Structural evolution and bonding of phosphorus-doped silicon clusters $\text{Si}_n\text{P}_m^{-/0/+}$ with $n = 1-10$, $m = 1,2$

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(Abstract)

The geometrical evolution, electronic structure and thermodynamic stability of a series of singly-doped Si_nP and doubly-doped Si_nP_2 silicon clusters with $n = 1-10$, in the neutral, cationic and anionic states were systematically investigated using DFT computations. The global minimum structures were identified using different search approaches. The isoelectronic structures including the neutral Si_nP , the cation $\text{Si}_{n-1}\text{P}_2^+$ and the anion Si_{n+1}^- exhibit a similar shape. Structural evolution of doubly P-doped Si_nP_2 was found to adopt a substitution mechanism rather than a cation pathway. Dissociation energies for various channels of Si_nP_2 clusters point out that the fragmentations generating P_2 atoms plus the corresponding Si_n host is the most preferred process. The closed-shell species Si_4P^- , Si_3P_2 , Si_7P^- and Si_6P_2 are found to have high thermodynamic stability with large binding energies and second-order difference energies. Their

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enhanced stability can be rationalized in terms of the Jellium shell model. The aromatic character was probed using the ring current maps of electron densities. The planar SiP_2 , Si_2P^- and Si_3P^- clusters feature an aromatic character, whereas only the five-membered plane of the bipyramid-like structures involving Si_6P^- and Si_5P_2 are locally aromatic.

Keywords: Silicon cluster; phosphorus doped silicon cluster; growth mechanism of silicon cluster; Electron localization function

1. Introduction

The cluster of semiconductor elements is increasingly attracted due to their physical and chemical properties are distinct from those of individual atoms, molecules or bulk matter [1,2,3,4,5]. In particular, silicon cluster has been attracted so much owing to their potential applications in modern microelectronic industry [6,7]. The thermodynamic, stability, chemical bonding and aromatic properties of silicon cluster are extensively and carefully investigated by both theoretical and experimental studies [8,9,10,11,12,13,14,15,16,17,18]. In view of the fact that pure silicon clusters are not thermodynamically stable, introduction of transition metal atoms (TM) to silicon host appears as an efficient way to release stable silicon clusters which can be used as building blocks to aggregate assembled materials. For example, MSi_{16} clusters ($\text{M} = \text{Sc}$, Ti and V), which are of high symmetry and stability, were theoretically predicted to form stable hetero-oligomers $\text{ScSi}_{16}\text{-VSi}_{16}$ and $\text{ScSi}_{16}\text{-TiSi}_{16}\text{-VSi}_{16}$ [19]. Additionally, TaSi_{16} cluster can contact with C_{60} cluster through covalence bond and thereby form $\text{TaSi}_{16}\text{-C}_{60}$ dimer [20]. On basis of BeSi_{12} hexagonal prism, a metal – silicon tubular structure was synthesized [21]. $\text{CrSi}_{20}\text{H}_{20}$ is a magnetic building unit having a sextet spin state for cluster-assembled materials

including the $(\text{CrSi}_{20}\text{H}_{16})-(\text{CrSi}_{20}\text{H}_{18})_2$ with 18 unpaired electrons, and $(\text{CrSi}_{20}\text{H}_{18})_6$ with 42 unpaired electrons [22]. The VSi_{12} hexagonal prism turns out to be a magnetic sheet in honeycomb-like framework [23]. Having also a tubular form, the anion $\text{V}_3\text{Si}_{12}^-$ presents with a particular structure in which three V atoms in a linear V-V-V form is placed inside the (2×6) hexagonal anti-prism Si_{12} [24]. The doubly Mn-doped $\text{Mn}_2\text{Si}_{15}$ cluster is stable in a tubular form, in which three Si_5 strings are joint in an anti-prism fashion, and the dimer Mn_2 is vertically placed inside that Si triple ring tube [25]. The stability of $\text{Mn}_2\text{Si}_{15}$ tubular structure was understood from two perspectives. On the one hand, the bonding and anti-bonding MOs of Mn-Mn are strongly stabilized by overlapping with MOs of the Si_{15} tube, and on the other hand, the empty levels of the Si_{15} tube are now fully occupied by dopant electrons, inducing thereby a high thermodynamic stabilization for the resulting tubular cluster. Such a stabilizing mechanism can be useful for building up TMs doped silicon tubes.

The main element also shows significant influence to stability of doped silicon cluster. While the TM-encapsulated silicon structure appears at the size of $n \geq 12$, the Be, B and C dopants already form encapsulated structure with only 8 Si atoms in a cubic shape [26]. The anion Si_9B^- and cation Si_{10}B^+ clusters, in which the B dopant occupies endohedral site, have electronic structure satisfying the electronic shell with 40 and 42 electrons, respectively, enhancing subsequently their stability [27]. Structural identification for silicon cluster doped C atom shows that geometry of Si_nC is slightly different from the pure Si_{n+1} structure [28]. Using both theoretical and experimental methods, structural characters and vibrational spectra of neutral Si_6X clusters with $\text{X} = \text{Be}, \text{B}, \text{C}, \text{N}$ and O were revealed. The Be, B and C dopants favor structure based on the Si_7 pentagonal bipyramid [29].

Of the main group elements, phosphorus is of particular interest, as it has one more electron than silicon, and thus corresponds to the anion Si^- . The electron number of the cation P^+ also equates to that of the Si atom and the Al^- anion. However, the investigations on geometric and electronic properties of silicon cluster doped by phosphorus is rather scarce. Using molecular orbital methods, Nigam *et al.* [30] explored geometric character of P-doped Si_nP clusters, with $2 \leq n \leq 13$, in which the structural behavior of the Si_nP is quite similar to its isoelectronic Si_{n+1}^- . Geometries of $\text{Si}_n\text{P}^{+/-}$ clusters with $n = 1-8$ were considered by Chang et al [31]. In this context, we set out to perform a systematic theoretical investigation on both singly and doubly P-doped silicon clusters in three different charged states in order to probe further on their growth pattern, aromatic feature and bonding phenomena.

2. Computational Methods

All electronic structure calculations are performed using the Gaussian 09 [32] suite of programs. The search for the energy global minima is approached in two different ways. The first is that we generate all possible structures using a stochastic generic algorithm [33]. Equilibrium structures are initially located using low-level computations, namely density functional theory with the hybrid B3LYP functional which has been shown to behave well for silicon clusters [34], in conjunction with the 6-31G(d) basis set. The lower-lying structures are then reoptimized by means of the same functional but with the larger 6-311+G(d) basis set. The use of a stochastic generic algorithm is efficient for multiply doped and large size clusters in which there is really a huge number of initial structures. In the second approach, initial guess structures are manually built by either substitution of a Si atom on the Si_{n+1} framework by a P atom, or by adding an P atom on different positions of a Si_n host. Combination of both

systematic searches ensures us to be able to locate the lowest-energy structure for each size and charge state at the level of theory employed.

Harmonic vibrational calculations are subsequently performed using the same level, B3LYP functional with the 6-311+G(d) basis set. For an analysis of the electronic distribution, in particular the aromatic character, we make use of canonical MOs, electron localization function (ELF) [35], and ring current calculations. The aromaticity feature is further probed using the ring current approach [36,37,38,39]. The ring current map is calculated using the electron densities at the B3LYP/6-311+G(d) level. Calculations on magnetic responses are carried out using the CTOCD-DZ method [37] implemented in the SYSMO program [40,41], which is connected to the GAMESS-UK package [42]. In the current density map, the contour and shading show the modulus of induced current electron density, and the narrows display its projection on the plotting plane. By definition, anticlockwise or clockwise electron circulations correspond to diatropic or paratropic currents, respectively. A diatropic ring current indicates an aromatic character, whereas a paratropic current shows an anti-aromatic feature.

3. Results and discussion

As for a convention, we label hereafter the structures considered as **x.y.M.z**, in which **x = n**, **c** and **a** stand for neutral, cationic and anionic (charged) states, respectively, **y** is the size of Si_n , **M = P** and **P2** corresponds to single and double doping, respectively, and finally **z = 1, 2, 3, ...** refers to the lower-lying isomers with an increasing relative energy ordering of the neutral state. For both ionic states, the same numbers **z** are used to indicate that the ionic structures have the same shape as the relevant neutrals, but the energy ordering could be changed. The structural shapes of singly doped $\text{Si}_n\text{P}^{-/0/+}$ clusters are displayed in Figures S1 and S2 of the Supplementary

Information (SI) file. The structural identification agrees well with earlier report on the singly neutral phosphorous doped silicon clusters [30,31], therefore we do not consider them further. For the sake of comparison, the main geometrical characteristics Si_nP in three charged states are also given in the electronic Supplementary Information (SI) file.

3.1 Structures of $\text{Si}_n\text{P}_2^{0/+/-}$

Figures 1 and 2 display the geometric shapes of the doubly P-doped Si clusters.

3.1.1 $\text{Si}_2\text{P}_2^{+0/+}$. For the tetraatomic cluster, the distorted rhombus **n.2.P2.1** ($C_{2v}^1A_1$) (Figure 1) is found as the lowest-energy isomer. The rhombus structure **n.2.P2.2**, ($D_{2h}^1A_g$) is 3.2 kcal/mol less stable than **n.2.P2.1**. The other planar isomers **n.2.P2.4** is 19.4 kcal/mol less stable, whereas its distorted structure **n.2.P2.3** is only 6.0 kcal/mol higher.

Regarding to the charged states, **c.2.P2.1** which is the corresponding cation of **n.2.P2.1** becomes destabilized, being 10.7 kcal/mol higher than the planar rhombus structure **c.2.P2.2** which is the global minimum structure of Si_2P_2^+ . The planar **c.2.P2.4** (C_s^2A'') is only 2.9 kcal/mol less stable, but the distorted **c.2.P2.3** (C_1^2A) is 8.9 kcal/mol higher than the global minimum **c.2.P2.2**.

For the negatively charged state, the distorted rhombus **a.2.P2.1** ($C_{2v}^2A_1$) is identified as the lowest energy structure. The planar rhombus isomer becomes less stable upon electron attachment, and the anion **a.2.P2.2** is 2.7 kcal/mol higher than its distorted counterpart.

3.1.2 $\text{Si}_3\text{P}_2^{+0/+}$. For the neutral state of the pentaatomic system, the triangular pyramid **n.3.P2.1** ($D_{3h}^1A_1'$), in which two P atoms add on two faces of the Si_3 triangle, is identified as the ground state. The next isomers **n.3.P2.2** (C_s^1A'), formed by addition of one P atom on an edge and the other on a face, is 3.0 kcal/mol less stable than the **n.3.P2.1**. The corresponding anion **a.3.P2.1** ($C_{2v}^2B_1$) is found to be the ground state for the Si_3P_2^- anion with a small distortion. The cations

c.3.P2.1 and **c.3.P2.2** are basically degenerate with a gap of 1.8 kcal/mol with respect to the ground state of Si_3P_2^+ .

3.1.3. $\text{Si}_4\text{P}_2^{-/0/+}$. On the basis of the Si_6 structure, three lower-lying isomers of Si_4P_2 including **n.4.P2.1** (C_s $^1A'$), **n.4.P2.2** (C_{2v} 1A_1) and **n.4.P2.3** (C_1 1A) are established upon substitution of Si by P atoms. The separation energy of these structures is only ~1.5 kcal/mol, making them likely competitive ground state for neutral Si_4P_2 . The next isomers are in higher energy as given in Figure 1.

For the cationic state, **c.4.P2.1**, cation of **n.4.P2.1**, is the lowest-energy isomer, whereas the two next isomers **c.4.P2.2** and **c.4.P2.3**, whose neutrals are degenerate with **n.4.P2.1**, are significantly less stable, being 5.9 and 5.6 kcal/mol higher than **c.4.P2.1**. In the negatively charged state, **a.4.P2.2** turns out to be the lowest-energy anionic isomer. The anions formed upon attachment of an electron to **n.4.P2.1** and **n.4.P2.3** are less stable.

3.1.4. $\text{Si}_5\text{P}_2^{-/0/+}$. In the neutral state of the heptaatomic system, the pentagonal pyramid **n.5.P2.1** (C_{2v} 1A_1), in which two P atoms substitute two Si positions in the pure Si_7 bipyramid, is identified as the ground state of Si_5P_2 . The next isomer **n.5.P2.2** (C_s $^1A'$), resulting from addition of two P atoms on a triangle of pyramid Si_5 , is 9.4 kcal/mol less stable than **n.5.P2.1**. However, the shape of **n.5.P2.2** is stabilized upon addition of an electron whereas **a.5.P2.1**, which is the actual anion state of **n.5.P2.1**, lies ~13 kcal/mol higher than **a.5.P2.2**. For cationic state, the corresponding cation **c.5.P2.1** of the neutral **n.5.P2.1** has a high stability, whereas the next isomer **c.5.P2.2** lies at 7.8 kcal/mol above.

3.1.5. $\text{Si}_6\text{P}_2^{-/0/+}$. In the neutral, the **n.6.P2.1** (C_{2v} 1A_1), a structure in which two P atoms replace two Si sites of the bare Si_8 cluster, is identified as the ground state. The next isomers being also produced by substitution of Si sites on Si_8 by P dopants are much higher in energy. Accordingly,

the position of P atoms is important. The cation **c.6.P2.1** is again identified as the lowest-energy structure of the positively charged state. **c.6.P2.2** is only 3.0 kcal/mol higher than **c.6.P2.1**, which can be considered as competitive in stability. For the anions, DFT calculations show that **a.6.P2.1** ($C_{2v} \ ^2B_1$) is the most stable structure being much lower in energy than the next isomers.

3.1.6 $Si_7P_2^{-/0/}$. As showed in Figure 2, the low symmetry **n.7.P2.1** is predicted as the most stable neutral Si_7P_2 . However, this structure is not observed as an equilibrium form in both charged states. The next neutral isomer, **n.7.P2.4** ($C_1 \ ^1A$), is only 2.8 kcal/mol less stable than **n.7.P2.1**. For the cationic state, **c.7.P2.2** ($C_1 \ ^2A$) and **c.7.P2.3** ($C_1 \ ^2A$), which have no corresponding neutral states, are found to be close with a small energy gap of 1.0 kcal/mol in such a way that they are both competing ground state of $Si_7P_2^+$. The other higher energy isomers of $Si_7P_2^+$ are displayed in Figure 2.

Turning now to the negatively charged state, **a.7.P2.2** ($C_s \ ^2A''$) is identified as the lowest-energy anion. The next isomer **a.7.P2.3** ($C_1 \ ^2A$) is 4.8 kcal/mol higher than **a.7.P2.2** whereas **a.7.P2.4** ($C_1 \ ^2A$) is only 2.7 kcal/mol less stable than the ground state. The neutral **n.7.P2.1** shape no longer exists as an energy minimum upon electron addition.

3.1.7 $Si_8P_2^{-/0+}$. DFT calculations identify the neutral **n.8.P2.1** ($C_s \ ^1A'$), which is characterized by substitution of two Si sites of the bare Si_{10} host, is the most stable neutral Si_8P_2 . The next isomers including **n.8.P2.3** ($C_s \ ^1A'$) and **n.8.P2.4** ($C_1 \ ^1A$) are only 1.9 and 1.5 kcal/mol less stable, respectively. They are thus considered as competitive for the ground state of Si_8P_2 . The isomers including **n.8.P2.5** ($C_1 \ ^1A$) and **n.8.P2.2** ($C_1 \ ^1A$) are 3.9 and 4.3 kcal/mol higher in energy, respectively.

In the cationic state, there is again a competition for the ground state. As in the case of their neutral counterparts, the energy separation between **c.8.P2.1** ($C_s \ ^2A''$) and **c.8.P2.2** amounts to

only ~1 kcal/mol as a result, they are competitive to be the global minimum of Si_8P_2^+ . The next isomer **c.8.P2.3**, ($C_s \ ^2A'$) is 4.9 kcal/mol less stable than the **c.8.P2.1**. The other structures including **c.8.P2.4** ($C_1 \ ^1A$, 10.9 kcal/mol) and **c.8.P2.5** ($C_1 \ ^1A$, 12.7 kcal/mol) are highly unstable than the ground state.

For the negatively charged state, the **a.8.P2.2** ($C_1 \ ^2A$) is emerged as the lowest-energy structure. The **a.8.P2.1** is 2.9 kcal/mol higher, and **a.8.P2.4** only 1.2 kcal/mol less stable than **a.8.P2.2**. The **a.8.P2.3** and **a.8.P2.5** anions are much less stable than **a.8.P2.2**.

3.1.8 $\text{Si}_9\text{P}_2^{-0/+}$. According to B3LYP/6-311+g(d) calculations, four neutral isomers including **n.9.P2.1** ($C_s \ ^1A'$), **n.9.P2.2** ($D_{3h} \ ^1A'$), **n.9.P2.3** ($C_1 \ ^1A$) and **n.9.P2.4** ($C_1 \ ^1A$) are identified to be close in energy content and they are all competitive for the ground state of Si_9P_2 . Actually, they are formed by a similar way in which two Si sites of the bare Si_{11} host are replaced by two P atoms, in different positions.

For the positively charged state, there is an important energy reversal. The **c.9.P2.5** ($C_1 \ ^2A$) is now found to be the most stable cation, whereas the cations corresponding to the four neutral state are getting destabilized. Regarding to the negatively charged state, the high symmetry **a.9.P2.2** ($D_{3h} \ ^2A_2''$), being the anion of **n.9.P2.2**, is identified as the lowest-energy isomer. The corresponding anions of **n.9.P2.1**, **n.9.P2.3** and **n.9.P2.4** are less stable by 2.7, 4.3 and 3.3 kcal/mol than **n.9.P2.2** in energy. The **a.9.P2.5** ($C_1 \ ^2A$) generated upon addition of an electron from the relevant neutral is not stable.

3.1.9 $\text{Si}_{10}\text{P}_2^{-0/+}$. For the neutral Si_{10}P_2 , three structures including **n.10.P2.1** ($C_1 \ ^1A$), **n.10.P2.2** ($C_1 \ ^1A$) and **n.10.P2.3** ($C_s \ ^1A'$) are again competitive for the global minimum status. Within these structure, two Si-positions of Si_{12} cluster are replaced by P dopants. Regarding to the cation state, the **c.10.P2.5** ($C_1 \ ^2A$) is the lowest-energy cation according to B3LYP/6-311+g(d)

calculations. The corresponding cations of neutral lowest-lying isomer involving **c.10.P2.1** (C_1 2A), **c.10.P2.2** (C_1 2A) and **c.10.P2.3** (C_s $^2A''$) are unstable. To the $Si_{10}P_2^-$ anion, the most stable isomer, **a.10.P2.1** (C_1 2A) structure, retains the shape of the most stable neutral structure.

3.2 Structural evolution

After describing the main structural characteristics of the singly (cf. the SI file) and doubly P-doped clusters, we now look at their evolution. As the cation P^+ , similar to the anion Al^- , is isoelectronic to the Si neutral atom, some similarities between their structural evolutions can be expected. On the basis of geometrical characteristics of $Si_nP_m^{+/0/-}$ and the combined results in previous investigations on the Si_nB^- , $Si_nAl_m^-$ clusters [27,43], the growth mechanism of the series of binary clusters Si_nB^- , Si_nAl^- , Si_nP^+ , $Si_{n-1}P_2$ and $Si_{n-1}Al_2^-$ can be revealed and shown in Figure 3.

For singly doped silicon clusters, the series of Si_nP^+ and Si_nAl^- exhibit a similar growth pattern, in which the P^+ or Al^- dopant replace a Si site of the Si_{n+1} hosts, giving rise subsequently to the Si_nP^+ and Si_nAl^- clusters. Although the B^- anion is isovalent to the Al^- , the growth sequence of Si_nB^- clusters behaves differently. As shown in Figure 3, Si_2B^- and Si_3B^- are formed by replacing one Si of the trimer Si_3 and tetramer Si_4 by a B^- dopant, whereas in the larger sizes $n = 5-9$, a Si_nB^- is released upon addition of a Si atom to the $Si_{n-1}B^-$ counterpart. In particular, the B^- dopant induces an endohedral structure in the size of $Si_{10}B^-$, whereas both Al^- and P^+ impurities tend to favour exohedral structures based on the pure Si_{11} cluster with substitution of a single Si atom. The B^- dopant is isovalent to both Al^- and P^+ , but its radius is obviously much shorter, and as a consequence, the B^- dopant is more apte to be inserted inside the Si cage to make an endohedral structure.

For the doubly doped silicon clusters, both P and Al dopants are again found to prefer a substitution growth mechanism. The $Si_nP_2^+$ clusters, except for the size $Si_8P_2^+$, are generated

upon direct derivation from the corresponding Si_{n+2}^- hosts, that are isoelectronic to Si_nP_2^+ cations, with substitution of two Si by two P atoms, as illustrated in Figure 3. Such a similarity in the growth sequence is also observed for the series of Si_nAl_2^- clusters, for which replacement of two Si atoms in Si_{n+2}^+ clusters yield directly the Si_nAl_2^- structures. Overall, the structures of both singly and doubly Al and P doped silicon clusters, involving the series of Si_nAl^- , Si_nP^+ , Si_nAl_2^- and Si_nP_2^+ are identified to be comparable with respect to the corresponding bare silicon hosts.

3.3 Energetic properties

3.3.1 Clustering energy

We now evaluate some energetic parameters that allow the thermodynamic stability of the clusters considered to be quantified. The relative stability of both series singly and doubly P-doped clusters in three charged states can be examined on the basis of binding energy (E_b) and the second-order difference energy (ΔE). The values on the binding energy of both $\text{Si}_n\text{P}^{-/0/+}$ and $\text{Si}_n\text{P}_2^{-/0/+}$ clusters are calculated by using the following expressions from (1) to (6):

$$E_b(\text{Si}_nP) = \frac{nE(\text{Si}) + E(\text{P}) - E(\text{Si}_nP)}{n + 1} \quad (1)$$

$$E_b(\text{Si}_nP_2) = \frac{nE(\text{Si}) + 2E(\text{P}) - E(\text{Si}_nP_2)}{n + 2} \quad (2)$$

$$E_b(\text{Si}_nP^+) = \frac{(n - 1)E(\text{Si}) + E(\text{Si}^+) + E(\text{P}) - E(\text{Si}_nP^+)}{n + 1} \quad (3)$$

$$E_b(\text{Si}_nP_2^+) = \frac{(n - 1)E(\text{Si}) + E(\text{Si}^+) + 2E(\text{P}) - E(\text{Si}_nP_2^+)}{n + 2} \quad (4)$$

$$E_b(\text{Si}_nP^-) = \frac{(n - 1)E(\text{Si}) + E(\text{Si}^-) + E(\text{P}) - E(\text{Si}_nP^-)}{n + 1} \quad (5)$$

$$E_b(Si_nP_2^-) = \frac{(n-1)E(Si) + E(Si^-) + 2E(P) - E(Si_nP_2^-)}{n+2} \quad (6)$$

where $E(Si)$, $E(Si^-)$, $E(Si^+)$ and $E(P)$ are the total energies of the Si atom, the anion Si^- , the cation Si^+ and the P atom, respectively. For their parts, the $E(Si_nP)$, $E(Si_nP^+)$, $E(Si_nP^-)$, $E(Si_nP_2)$, $E(Si_nP_2^-)$ and $E(Si_nP_2^+)$ correspond to the total energies of the Si_nP , Si_nP^+ , Si_nP^- , Si_nP_2 , $Si_nP_2^-$ and $Si_nP_2^+$ clusters, respectively. The second-order difference energy of the singly and doubly doped cluster considered can be obtained using the following equations, from (7) to (12):

$$\Delta E(Si_nP) = E(Si_{n+1}P) + E(Si_{n-1}P) - 2E(Si_nP) \quad (7)$$

$$\Delta E(Si_nP_2) = E(Si_{n+1}P_2) + E(Si_{n-1}P_2) - 2E(Si_nP_2) \quad (8)$$

$$\Delta E(Si_nP^-) = E(Si_{n+1}P^-) + E(Si_{n-1}P^-) - 2E(Si_nP^-) \quad (9)$$

$$\Delta E(Si_nP_2^-) = E(Si_{n+1}P_2^-) + E(Si_{n-1}P_2^-) - 2E(Si_nP_2^-) \quad (10)$$

$$\Delta E(Si_nP^+) = E(Si_{n+1}P^+) + E(Si_{n-1}P^+) - 2E(Si_nP^+) \quad (11)$$

$$\Delta E(Si_nP_2^+) = E(Si_{n+1}P_2^+) + E(Si_{n-1}P_2^+) - 2E(Si_nP_2^+) \quad (12)$$

The profiles of binding energies of $Si_nP^{-/0/+}$ and $Si_nP_2^{-/0/+}$ clusters are schematically given in Figures 4a and 4b, whereas Figures 4c and 4d illustrate the evolution of the second-order difference energies. In order to emphasize the effect of the P dopants, the binding and second-order difference energy values of the pure clusters Si_{n+1} and Si_{n+2} are also determined using the same method, and also reported in Figure 4 together with $Si_nP^{-/0/+}$ and $Si_nP_2^{-/0/+}$, respectively.

The binding energy of the singly doped clusters, as given in Figure 4a, increases with the cluster sizes. The anionic state is significantly more stabilized than the other charged states, and the cationic state of the doped series is more stable than the isoelectronic pure Si_{n+1} clusters. As a

consequence, introduction of the P dopant tends to enhance the thermodynamic stability of the resulting doped clusters.

In the case of the doubly doped Si_nP_2 clusters, the E_b is also enlarged with the increasing size, due to the additional chemical bonds and electrons brought about by P atoms. The negatively charged state again holds the higher stability than the neutral counterparts. As a result, the doubly P-doped Si clusters are able to more easily donate and accept electron. As given in Figure 4c, the notably large value of the second-order difference is identified for two anions Si_4P^- and Si_7P^- , clearly demonstrating that they are of higher stability among the singly doped clusters. Their isoelectronic structures including Si_3P_2 and Si_6P_2 are equally determined to have remarkably large ΔE values, indicating that they are more stable than the other doubly doped members.

3.3.2 Dissociation energy

In order to probe further their relative stability, the dissociation energies (DE) associated with various channels are examined and listed in Tables 1 and 2.

For the singly doped clusters, dissociation energies of neutral Si_nP for the Si-loss channel 1: $\text{Si}_n\text{P} \rightarrow \text{Si}_{n-1}\text{P} + \text{Si}$ turns out to be preferred over the channel 2: $\text{Si}_n\text{P} \rightarrow \text{Si}_n + \text{P}$ at the sizes of 1-5. In the larger sizes, the P-loss channel becomes more favored. In the charged state, the Si-elimination channel in which Si_nP^q clusters with $q = -1$ and 1 are fragmented generating a Si atom and the corresponding charged $\text{Si}_{n-1}\text{P}^q$ species, is identified in most cases as the preferential channel.

Regarding to doubly doped series, the fragmentation pathway 3 in which the neutral parent cluster is dissociated generating a Si_n host plus the P_2 dimer, is characterized by the smallest DE values. This result agrees well with the growth pattern identified above for the neutral Si_nP_2 . A

similar pathway is also observed for the cationic state in which the Si-elimination channel 1': $\text{Si}_n\text{P}_2^+ \rightarrow \text{Si}_{n-1}\text{P}_2^+ + \text{Si}$, and P-loss (2'): $\text{Si}_n\text{P}_2^+ \rightarrow \text{Si}_n\text{P}^+ + \text{P}$ are more difficult to achieve than the pathway 3': $\text{Si}_n\text{P}_2^+ \rightarrow \text{Si}_n^+ + \text{P}_2$ as suggested by the dissociation energy. Likewise, the channel generating the negatively charged Si_n^- counterpart plus the P_2 dimer (pathway D3'') is determined as the most preferred one. It can be seen that the doubly doped clusters Si_nP_2^q tend to be fragmented generating the bare Si_n^q counterpart together with P_2 dimer.

3.4 Phenomenological shell model

As for a rationalization of the relative stability of doped silicon clusters, their MO shapes are now re-examined under the viewpoint of the Jellium shell model (JSM) [44], which has been successfully applied to interpret the stability of binary atomic clusters in recent reports [33, 45,46,47,48].

According to this simple model, the valence electrons are assumed to be freely itinerant in the mean-field potential formed by particles including the nuclei of atoms and core electrons (that can be regarded as ions), and the valence electrons occupy orbitals whose patterns are described as $[1\text{S}^2 1\text{P}^6 1\text{D}^{10} 2\text{S}^2 1\text{F}^{14} 2\text{P}^6 1\text{G}^{18} 2\text{D}^{10} \dots]$. Within this model, the number of electrons of 8, 20, 34, 40, 58 and 68 emerge as the magic numbers that actually corresponds to a complete filling of the successive electron shells.

As for a typical example, let us consider the valence configuration of neutral Si_6P_2 and its isoelectronic Si_7P^- , that are explored in view of their high thermodynamic stability as indicated by the binding and second-order difference energies (see above). Figure 5 displays the electron shell configuration for Si_6P_2 and Si_7P^- clusters.

The neutral Si_6P_2 ($^1\text{A}_1 \text{C}_{2v}$) possesses a valence orbital configuration as follows:

$$\text{Si}_6\text{P}_2 (^1\text{A}_1 \text{ } C_{2v}): (1\text{A}_1)^2 (1\text{B}_2)^2 (2\text{A}_1)^2 (1\text{B}_1)^2 (2\text{B}_2)^2 (3\text{A}_1)^2 (2\text{B}_1)^2 (4\text{A}_1)^2 (1\text{A}_2)^2 (5\text{A}_1)^2 (3\text{B}_2)^2 (4\text{B}_2)^2 (6\text{A}_1)^2 (3\text{B}_1)^2 (2\text{A}_2)^2 (4\text{B}_1)^2 (7\text{A}_1)^2 (5\text{B}_1)^0,$$

whereas the valence orbital configuration of the anion $\text{Si}_7\text{P}^- (^1\text{A}_1 \text{ } C_{3v})$ can be written as:

$$\text{Si}_7\text{P}^- (^1\text{A}_1 \text{ } C_{3v}): (1\text{A}_1)^2 (2\text{A}_1)^2 (1\text{E})^2 (2\text{E})^2 (3\text{A}_1)^2 (3\text{E})^2 (4\text{E})^2 (4\text{A}_1)^2 (5\text{E})^2 (6\text{E})^2 (5\text{A}_1)^2 (7\text{E})^2 (8\text{E})^2 (6\text{A}_1)^2 (9\text{E})^2 (10\text{E})^2 (1\text{A}_2)^2 (11\text{E})^0.$$

Both orbital configurations can be assigned to the corresponding electronic shell model [$1\text{S}^2 1\text{P}^6 1\text{D}^{10} 2\text{S}^2 1\text{F}^{14}$]. As a consequence, the driving force for the higher stability of the neutral Si_6P_2 and the anion Si_7P^- is that their 34 valence electrons fully fill up to the (1F) level of the Jellium shells. In this case, the density of states (DOS, Figure 5) of both Si_6P_2 and Si_7P^- molecules turn out to have many similarities, even though they are in different C_{2v} and C_{3v} point groups, respectively. The partial pDOS plots (Figure 5) of these molecules also reveal that the s-AO(Si) and p-AO(Si) of Si atoms bring in the main contributions to the orbitals included in the shell model.

The valence orbital configurations of Si_3P_2 and Si_4P^- are:

$$\text{Si}_3\text{P}_2 (D_{3h} ^1\text{A}_1'): \dots (1\text{A}_1')^2 (1\text{A}_2'')^2 (1\text{E}')^2 (2\text{E}')^2 (2\text{A}_1')^2 (1\text{E}'')^2 (2\text{E}'')^2 (3\text{A}_1')^2 (2\text{A}_2'')^2 (3\text{E}')^2 (4\text{E}')^2 (5\text{E}')^0$$

$$\text{and } \text{Si}_4\text{P}^- (C_{2v} ^1\text{A}_1): (1\text{A}_1)^2 (1\text{A}_1)^2 (1\text{B}_1)^2 (2\text{A}_1)^2 (1\text{B}_2)^2 (3\text{A}_1)^2 (2\text{B}_1)^2 (4\text{A}_1)^2 (1\text{A}_2)^2 (2\text{B}_2)^2 (5\text{A}_1)^2 (3\text{B}_1)^2 (3\text{B}_2)^0$$

and both structures also identified to have a higher stability on the basis of the E_b and ΔE quantities.

Both electronic configurations can be assigned to the corresponding shell configurations of [$1\text{S}^2 1\text{P}^6 1\text{D}^{10} 1\text{F}^2$]. In this case, the number of valence electrons of both neutral Si_3P_2 and anion

Si_4P^- again fully fill up to the 1D^{10} subshell, and as a result, their stability is significantly enhanced.

3.5 Electron localization function

In an attempt to more deeply understand the influence of the P dopant on the stability of Si clusters, the electron localization function (ELF) maps are constructed and shown in Figure 6. The ELF technique is a conventional tool for the partition of the total electron density into different basins. The basins located indicate to the chemical bond regions, due to the fact that this function relates to the real spaces of molecule where the electrons are likely to occupy. Accordingly, the basins corresponding to the bonds, lone pairs,... can be assigned. In this context, the ELF maps of both isoelectronic 34 electrons, Si_6P_2 and Si_7P^- , and isoelectronic 22 electrons systems Si_3P_2 and Si_4P^- are plotted as for typical examples for the series considered.

It is clear from Figures 6a and 6b that the localization domain pattern of both neutral Si_6P_2 and anionic Si_7P^- show many similarities. This result is highly consistent with the similar shell structures obtained above by using the Jellium model. In both cases, three localization domains are identified corresponding to the di-synaptic basin $V(\text{Si},\text{P})$, occupied by 1.6 electron for Si_6P_2 and 1.7 electron for Si_7P^- . Thus, the P dopant uses its three 3p valence electrons to form three P-Si bonds. A similar behavior is also observed for Si_3P_2 , in which there are three localization domains assigned for P dopant, but with smaller bifurcation value ($\text{ELF} = 0.8$). In the anion Si_4P^- , the P dopant and Si host prefer to be connected with each other through an electrostatic interaction, rather than via a covalent bond. In general, the P dopant, possessing three unpaired electrons on the 3p-AOs, is likely to be located on the position having coordination number of 3, due to the fact that this kind of dopant offers formation of three Si-P bonds.

3.6 Aromaticity of planar and bipyramid structures

Recently, the aromaticity of planar silicon clusters has been reexamined using the ring current density method. The σ aromaticity has been identified in some small pure Si cluster [13,49]. To establish the effects of P dopants on the aromatic feature of planar silicon forms, some current density maps are plotted and given in Figure 7. The triatomic P_2Si and its isoelectronic Si_2P^- produce strongly diatropic ring current in terms of magnetic responses, therefore they are classified as aromatic species. As shown in Figure 7, the ring current density map of the dianion Si_3^{2-} , which is isoelectronic to P_2Si and Si_2P^- , is also strongly diatropic. This result points out that P-dopant maintains the aromatic characteristic of the triatomic Si ring.

The tetraatomic anion Si_3P^- raises a diatropic current density, as given in Figure 7, and therefore it should be classified as aromatic specie. For the pentaatomic Si_3P_2 having a 3D structure, a ring current density moving over the whole Si_3 plane is not observed. The Si_3 ring is not active in term of magnetic responses (Figure 7). However, a strongly diatropic ring current is found for the $PSiP$ plane (Figure 7). This result illustrates clearly that the local aromatic feature of Si_3P_2 arises mainly from electrons of lying within the $PSiP$ plane.

For the bipyramid structures Si_5P_2 and Si_6P^- , the ring current maps are shown in Figure 8. Accordingly, the five-membered ring of the bipyramid plays an important role in characterizing its aromaticity. Strongly diatropic current maps are observed within the five-membered rings involving Si_3P_2 and Si_4P , thus giving rise to an aromatic character. As a consequence, both Si_5P_2 and Si_6P^- are locally aromatic in the plane containing five atoms. For a comparison, the current density maps of Si_7 and Si_5Li_2 bipyramids are produced, and they also show the diatropic current densities in the Si_5 plane. On the other hand, the presence of P-dopants maintains an aromatic feature of silicon cluster in the plane containing five atoms. Another plane could also be considered by using ring current technique, which contains the apex atoms and is called as side-

plane. As shown in Figure 8, a paratropic current density is observed for Si_5P_2 indicating an anti-aromatic character in the side-plane. Similarly, the Si_6P^- exhibits a slightly paratropic ring current map in side-plane. However, this cluster could better be classified as non-aromatic, due to low intensity of the contour moving around the nuclei. For the bare Si_7 cluster, the side-plane does not have any ring current density at all. In other words, there is no aromatic character in this plane. Accordingly, the P dopants significantly influence the electron distribution of in side-planes of 3D silicon clusters. The doping of two P atoms induces a locally anti-aromatic Si_5P_2 molecule, whereas insertion of one P atom results in a non-aromatic Si_6P^- structure in the side-plane.

4. Concluding Remarks

In the present theoretical article, we reported on a systematic theoretical investigation on the geometrical evolution, stability, chemical bonding and aromaticity of both series of singly and doubly P-doped silicon clusters. The global energy minima of clusters considered were identified by mean of DFT computations (B3LYP/6-311+G(d) + ZPE). The structural evolution was revealed on the geometric characteristics of the global minimum structures. The P^+ dopant, similar to the Al^- anion, was found to favour a substitution mechanism over a caption pathway, due to the fact that they are isoelectronic with the Si atom.

Their relative stability was explored using both binding energy and second order difference energy. The species Si_4P^- , Si_3P_2 , Si_7P^- and Si_6P_2 were found to have enhanced stability. The canonical MO analysis confirmed that the electronic structure of these species satisfy the Jellium shell model for 22 and 34 electrons. The results obtained from electron localization function maps demonstrate that the P dopant tends to form three classical (2c-2e) Si-P bonds using its three unpaired valence electrons.

The various fragmentation channels of the P-mixed clusters considered were studied by using values of dissociation energies. Fragmentation generating the P₂ dimer plus the corresponding Si_n^q host is the preferential channel. The planar clusters including SiP₂, Si₂P[−] and Si₃P[−] moieties exhibit aromatic character according to the ring current density maps. On the contrary, the bipyramid-like structures (Si₇, Si₆P[−] and Si₅P₂) have a local aromatic character only in the five-membered plane. In the side-plane, the Si₇, Si₆P[−] are non-aromatic whereas the Si₅P₂ is anti-aromatic.

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Table 1. Dissociation energies (kcal/mol) of Si_nP^{−/0/+} clusters for various channels.

n	Neutrals		Cations				Anions			
	D1	D2	D1'	D2'	D3'	D4'	D1''	D2''	D3''	D4''
2	89.06	103.44	124.11	164.25	135.47	97.40	72.84	134.51	105.87	133.68
3	75.79	92.40	89.07	166.49	113.73	97.41	73.74	121.43	89.44	118.37
4	81.54	79.38	65.75	137.68	79.80	87.38	99.93	126.80	99.16	142.51
5	72.39	76.76	95.48	158.15	102.24	101.31	61.56	113.35	78.12	122.53
6	74.82	64.49	81.70	152.76	87.63	110.63	73.40	99.66	72.50	123.54
7	79.31	59.66	70.55	139.18	77.90	106.36	98.22	113.74	89.33	146.94
8	69.48	72.55	81.61	164.20	85.66	108.67	63.79	120.94	91.37	131.42
9	85.75	74.29	83.90	164.10	95.27	123.09	84.02	120.96	91.42	145.96
10	63.78	50.22	66.24	142.48	78.28	103.58	73.59	106.69	73.15	133.81

D1: Si_nP → Si_{n-1}P + Si

D2: Si_nP → Si_n + P

D1' : Si_nP⁺ → Si_{n-1}P⁺ + Si

$$D2' : Si_n P^+ \rightarrow Si_n + P^+$$

$$D3' : Si_n P^+ \rightarrow Si_n^+ + P$$

$$D4' : Si_n P^+ \rightarrow Si_{n-1} P + Si^+$$

$$D1'' : Si_n P^- \rightarrow Si_{n-1} P^- + Si$$

$$D2'' : Si_n P^- \rightarrow Si_n + P^-$$

$$D3'' : Si_n P^- \rightarrow Si_n^- + P$$

$$D4'' : Si_n P^- \rightarrow Si_{n-1} P^- + Si^-$$

Table 2. Dissociation energies (kcal/mol) of $\text{Si}_n\text{P}_2^{-/0/+}$ clusters for various channels.

n	Neutrals			Cations			Anions		
	D1	D2	D3	D1'	D2'	D3'	D1''	D2''	D3''
2	75.11	80.26	75.32	87.12	73.08	100.17	82.22	73.83	71.32
3	87.26	91.74	75.76	83.70	67.71	73.06	83.67	83.75	64.82
4	63.55	73.74	44.74	79.86	81.82	53.24	74.93	58.75	49.53
5	68.71	70.06	38.44	78.90	65.25	59.11	69.20	66.39	36.14
6	100.74	95.98	52.09	83.84	67.39	46.64	92.09	85.08	49.20
7	59.48	76.16	27.44	74.59	71.43	40.94	73.48	60.35	41.29
8	79.08	85.75	49.92	82.94	72.76	50.04	75.63	72.18	55.17
9	74.08	74.09	40.00	74.92	63.78	50.67	83.99	72.16	55.20
10	74.27	84.58	26.42	79.47	77.01	46.91	75.98	74.54	39.31

D1: $\text{Si}_n\text{P}_2 \rightarrow \text{Si}_{n-1}\text{P}_2 + \text{Si}$

D2: $\text{Si}_n\text{P}_2 \rightarrow \text{Si}_n\text{P} + \text{P}$

D3: $\text{Si}_n\text{P}_2 \rightarrow \text{Si}_n + \text{P}_2$

D1': $\text{Si}_n\text{P}_2^+ \rightarrow \text{Si}_{n-1}\text{P}_2^+ + \text{Si}$

D2': $\text{Si}_n\text{P}_2^+ \rightarrow \text{Si}_n\text{P}^+ + \text{P}$

D3': $\text{Si}_n\text{P}_2^+ \rightarrow \text{Si}_n^+ + \text{P}_2$

D1'': $\text{Si}_n\text{P}_2^- \rightarrow \text{Si}_{n-1}\text{P}_2^- + \text{Si}$

D2'': $\text{Si}_n\text{P}_2^- \rightarrow \text{Si}_n\text{P}^- + \text{P}$

D3'': $\text{Si}_n\text{P}_2^- \rightarrow \text{Si}_n^- + \text{P}_2$

Figure captions

Figure 1. Shapes, point groups and relative energies of the doubly doped $\text{Si}_n\text{P}_2^{-/0/+}$ with $n = 1-6$. Relative energy is showed as: Upper panel: neutral; Middle panel: cation and Lower panel: anion (B3LYP/6-311+G(d) + ZPE, kcal/mol)

Figure 2. Shapes, point groups, electronic states and relative energies of the doubly doped $\text{Si}_n\text{P}_2^{-/0/+}$ with $n = 7-10$. Relative energy is showed as follows: Upper panel: neutral; Middle panel: cation, and Lower panel: anion (B3LYP/6-311+G(d) + ZPE, kcal/mol).

Figure 3. A comparison of the growth mechanism of the singly and doubly P and Al doped silicon clusters. Right: $\text{Si}_{n-1}\text{Al}_2^-$ and $\text{Si}_{n-1}\text{P}_2^+$, and left: Si_nB^- , Si_nAl^- and Si_nP^+ .

Figure 4. Binding energies (E_b) and second-order energies (ΔE), given in kcal/mol, of $\text{Si}_n\text{P}^{-/0/+}$ and $\text{Si}_n\text{P}_2^{0/-/+}$. **a)** E_b of $\text{Si}_n\text{P}^{-/0/+}$ and **b)** E_b of $\text{Si}_n\text{P}_2^{0/-/+}$; **c)** ΔE of $\text{Si}_n\text{P}^{-/0/+}$ and **d)** ΔE of $\text{Si}_n\text{P}_2^{0/-/+}$ (B3LYP/6-311+G(d) + ZPE).

Figure 5. The total (DOS) and partial (pDOS) densities of state of **(a)** Si_7P^- and **(b)** Si_6P_2 (B3LYP/6-311+G(d))

Figure 6. The ELF isosurface maps of **(a)** anion Si_7P^- and **(b)** neutral Si_6P_2 , at the bifurcation value $\text{ELF} = 0.85$, and **(c)** anion Si_4P^- and neutral Si_3P_2 , at the bifurcation value $\text{ELF} = 0.80$ (B3LYP/6-311+G(d))

Figure 7. Ring current density maps of SiP_2 , Si_2P^- , Si_3P^- and Si_3P_2 . The ring current densities were performed using B3LYP/6-311+G(d) calculations.

Figure 8. Ring current density maps of Si_6P^- , Si_5P_2 , Si_7 and Si_5Li_2 . The ring current densities were performed using B3LYP/6-311+G(d) calculations.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

a)

Si_3P_2

b)

Figure 7

Si_5P_2

Si_6P^-