Probing the structures and electronic properties of dual-phosphorus-
doped gold cluster anions (Au$_n$P$_2$, $n=1$–8): A density functional theory investigation

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The geometries of gold clusters doped with two phosphorus atoms, Au$_n$P$_2$ ($n=1$–8), were investigated using density functional theory (DFT) methods. Various two-dimensional (2D) and three-dimensional (3D) structures of the doped clusters were studied. The results indicate that the structures of dual-phosphorus-doped gold clusters exhibit large differences from those of pure gold clusters with small cluster sizes. In our study, as for Au$_n$P$_2$, two cis-trans isomers were found. The global minimum of Au$_8$P$_2$ presents a similar configuration to that of Au$_{20}$, a pyramid-shaped unit, and the potential novel optical and catalytic properties of this structure warrant further attention. The higher stability of Au$_n$P$_2$ clusters relative to Au$_n$ ($n=1$–8) clusters was verified based on various energy parameters, and the results indicate that the phosphorus atom can improve the stabilities of the gold clusters. We then explored the evolutionary path of Au$_n$P$_2$ ($n=1$–8) clusters. We found that Au$_n$P$_2$ clusters exhibit the 2D–3D structural transition at $n=6$, which is much clearer and faster than that of pure gold clusters and single-phosphorus-doped clusters. The electronic properties of Au$_n$P$_2$ ($n=1$–8) were then investigated. The photoelectron spectra provide additional fundamental information on the structures and molecular orbitals shed light on the evolution of Au$_n$P$_2$ ($n=1$–8). Natural bond orbital (NBO) described the charge distribution in stabilizing structures and revealed the strong relativistic effects of the gold atoms.

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1. Introduction

Gold is an element whose unique properties are strongly influenced by relativistic effects [1–3]. Haruta [4] first reported that gold nano-clusters exhibit catalytic properties; since that report, the structures of gold nano-clusters have received considerable attention [1–3,5]. A series of experimental and theoretical studies have examined the unique structures and exciting properties of small-to-medium pure gold clusters [6–23]. Gold clusters doped with metal/nonmetal species have also been widely investigated based on the expectation that varying the dopant alters the size and shape of the clusters in addition to tailoring the properties of the nano-clusters [24–46].

Phosphorus-doped gold clusters have received significant attention, in part due to interest in understanding the fascinating properties of these materials, particularly their semiconductivity and unique optical properties [47,48]. A number of experimental [49–55] and theoretical [56–60] investigations have also been reported on the reactivities of gold clusters doped with phosphorus.

Jeitschko and Moller [49] investigated the Au–Au interaction in the crystal structure of the well-known Au$_3$P$_3$ structure. Eschen and Jeitschko [50] reported the network crystal structure of Au$_n$MP$_2$ ($M=Pb$, TI, and Hg) in three dimensions with condensed 8-membered Au$_4$P$_6$ and 10-membered Au$_6$P$_8$ rings. Weizer and Fatemi [51] reported the contact resistance of a Au$_2$P$_2$ layer, which was found to be very sensitive to the growth rate of the interfacial Au$_2$P$_2$ layer. Henkes et al. [52] reported on Au$_3$P$_2$ and other metal phosphides synthesized using hot tricoxyphosphine (TOP) as a solvent. A study on the generation of Au$_n$P$_m$ using a Nd:YAG (532 nm) laser was reported by Zheng and co-workers [53]. Recently, Panyala et al. [54] also studied Au$_n$P$_m$ clusters with different $m$.
and $n$ values using laser ablation coupled with TOF-MS, the new gold phosphides generated might inspire synthesis of new Au–P materials with specific properties. Careno et al. [55] developed a versatile route for investigating the formation of Au$_n$P$_3$ nanostructures.

In contrast, there have been few theoretical studies on the structural and bonding properties of Au–P clusters using different calculation methods based on density functional theory (DFT) [57–60]. Theoretical studies on the electronic structures of Au$_n$MP$_2$ ($M = \text{Pb, Ti, and Hg}$) have been undertaken by Wen et al. [56]. Similar results have been reported by Eschen and Jeitschko [50] for the network crystal structure of Au$_n$MP$_2$ ($M = \text{Pb, Ti, and Hg}$). Li et al. [57] studied the geometries, stabilities, and electronic properties of neutral Au$_n$P$_3$ ($n = 1–8$) clusters, and Zhao et al. [58] reported findings for neutral Au$_{12}$ clusters doped with secondary periodic elements based on DFT. The atomic and electronic structures of Au$_n$M ($M = \text{Na, Mg, Al, Si, P, and S}$) [60] and M$_2$Au$_n$ ($M = \text{Al, Si, P, S, Cl, and Ar}$) [59] clusters have been investigated using DFT with a scalar relativistic effective core potential basis set. However, to the best of our knowledge, no systematic investigations of anionic phosphorus-doped gold clusters have been reported in the literature.

Herein, we report a density functional theory study of a series of small gold clusters doped with two phosphorus atoms (Au$_n$P$_2$ ($n = 1–8$)). This study is a follow-up to our previous work which focused on single-phosphorus-doped gold clusters [61]. We selected this size range to probe how isoelectronic substitutions affect the structures of pure gold clusters. We observed the two- or three-dimensional (2D–3D) structural transition at $n = 6$, which is earlier than that of pure gold clusters and much clearer than that of single-phosphorus-doped gold clusters (Au$_n$P$_2^-$), which show an even–odd oscillation in 2D/3D transition. The unique pyramid-shaped structure substitutes the planar Au$_{10}$ cluster to afford the global minimum of Au$_{10}$P$_3$.

2. Theoretical methods

The basin-hopping (BH) global search method [62–66] coupled with DFT was employed to search for low-lying isomers of phosphorus-doped clusters of the type Au$_n$P$_2$ ($n = 1–8$). The original BH algorithm fundamentally combined the Metropolis random sampling technique and local optimization procedures. Two steps were included in this method: a new structure was generated via the random displacement of atoms and then optimized to the local minimum; this local energy minimum was used as a criterion to accept the initial generated structure spaces with the Boltzmann weight at a finite temperature. In our study, randomly produced structures of each species were used as the initial inputs for the BH search method, and 200 initial low-lying isomers were generated after 200–300 BH moves. Considering the inevitable errors of DFT methods when applied to total energy calculations, several additional techniques were chosen for the DFT optimization, including the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) [67], hybrid generalized gradient approximation (hybrid-GGA) in the Becke 3-parameter exchange and the Lee–Yang–Parr correlation (B3LYP) [68–70] functional forms coupled with four basis sets [61]. As shown the selection and verification on the functional and basis set for Au/P systems, PBE functional coupled with CRENBL basis set used for Au and P was selected for the optimization calculations; all approaches were implemented in the NWChem 5.1.1 software package [71,72].

The top 10 isomers with relatively low energies were then selected for single-point energy calculations at the PBE0 [73]/CRENBL level of theory. Because of the strong relativistic effects of the gold atom, the spin orbit (SO) coupling effect [74] also must be considered for heavy atoms such as gold. The PBE0/CRENBL level and SO effects were carefully selected for the gold atom to achieve quantitative agreement between the experimental and theoretical PES spectra [64,75–79].

Simulated photoelectron spectra of the selected low-lying isomers were generated for comparison with the experimental data to further identify the Au$_n$P$_2^-$ ($n = 1–8$) clusters. The first vertical detachment energies (VDEs) of the anion clusters were calculated as the difference between the energies of the neutral and anionic species of each isomer. The binding energies of all deeper occupied orbitals were then added to the first VDE to simulate the detachment features of the valence electrons as a line spectrum. Each line in the obtained spectra was then fitted with a Gaussian width of 0.04 eV to obtain continuous spectra.

3. Results and discussion

This section consists of two parts: the geometric structures and the electronic properties. In the first part, we focus on the geometric structures of Au$_n$P$_2$ ($n = 1–8$) at the PBE0/CRENBL level of theory. The global minima of the species are explored. Next, we discuss the stabilities of these lowest-energy isomers. We also attempt to describe the possible evolutionary process of dual-phosphorus-doped gold clusters. In the second part of this section, the theoretically simulated photoelectron spectra of the low-lying isomers and the corresponding HOMO–LUMO gaps are discussed to support the first part of this section and the molecular orbital analysis. Finally, natural bond orbital (NBO) [80,81] provides intuitive information of the natural population analysis (NPA) [82] assigning atomic charge and the natural electron configuration (NEC) in the clusters.

3.1. Geometric structures

3.1.1. Low-lying structures

Au$_{P2}^-$: Two low-lying isomers of Au$_{P2}^-$ at the PBE0/CRENBL SO level of theory are presented in Fig. 1. The global minimum (Isomer 1) of Au$_{P2}^-$ is a C$_5$ structure with a middle-positioned P atom, and the isomer prefers an obtuse angle $\angle\text{Au–P–P}$. The other isomer is an acute-triangle-shaped structure with a relatively high energy of 1.645 eV, which has a low probability of being the global minimum.

Au$_{P2}^-$: The global minimum of the Au$_{P2}^-$ cluster (Fig. 1) is an axe-like structure (C$_4$), the same configuration of the major isomer of Au$_{P}^-\text{ }$ in our previous study [61]. Isomer 2 (D$_{2h}$) is a high-symmetry structure with a 0.929 eV higher energy than the Isomer 1. The difference between Isomers 3 (C$_5$) and 4 (C$_{2v}$) lies in the Au–Au bond of Isomer 3. Isomer 5, as well as Isomers 2–4, with a greater energy difference than Isomer 1, shows a low probability of being the global minimum. The global minimum of the anion (Au$_{P2}^-\text{ }$) differs somewhat from the neutral configuration (Au$_{P2}^-$) reported by Li et al. [57], which is expected because of the interaction of an additional electron in the structures [40,57,83,84].

Au$_{S3}^-$: The first five low-lying isomers of which possess a P–P bond are presented in Fig. 1. The lowest-energy isomer (Isomer 1) is a pentagon structure with an inner Au–Au bond. Isomer 2 is a zigzag structure evolved from the global minimum of Au$_{S3}^-\text{ }$ by bonding an additional Au atom to the edge-positioned P atom. However, the energy of this isomer is considerably higher than Isomer 1. Different with Isomer 2, Isomer 3 evolves from the global minimum of Au$_{S3}^-\text{ }$ by adding the extra Au atom on the same side of the P–P bond with its energy a slightly higher than Isomer 2. Isomer 4 has an hourglass-like structure, and the energy of this isomer is 0.677 eV greater than that of Isomer 1. Additionally, the energy of Isomer 5, in which all 3 gold atoms are linearly bonded,
is 0.907 eV greater than that of Isomer 1. Isomers 2–5 are also unlikely to be the global minimum. The low isomers of Au\textsubscript{3}P\textsubscript{2}/C\textsubscript{0}/2 are much different from that of the meta-stable phase of Au\textsubscript{2}P\textsubscript{2}/C\textsubscript{0}/3 [84].

Au\textsubscript{4}P\textsubscript{2}⁻: For Au\textsubscript{4}P\textsubscript{2}⁻ in Fig. 1, the global minimum for the species is a planar structure (Cs). The isomer can clearly be envisioned as resulting from the attachment of an additional gold atom to the pentagon structure of Au\textsubscript{3}P\textsubscript{2}⁻. Isomer 2 is 0.133 eV higher than Isomer 1 as a result of moving the Au atom from the upper right corner to the lower right corner. Isomers 3, 4, and 5 are unlikely to be the global minimum structures due to their relatively high energies. Isomer 5 and Isomer 1 differ by only one Au–Au bond; however, the 0.287 eV energy difference affords Isomer 5 with a low probability of being the most stable structure.

Au\textsubscript{6}P\textsubscript{2}⁻: As shown in Fig. 1, there are two co-existing low-lying isomers for Au\textsubscript{6}P\textsubscript{2}⁻. Two dangling Au atoms bond with one phosphorus atom. The difference between the two isomers lies in the relative position of the two dangling gold atoms. We refer to Isomers 1 and 2 as the “cis-isomer” and “trans-isomer”, respectively, borrowing from the molecular naming rules of organic chemistry. The energy of the cis-isomer is slightly lower than that of the trans-isomer. Seven other density functional theory methods

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Footnotes:

1. The top-5 isomers are ranked according to their relative energies for Au\textsubscript{n}P\textsubscript{2}⁻ (n = 2–8), whereas the top-2 isomers are ranked for AuP\textsubscript{2}.
also confirm the energy rankings of the two isomers (Table S1, Supplementary material). Isomer 3 is a $C_{2v}$ structure, and its energy is also within 0.1 eV. Thus, it may be a local minimum. Isomers 4 and 5 exhibit a unique phenomenon in which one gold atom interacts with different phosphorus atoms of the quasi-planar Au$_8$P$_2$ base. The energy difference between Isomer 4 and Isomer 5 is large due to the different positions of the gold atoms.

Au$_8$P$_2^-$: The global minimum is a $C_{2v}$ structure at the PBE0/CRENBL level in our study (Fig. 1). It is an irregular olive-shaped structure with a 1–2–3–2–1 formation ranked according to the number of atoms from the top to the bottom of the structure. Two phosphorus atoms are separated by a gold atom. Isomer 2 is a sailboat-type structure with two phosphorus atoms located at both ends of the sailboat. The structure is slightly distorted, and its energy is somewhat higher than that of Isomer 1. Isomer 3 is a quasi-tetrahedron-type structure, and the clear 3-layer structure makes it highly symmetrical. Isomers 4 and 5 are somewhat disordered structures.

Au$_8$P$_2$: It is very interesting that the global minimum of Au$_8$P$_2$ in our study is a pyramid-shaped structure, as shown in Fig. 1. The structure will exhibit very high symmetry if the two phosphorus atoms are substituted by gold atoms. Unfortunately, previous studies [7,8,11] have already reported that the global minimum of the Au$_{10}$ cluster is a planar structure, whereas the Au$_{10}$ cluster was confirmed to be a 4-layer pyramid-shaped (Td) structure with high chemical inertia and potential novel optical and catalytic properties [11]. This structure may be a basic unit for a large cluster configuration, which requires further exploration. Isomers 2 and 3 can be easily envisioned as resulting from substituting one gold atom for the phosphorus at the corresponding position. Both Isomer 4 and Isomer 5 have a relatively large energy difference from the lowest-energy isomer and are not common structures of Au$_8$P$_2$.

3.1.2. Relative stabilities

To predict the relative stabilities of the Au$_n$P$_m^-$ clusters, the average atomic binding energies $E_b$, dissociation energies $\Delta E$, and the second-order difference of energies $\Delta^2 E$ for the global minima are examined. The global minima of Au$_{n-2}$ (n = 1–8) (Fig. S1, Supplementary material) are used for comparison. For the Au$_n$P$_m^-$ clusters, $E_b$, $\Delta E$, and $\Delta^2 E$ are defined as functions of the number of gold atoms n as follows:

$$E_b(n) = \left(\frac{(n - 1)E(Au) + 2E(P) + E(Au^-) - E(Au_{n-2})}{n}\right)$$

$$\Delta E(n) = E(Au_{n-1}P_2^-) + E(Au) - E(Au_{n-2}^-)$$

where $E(Au)$, $E(P)$, $E(Au^-)$, $E(Au_{n-1}P_2^-)$, $E(Au_{n-2}^-$), and $E(Au_{n-1}P_2^-)$ denote the total energies of the Au, P, Au$^-$, Au$_{n-1}$P$_2^-$, Au$_{n-2}^-$, and Au$_{n-1}$P$_2^-$ clusters, respectively. For the Au$_n$ clusters, $E_b$, $\Delta E$, and $\Delta^2 E$ are defined as functions of the number of gold atoms n as follows:

$$E_b(n + 2) = \left(\frac{(n + 1)E(Au) + E(Au^-) - E(Au_{n-2}^-)}{n + 2}\right)$$

$$\Delta E(n + 2) = E(Au_{n-1}^-) + E(Au) - E(Au_{n-2}^-)$$

$$\Delta^2 E(n + 2) = E(Au_{n-1}^-) + E(Au_{n-2}^-) - 2E(Au_{n-3}^-)$$

As shown in Fig. 2(a), $E_b$ of the Au$_8$P$_2$ clusters (red triangles) are higher than those of the Au$_{n-2}$ clusters (blue blocks) at the same n value, indicating that the substitution of Au by P could improve the overall stability. The binding energy of two species of clusters generally increases with increasing cluster size (n), which could explain for the stabilities increase as the clusters size increasing.

$\Delta E$ represents the difficulty with which one Au atom is removed from the clusters, the higher the value is, the more stable the structure will be. Fig. 2(b) shows that $\Delta E$ of the Au$_8$P$_2^- (n = 1–8)$ clusters exhibits an odd–even oscillation as well as pure gold clusters [42,85]. It is more difficult to remove one gold atom from Au$_8$P$_2^- (n = 1, 3, 5, 7)$ than from Au$_8$P$_2^- (n = 2, 4, 6, 8)$ or Au$_{n-2}^-$. This should be due to the clusters with odd n values have an even number of electrons, forming a closed-shell configuration affected by the odd–even electron pairing effect. Therefore, removing one Au atom from closed-shell structure is more difficult than the corresponding open-shell structure.

The odd–even effect considering the second-order difference in energies $\Delta^2 E$ is also illustrated in Fig. 2(c). For clarity, we denote n + 2 by m; thus, formula (6) can also be presented as (7) based on formula (5).

$$\Delta^2 E(m) = \Delta^2 E(m) - \Delta^2 E(m + 1)$$

$$\Delta^2 E(m + 2) = \Delta^2 E(m + 2) - 2\Delta^2 E(m + 3)$$

From formula (7), we can see that $\Delta^2 E$ is the dissociation energy difference between the corresponding cluster and its next order by the sharp oscillation. This parameter provides information about the values evenly distributed on both sides of the zero axis.
Odd-numbered Au atomic clusters possess positive values, whereas even-numbered clusters possess negative values. The definition illustrated in Eqs. (6) and (7) indicates that clusters with positive $A_E$ values are more stable.

3.1.3. Evolution of the structures

Fig. 3 shows a possible evolutionary path from $\text{Au}_n\text{P}_2$ to $\text{Au}_n\text{P}_2^-$ to identify a rule that governs the growth of small-to-medium dual-phosphorous-doped gold clusters.

As mentioned above, $\text{Au}_n\text{P}_2$, a $C_{2v}$ symmetric structure, can easily evolve into $\text{Au}_2\text{P}_2^-$ by bonding an additional gold atom (labeled No. 2) to the original gold atom. The pentagon-shaped structure of $\text{Au}_n\text{P}_2$ can be obtained by attaching an additional Au (1) atom to Au (2) and P (a), forming a closed-loop structure. The global minimum of $\text{Au}_n\text{P}_2$ is also a planar structure, and it can be envisioned as the pentagon structure of $\text{Au}_n\text{P}_2^-$ with a Au (3) atom added at the corner of the isomer. The Au (3) atom bonds with Au (2) and one Au (1). The evolution path from $\text{Au}_n\text{P}_2^-$ to $\text{Au}_n\text{P}_2$ is apparent. An additional Au (3) atom is added to the upper left corner of $\text{Au}_n\text{P}_2^-$, yielding a $C_{2v}$ symmetric structure. Noting that the Au (1)–Au (1) bond breaks due to the atomic interaction caused by the two Au (3) atoms at each side bonding with two Au (1) atoms, the interaction pulls the two Au (1) atoms away, breaking the Au (1)–Au (1) bond.

Beginning with $\text{Au}_n\text{P}_2^-$, a different path appeared to explain the evolutionary progress of the $\text{Au}_n\text{P}_2^-$ species. As shown in Fig. 3, the global minimum of $\text{Au}_n\text{P}_2$ is a 3D structure with two separated P atoms. The evolutionary path may trace back to the precursor, which is not the global minimum. Isomer (II) of $\text{Au}_n\text{P}_2$ is a dangling structure that is similar to the global minimum of $\text{Au}_n\text{P}$. Isomer (II) is 0.305 eV higher than the global minimum of $\text{Au}_n\text{P}_2$. This high-energy isomer may also evolve from $\text{Au}_n\text{P}_2^-$. The $C_{2v}$ symmetric structure will be more stable.

Odd-numbered Au atomic clusters possess positive values, whereas even-numbered clusters possess negative values. The definition illustrated in Eqs. (6) and (7) indicates that clusters with positive $A_E$ values are more stable.

3.2. Electronic properties

3.2.1. Simulated photoelectron spectra and HOMO–LUMO gap

Fig. 4 shows simulated photoelectron spectra of the global minimum (Isomer 1) of $\text{Au}_n\text{P}_2$ ($n = 1–8$) at the PBE0/CRENBL level of theory. The global minimum of $\text{Au}_n\text{P}_2$ exhibits low vertical detachment energy (VDE) and a large HOMO–LUMO gap. Isomer 1 of $\text{Au}_n\text{P}_2$ also exhibits a relative low VDE and a larger HOMO–LUMO. Isomer 1 of $\text{Au}_n\text{P}_2$ has three distinct isolated peaks, predicting the change of the configuration which is different from the former isomers mentioned above. Isomer 1 of $\text{Au}_n\text{P}_2^-$ shown in figure presents a scaled-down three peak compared with $\text{Au}_n\text{P}_2$ and suggests the internal relation on the configurations. Isomer 1 of $\text{Au}_n\text{P}_2$ has a somewhat large HOMO–LUMO gap, and the neutral structure of this complex is a high-stability candidate for the species. Different from above, $\text{Au}_n\text{P}_2^-$ have two co-existed lowest-lying isomers as the simulated photoelectron spectra are shown in Fig. 4 ($\text{Au}_n\text{P}_2^-$ (I) & (II)). Although the structures have only a slight difference in cis–trans location of one Au atom, the VDE values, HOMO–LUMO gaps are large differences for obvious distinction. Additionally, this result also confirms that the PES is sensitive function to the configuration. The global minimum of $\text{Au}_n\text{P}_2^-$ has a large VDE (4.04 eV, Table S2, Supplementary material) and five single peak indicating the high stability and different-typed atoms of the configuration, respectively. The PES of
3.2.2. Molecular orbital analysis

Fig. 5 shows the frontier molecular orbitals of the global minimum of each species of Au$_n$P$_2$ ($n = 1$–8). Selected information obtained from the figures is summarized below.

1. Au$_2$P$_2$ & Au$_3$P$_2$, Au$_4$P$_2$ & Au$_5$P$_2$, and Au$_6$P$_2$ & Au$_7$P$_2$ can be treated as distinct groups because of their similar HOMO and LUMO values. This result indicates that the clusters of each group have similar orbital types. The precursor of each group is an open shell, whereas the later structure with an additional gold atom yields a closed shell with an even number of valence electrons. Hence, it is straightforward to transform from an open-shell cluster to a closed-shell cluster, with slight changes identified using molecular orbital theory. Meanwhile, a very large change is required to transform from the closed-shell structure of Au$_6$P$_2$ to the open-shell structure of Au$_5$P$_2$. The results of orbital hybridization indicate that the global minimum of Au$_6$P$_2$ does not have the lowest-energy isomer as its processor. This finding helps explain the change from Au$_5$P$_2$ to Au$_6$P$_2$.

2. It was observed that closed-shell clusters, such as Au$_n$P$_2$ ($n = 1, 3, 5, 7$), add 10 molecular orbitals to the open-shell clusters, i.e., Au$_n$P$_2$ ($n = 2, 4, 6, 8$). In contrast, 9 orbitals were added when an open-shell structured transitioned to a closed-shell structure. It is also known that gold atoms share the 6s$^1$ atomic orbital. The single valence electron can combine with the open-shell orbital to form a closed-shell orbital when a gold atom is added to the open-shell cluster, affording Au$_n$P$_2$ ($n = 1, 3, 5, 7$). This removes one occupied molecular orbital.

3.2.3. Natural bond orbital (NBO) analysis

We have summarized Natural population analysis (NPA) and natural electron configuration (NEC) from NBO [80,81] analysis of the global minima within the low-lying isomers of the Au$_n$P$_2$ ($n = 1$–8) clusters in Fig. 6. The atomic charge is labeled in square brackets above the atom, and the electron configuration of each atom is provided below the atom. Atoms are also labeled in proper sequence.

Structures with high symmetry have some of the same types of gold or phosphorus atoms. The classification is shown in the figure. The species have 1, 2, 2, 4, 3, 4, 3, and 4 types of Au atoms from $n = 2$ to 8, respectively (two isomers for $n = 6$). When $n$ is less than or equal to 5, the two bonded phosphorus atoms share no more than 0.5 units of charge, except for Au$_5$P$_2$. When $n$ is greater than 5, the two phosphorus atoms separated from each other share more charge than all of the other gold atoms.
atoms. In addition, the overall negative charge distribution of clusters prefers to localize on the apex atoms rather than the edge atoms. One possible explanation is that the repulsive interaction of the outside valence electrons stabilizes the structures with the weakest repulsive interaction. $\text{Au}_6\text{P}_2\text{C}_0^2$ is unique because it possesses two global minima that are mutual cis–trans isomers. We searched for insights to better understand the difference between these isomers. The steric hindrance effect of $\text{Au}_6\text{P}_2\text{C}_0^2(\text{II})$ is smaller than that of $\text{Au}_6\text{P}_2\text{C}_0^2(\text{I})$, and the phosphorus atoms share more natural charge. In $\text{Au}_7\text{P}_2\text{C}_0^2$, 5 of the 7 gold atoms are adjacent to phosphorus and have a positive natural charge. This result means that the gold atoms act as an electron donor, losing an electron to their surrounding environment. Additionally, the other four electron acceptors are in apex positions. $\text{Au}_8\text{P}_2^-$, a 3D pyramidal configuration with $C_2v$ symmetry, as mentioned above, has 4 types of Au atoms, 5–6–7–9, 3–8, 4 and 10. As shown, the four apex atoms of the pyramidal structure possess a higher charge than the edge atoms. $\text{Au}_{10}$ possesses a positive charge of 0.030, indicating that it is an electron donor.

To better understand the above phenomenon, the NEC is also considered. As shown in Fig. 6, the electrons on the phosphorus atom are mainly in the 3s and 3p orbitals; the 4p orbital also

![Fig. 5. Frontier molecular orbitals of $\text{Au}_n\text{P}_2^-$ ($n = 1–8$).](image)

![Fig. 6. Natural population analysis (NPA) (a.u.) and natural electron configuration (NEC) of $\text{Au}_n\text{P}_2^-$ at the PBE/CRENBL level.](image)
accepts small amount of charge. The electrons on the gold atoms are mainly concentrated in the 5d and 6s orbitals. Due to the strong relativistic effects of the heavy gold atoms contracting the 6s orbital, the energies of the 5d and 6s orbitals reverse as the valence electron configurations of gold atom is 5d^106s^2, and these orbitals hybridize with each other on gold atoms. Au5 of AuP_2 and Au4 of AuP_2 also have electrons that localize due to the explicit interaction of the repulsive interactions of electrons and the attractive interactions of nuclei.

4. Conclusions

In conclusion, we have presented a theoretical study on the structural and electronic properties of Au_nP_2 clusters in the size range of 1–8 atoms. The results indicate that the structures of Au_nP_2 clusters have one clear global minimum structure, with the exception of AuP_2 due to its two cis–trans isomers of similar energies. In particular, the global minimum of AuP_2 is a pyramidal-shaped structure that is similar to that of Au_3 and with potential characteristics of the phosphorus dopants. Provides only theoretically simulated photoelectron spectra. In our study proves necessary to determine their sizes and shapes, as our study provides only theoretically simulated photoelectron spectra. In our study proves necessary to determine their sizes and shapes, as our study provides only theoretically simulated photoelectron spectra.

Experimental studies of phosphorus-doped clusters remain necessary to determine their sizes and shapes, as our study provides only theoretically simulated photoelectron spectra. In our future work, we will investigate medium- to large-sized phosphorus-doped clusters and pay more attention to possible notable characteristics of the phosphorus dopants.

Conflict of interest

The authors declared no conflict of interest in this paper.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemphys.2015.04.019.

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