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Theoretical study of the XP_3 (X = Al, B, Ga) clusters

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ABSTRACT

The lowest singlet and triplet states of AlP_3, GaP_3 and BP_3 molecules with C_s, C_{2v} and C_{3v} symmetries were characterized using the B3LYP functional and the aug-cc-pVTZ and aug-cc-pVQZ correlated consistent basis sets. Geometrical parameters and vibrational frequencies were calculated and compared to existent experimental and theoretical data. Relative energies were obtained with single point CCSD(T) calculations using the aug-cc-pVTZ, aug-cc-pVQZ and aug-cc-pV5Z basis sets, and then extrapolating to the complete basis set (CBS) limit.

1. Introduction

Clusters have been receiving a great deal of attention since they are important intermediates between isolated molecules and bulk material. Understanding their physical properties may allow better design of systems of potential technological interest. For these reasons clusters formed by III–V semiconductor have been subjected to both experimental and theoretical studies [1–7]. These studies were undertaken to understand their structures, spectroscopy, chemical reactivity and the changes of properties when these materials are reduced to the nanometer scale.

A series of aluminum clusters doped with phosphorus have already been observed in a few experimental works [1,2,8]. Liu et al. [1] synthesized and studied the mass distribution of aluminum phosphide clusters in the gas phase by laser ablation of solid samples of aluminum compound in high vacuum. Anion photoelectron spectra was used by Gomez et al. [2] to measure electron affinities, vertical detachment energies, and vibrational frequencies of the corresponding neutral and anion of Al_xP_y ($x, y \leqslant 4$) clusters. De Maria et al. [8] determined the dissociation energy of the gaseous AlP molecule with Knudsen-cell-mass-spectrometer. There are substantially more theoretical works related to Al and P clusters [9–21]. Specifically for the AlP_3 system, the first theoretical work was made by Feng and Balasubramanian [3], using MCSCF, CASSCF and MRSDCI methods, with the ground state ($^3A_2$) presenting C_{3v} symmetry. This conclusion changed with the work of Archibong et al. [4] using the B3LYP, MP2 and single-point CCSD(T) methods in which two singlet states, $^1A_1$ (C_{2v}) and $^1A'$ (C_s) are found more stable and almost degenerate, while the triplet $^3A_2$ (C_{3v}) lying at least 0.5 eV higher. Guo et al. [22,23] calculated the adiabatic electron affinities and vertical detachment energies of several Al_nP_m ($n + m = 3–6$) neutral and anionic isomers, with the AlP_3 isomer ground state related to a singlet C_{2v} structure. More recently, Guo et al. [24] have characterized the Al_mP_n ($m + n = 2–5$) clusters, neutral and anions, using DFT methodology with several functionals. The relative stability of the two lowest singlet states with C_{2v} and C_s symmetries were studied by Malaspina et al. [25] using ab initio (MP2 and CCSD(T)), DFT (B3LYP and B3PW91 functionals) and Brueckner orbital methods, with cc-pVXZ ($X = 2, 3, 4$ and 5) basis set. The C_{2v} structure was found to be more stable than the C_s one, with their best results calculated at the CCSD(T)/CBS//B3LYP-cc-pVTZ level and differing by only 1.57 kcal mol^{-1}. The relative abundance and interconversion ratio of these two lowest structures were also analyzed by Malaspina and Canuto [26].

Experimentally, there are some works related to clusters containing gallium and phosphorus elements. Li et al. [6] prepared GaP, Ga_2P and GaP_2 clusters by laser vaporization and observed the vibrational spectra of these clusters at 4 K. Taylor and coworkers reported photoelectron spectroscopy of gallium and phosphorus anion clusters [27–29] to determine adiabatic electron

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affinities and vertical detachment energies. Ga_3P nanocrystals under solvothermal conditions in benzene were studied by Gao et al. [30]. Theoretically, the structure, stability and melting point of small GaP clusters were first studied by Andreoni [31] using molecular dynamics. Feng and Balasubramanian [32–35] characterized the geometry and the energy stability of the low-lying states of several GaP clusters employing CASSCF and MRSDCI. Archibong et al. [36–39] computed the geometry, vibrational frequencies and electron affinities of small gallium clusters doped with phosphorus employing MP2, CCSD(T) and DFT methods. The geometry and vibrational frequencies of several isomers of small $(MX)_n$ clusters ($n = 1, 2, 3$; M = Al, Ga, In; X = P, As) were investigated using DFT method by Costales et al. [40]. Using B3LYP/6-31G(d) methodology, Jia and Wu [41] studied the structure and photoelectron spectra of some Ga_nP_m ($n < 5$, $m < 5$) clusters, and Li et al. [7] have examined the Ga_nP and Ga_nP_2 ($n = 1$–7) clusters. The structure, electron affinities and vibrational frequencies of Ga_mP_n ($m + n = 2$–5), neutral and anion clusters were studied by Guo and Wu [42] using four different DFT functionals.

There are significantly less works related to boron and phosphorus clusters in comparison to aluminium and gallium clusters doped with phosphorus. Experimentally, the only cluster studied is the boron monophosphide, BP, in which Gingerich applied Knudsen mass spectrometry [43] to determine its dissociation energy. Theoretically, the dissociation energy and other molecular parameters were reported by Boldyrev et al. [44,45], Gan et al. [46] and Chan and Handy [47]. Also, Bruna and Grein calculated the electron-spin g-shifts, ground state equilibrium geometry and vertical excitation energies of BP [48], while Miguel et al. [49] used MRDCI to study the ground and excited states of the BP molecule. For small clusters, Burrill and Grein investigated the geometries and electronic states of B_2P_2 [50]. Linguerri et al. [5] studied the anion and cation structures of BP and B_2P_2 using MRCI and RCCSD(T) methods. The stability and structure of $(BP)_n$ ($n = 2$–4) clusters have been calculated by Qu et al. [51], and987Ončák and Srnec [52] studied the electronic structure of various IIIa–Va clusters, including $(BP)_n$ ($n = 1$–3), using ab initio and DFT methods. To the best of our knowledge, there are no data related to BP_3 molecule, and this work is the first study of the relative stability of its lowest states.

This work aims at providing accurate data related to electronic and structural parameters of AlP_3, BP_3, GaP_3 clusters using the B3LYP functional and the CCSD(T) method, with the use of the aug-cc-pVTZ, aug-cc-pVQZ and aug-cc-pV5Z correlated consistent basis sets. More accurate determination of the energetic parameters was obtained with extrapolation to the complete basis set (CBS) limit. In this way, this article provides improved information and a detailed and unified study of these clusters now computed at the same level to facilitate comparison.

2. Methodology

The geometrical optimization and vibrational harmonic frequencies of all isomers and electronic states of AlP_3, BP_3, GaP_3 clusters were calculated employing the B3LYP density functional [53,54]. The relative energies were calculated with the B3LYP functional and also employing single-point coupled cluster calculations at the level of coupled cluster with single and double excitations and perturbed triple excitation (CCSD(T)) [55] using B3LYP optimized geometry.

Relative energies, including extrapolation correction and ZPE, were calculated with B3LPY/aug-cc-pVXZ (X = T, Q) and CCSD(T)/aug-cc-pVXZ (X = T, Q, 5)//B3LPY/aug-cc-pVQZ, for the lowest singlet and triplet energy states with C_s, C_{2v} and C_{3v} symmetries. The basis sets used in this study were the correlated consistent aug-cc-pVTZ, aug-cc-pVQZ and aug-cc-pV5Z of Dunning and collaborators [56,57]. Total energies were extrapolated to the complete basis set (CBS) limit by using an extrapolation procedure developed by Halkier et al. [58],

$$E_{CBS} = \frac{[E(n) \times n^3] - [E(n-1) \times (n-1)^3]}{n^3 - (n-1)^3},$$

where n is equal to 5 for the aug-cc-pV5Z basis set.

All calculations were carried out with Gaussian03 [59] suite of program.

3. Results and discussion

3.1. AlP_3 cluster

The AlP_3 is a relatively well studied molecule where the main objective has been related to the relative stability of the different isomers. The geometrical parameters of the lowest singlet and triplet states with C_s, C_{2v} and C_{3v} symmetries were obtained with the B3LYP functional using both the aug-cc-pVTZ and aug-cc-pVQZ basis sets. The structures related to these symmetries that were optimized for BP_3, AlP_3 and GaP_3 are displayed in Fig. 1. All structural and vibrational frequencies data are available in the Supporting material.

The increase in atomic basis set size leads to a small decrease in the bond length distances by about 0.007 Å, while the angles remained almost the same. The geometry optimization using B3LYP functional were also carried out in the previous works [4,22,24,26]. Malaspina and Canuto [26] have also optimized both singlet C_s and C_{2v} lowest energy structures using the B3LYP/aug-cc-pVTZ method obtaining the same geometrical parameters, as expected. Archibong et al. [4] and Guo et al. [24] investigated several electronic states using the 6-311+G (2df) basis set with similar geometrical parameters. The geometry of the C_{2v} ($^1A_1$) ground state were also optimized by Guo et al. [24] using BHLYP, BP86 and BLYP functionals and 6-311+G (2df) basis set, and the results show that the BHLYP method predict smaller bond distances. Ab initio MP2 optimizations were made by Malaspina and Canuto [26] and Archibong et al. [4]. The post-HF CASSCF and MRSDCI methods were employed by Feng and Balasubramanian [3] in the study of singlet and triplet C_{3v} states, but in all cases these states do not correlate to our optimized states.

The values of the vibrational frequencies calculated at the B3LYP/aug-cc-pVXZ (X = T, Q) levels present, in general, a slight increase with the basis sets changing from aug-cc-pVTZ to aug-cc-pVQZ. The frequencies calculated by Malaspina and Canuto [26] for the singlet C_s and C_{2v} states are identical to the present results, as expected. The vibrational frequencies were also calculated by Guo et al. [24] and Archibong et al. [4] using the B3LYP functional with different basis set, and their values differ no more than 5 cm^{-1}, compared to the present results. The C_s electronic states ($^3A'$ and $^1A'$) and the C_{2v} states ($^3A_2$ and $^3B_2$) were characterized as transition states with one imaginary frequency, as already calcu-

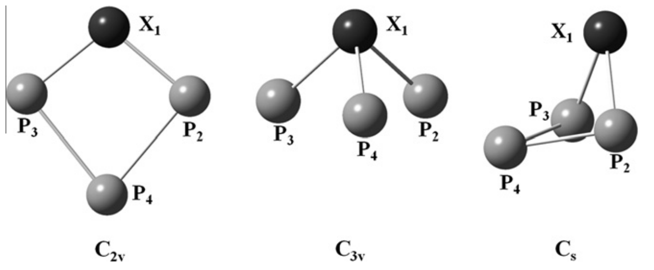

Fig. 1. Structures of XP_3 (X = B, Al, Ga) clusters.

lated by Archibong et al. [4]. The previous results using different functionals (BHLYP, BP86, BLYP) were calculated only for the singlet ground state with symmetry C_{2v} ($^1A_1$) [24], with BLYP and BHLYP giving, respectively, smaller and greater values compared to the present results. Compared to the present B3LYP frequencies, the inclusion of correlation effects with MP2/6-311+G (2df) [4,26] lead to similar frequencies for the singlet C_s and C_{2v} states, although there is a small tendency to give higher values. However, for the triplet C_{2v} and C_{3v} states all MP2 frequencies present considerable differences to our optimized states.

As mentioned before, the question of the relative stability of the electronic states has been the main objective of several works related to AlP_3 molecule. In Table 1 are presented the relative energies of the lowest energy states with C_s, C_{2v} and C_{3v} symmetries. The data presented in Table 1 indicate clear presence of two states of lowest energy, C_{2v} ($^1A_1$) and C_s ($^1A'$) which are almost degenerate. In all cases the C_{2v} state is the ground state, and the separation energy gets larger increasing the basis set. The B3LYP/aug-cc-pVQZ separation energy is equal to 1.10 kcal/mol and the single point CCSD(T)/aug-cc-pV5Z and CCSD(T)/CBS results are respectively equal to 1.73 and 2.01 kcal/mol. These results are in good agreement with previous works [4,22,25]. Archibong et al. [4] using B3LYP, MP2 and single-point CCSD(T) methods with the 6-311+G(2df) basis set, concluded that singlet the C_{2v} ($^1A_1$) is the ground state, but almost degenerate with the C_s ($^1A'$) state with an stability of only 0.23 kcal/mol (CCSD(T)//MP2) or 0.46 kcal/mol (CCSD(T)//B3LYP) higher than the C_{2v} state. Guo et al. [22] using the B3LYP/6-311G$*$ method also obtained the singlet C_{2v} state to be the ground state, but the singlet C_s state located only 1.84 kcal/mol above. Malaspina et al. [25] employing ab initio and DFT methods also studied the relative energy of the lowest states C_{2v} ($^1A_1$) and C_s ($^1A'$), presenting in all cases the C_{2v} ($^1A_1$) state as ground state. In their best results calculated using the geometries optimized at B3LYP/cc-pVTZ level, the C_s state is 1.55 kcal/mol above the ground state at CCSD(T)/cc-pV5Z level, and is 1.57 kcal/mol calculated at CCSD(T)/CBS. These values can be compared with the present results at CCSD(T)/aug-cc-pV5Z level, equal to 1.73 kcal/mol, while, at the CCSD(T)/CBS it is equal to 2.01 kcal/mol. However, the CBS results are calculated using different extrapolation schemes. Using the Halkier et al. extrapolation procedure [58], the Malaspina et al. [25] result changes to 1.81 kcal/mol, and our result using the extrapolation proposed by Varandas [60], as used by Malaspina et al. [25], changes to 1.76 kcal/mol. One could also use the exponential expression proposed by Peterson and Dunning [61], to obtain an extrapolated value of 2.01 kcal/mol for our results and 1.90 kcal/mol using Malaspina et al. results. From these works, one can note that the separation energy increases with the basis set quality, as well as with the use of highly correlated method. Thus all considered we conclude that the C_s state should be higher than the C_{2v} state by 1.5–2.0 kcal/mol.

Table 1
Relative energies (in kcal/mol) of AlP_3 low-lying states. The B3LPY/aug-cc-pVXZ (X = T, Q) results include ZPE and CCSD(T)/aug-cc-pVXZ (X = T, Q, 5)//B3LPY/aug-cc-pVQZ results are without ZPE.

State	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pV5Z	CBS
C_s ($^1A'$)	0.73[a] 0.50[b]	1.10[a] 1.46[b]	1.73[b]	2.01[b]
C_s ($^1A'$)	11.75[a] 11.30[b]	12.19[a] 12.70[b]	13.11[b]	13.54[b]
C_s ($^3A''$)	12.43[a] 16.87[b]	12.80[a] 18.12[b]	18.66[b]	19.23[b]
C_s ($^3A'$)	18.51[a] 17.51[b]	18.83[a] 17.87[b]	17.87[b]	17.87[b]
C_{2v} ($^1A_1$)	0.00[a,b]	0.00[a,b]	0.00[b]	0.00[a,b]
C_{2v} ($^3A_2$)	19.23[a] 24.31[b]	19.71[a] 25.86[b]	26.49[b]	27.15[b]
C_{2v} ($^3B_2$)	24.96[a] 35.89[b]	25.39[a] 30.26[b]	30.85[b]	31.47[b]
C_{3v} ($^1A_1$)	40.37[a] 37.10[b]	40.62[a] 36.84[b]	36.61[b]	36.37[b]
C_{3v} ($^3A_1$)	11.37[a] 13.26[b]	11.81[a] 14.82[b]	15.22[b]	15.64[b]

[a] This work results obtained with B3LYP/aug-cc-pVXZ (X = T, Q). Ground state, C_{2v} ($^1A_1$), total energies: T = –1266.6117626 au; Q = –1266.6263573 au.

[b] This work results obtained with CCSD(T)/cc-pVXZ//B3LPY/aug-cc-pVQZ. Ground state, C_{2v} ($^1A_1$), total energies: T = –1264.7458098 au; Q = –1264.7870134 au; 5 = –1264.8026899 au.

As characterized by Archibong et al. [4], the next excited structure is also a C_s ($^1A'$) state, which is 13.54 kcal/mol above the ground state using the CCSD(T)/CBS method. Note that this structure has an imaginary frequency and it is only 2.10 kcal/mol below the triplet C_{3v} structure at the CCSD(T)/CBS level, but at the B3LYP level the C_{3v} structure presents the lowest energy. Next in the energy ordering are the C_s ($^3A'$) and C_s ($^3A''$) structures, respectively 17.87 and 19.23 kcal/mol above the ground state, followed by two C_{2v} triplet states, but both states present an imaginary frequency. Note that the singlet C_{3v} ($^1A_1$) structure is located very high energetically.

3.2. GaP_3 cluster

Although there are several studies related to gallium phosphides, there are no experimental data related specifically to GaP_3 cluster and scarce theoretical works. The B3LYP geometrical parameters and vibrational frequencies for the ground and low-lying states of GaP_3 are available in the Supporting material.

As observed for AlP_3, the change in the basis set from aug-cc-pVTZ to aug-cc-pVQZ gives, in general, a small reduction of internuclear distances, and small variation of angles. The ground state C_s ($^1A'$) was also optimized by Archibong and Mvula [39] and Guo and Wu [42] using MP2 and B3LYP, BLYP and BP86 functionals and with the 6-311+G(2df) basis set. In general the results are similar, although the BHLYP predicts smaller distances and the BLYP greater ones. The first excited C_{2v} ($^1A_1$), C_{3v} ($^3A_2$) and the second C_s ($^1A'$) states were also optimized by Archibong and Mvula [39] using the DFT B3LYP and the MP2 method. The C_{3v} ($^3A_2$) state was also optimized by Feng and Balasubramanian [35] with the use of CASSCF and MRSDCI methods. The two latter methods give computed bond lengths which are, in general, very close, but with the MP2 [39] and MRSDCI [35] results presenting the smallest values, as expected. As calculated for AlP_3, we have also optimized several other structures of C_s, C_{2v} and C_{3v} symmetries not previously characterized.

The change in basis set did not alter substantially the calculated values of frequencies. The C_s ($^1A'$), C_{2v} ($^1A_1$) and C_{3v} ($^3A_2$) states were studied theoretically by Archibong and Mvula [39], with B3LYP giving frequencies results that are very similar to our data and MP2 frequencies, in general, greater than those calculated with B3LYP. The frequencies of GaP_3 were also calculated by Guo and Wu [42] using four different functionals, with similar data, differing no more than 40 cm^{-1}. As obtained for AlP_3, the second singlet, C_s ($^1A'$), and the two triplet, C_{2v} ($^3A_2$ and $^3B_2$) states have one imaginary frequency.

In Table 2 are presented the relative energies of the low-lying states calculated using the B3LYP functional and single-point CCSD(T). All calculations clearly indicate the singlet C_s ($^1A'$) structure is the ground state, in agreement to Archibong and Mvula [39] and differing from the results obtained by Feng and Balasubramanian [35], which indicated the $^3A_2$ (C_{3v}) structure as the ground state. At the B3LYP level, the three low-lying states, C_{3v} ($^3A_1$), C_{2v} ($^1A_1$) and C_s ($^1A'$) are respectively 7.41, 7.53 and 8.54 kcal/mol above the ground state and they are almost degenerate. However, at the CCSD(T)/CBS single point calculations the first excited

Table 2
Relative energies (in kcal/mol) of GaP_3 low-lying states. The B3LPY/aug-cc-pVXZ (X = T, Q) results include ZPE and CCSD(T)/aug-cc-pVXZ (X = T, Q, 5)//B3LPY/aug-cc-pVQZ results are without ZPE.

State	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pV5Z	CBS
C_s ($^1A''$)	0.00[a,b]	0.00[a,b]	0.00[b]	0.00[a,b]
C_s($^1A'$)	8.52[a] 9.70[b]	8.54[a] 10.20[b]	9.96[b]	9.71[b]
C_s($^3A'''$)	16.63[a] 19.67[b]	16.77[a] 20.59[b]	21.16[b]	21.76[b]
C_s($^3A'$)	31.61[a] 24.91[b]	31.76[a] 25.31[b]	25.98[b]	26.68[b]
C_{2v}($^1A_1$)	7.68[a] 4.37[b]	7.53[a] 4.46[b]	4.56[b]	4.66[b]
C_{2v}($^3A_2$)	23.10[a] 27.76[b]	23.34[a] 28.88[b]	29.38[b]	29.90[b]
C_{2v}($^3B_2$)	32.27[a] 31.62[b]	32.53[a] 33.25[b]	33.91[b]	43.60[b]
C_{3v}($^1A_1$)	57.85[a] 46.96[b]	57.96[a] 47.25[b]	48.08[b]	48.95[b]
C_{3v}($^3A_1$)	7.44[a] 11.26[b]	7.41[a] 11.14[b]	11.36[b]	11.59[b]

[a] This work results obtained with B3LYP/aug-cc-pVXZ (X = T, Q). Ground state, C_s (1A′), total energies: T = −2949.1094252 au; Q = −2949.1238158 au.

[b] This work results obtained with CCSD(T)/cc-pVXZ//B3LPY/aug-cc-pVQZ. Ground state, C_s ($^1A'$), total energies: T = −2946.1966255 au; Q = −2946.3012999 au; 5 = −2946.3989298 au.

structure is the C_{2v} ($^1A_1$), which is 4.66 kcal/mol above the ground state followed by the C_s ($^1A'$) (9.71 kcal/mol) and C_{3v} ($^3A_1$) (11.59 kcal/mol) states. These results are in agreement with the previous assignment of Archibong and Mvula [39], calculated at CCSD(T)//MP2 level with the C_{2v} ($^1A_1$), C_s ($^1A'$) and C_{3v} ($^3A_1$) states lying at 6.47, 8.76 and 10.15 kcal/mol above the ground state, respectively. The other excited states are very high energetically and were not studied previously.

3.3. BP_3 cluster

In the literature, there are substantially less studies of clusters of boron with phosphorus in comparison with the combination of aluminium and gallium with phosphorus. To the best of our knowledge, there are no experimental data and theoretical works on BP_3 cluster for comparison. In the Supporting material are presented optimized geometrical parameters using the B3LYP functional with aug-cc-pVTZ and aug-cc-pVQZ basis sets for the low-lying singlet and triplet states at the C_s, C_{2v} and C_{3v} symmetries, together with the harmonic vibrational frequencies.

There is a small effect on the geometrical parameters when the basis set is increased from aug-cc-pVTZ to aug-cc-pVQZ, as already observed for the other clusters. The distances decrease, but no more than 0.017 Å, and the angles also present a small decrease. The harmonic frequencies also do not change substantially with the basis set increase.

The relative energies of the lowest states are presented in Table 3. The ground state of the BP_3 cluster is determined to be a singlet C_{2v} ($^1A_1$) as calculated at both B3LYP and single point CCSD(T) methods. Calculations at the CCSD(T)/CBS level also show that the first excited state is the triplet C_{2v} ($^3B_2$) lying at 16.51 kcal/mol above the ground state. The next excited structures are the C_{3v} ($^1A_1$) and C_s ($^1A'$) states, which are almost degenerate, lying 23.29 and 24.36 kcal/mol above the C_{2v} ($^1A_1$) ground state. The next state, C_{3v} ($^3A_1$), was characterized as a transition state and the C_{3v} ($^3A_1$) state is very high energetically.

Table 3
Relative energies (in kcal/mol) of BP_3 low-lying states. The B3LPY/aug-cc-pVXZ (X = T, Q) results include ZPE and CCSD(T)/aug-cc-pVXZ (X = T, Q, 5)//B3LPY/aug-cc-pVQZ results are without ZPE.

State	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pV5Z	CBS
C_s($^1A'$)	28.87[a] 24.30[b]	29.07[a] 24.46[b]	24.41[b]	24.36[b]
C_s($^3A''$)	31.90[a] 31.53[b]	32.02[a] 31.76[b]	31.68[b]	31.59[b]
C_{2v}($^1A_1$)	0.00[a],[b]	0.00[a],[b]	0.00[b]	0.00[a],[b]
C_{2v}($^3B_2$)	9.95[a] 13.89[b]	10.33[a] 15.24[b]	15.86[b]	16.51[b]
C_{3v}($^1A_1$)	25.12[a] 23.30[b]	25.33[a] 23.19[b]	23.24[b]	23.29[b]
C_{3v}($^3A_1$)	67.72[a] 67.52[b]	68.39[a] 68.55[b]	68.61[b]	68.67[b]

[a] This work results obtained with B3LYP/aug-cc-pVXZ (X = T, Q). Ground state, C_{2v} ($^1A_1$), total energies: T = −1048.9712998 au; Q = −1048.9837314 au.

[b] This work results obtained with CCSD(T)/cc-pVXZ//B3LPY/aug-cc-pVQZ. Ground state, C_{2v} ($^1A_1$), total energies: T = −1047.4905403 au; Q = −1047.5307427 au; 5 = −1047.5457698 au.

3.4. Comparison between BP_3, AlP_3 and GaP_3 cluster

As previously discussed, the ground state structure of BP_3, AlP_3 and GaP_3 have singlet C_{2v}, C_{2v} and C_s symmetries, respectively, which reflect the change in the atomic radii of the IIIA elements. For the BP_3 cluster, at the CCSD(T)/CBS level, the singlet C_{2v} structure is more stable than the C_s by as much 24.4 kcal/mol in clear distinction with the AlP_3 cluster where the two singlet structures are very close in energy, (C_{2v} more stable by about 2.0 kcal/mol). For the GaP_3 cluster the relative stability changes and the singlet C_s structure becomes more stable than the C_{2v} structure by 4.7 kcal/mol. The change from B to Al doped atom in the XP_3 (X = B, Al, Ga) clusters lead, as expected, to a considerable increase in the X–P distance (1.810–2.296 Å), a small increase in the P_2P_3 distance (3.410–3.624 Å) and the angle PXP decreases from 140.8°–104.2°. The other P_2P_4 distance decrease (2.161–2.091 Å) and there is a considerable increase in the PPP angle (104.1°–120.1°). The change to Ga atom increases even more the metal-P distance (2.512 Å in GaP_3) and reduce the PPP angle to 71.7°, which leads the three P atoms structure close to a P_3 molecule [62,63].

4. Conclusions

Geometrical parameters and vibrational frequencies of AlP_3, GaP_3 and BP_3 molecules were obtained using the B3LYP functional and correlation consistent basis sets of Dunning, and the results are compared to other results when possible. The main issue related to these species is the question of the relative energy of their various isomers. The AlP_3 cluster has two lowest C_{2v} ($^1A_1$) and C_s ($^1A'$) states which are very close in energy. In all calculations the C_{2v} state is found to be the ground state, which is in agreement to most recent works, while the C_s state, calculated with CCSD(T)/aug-ccpV5Z and CCSD(T)/CBS methods are located above by, respectively, 1.7 and 2.0 kcal/mol. In relation to GaP_3, the singlet C_s ($^1A'$) is clearly the ground state, followed by C_{2v} ($^1A_1$), which is 4.7 kcal/mol above the ground state followed by the C_s ($^1A'$) (9.7 kcal/mol) and C_{3v} ($^3A_1$) (11.6 kcal/mol) states computed at the CCSD(T)/CBS level. The electronic ground state of BP_3 molecule was unambiguously characterized by the first time as a singlet C_{2v} ($^1A_1$) in both B3LYP and single-point CBS calculations using the CCSD(T) method. The first excited electronic state is the triplet C_{2v} ($^3B_2$) lying at 16.5 kcal/mol above the ground state. The next excited structures have symmetries C_{3v} ($^1A_1$) and C_s ($^1A'$), which are 23.3 and kcal/mol above the ground state. Other excited states were also characterized.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemphys.2011.06.004.

References

[1] Z.Y. Liu, C.R. Wang, R.B. Huang, Int. J. Mass Spectrom. Ion Proc. 141 (1995) 201.
[2] H. Gomez, T.R. Taylor, D.M. Neumark, J. Phys. Chem. A 105 (2001) 6886.
[3] P.Y. Feng, K. Balasubramanian, Chem. Phys. Lett. 301 (1999) 458.
[4] E.F. Archibong, S.K. Goh, D.S. Marynick, Chem. Phys. Lett. 361 (2002) 214.
[5] R. Linguerri, N. Komiha, R. Oswald, A. Mitrushchenkov, P. Rosmus, Chem. Phys. 346 (2008) 1.
[6] P. Pichini, A. Fazzio, S. Canuto, Nanostruct. Mater. 10 (1998) 635.
[7] E.-L. Li, X.-M. Luo, W. Shi, X.-W. Wang, J. Mol. Struct. (Theochem) 723 (2005) 79.
[8] G. De Maria, K.A. Gingerich, L. Malaspina, V. Piacente, J. Chem. Phys. 44 (1966) 2531.
[9] D.W. Liao, K. Balasubramanian, J. Chem. Phys. 96 (1992) 8938.
[10] M.A. Al-Laham, G.W. Trucks, K. Raghavachari, J. Chem. Phys. 96 (1992) 1137.
[11] A. Tomasulo, M.V. Ramakrishna, J. Chem. Phys. 105 (1996) 10449.
[12] A. Tomasulo, M.V. Ramakrishna, Z. Phys. D 40 (1997) 483.
[13] P.Y. Feng, K. Balasubramanian, Chem. Phys. Lett. 318 (2000) 417.
[14] E.F. Archibong, R.M. Gregorius, S.A. Alexander, Chem. Phys. Lett. 321 (2000) 253.
[15] L. Guo, H.-S. Wu, Z.-H. Jin, J. Mol. Struct. (Theochem) 680 (2004) 121.
[16] Y. Qu, X. Bian, J. Comput. Chem. 26 (2005) 226.
[17] J.J. Zhao, L. Wang, J. Jia, X.S. Chen, X.L. Zhou, W. Lu, Chem. Phys. Lett. 443 (2007) 29.
[18] P. Karamanis, J. Leszczynski, J. Chem. Phys. 128 (2008) 154323.
[19] L. Guo, H. Wu, J. Nanopart. Res. 10 (2008) 341.
[20] L. Guo, Mater. Chem. Phys. 115 (2009) 612.
[21] L. Guo, J. Alloys Compd. 490 (2010) 78.
[22] L. Guo, H.-S. Wu, Z.-H. Jin, J. Mol. Struct. (Theochem) 684 (2004) 67.
[23] H.-S. Wu, L. Guo, Z.-H. Jin, J. Mol. Struct. (Theochem) 683 (2004) 43.
[24] L. Guo, H.-S. Wu, Z.-H. Jin, Int. J. Mass Spectrom. 240 (2005) 149.
[25] T. Malaspina, K. Coutinho, S. Canuto, Chem. Phys. Lett. 411 (2005) 14.
[26] T. Malaspina, S. Canuto, Chem. Phys. Lett. 444 (2007) 247.
[27] T.R. Taylor, K.R. Asmis, C. Xu, D.M. Neumark, Chem. Phys. Lett. 297 (1998) 133.
[28] T.R. Taylor, K.R. Asmis, H. Gomez, D.M. Neumark, Eur. Phys. J. D 9 (1999) 317.
[29] T.R. Taylor, H. Gomez, K.R. Asmis, D.M. Neumark, J. Chem. Phys. 115 (2001) 4620.
[30] S. Gao, J. Lu, Y. Zhao, N. Chen, Y. Xie, Eur. J. Inorg. Chem. 9 (2003) 1822.
[31] W. Andreoni, Phys. Rev. B 45 (1992) 4203.
[32] P.Y. Feng, K. Balasubramanian, Chem. Phys. Lett. 258 (1996) 387.
[33] P.Y. Feng, K. Balasubramanian, Chem. Phys. Lett. 265 (1997) 41.
[34] P.Y. Feng, K. Balasubramanian, Chem. Phys. Lett. 265 (1997) 547.
[35] P.Y. Feng, K. Balasubramanian, Chem. Phys. Lett. 288 (1998) 1.
[36] E.F. Archibong, A. St-Amant, Chem. Phys. Lett. 316 (2000) 151.
[37] E.F. Archibong, A. St.-Amant, Chem. Phys. Lett. 330 (2000) 199.
[38] E.F. Archibong, A. St-Amant, S.K. Goh, D.S. Marynick, Chem. Phys. Lett. 361 (2002) 411.
[39] E.F. Archibong, E.N. Mvula, Chem. Phys. Lett. 391 (2004) 325.
[40] A. Costales, A.K. Kandalam, R. Franco, R. Pandey, J. Phys. Chem. B 106 (2002) 1940.
[41] W.H. Jia, H.S. Wu, Acta Phys. Sin. 53 (2004) 1056.
[42] L. Guo, H. Wu, Int. J. Quantum Chem. 106 (2006) 968.
[43] K.A. Gingerich, J. Chem. Phys. 56 (1972) 4239.
[44] A.I. Boldyrev, J. Simons, J. Phys. Chem. 97 (1993) 6149.
[45] A.I. Boldyrev, N. Gonzales, J. Simons, J. Phys. Chem. 98 (1994) 9931.
[46] Z. Gan, D.J. Grant, R.J. Harrisson, D.A. Dixon, J. Chem. Phys. 125 (2006) 124311.
[47] G.K-L. Chan, N.C. Handy, J. Chem. Phys. 112 (2000) 5639.
[48] P.J. Bruna, F. Grein, J. Phys. Chem. A 105 (2001) 3328.
[49] B. Miguel, S. Omar, P. Mori-Sánchez, J.M.G. de la Vega, Chem. Phys. Lett. 381 (2003) 720.
[50] S. Burrill, F. Grein, J. Mol. Struct. (Theochem) 757 (2005) 137.
[51] Y. Qu, W. Ma, X. Bian, H. Tang, W. Tian, Int. J. Quantum Chem. 106 (2006) 960.
[52] M. Ončák, M. Srnec, J. Comput. Chem. 29 (2008) 233.
[53] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[54] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[55] K. Raghavachari, G.W. Trucks, J.A. Pople, M. Head-Gordon, Chem. Phys. Lett. 157 (1989) 479.
[56] R.A. Kendall, T.H. Dunning Jr., R.J. Harrison, J. Chem. Phys. 96 (1992) 6796.
[57] D.E. Woon, T.H. Dunning Jr., J. Chem. Phys. 98 (1993) 1358.
[58] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, A.K. Wilson, Chem. Phys. Lett. 286 (1998) 243.
[59] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B.J. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision A.1, Gaussian Inc., Pittsburgh, PA, 2003.
[60] A.J.C. Varandas, J. Chem. Phys. 113 (2000) 8880.
[61] K.A. Peterson, T.H. Dunning Jr., J. Chem. Phys. 102 (1995) 2032.
[62] N.J. Fitzpatrick, P.J. Groarke, Polyhedron 11 (1992) 2517.
[63] D. Wang, C. Xiao, W. Xu, J. Mol. Struct. (Theochem) 759 (2006) 225.