

Research Article

Spectroscopic properties of Boron phosphide diamondoid structure using Density functional theory

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Abstract

IR and Raman spectra of BP vibrational properties are investigated using density functional theory at the PBE/6-31G(d) level and basis including polarization functions. The frequencies in the vibrational spectrum are analyzed against reduced masses, force constants and intensities of vibration. An analysis of vibrational modes, in terms of reduced masses, force constants and IR intensity, was then performed. The size-related change of certain vibrational frequencies of BP diamondoids was compared with the experimental bulk. The spectrum can be divided into two regions depending on the properties of the vibrations or the gap separating them. In the first region, results show good matching to several experimentally obtained lines. The 500 cm^{-1} broad-peak region is characterized by pure B-P vibrations. In the second region the matching also extends to B-H,P-H vibration frequencies that include different modes such as symmetric, asymmetric, wagging, scissor, rocking and twisting modes. Radial breathing mode frequency began from 550 cm^{-1} for the smallest molecule BPH₆ and decreased with fluctuations. Longitudinal optical mode began from 500 cm^{-1} for the smallest molecule and increased with fluctuations, heading to 800 cm^{-1} (24 THz) as its bulk limit.

Keywords: BP, infrared spectroscopy, DFT

1. Introduction

The theoretical calculations of vibrational infrared frequency and Raman lines of BP nanocrystal cluster and the variation of these vibrations from molecular to bulk size is investigated (S. M. Sze and K. K. Ng., 2007). The cluster full geometrical optimization calculation are available to run with DFT in Gaussian 09 program (J.B. Foresman *et al.*, 1996). The present work is concerned with the theoretical calculation of vibrational infrared frequency lines of diamond nanocrystals and the variation of these vibrations from molecular to bulk sizes (M. A. Abdulsattar, 2013). An appreciation of the variation of different properties from the molecular to then nano - and bulk-scales is important in order to understand how to deal with these materials in their nanotechnology applications. Recently, a collection of molecules with an increasing number of atoms and varying sizes, called diamondoids, were found to be the building blocks of nano materials (de Araujo P L B *et al.*, 2012). 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 (M.T. Hussein *et al.*, 2014).

Theory

Physical properties and size effect on various nanostructures properties can be explored using wide variety of spectroscopic techniques and methods. Some of these methods are IR, Raman spectroscopes that will be used in the present work to investigate BP diamondoids structures. To perform this task, we used all electron density functional theory at the level of Perdew, Burke and Ernzerhof (PBE). PBE/6-31G(d) method and basis set that include polarization functions are suitable for performing the present tasks from the point of view of computational resources and capabilities of Gaussian09 program used in the present work (M. A. Abdulsattar *et al.*, 2015). Frequencies are multiplied by appropriate scaling factor (0.986) usually assigned to present method and basis set (PBE/6-31G(d)) (M. A. Abdulsattar *et al.*, 2015). The molecular approach to nanocrystal or bulk properties is an interesting approach. This approach can be used to calculate many properties that are sometimes difficult to calculate using solid-state theories. In the present

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work, we shall build BP nanocrystals starting from the smallest BP molecules and diamondoids. These molecules include BPH₆, linear molecules, BP-cyclohexane (B₃P₃H₁₂), BP-diamantane (B₇P₇H₂₀), BP-tetramantane (B₁₁P₁₁H₂₈), BP-hexamantane (B₁₃P₁₃H₃₀), BP-octamantane (B₂₀P₂₀H₄₂), and BP-decamantane (B₂₂P₂₂H₄₂). The number of cages of these diamondoids is obvious from the nomenclature of the latter five. The first two molecules (which are not diamondoids) were added to complete the overview and range of energy and vibrational spectra (Tobias Z. et al, 2013).

Results and discussion

The program Gaussian 09 is used to optimize the geometries and calculate the vibrational spectra of BP diamondoids nanocrystals (diamantane, tetramantane, hexamantane, octamantane). The calculated frequency error that results from ab-initio calculation (Blakemore J. S. , 1982). The previous estimation of this scale factor for PBE theory by using 6-31G(d) basis is 0.986 [10]. 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. Fig (1) shows geometrical optimization method is used in the present work to obtain of BP molecules as while as infrared spectrum as a function of frequency. These include cage like molecules as following diamantane B₇P₇H₂₀, tetramantane B₁₁P₁₁H₂₈, hexamantane B₁₃P₁₃H₃₀ and octamantane B₂₀P₂₀H₄₂.

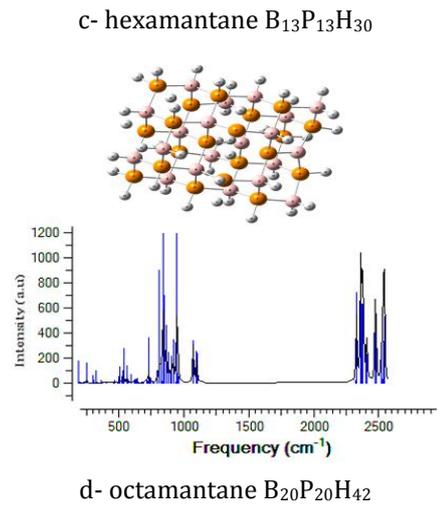
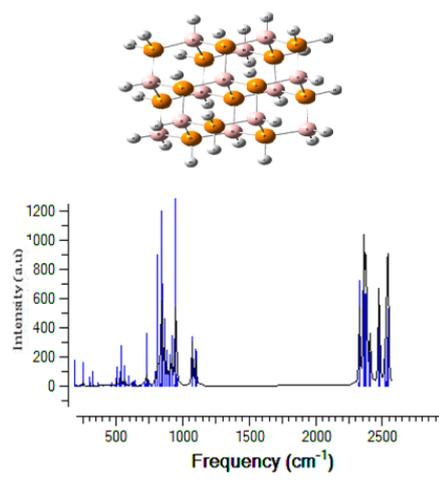
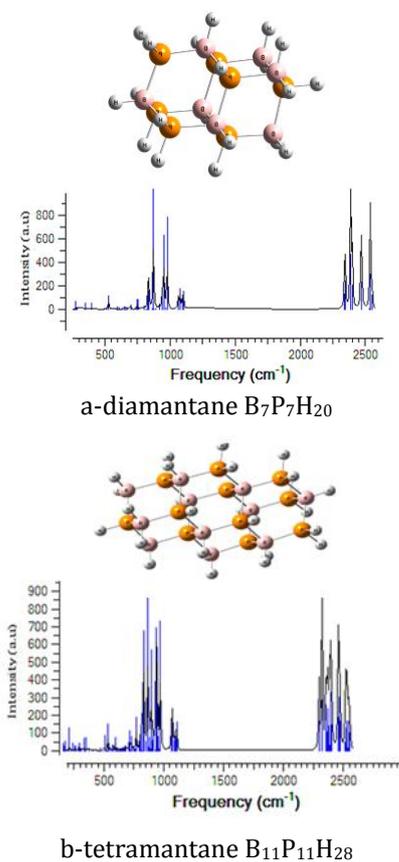
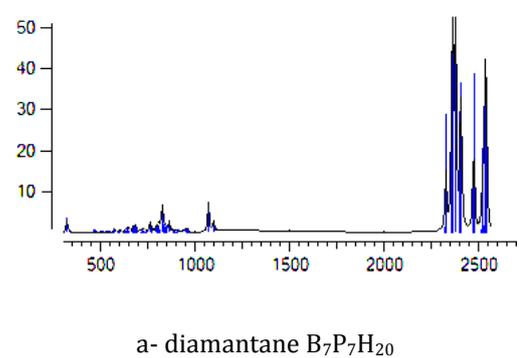


Fig.1: Shape of geometrically optimized and I.R spectra of BP- diamantoids as a function of frequency of a- diamantane B₇P₇H₂₀, b-tetramantane B₁₁P₁₁H₂₈, c- hexamantane B₁₃P₁₃H₃₀ , d- octamantane B₂₀P₂₀H₄₂

Bulk Bp is identified by its IR absorption at approximately 0-500 cm⁻¹ vibrational mode peak. The highest intensity line in the presently calculated (Fig. 1) for Bp diamondoids is at 865 cm⁻¹ while is octamantan is at 985cm⁻¹. We notice a shift in the intensity maxima toward right side of the infrared vibrational frequencies. This includes the 954–2540 cm⁻¹ modes in the B-H and P-H vibrational region. The region around the broad peak at 865 cm⁻¹ has B–P.



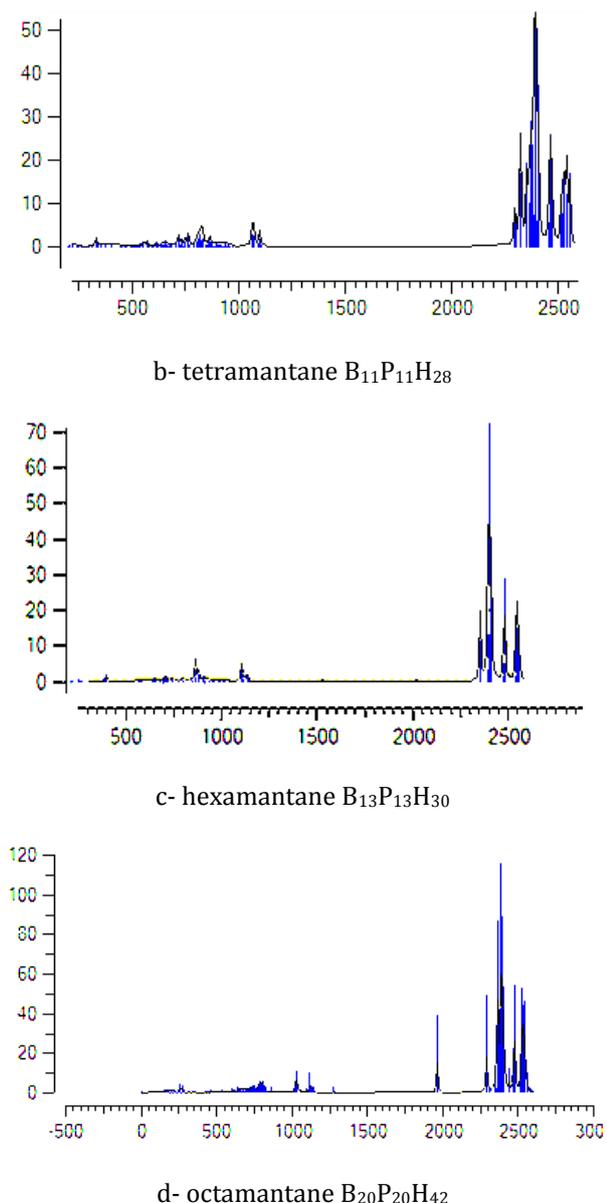


Fig.2: Raman intensities of BP-diamondoids of infrared spectrum as a function of frequency of a- diamantane B₇P₇H₂₀, b- tetramantane B₁₁P₁₁H₂₈, c- hexamantane B₁₃P₁₃H₃₀, d- octamantane B₂₀P₂₀H₄₂

Fig.2 represents the Raman vibrational frequencies, the highest intensity line in the presently calculation for Bp diamantane is at 2354 cm⁻¹, tetramantane is at 2358 cm⁻¹ and hexamantane is at 2347 cm⁻¹ octamantane 2355 cm⁻¹. The shift in the intensity maxima of about 2300 cm⁻¹. This includes the 1100–2500 cm⁻¹ modes in the B-H and P-H vibrational region.

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

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \tag{1}$$

The reduced mass μ of two particles of masses m_1 and m_2 is given by:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{2}$$

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 BP-diamondoids vibrations, the left parts of B-P 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 diamantane Fig (3-a) is larger than of the other diamondoids.

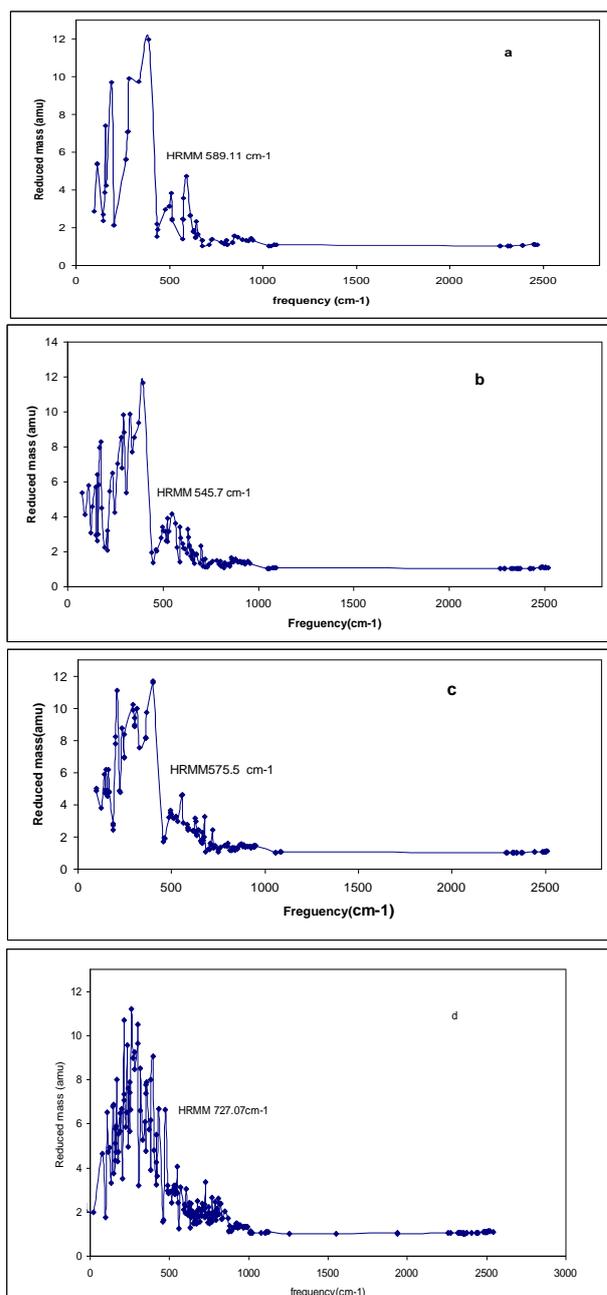


Fig.3: BP-diamondoids reduced mass as a function of vibration frequency of a- diamantane B₇P₇H₂₀, b- tetramantane B₁₁P₁₁H₂₈, c- hexamantane B₁₃P₁₃H₃₀, d- octamantane B₂₀P₂₀H₄₂

Fig (4) shows BP-diamondoids force constants as a function of vibration frequency. A part from the statistical difference between the numbers of vibration frequencies of all BP-diamondoids, The shapes in Fig (4) begin from approximately 0 cm^{-1} of B-P vibrations and ends at less than 1000 cm^{-1} , whereas right parts of H vibrations starts at approximately above 1000 cm^{-1} and ends at nearly 2500 cm^{-1} . The bulk experimental BP longitudinal optical (LO) vibration frequency, about 800 cm^{-1} (24 THz) which agreement with octamantane diamondoids structure as shown in Fig(4-d) (Otfried Madelung *et. al*, 2012).

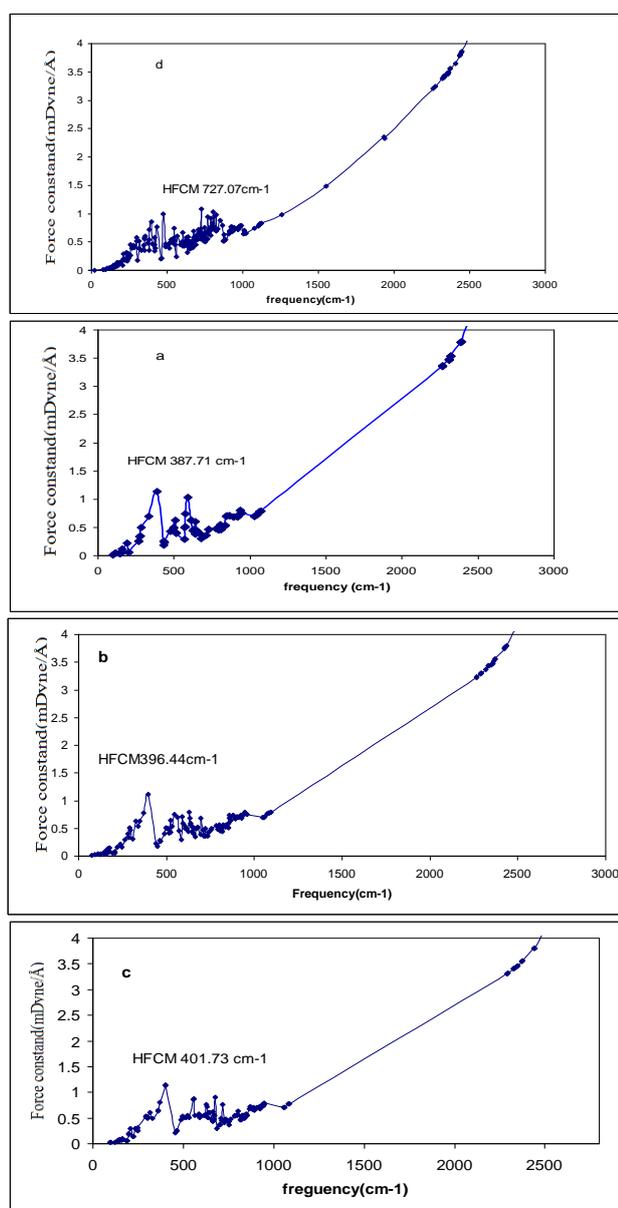


Fig.4: Force constant of BP- diamondoids as a function of frequency of a- diamantane $\text{B}_7\text{P}_7\text{H}_{20}$, b tetramantane $\text{B}_{11}\text{P}_{11}\text{H}_{28}$, c- hexamantane $\text{B}_{13}\text{P}_{13}\text{H}_{30}$ d- octamantane $\text{B}_{20}\text{P}_{20}\text{H}_{42}$

The two hydrogen-surface vibrational modes in Fig. (5) are nearly constant throughout the different sizes of BP diamondoids and molecules. The frequency of this

vibration should converge to 0 cm^{-1} as we reach bulk sizes (Kittel C. *et al*, 2005). The two modes meet at 550 cm^{-1} in the BPH_6 molecule. To complete the view of frequency range, we added the highest asymmetric surface hydrogen vibrations with both B and P atoms (B-H_2 and P-H_2) to Fig (5).

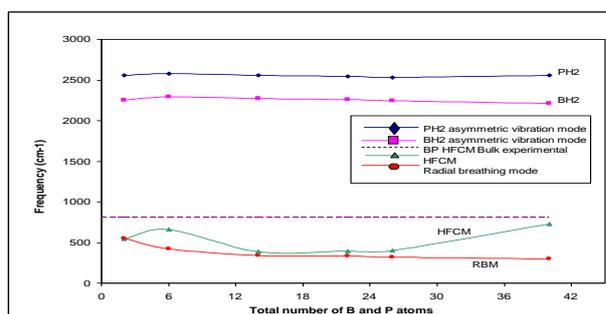


Fig. 5: Molecular size effects on various BP diamondoid molecular vibrations, RBM, HFCM and asymmetric hydrogen surface vibration modes are shown. The dashed line represents the experimental bulk BP LO vibration frequency (Otfried Madelung *et. al*, 2012).

Conclusions

The IR vibrational spectra of BP diamondoids are divided into two parts. The first part is mainly B-P vibrations; this part is located approximately within the range of 0-550 cm^{-1} . This part is distinguished by a reduced mass that is larger than 1. The second part – in the range 954–2540 cm^{-1} , Is made up exclusively of hydrogen vibrational modes with a reduced mass very close to 1. The first part encounters vibrational frequency shifts as the size of diamondoids change. The region around the broad peak at 550 cm^{-1} has pure B-P vibrations and is a sign of diamondoids structure in nanocrystals. The present theory reproduces adequately various B-H , P-H vibrations, which include symmetric, asymmetric, wagging, scissor, rocking and twisting modes.

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