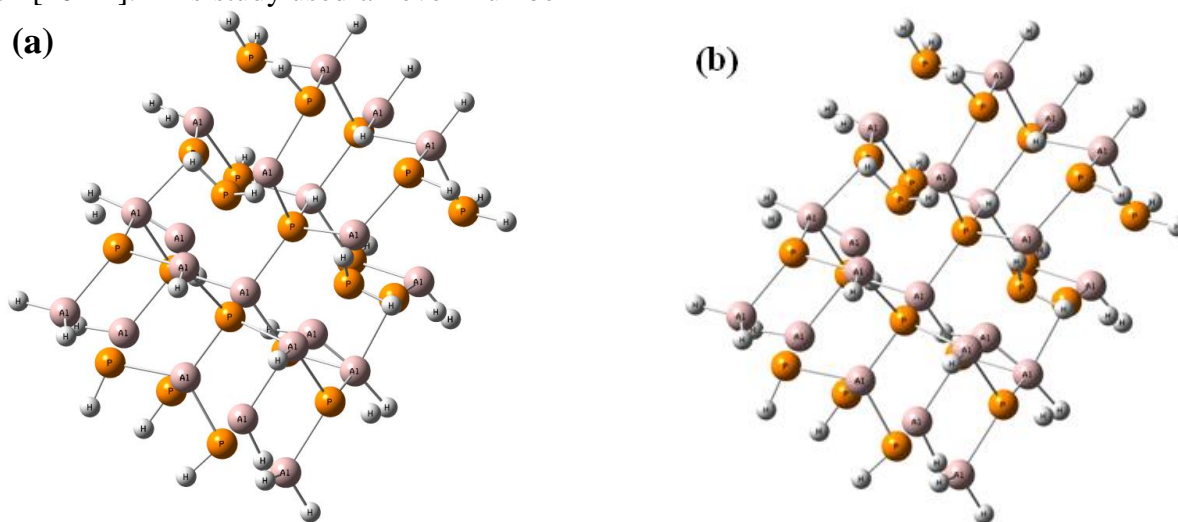


Figure 1. Geometrically optimized a) AIP-tetramantane (Al₁₁P₁₁H₂₈), b) AIP-octamantane (Al₂₀P₂₀H₄₂) diamondoids structure molecules. (by GaussView5.0w).

RESULTS AND DISCUSSION

The use of Raman and IR vibrational spectroscopy for realizing materials is a commonly used in spectroscopy techniques. As a result, it's uncommonly employed to make nanocrystals or determine particle molecular size. The appropriateness of such spectroscopic approaches for creating nanocrystals, AIP diamondoids, and their sizes will be discussed in this paper. Force constants, reduced masses, and vibrations in the Raman spectrum, the reduced mass μ of 2 particles with masses m_b and m_a is calculated as follows [14]:

$$\frac{1}{\mu} = \frac{1}{ma} + \frac{1}{mb} \quad (1)$$

Figures 2 a,b show reduced masses as a function of frequency for both AIP-tetramantane and AIP-octamantane. The vibrations beyond the frequency of 400-438 cm^{-1} AIP-tetramantane and AIP -octamantane belong to hydrogen-associated vibrations, most of the molecules reduced mass to more than 1 amu. While the reduced molecular masses after 400-438 cm^{-1} are all approximately equal to 1amu which represents H vibrations.

Figure 3. illustrates the force constants as a function of frequency for AIP-tetramantane and AIP -octamantane. From this figure can be shown

force constants keep on increasing, due to the fact that the vibration frequency is considered to be proportionate to square root related to force constant according to the following equation [15]:

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

where k denotes force constant, and μ' denotes the reduced mass.

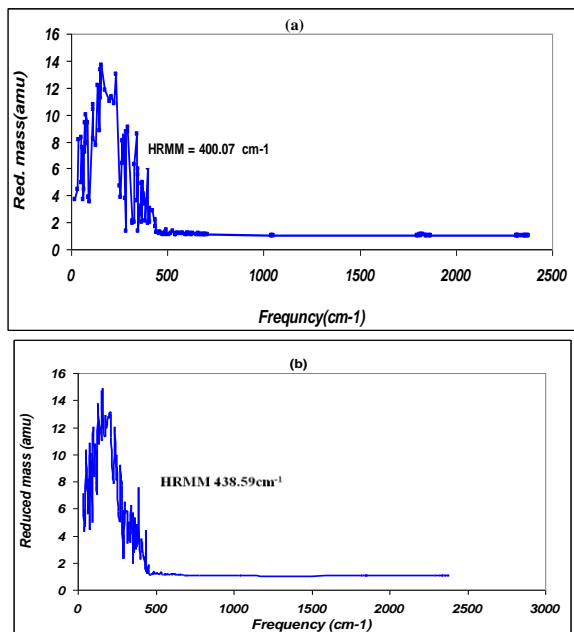


Figure 2. a) AIP-tetramantane reduced mass as a vibration frequency function and b) AIP-octamantane reduced mass as a vibration frequency function.

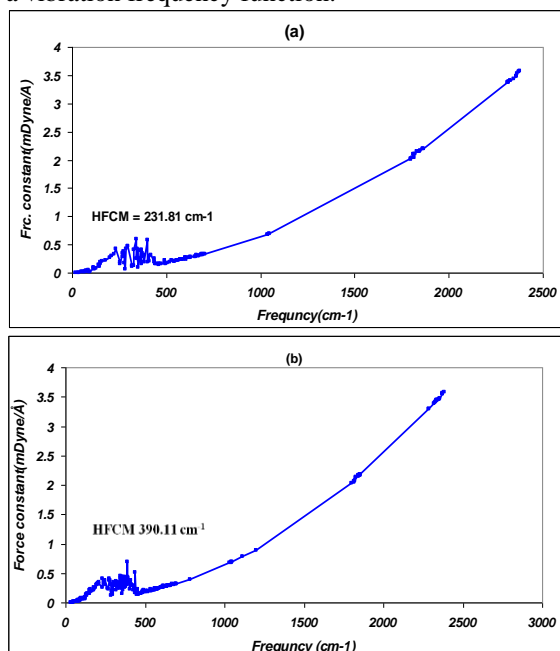


Figure 3. a) AIP-tetramantane force constant as a vibration frequency function and b) AIP-octamantane force constant as a vibration frequency function.

Figure 3a and 3b are almost similar in shape and behaviour, these figures might be divided to 2 parts. The first one starts from about 0cm^{-1} and ends at not more than $231\text{-}390\text{cm}^{-1}$, while the second one begins at $231\text{-}390\text{cm}^{-1}$ and ends at about 2400cm^{-1} . The second part in Figure 3 can easily explain the parabola shape, because reduced mass is fairly constant and equals 1. It can be seen in the second part of Figure 2 and Figure 3 have similar shapes and values compared to the first part for the same figures.

High reduced mass mode (HRMM) and high force constant mode (HFCM) with different AIP diamondoids are shown in Table 1. Tetramantane diamondoids' (HRMM) and (HFCM) structures are smaller than those of octamantane.

Table 1. High Reduced Mass Mode (HRMM) and High Force Constant Mode (HFCM).

AIP diamondoids	High Reduced Mass Mode (HRMM) cm^{-1}	High Force Constant Mode (HFCM) cm^{-1}
Tetramantane (A111P11H28)	400.07	231.81
Octamantane (A120P20H42)	438.59	390.11

Figure 4 shows the AIP diamondoid size variations of the 4 different sizes. Longitudinal Optical-Highest reduced Mass Mode (LO-HMM), Radial Breathing Mode (RBM), and A1-2H and P-2H asymmetrical vibrations are among such vibrations. Through the observation of the atomic displacement regarding such vibration, RBM can be achieved. In this mode, the majority of atoms move in phase along the molecule's radius [16]. When reaching bulk sizes, the vibration frequency must converge to 0cm^{-1} [17]. The LO-HRMM, on the other hand, converges to 441cm^{-1} [18]. In the AIPH6 molecule, the 2 modes meet at 240cm^{-1} . Therefore, RBM is blue shifted as it moves from bulk to nanoscale and molecular limits, whereas LO-HRMM is red shifted. HRMM and RBM, on the other hand, vary in size and might be utilized as size directors for those diamondoids.

Figures 5a and 5b illustrate the IR spectra as a function of frequency for AIP-tetramantane and AIP-octamantane diamondoids structure molecules respectively.

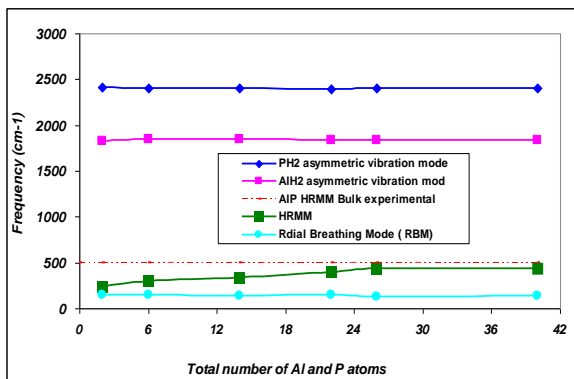


Figure 4. Molecular size effects on various AIP diamondiod molecular vibration values, HRMM, RBM, and asymmetric hydrogen surface vibration modes are seen. The dashed line denotes experimental bulk AIP LO vibration frequency [18].

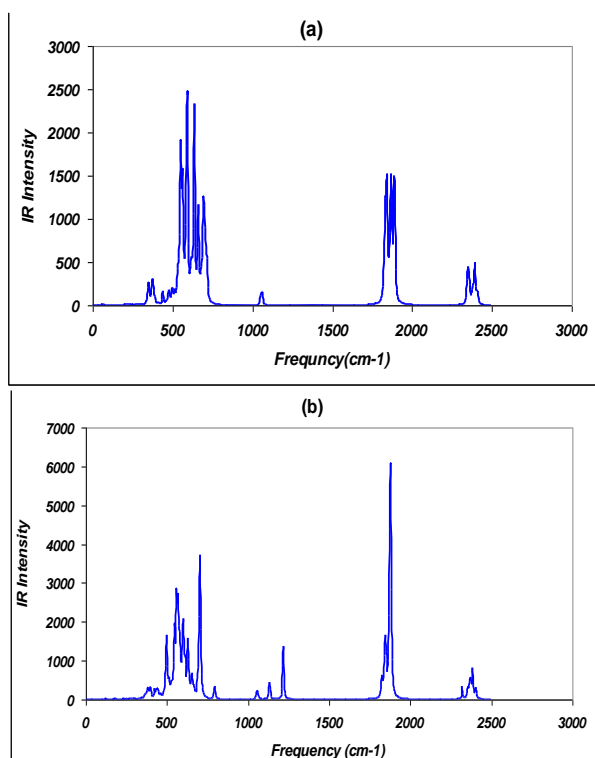


Figure 5. IR spectra as a function of frequency for a) AIP-tetramantane b) AIP-octamantane diamondoids structure molecules.

There are 2 regions based on the characteristics of vibration or gap separation. In the first region, the results indicate good matching to experimentally acquired lines. The $(0-570) \text{ cm}^{-1}$ region is characterized by pure AIP. Notice a shift in the intensity maxima toward the right side of the infrared vibrational frequencies which is indicative of the presence H surface atoms. The second region includes the $1066-1870 \text{ cm}^{-1}$ modes in the Al-H and P-H vibrational regions.

Figures 6a and 6b show the Raman spectra as a function of frequency for AIP-tetramantane and

AIP-octamantane diamondoids structure molecules.

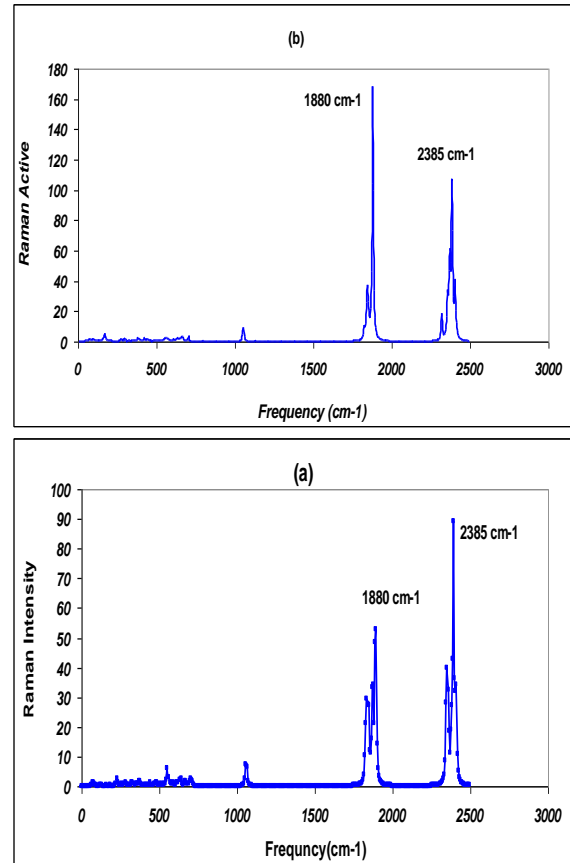


Figure 6. Raman spectra as a function of frequency for (a) AIP-tetramantane (b) AIP-octamantane diamondoids structure molecules.

Raman spectra for AIP diamondoid structure are between the $1880-2385 \text{ cm}^{-1}$ modes in the Al-H and P-H vibrational region including stretching (symmetrical and asymmetrical) and bending vibration mode (wagging, rocking, scissoring, and twisting). The corresponding Raman spectra share almost identical characteristics as the IR spectra, however, with different selection rules. The chance of absorbing a specific wave length photon determines the peak intensities in the Raman spectrum. These results have been discovered to be in consistency with other theoretical values in reference [19].

CONCLUSIONS

The AIP vibration and characteristics estimated with the use of the DFT approach are found to be in good agreement with experimental bulk limits in the current study. Various spectroscopic and structural features were investigated using molecular calculations. The theoretically sensitive size variations of AIP diamondoids have been demonstrated using IR Raman spectroscopic techniques. There are two parts to the vibrational force constant for AIP diamondoids. The first

consists primarily of AIP vibrations with a decreased mass of more than 1 amu and a range of around $0\text{-}231\text{ cm}^{-1}$. The second part, which is in the range $1228\text{-}2400\text{ cm}^{-1}$ and has a decreased mass of very near to 1 amu, is made up entirely of hydrogen vibrational modes. When moving from the bulk to nanoscale or molecular, RBM experiences a blue shift; while when moving from the bulk to molecular or nanoscale, LO-HRMM experiences red shift.

Disclosure and conflict of interest: The authors declare that they have no conflicts of interest.

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