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Ga_xP_y(x+y=8)及其阴离子团簇的结构与性质的 DFT 研究

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摘要 用密度泛函理论方法对半导体二元微团簇Ga_xP_y和Ga_xP_y⁻(x+y=8)的几何结构、电子态、能量等进行了计算, 在B3LYP/6-311+G(2df)水平下完成结构优化和频率分析. 讨论了电荷诱导结构发生变化情况, 与中性团簇相比, 在阴离子团簇中, Ga—P键较P—P键有利于形成. 预测了未知Ga₁P₇⁻、Ga₂P₆⁻、Ga₃P₅⁻、Ga₄P₄⁻和Ga₇P₁⁻化合物的最稳定结构存在的可能性, 得出在Ga_xP_y和Ga_xP_y⁻(x+y=8)中, Ga₄P₄和Ga₄P₄⁻比较稳定. 给出了两种能差即绝热电子亲合势(ΔE_{AEA})和垂直电离能(ΔE_{VDE}), 并与相关文献作比较. Ga₄P₄和Ga₅P₃的绝热电子亲合势与实验值相当吻合. 布居分析表明, 磷化镓团簇的成键属于混合键型.

关键词: 密度泛函理论, Ga_xP_y和Ga_xP_y⁻团簇, 布居分析, 垂直电离能, 绝热电子亲合势

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Study on the Structure and Property of the Neutral Ga_xP_y (x+y=8) and Anionic Gallium Phosphide Clusters Using DFT

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Abstract Structure, electronic state, and energy of semiconductor binary micro-clusters, Ga_xP_y and Ga_xP_y⁻, having eight atoms have been computed using density functional theory (DFT) method. Structural optimization and frequency analysis are performed at the B3LYP/6-311+G(2df) level. The charged-induced structural changes of these anions have been discussed. The strong Ga—P bond is favored over the P—P bond in Ga_xP_y⁻ (x+y=8), in comparison with the corresponding neutral cluster. The calculations predict the existence of previously unknown isomers (i.e. Ga₁P₇⁻, Ga₂P₆⁻, Ga₃P₅⁻, Ga₄P₄⁻, and Ga₇P₁⁻). Among different Ga_xP_y and Ga_xP_y⁻ (x+y=8) clusters, Ga₄P₄ and Ga₄P₄⁻ are more stable. Two types of energy separations are reported in this study, adiabatic electron affinities (ΔE_{AEA}) and vertical detachment energies (ΔE_{VDE}), wherever applicable, and are compared with those described in other published data in the literature. Adiabatic electron affinities for Ga₄P₄ and Ga₅P₃ are in good agreement with those obtained in the experiments. Mulliken population analyses indicate that the bonding in GaP clusters is of a mixed type.

Keywords: Density functional theory, Ga_xP_y and Ga_xP_y⁻ clusters, Mulliken population analysis, Vertical detachment energies, Adiabatic electron affinities

Theoretical and experimental studies on the electronic and geometric properties of main group III-V clusters continue to be an active area of research because of their rich chemistry and physics, and perhaps more importantly because of their potential application in the electronics industry^[1-2]. An important aspect

of the chemistry and physics of small clusters involves understanding the change in their geometric and electronic properties with an increase in size. Furthering the efforts of several research groups on III-V clusters, Neumark and coworkers^[3] experimentally investigated the evolution of electronic structure as a

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function of size in gallium phosphide semiconductor clusters. In a subsequent work, the authors reported vibrationally resolved anion photoelectron spectra of the low-lying electronic states of small clusters with up to 5 atoms comprehensively^[4-5]. Before the study conducted by Neumark and coworkers, Weltner and his associates^[6] had investigated the IR absorption spectra of GaP, GaP₂ and Ga₂P isolated in a 4 K argon matrix.

Several theoretical investigations of gallium phosphide clusters have been carried out^[7-19]. Andreoni^[7] employed the Car-Parrinello molecular dynamics method to study the structure, stability, and melting point of (GaP)_n clusters with $n=2\sim 5$. Costales *et al.*^[8] studied the structural and vibrational properties of small stoichiometric (GaP)_n clusters with $n=1\sim 3$ within the framework of density functional theory (DFT). The first small GaP fullerene cage was proposed with *ab initio* molecular dynamics simulations^[10]. Korambath *et al.*^[17] studied the (hyper) polarizability of GaP clusters by *ab initio* time-dependent Hartree-Fock method. Inspired by the pioneering work of Neumark and coworkers on anion photoelectron spectra of Ga_xP_y clusters^[3] and based on the previous reports on binary semiconductor clusters^[9-15], the structures, electronic states and vibrational frequencies for Ga_mP_n⁻ ($m+n\leq 5$) clusters have been investigated in this study using B3LYP/6-31G(*d*) method^[18]. In the near past, Li *et al.*^[19] studied the geometric, electronic state of Ga_nP and Ga_nP₂ ($n=1\sim 7$) clusters at the B3LYP/6-31G(*d*) level.

Although several studies have been carried out on gallium phosphide, the investigations on larger clusters have scarcely been reported, and calculations of Ga_xP_y and Ga_xP_y⁻ ($x+y=8$) clusters have neither been systemically studied. In the present study, the calculations on Ga_xP_y and Ga_xP_y⁻ ($x+y=8$) species were performed using the B3LYP level of DFT to provide more reliable ground state geometries, the highest occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO-LUMO) energy gap, and theoretically calculated IR vibrational frequencies at the corresponding optimum structures. A reliable theoretical prediction would be established for those gallium phosphides in the absence of experimental results and in some cases to challenge existing experiments.

The choice of DFT has been fully justified for studies on semiconductor system due to the fact that it is an *ab initio* tool and includes the electron correlation effect which has been found necessary for gallium phosphide clusters at relatively low computational cost^[18-19] and other aspect.

1 Computation method

The basis set followed in this study was the 6-311+G(2*df*) one-particle basis set^[20-21]. Restricted methods were used for all closed-shell systems, whereas unrestricted methods were employed for the open-shell species. Geometrical optimizations were computed using the B3LYP functional. Frequency analyses are also performed at the same theoretical level to check whether the optimized structures are transition states or true minima on the potential energy surfaces of corresponding clusters. All the most stable Ga_xP_y and Ga_xP_y⁻ clusters that were obtained were characterized as true minima without imaginary frequencies. Furthermore, adiabatic electron affinities (ΔE_{AEA}) of Ga_xP_y and vertical detachment energies (ΔE_{VDE}) of Ga_xP_y⁻ were calculated. Some of them are compared with the available experimental values.

The adiabatic electron affinity is defined as the energy difference between the neutral cluster and its corresponding anion, that is $\Delta E_{\text{AEA}} = E_{(\text{optimized neutral})} - E_{(\text{optimized anion})}$, where both the neutral cluster and its radical anion are in the lowest electronic states. The vertical detachment energy is defined as the energy difference between the fully optimized anion cluster and the related neutral cluster without relaxation, that is $\Delta E_{\text{VDE}} = E_{(\text{neutral at optimized anionic geometry})} - E_{(\text{optimized anion})}$. All calculations were carried out using the Gaussian 03 program^[22].

2 Results and discussion

2.1 Geometry

The ground state geometric sketch figures of Ga_xP_y and Ga_xP_y⁻ ($x+y=8$) clusters are shown in Fig.1, where “n” represents neutral clusters and a represents anion clusters. The corresponding geometric parameters of Ga_xP_y and Ga_xP_y⁻ ($x+y=8$) are listed in Table 1.

2.1.1 Ga₁P₇ and Ga₁P₇⁻

The equilibrium geometries of the ¹A' ground state of neutral Ga₁P₇ and the ²A' ground state of Ga₁P₇⁻ are displayed in Fig.1 (1n and 1a). The neutral Ga₁P₇ structure is similar to the ground state of P₈^[23], the substitution of one P atom by one Ga atom in the wedge-shaped C_{2v} configuration of P₈^[23], and the C_s could be considered as the distortion of C_{2v}. There exist two kinds of Ga—P bonds and five kinds of P—P bonds in structure (1n). With the addition of an extra electron to Ga₁P₇ to form Ga₁P₇⁻, the symmetry does not change, but bond distances and bond angles change. For example, bond distances $R_{\text{Ga2-P3}}$ and $R_{\text{Ga2-P4}}$ are

all longer than those of the neutral cluster by about 5.0% and 6.3%, bond angles $\alpha_{\text{P3-Ga2-P7}}$ and $\alpha_{\text{P3-Ga2-P4}}$ decrease in size by 16.1% and 7.2%, respectively. And P—P bond lengths are all shorter than those of the neutral cluster. Although no experimental or theoretical data are available for either Ga_1P_7 or Ga_1P_7^- , the calculations in this study should facilitate the analysis of future data.

The theoretical ΔE_{AEA} and ΔE_{VDE} are 2.20 eV and 2.66 eV, respectively. The difference between ΔE_{AEA} and ΔE_{VDE} is attributed to the considerable geometric distortions in geometry between Ga_1P_7 and Ga_1P_7^- .

2.1.2 Ga_2P_6 and Ga_2P_6^-

The geometries of the 1A_1 ground state of Ga_2P_6 and its 2A ground state anion are shown in Fig.1 (2n and 2a). As was the case for Ga_2P_6 , the optimized structure is a distorted cube structure with a C_{2v} symmetry that is similar to the low-lying state of P_8 (O_h), which was derived by the substitution of two P atoms with two Ga atoms in the structure of P_8 ^[23]. With the addition of an extra electron to Ga_2P_6 to form the anion, large distortions occurred in geometry because of John-Teller effect. The Ga_2P_6^- anion displays C_1 wedge-shaped structure, which is similar to structure (1a).

The calculated values of ΔE_{AEA} and ΔE_{VDE} are 1.56 eV and 2.64 eV, respectively. The difference between ΔE_{AEA} and ΔE_{VDE} is due to the strong distortion in geometry between Ga_2P_6 and Ga_2P_6^- .

2.1.3 Ga_3P_5 and Ga_3P_5^-

The ground state of Ga_3P_5 has C_{3v} (1A_1) structure (3n), which can be derived from the structure of P_8 by the substitution of three P atoms by three Ga atoms. The anion Ga_3P_5^- also has C_{3v} symmetry (3a), and the addition of an electron to the neutral isomer results in an increase in bond length $R_{\text{P-P}}$ and a decrease in bond angle $\alpha_{\text{P2-P1-P5}}$. There are two kinds of Ga—P bonds and one kind of P—P bonds in structures (3n) and (3a). The calculations of this study predict that the ΔE_{AEA} and ΔE_{VDE} are 2.00 eV and 2.13 eV, respectively. No photoelectron measurements have yet been performed for this cluster. The values of ΔE_{AEA} and ΔE_{VDE} are close to each other because of the small geometric changes between the neutral and its corresponding anion.

2.1.4 Ga_4P_4 and Ga_4P_4^-

The lowest energy structure of Ga_4P_4 has C_2 (1A) symmetry, which can be derived from the amalgamation of Ga—Ga edges of two trigonal bipyramidal structures of Ga_3P_2 ^[18] and then the

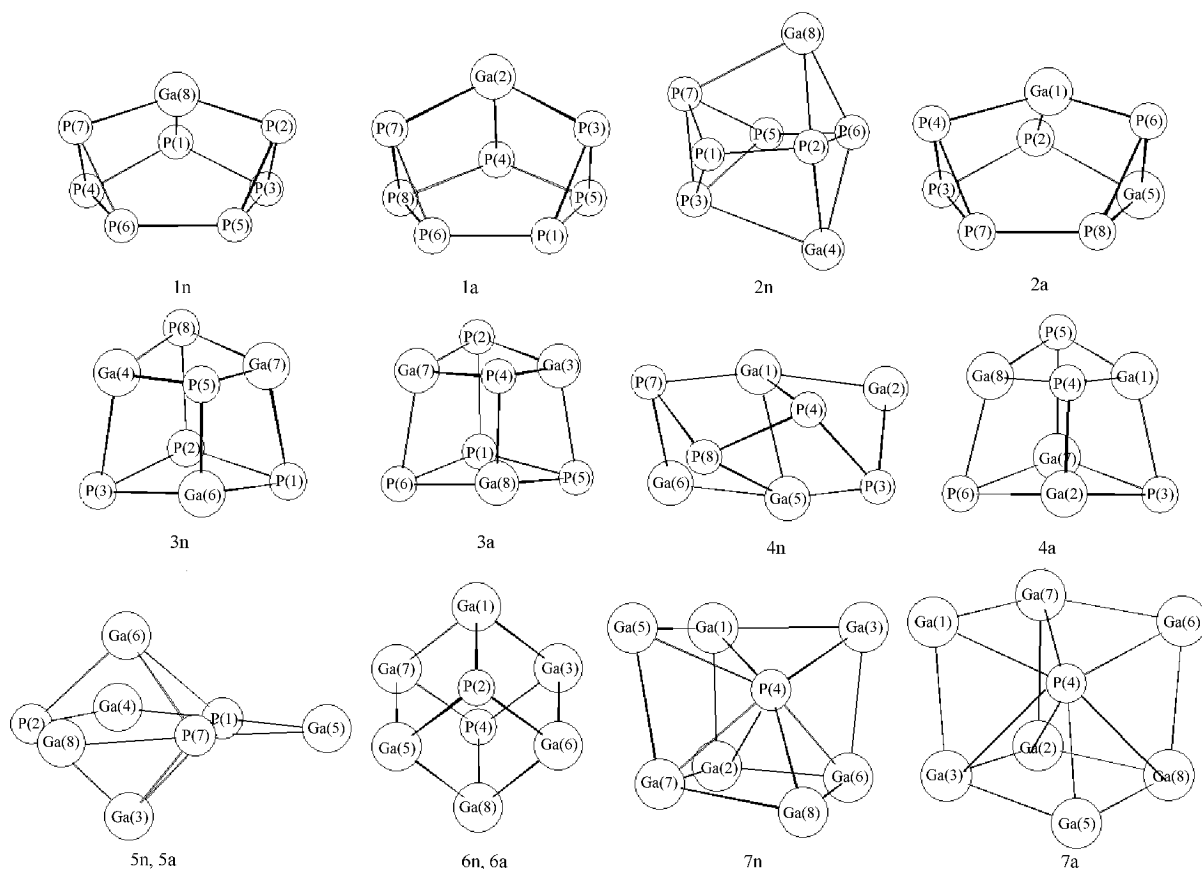


Fig.1 The lowest electronic state geometries of Ga_xP_y and Ga_xP_y^- ($x+y=8$) clusters

n denotes neutral clusters and a denotes anion clusters.

formation of one additional P—P bond. A $T_d(^1A_1)$ isomer locates at 1.11 eV above the ground state. With the addition of an extra electron to the neutral Ga_4P_4 to form the anion Ga_4P_4^- , the symmetry changes from C_2 to T_d . The ground state of Ga_4P_4^- has $T_d(^2A_1)$ structure (4a) and is the most energetically favored among isomers. It can be viewed as a fusion of two tetrahedrons of GaP_3 and PGa_3 which are rotated with respect to each other. As was case for Ga_4P_4^- , bond lengths of 0.2421 nm was obtained using the calculations described in this study for the identical Ga—P bonds.

The calculated values of ΔE_{AEA} and ΔE_{VDE} are predicted to be 2.26 eV and 3.42 eV, respectively. The predicted ΔE_{AEA} for Ga_4P_4 is in satisfactory agreement with the PE spectrum given by Neumark *et al.*^[9]. The PE spectrum gives a ΔE_{VDE} of (2.59±0.15) eV for Ga_4P_4^- , which is smaller than the predicted values obtained in this study.

2.1.5 Ga_3P_3 and Ga_3P_3^-

The ground state of Ga_3P_3 has $C_s(^1A')$ structure(5n). The HOMO-LUMO gap of structure (5n) is greater than that of any other low-lying states, and the energy of structure (5n) is the lowest of all the low-lying states. These may explain the stabilization of the structure (5n). Strong P—P bond is favored over Ga—P bonds in Ga_3P_3 . With an additional electron to the neutral to form Ga_3P_3^- (5a), the symmetry does not change; however, the bond distances and bond angles changed. The P—P bond in the anion is shorter than that in the neutral cluster, which indicates that the interaction between the two P atoms is enhanced.

The calculated values of the ΔE_{AEA} for Ga_3P_3 and the ΔE_{VDE} for Ga_3P_3^- are 2.22 eV and 2.60 eV, respectively. The theoretical values of ΔE_{AEA} and ΔE_{VDE} are lower than the corresponding experimental values ((2.67±0.15) eV for ΔE_{AEA} and (3.42±0.15) for ΔE_{VDE})^[31]. The energy difference between ΔE_{AEA} and ΔE_{VDE} is attributed to structural relaxation.

2.1.6 Ga_6P_2 and Ga_6P_2^-

Li *et al.*^[19] calculated the geometry and energy gap of Ga_6P_2 cluster. They predicted that the ground state of Ga_6P_2 has strong P—P bond at B3LYP/6-31G(d) level. However, in the calculation obtained in this study, it has been found that the $D_{3d}(^1A_{1g})$ structure (6n) with strong Ga—P bonds is more stable in energy by 72.7 kJ·mol⁻¹ than the $C_s(^1A')$ structure^[19] at the same level. The HOMO-LUMO energy gap of structure (6n) is also 0.30 eV greater than that of Li's structure. Hence the stabilization of structure (6n) should be accounted for. The ground state of Ga_6P_2

Table 1 Distances between two atoms in Ga_xP_y and Ga_xP_y^- ($x+y=8$) clusters

Clusters	Bond type	Bond length(nm)	Clusters	Bond type	Bond length(nm)	
1n ⁺	P(1)–P(3)	0.2295	1a ⁺	P(1)–P(3)	0.2213	
	P(2)–P(3)	0.2304		P(1)–P(5)	0.2236	
	P(2)–P(5)	0.2220		P(1)–P(6)	0.2268	
	P(3)–P(5)	0.2244		Ga(2)–P(3)	0.2487	
	P(5)–P(6)	0.2306		Ga(2)–P(4)	0.2492	
	Ga(8)–P(1)	0.2345		P(3)–P(5)	0.2282	
2n	Ga(8)–P(2)	0.2368	2a	P(4)–P(5)	0.2250	
	P(1)–P(2)	0.2215		Ga(1)–P(2)	0.2348	
	P(1)–P(3)	0.2256		Ga(1)–P(4)	0.2437	
	P(2)–Ga(4)	0.2612		Ga(1)–P(6)	0.2295	
	P(2)–P(6)	0.2263		P(2)–P(3)	0.2256	
	P(3)–P(7)	0.2233		P(2)–Ga(5)	0.2546	
3n	P(1)–P(2)	0.2237	3a	P(3)–P(4)	0.2254	
	P(1)–Ga(6)	0.2427		P(3)–P(7)	0.2308	
	Ga(4)–P(5)	0.2385		P(4)–P(7)	0.2206	
4n	Ga(1)–Ga(2)	0.2738	4a	Ga(5)–P(6)	0.2624	
	Ga(1)–P(4)	0.2599		Ga(5)–P(8)	0.2425	
	Ga(1)–Ga(5)	0.2705		P(6)–P(8)	0.2288	
	Ga(1)–P(7)	0.2354		P(7)–P(8)	0.2262	
	Ga(2)–P(3)	0.2687		5a	P(1)–P(2)	0.2295
	P(3)–P(4)	0.2163			P(2)–Ga(3)	0.2422
	P(4)–P(8)	0.2257			Ga(3)–P(4)	0.2411
	5n	P(1)–Ga(3)			0.2467	4a
P(1)–Ga(4)		0.2662	5a	P(1)–Ga(3)	0.2586	
P(1)–Ga(5)		0.2658		P(1)–Ga(4)	0.2632	
P(1)–P(7)		0.2389		P(1)–Ga(5)	0.2549	
P(2)–Ga(3)		0.2438		P(1)–P(7)	0.2279	
P(2)–Ga(4)		0.2656		P(2)–Ga(3)	0.2545	
6n	Ga(1)–P(2)	0.2387		6a	P(2)–Ga(4)	0.2582
	Ga(1)–Ga(3)	0.2795	Ga(1)–P(2)		0.2414	
7n	Ga(1)–Ga(2)	0.2615	7a	Ga(1)–Ga(3)	0.2762	
	Ga(1)–Ga(3)	0.2898		Ga(1)–Ga(3)	0.2716	
	Ga(1)–P(4)	0.2624		Ga(1)–P(4)	0.2593	
	Ga(2)–P(4)	0.2734		Ga(2)–Ga(3)	0.2658	
	Ga(3)–P(4)	0.2537		Ga(2)–P(4)	0.2710	
				Ga(3)–P(4)	0.2685	

ⁿ denotes neutral clusters and a denotes anion clusters.

has six identical Ga—Ga bonds and six identical Ga—P bonds. With the addition of an extra electron to the neutral Ga_6P_2 to form Ga_6P_2^- , the symmetry remains unchanged; however, the geometric parameters change slightly. Compared with the neutral cluster, the Ga—P bond distance is longer by 1.4% and the Ga—Ga bond distance is shorter by 0.9% in the anion.

The theoretical values of ΔE_{AEA} and ΔE_{VDE} are 2.00 eV and 2.44 eV, respectively. Although no photoelectron measurements are available for this cluster at present, the calculations described

Table 2 Harmonic vibrational frequencies and IR intensities of the ground state of Ga_xP_y and Ga_xP_y⁻ (x+y=8) clusters

Species	Vibrational mode frequency, (cm ⁻¹), and IR intensity (km ² ·mol ⁻¹ , in parentheses)		
Ga ₇ P ₁	A':116.5(1.1)	A'':371.2(6.8)	A':490.5(1.7)
Ga ₂ P ₆	A ₁ :50.7(1.2)	B ₁ :278.8(60.6)	A ₁ :513.2(0.3)
Ga ₃ P ₅	E:141.5(0.0)	A ₁ :386.3(6.5)	E:442.2(5.0)
Ga ₄ P ₄	A:43.4(0.0)	B:140.0(16.2)	B:463.8(8.0)
Ga ₅ P ₃	A':10.4(0.0)	A'':280.8(63.8)	A':364.8(17.5)
Ga ₆ P ₂	E _g :39.3(0.0)	A _{2g} :314.6(30.5)	A _{1g} :325.4(0.0)
Ga ₇ P ₁	A:32.7(0.0)	E:319.6(71.7)	E:319.6(71.7)
Ga ₈ P ₀	A':115.1(0.7)	A':269.7(7.0)	A'':487.5(1.1)
Ga ₂ P ₆ ⁻	A:83.6(1.4)	A:399.7(12.3)	A:487.3(5.2)
Ga ₃ P ₅ ⁻	E:5.2(8.9)	A ₁ :352.1(15.0)	E:379.9(8.9)
Ga ₄ P ₄ ⁻	E:135.9(0.0)	T ₂ :349.9(26.3)	T ₂ :349.9(26.3)
Ga ₅ P ₃ ⁻	A'':29.2(0.4)	A':301.8(75.3)	A':380.6(0.5)
Ga ₆ P ₂ ⁻	E _g :36.0(0.0)	A _{2g} :333.4(55.3)	A _{1g} :343.8(0.0)
Ga ₇ P ₁ ⁻	A:43.5(0.0)	E:269.9(35.8)	E:269.9(35.8)

Table 3 Total energies, zero-point vibrational energies, and energy gaps of Ga_xP_y and Ga_xP_y⁻ clusters

Cluster	Symmetry	State	Total energies (a.u.)	Zero energy (kJ·mol ⁻¹)	Energy gaps(eV)	
				α [*]		β [*]
Ga ₁ P ₇	C _s	¹ A'	-4314.61971	32.795	2.82	
Ga ₂ P ₆	C _{2v}	¹ A ₁	-5898.13897	28.696	3.50	
Ga ₃ P ₅	C _{3v}	¹ A ₁	-7481.62957	28.976	2.83	
Ga ₄ P ₄	C ₂	¹ A	-9065.12882	23.412	2.62	
Ga ₅ P ₃	C _s	¹ A'	-10648.61680	18.837	2.62	
Ga ₆ P ₂	D _{3d}	¹ A _{1g}	-12232.12469	16.878	2.35	
Ga ₇ P ₁	C _{3v}	¹ A ₁	-13815.60456	13.903	2.08	
Ga ₈ P ₀	C _s	² A'	-4314.70041	31.791	2.75	2.21
Ga ₂ P ₆ ⁻	C ₁	² A	-5898.19622	28.394	2.15	1.79
Ga ₃ P ₅ ⁻	C _{3v}	² A ₁	-7481.70310	25.162	1.54	2.78
Ga ₄ P ₄ ⁻	T _d	² A ₁	-9065.21198	25.232	3.11	1.74
Ga ₅ P ₃ ⁻	C _s	² A'	-10648.69841	18.045	2.27	2.13
Ga ₆ P ₂ ⁻	D _{3d}	² A _u	-12232.19851	16.640	1.65	1.64
Ga ₇ P ₁ ⁻	C _{3v}	² A ₂	-13815.68520	14.585	2.36	1.67

*α and β denote different orbitals respectively.

Table 4 Mulliken population analyses for the ground electronic state of Ga_xP_y clusters

Structure	Gross population (q)		Natural electron configuration	Charge (e)
1n	Ga (8)	2.42	4s(1.22) 4p(1.18) 4d(0.01) 7p(0.01)	0.578
	P (1)	5.24	3s(1.72) 3p(3.47) 3d(0.04) 5p(0.01)	-0.251
	P (2, 7)	5.17	3s(1.75) 3p(3.36) 3d(0.05) 5p(0.01)	-0.174
	P (3, 4)	4.97	3s(1.73) 3p(3.18) 3d(0.05) 5p(0.01)	0.019
	P (5, 6)	5.00	3s(1.70) 3p(3.24) 3d(0.05) 5p(0.01)	-0.009
2n	Ga (4, 8)	2.45	4s(1.89) 4p(0.54) 4d(0.01) 7p(0.01)	0.550
	P (1, 5)	5.01	3s(1.69) 3p(3.26) 3d(0.05) 5p(0.01)	-0.012
	P (2, 6)	5.50	3s(1.71) 3p(3.72) 3d(0.05) 4p(0.01) 5p(0.01)	-0.499
	P (3, 7)	5.04	3s(1.75) 3p(3.22) 3d(0.06) 5p(0.01)	-0.039
3n	Ga (4, 6, 7)	2.58	4s(1.25) 4p(1.30) 4d(0.01) 6p(0.01) 7p(0.01)	0.436
	P (1, 3, 8)	5.26	3s(1.75) 3p(3.46) 3d(0.04) 5p(0.01)	-0.267
	P (2)	4.97	3s(1.57) 3p(3.31) 3d(0.07) 4p(0.01) 5p(0.01)	0.022
	P (5)	5.51	3s(1.73) 3p(3.74) 3d(0.04)	-0.528
4n	Ga (1, 5)	2.89	4s(1.44) 4p(1.41) 4d(0.02) 6p(0.01) 7p(0.01)	0.121
	Ga (2, 6)	2.52	4s(1.83) 4p(0.67) 4d(0.01) 6p(0.01)	0.482
	P (3, 7)	5.42	3s(1.73) 3p(3.63) 3d(0.05) 5p(0.01)	-0.427
	P (4, 8)	5.17	3s(1.67) 3p(3.43) 3d(0.06) 4p(0.01)	-0.175
5n	Ga (3)	2.74	4s(1.42) 4p(1.29) 4d(0.02) 6p(0.01)	0.269
	Ga (4, 8)	2.48	4s(1.85) 4p(0.61) 4d(0.01) 6p(0.01)	0.518
	Ga (5)	2.35	4s(1.92) 4p(0.42) 6s(0.01)	0.653
	Ga (6)	2.71	4s(1.42) 4p(1.29) 4d(0.02) 6p(0.01)	0.268
	P (1, 7)	5.71	3s(1.73) 3p(3.92) 3d(0.05) 4p(0.01)	-0.721
	P (2)	5.78	3s(1.76) 3p(3.97) 3d(0.05)	-0.784
6n	P	5.13	3s(1.74) 3p(4.33) 3d(0.06)	-1.136
	Ga	2.62	4s(1.59) 4p(1.00) 4d(0.01) 6p(0.02)	0.379
7n	Ga (1, 6, 7)	2.86	4s(1.71) 4p(1.12) 4d(0.02) 6p(0.01)	0.138
	Ga (2)	3.15	4s(1.61) 4p(1.47) 4d(0.05) 6p(0.02)	-0.139
	Ga (3, 5, 8)	2.54	4s(1.79) 4p(0.73) 4d(0.01) 6p(0.01)	0.456
	P (4)	6.63	3s(1.68) 3p(4.89) 4s(0.01) 3d(0.05)	-1.643

in this study are useful for further experiments.

2.1.7 Ga₇P₁ and Ga₇P₁⁻

The equilibrium geometries of the ¹A₁ ground state of neutral Ga₇P₁ and the ²A₂ ground state of Ga₇P₁⁻ are given in Fig.1(7n). Li *et al.*^[19] performed B3LYP-DFT calculations of Ga₇P₁ cluster and predicted that the ground state of Ga₇P₁ has C_s(¹A') structure. In the calculations described in this study, the energy of the C_{3v}(¹A₁) structure is nearly equal to that of the C_s(¹A') structure, when the same method was used. Thus, the result (7n) is almost identical to that obtained by Li *et al.*^[19]. For the ²A₂ ground state of Ga₇P₁⁻, the symmetry does not change; however, the bond distances and bond angles change to a certain extent compared with the neutral Ga₇P₁. The calculations described in this study predict the ΔE_{AEA} and ΔE_{VDE} to be 2.19 eV and 2.53 eV, respectively. Experimental data on the ΔE_{AEA} and ΔE_{VDE} are not available at present.

The foregoing ΔE_{VDE} of Ga₇P₁⁻ can be used to facilitate characterization of these novel structures in photoelectron spectroscopy measurements in future.

2.2 Vibrational frequency analysis and stability

A vibrational frequency calculation is important to predict molecular stability. To determine the ground state of clusters, the vibrational frequencies were calculated for these clusters at the B3LYP/6-311+G(2df) level. All the ground states that were reported are actually equilibrium states without imaginary frequencies. Three kinds of infrared vibrational frequencies, which involve the lowest frequency, the strongest IR frequency, and the highest frequency, are reported to aid future assignment of the vibrationally resolved spectrum. The results are listed in Table 2. The calculated energies are tabulated in Table 3.

As shown in Table 3, the HOMO-LUMO energy gaps (ΔE_g) for Ga_xP_y clusters were found to decrease with the increas-

Table 5 Mulliken population analyses for the ground electronic state of Ga_xP_y⁻ clusters

Structure	Gross population (<i>q</i>)		Natural electron configuration	Charge (<i>e</i>)
1a	Ga (2)	2.69	4s(1.42) 4p(1.23) 5s(0.01) 4d(0.01) 5p(0.01) 6p(0.01)	0.312
	P (4)	5.37	3s(1.70) 3p(3.62) 3d(0.04) 4p(0.01)	-0.375
	P (1, 6)	5.08	3s(1.68) 3p(3.34) 3d(0.05) 4p(0.01)	-0.086
	P (3, 7)	5.32	3s(1.74) 3p(3.53) 3d(0.04) 4p(0.01)	-0.334
	P (5, 8)	5.04	3s(1.70) 3p(3.28) 3d(0.05) 4p(0.01)	-0.048
2a	Ga (1)	2.49	4s(1.16) 4p(1.30) 4d(0.01) 5p(0.02)	0.506
	Ga (5)	2.73	4s(1.49) 4p(1.22) 4d(0.01) 5p(0.01)	0.263
	P (2)	5.52	3s(1.72) 3p(3.75) 3d(0.04) 4p(0.01)	-0.515
	P (3)	5.05	3s(1.70) 3p(3.29) 3d(0.05) 4p(0.01)	-0.066
	P (4)	5.25	3s(1.73) 3p(3.46) 3d(0.05) 4p(0.01)	-0.250
	P (6)	5.54	3s(1.73) 3p(3.76) 3d(0.04) 4p(0.01)	-0.550
	P (7)	5.05	3s(1.69) 3p(3.30) 3d(0.05) 4p(0.01)	-0.061
	P (8)	5.31	3s(1.69) 3p(3.57) 3d(0.04) 4p(0.01)	-0.328
3a	Ga (3, 7, 8)	2.67	4s(1.28) 4p(1.37) 4d(0.01) 5p(0.01)	0.327
	P (2, 5, 6)	5.45	3s(1.74) 3p(3.66) 3d(0.04) 4p(0.01)	-0.441
	P (1)	5.01	3s(1.65) 3p(3.28) 3d(0.06) 4p(0.02)	-0.013
	P (4)	5.64	3s(1.73) 3p(3.87) 3d(0.04)	-0.644
4a	Ga (1, 2, 7, 8)	2.57	4s(1.16) 4p(1.38) 4d(0.01) 5p(0.02)	0.422
	P (3, 4, 5, 6)	5.66	3s(1.72) 3p(3.90) 3d(0.04)	-0.672
5a	Ga (3, 6)	2.79	4s(1.62) 4p(1.15) 4d(0.01) 5p(0.01)	0.208
	Ga (4, 8)	2.69	4s(1.80) 4p(0.87) 4d(0.01) 5p(0.01)	0.308
	Ga (5)	2.56	4s(1.87) 4p(0.67) 5s(0.01) 5p(0.01)	0.447
	P (2)	5.94	3s(1.75) 3p(4.15) 3d(0.04)	-0.948
	P (1, 7)	5.76	3s(1.70) 3p(4.00) 3d(0.05) 4p(0.01)	-0.766
6a	P	5.99	3s(1.73) 3p(4.21) 3d(0.05)	-0.997
	Ga	2.84	4s(1.54) 4p(1.26) 4d(0.02) 5p(0.02)	0.166
7a	Ga (1, 5, 6)	2.82	4s(1.71) 4p(1.09) 4d(0.01) 5p(0.01)	0.185
	Ga (2)	3.12	4s(1.60) 4p(1.52) 4d(0.03) 5p(0.01)	-0.169
	Ga (3, 7, 8)	3.03	4s(1.64) 4p(1.36) 4d(0.02) 5p(0.01)	-0.024
	P (4)	6.31	3s(1.67) 3p(4.59) 4s(0.01) 3d(0.04)	-1.315

ing of Ga atom except for Ga_2P_6 cluster. A very large gap is found for Ga_2P_6 cluster. It is found that Ga_2P_6 is more stable than $2\text{GaP}_3^{[18]}$ by $227.4 \text{ kJ}\cdot\text{mol}^{-1}$. The HOMO-LUMO energy gap for Ga_2P_6 is 1.0 eV larger than that for GaP_3 . In consideration of the total energy and HOMO-LUMO energy gap, the existence of Ga_2P_6 cluster is favored. It has also been found that Ga_6P_2 is energetically more stable than $2\text{Ga}_3\text{P}^{[18]}$ by $155.9 \text{ kJ}\cdot\text{mol}^{-1}$, which supports the possibility of the existence of Ga_6P_2 cluster. The above predictions are yet to be confirmed experimentally. With regard to the anion clusters, Ga_4P_4^- cluster has the largest energy gap of 3.11 eV, which may be the reason that it had been observed.

2.3 Mulliken population analysis and natural charge

Table 4 shows the Mulliken populations of the lowest electronic states of Ga_xP_y ($x+y=8$) that has been considered here. In the electronic states of neutral clusters the P populations are uniformly larger than 5.00 except P(3,4) of Ga_1P_7 and P(2) of Ga_3P_5 , whereas the Ga populations are uniformly smaller than 3.00 except Ga(2) of Ga_7P_1 , consistent with the Ga^+P^- ionic bonding in these species and indicating orbital mixing within the framework DFT. Both Ga $4s$ and $4p$ orbitals lose electronic charge to the P $3p$ orbital, as evident from the enhancement of the $3p$ populations of the P atoms in all of the electronic states. Both Ga and P atoms exhibit non-zero d populations, which underscore the importance of the polarization functions.

The natural charges provide interesting insights into the distribution of charge within the molecules. The calculations described in this study present the natural charge of all atoms of clusters that have been considered here. Table 5 shows that addition of an electron to the neutral species results in electronegative enhancement of Ga atoms and P atoms (close to Ga atoms) for the P-rich clusters. For the Ga-rich clusters, the addition of an electron to the neutral species results in electronegative enhancement of P atoms and Ga atoms (close to P atoms). In the anion clusters, the bondings between Ga and P atoms are enhanced.

3 Conclusions

Geometries, electronic states and energies of Ga_xP_y and Ga_xP_y^- ($x+y=8$) clusters have been investigated using DFT with 6-311+G(2df) basis set. In comparison with the corresponding neutral clusters, the results show that the strong Ga—P bond is favored over P—P bond in Ga_xP_y^- ($x+y=8$) clusters. Two types of energy separations reported in this work are the adiabatic electron affinity (ΔE_{AEA}) and the vertical detachment energy (ΔE_{VDE}), wherever applicable, and are compared with described

in other published data in the literature. ΔE_{AEA} and ΔE_{VDE} are predicted to be 2.20 and 2.66 eV (Ga_1P_7), 1.56 and 2.64 eV (Ga_2P_6), 2.00 and 2.13 eV (Ga_3P_5), 2.26 and 3.42 eV (Ga_4P_4), 2.22 and 2.60 eV (Ga_5P_3), 2.00 and 2.44 eV (Ga_6P_2), 2.19 and 2.53 eV (Ga_7P_1). ΔE_{AEA} for Ga_4P_4 and Ga_5P_3 are in good agreement with the experiment values; however, their ΔE_{VDE} are larger than the experimental values. For other clusters, the prediction of this study are useful for future experimental investigations.

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