Formation, photodissociation, and structure studies of group 14(Si, Ge, Sn, and Pb)/P binary cluster ions

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Abstract

Group 14(Si, Ge, Sn, and Pb)/P binary cluster ions have been produced by laser ablation, photodissociated by UV laser and detected with a tandem time-of-flight mass spectrometer. As expected on the double periodicities of group 14 elements, Si/P and Ge/P binary cluster ions, whereas Sn/P and Pb/P binary cluster ions, have similar compositions, respectively. The stabilities of these binary phosphide cluster ions depend on their electronic and geometric structures, and the influence of geometric structures on the stabilities is increasing from Si/P cluster ions to Pb/P cluster ions. “Magic numbers” are observed in two types of binary phosphide cluster ions. One type of magic numbered binary cluster ions is isoelectronic to Zintl polyatomic anions (e.g. Pb522−) in condensed phases. These binary cluster ions are composed of group 14 metals mainly, containing only one or two phosphorus atoms. The structures and bonding scheme of these binary cluster ions can be predicted by using Wade’s electron counting rule. Another type of magic numbered binary cluster ions is isoelectronic either to the neutral group 14 clusters or to the neutral phosphorus clusters, and thus may present similar structures as their neutral analogues. The possible structures and bonding of the magic numbered cluster ions are further investigated with density functional theory Becke-style 3 parameter using the Lee-Yang-Parr correlation functional calculations. (Int J Mass Spectrom 202 (2000) 261–271) © 2000 Elsevier Science B.V.

Keywords: Group 14/phosphorus cluster ions; Laser ablation; Time-of-flight mass spectrometer; Photodissociation; Density functional theory calculations

1. Introduction

Group 14 (C, Si, Ge, Sn, and Pb) is an interesting series of elements because the bonding changes from covalent to metallic in going from the lightest to the heaviest element. Carbon has a strong covalent character, silicon and germanium are of the semiconductor type, whereas tin and lead are typical metals. This systematic variation in properties through the group is also presented in the gas phase clusters composed of group 14 elements. Carbon clusters Cn of a small size (n < 10) have chain structures, and the stabilities of cluster ions Cn+ are dominated by the electronic structures and spin states [1–3]. Silicon clusters Si_n and germanium clusters Ge_n have similar compositions and structures but differ substantially from small carbon clusters [4–8]. Cyclic or closed structures are clearly more favorable for silicon clusters and germanium clusters over linear structures and there exist

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local maximum intensities (magic numbers) at $n = 6, 10$ for neutral Si$_n$, Ge$_n$, and cations Si$_n^+$, Ge$_n^+$ [5]. Such similarities between silicon clusters and germanium clusters arise from the similarities in the valence wave functions of silicon and germanium. This effect is well known as “d-block screening”, and a parallel effect leads to similarities between tin clusters Sn$_n$ and lead clusters Pb$_n$. Both Sn$_n$ and Pb$_n$ have close packing geometries and the magic numbers $n = 7, 10$ [9,10].

From the comparison of these clusters, we can see obviously that the dominance of geometric structures on stabilities of group 14 clusters is gradually increased from the top element (C) to the bottom element (Pb), i.e. the close packing structures become more favorable when covalent bonding interaction is weakened. These trends could be attributed to many factors, such as valence electrons, ionization energies, electron affinities, atom sizes, etc., whereas the most profound factor is their bonding properties. However, since there is not enough experimental structure data available for gas phase group 14 clusters, it is still difficult to draw a general pattern governing their structures and stabilities in the gas phase.

In contrast to the gas phase group 14 cluster ions, the condensed phase group 14 cluster ions, particularly the condensed phase group 14 metal (also called post-transition metal) cluster ions, have been studied for many years. The most interesting result from condensed phase studies is that group 14 metals can form polyatomic Zintl ions, such as Ge$_5^{2-}$, Sn$_5^{2-}$, and Pb$_5^{2-}$ [11], in which the bonding and structures can be followed by a simple electron counting scheme outlined in the form of Wade’s rule [12–14]. In brief, for a polyhedron with $N$ atoms, enhanced stability is expected for species containing $2N + 2$, $2N + 4$, and $2N + 6$ skeleton electrons. These electron counts define closo-(closed), nido-(nest-like) and arachno-(cobweb) cluster structures and determine the expected patterns in cluster bonding [15]. Zintl ions are normally produced in condensed phases, but it is now recognized that Zintl ions can also be produced in gas phase. It has been shown, for example, that the bonding in gas phase binary cluster ions Cs$_3$Sn$_5^+$, Sn$_5$Bi$_3^+$, and Pb$_5$Bi$_3^+$ are all related through this simple electron counting patterns [16–18]. The cesium atoms in Cs$_5$Sn$_5^+$ act as electron donors to match the electronic structure of Sn$_5^{2-}$. The tin, lead, and bismuth atoms in Sn$_2$Bi$_3^-$ or in Pb$_2$Bi$_3^+$ all participate in the construction of the closo skeletons to form ions isoelectronic to Sn$_5^{2-}$ or Pb$_5^{2-}$. Martin has reported that binary clusters containing five lead atoms and a less electronegative element have a tendency to cluster into Pb$_5^{2-}$ polyanions [15], which may also be explained by Wade’s rule.

In this article gas phase binary cluster ions composed of group 14 element (Si, Ge, Sn, and Pb) and phosphorus are studied. The purpose of this investigation is to provide more insight into the role of the periodicity on group 14 clusters. Phosphorus can combine with every element of group 14 to form various phosphide compounds [18]. Liu et al. have reported the study of C/P binary cluster anions with the compositions of C$_n$P$_m^-$ [19]. In each composition the number of carbon atoms is much larger than that of phosphorus atoms, and the main compositions can be indicated as C$_n$P$_m^-$ and C$_n$P$_2^+$. For the species C$_n$P$_m^-$, there is an odd/even oscillation in intensity, and the intensities with odd $n$ are more intense than those with even $n$. Fisher et al. have performed density functional theory (DFT) calculations on the structures of C$_n$P$_m^-$ and C$_n$P$_2^+$, and have shown that C$_n$P$_m^-$ and C$_n$P$_2^+$ have optimized linear structures with P at one end of C$_n$P$_m^-$ or two ends of C$_n$P$_2^+$, respectively [20]. From the present studies of Si, Ge, Sn, and Pb/P binary cluster ions, we expect to complete a systematical investigation of group 14 phosphide binary cluster ions, including the cluster compositions, electronic bonding, and geometric structures. From such studies we hope to understand the clustering properties of group 14 elements from another viewpoint.

Moreover, we also expect to examine the applicability of Wade’s rule for these gas phase binary systems. Pure clusters of germanium, tin and lead since they contribute two $p$ electrons for bonding per atom [14], are electron deficient. Their total valence electrons $2 \times N$ ($N =$ atom number) is less than...
2N + 2, 2N + 4, ..., and they exist as multi-charged Zintl anions as Ge\textsuperscript{5−}, Sn\textsuperscript{5−}, and Pb\textsuperscript{5−} in condensed phases. A phosphorus atom, on the other hand, contributes three \( p \) electrons per atom and thus is electron rich. These trends average out in the group 14 phosphide cluster ions and thus precise electron counts (2N + 2, 2N + 4, and 2N + 6) can be achieved for single charged binary cluster ions in the gas phase. These binary clusters, therefore, provide another interesting test for Wade’s rule in the gas phase because only certain stoichiometries can achieve desirable electron counts. Preferential combinations of elements according to Wade’s electron counting rule, therefore, should appear as “magic numbered” peaks in the laser ablation time-of-flight (TOF) mass spectra.

2. Experiment and calculation

2.1. Experiment

The mixed samples were prepared by grinding the mixture of group 14 element (purity 99%) and red phosphorus (purity 99%) into fine powders, and pressing it into a tablet of 12 mm in diameter and 5 mm in thickness to form the laser target. The molar ratio for group 14 element to phosphorus in the mixed samples was varied from 1:1 to 1:8. Red phosphorus powder was pretreated to eliminate oxide impurities and kept dry in a phosphoric anhydride desiccator.

Experiments were performed on a homemade tandem time-of-flight mass spectrometer (TOFMS), the details of which were published elsewhere [21]. In brief, the sample target was mounted in the source chamber of the tandem TOFMS, which was evacuated to 10^{-4} Pa before laser ablation. The laser ablation was carried out by the second harmonic of a pulsed Nd:YAG laser (532 nm wavelength, 10 ns pulse width, 10 Hz, 10–20 mJ/pulse). The laser beam was focused with a lens (\( f = 50 \text{ cm} \)) to a spot of diameter 0.5 mm on the target with the power density in order of 10^7 W/cm^2. The target surface under ablation was vaporized into a plume of plasma state consisting of electrons, ions, atoms, and cluster species formed from the ablation process and ion molecule reaction [22]. The cluster ions were extracted and accelerated by a pulsed voltage of 1.2 kV and then allowed to drift in a field-free region. After transmission through 3.5 m long field-free flight tube, the cluster ions with different masses were separated and detected by a dual microchannel plate detector. The mass resolution of the first stage of the tandem TOFMS is about 300. The cluster cations with a specific mass were selected by a mass gate at the end of the flight tube. The selected ions were decelerated by a retarding field of 0.9 kV and then photodissociated by an excimer laser beam (Lambda Physik LPX 300, KrF, 248 nm wavelength, 4 ns pulse width, 10 Hz, 200 mJ/cm^2). Following photodissociation, both the remaining parent ions and the fragment ions were reaccelerated and then mass analyzed by the second stage of the tandem TOFMS, which was perpendicular to the first stage. The signals from either the first stage or the second stage were recorded with a 10 MHz transient recorder, preamplified and stored in a PC computer. The final digitized mass spectrum was time averaged for over 2000 shoots.

2.2. Density function theory (DFT) calculation

Full geometry optimization was performed on selected binary cluster ions at several initial geometries, using the density functional method B3LYP (Becke-style 3-parameter using the Lee-Yang-Parr correlation functional) [23]. Vibrational analysis was performed on the optimized structures until a minimum with no imaginary vibrational frequencies was located. The basis set LANL2DZ was used for group 14 metal atoms [24]. For phosphorus, the basis set 6-31G(\( d \)) was used. All calculations were carried out by running GAUSSIAN 94 [25].
generated by laser ablation while $Si^+_n$ can only be produced to $n = 10$ under the same experimental condition.

The distribution of Si/P cluster anions is similar to that reported by Liu et al. before [19], which contains $Si^-_n P^+_m$, $Si^-_n$, and $P^-_m$ [Fig. 1(b)]. The size of Si/P cluster anions is larger than that of Si/P cluster cations. Furthermore, the intensities of $Si^-_n P^+_m$ are oscillating with the number of phosphorus atoms, and the intensities of cluster anions with odd $m$ are much more intense than those of the neighboring even $m$’s. For example, $Si^-_n P^+_m$ with $n + m = 5$, intense peaks are corresponding to $Si^-_4 P^+_5$, $Si^-_2 P^+_3$, and $P^-_5$, whereas the peaks of $Si^-_1 P^-_2$ and $Si^-_1 P^-_4$ are either much lower or absent in the mass spectrum. The odd/even oscillation of the intensity appears to correlate with the number of valence electrons in clusters. The valence electron number of the silicon atom is 2, and thus the number of clustered silicon atoms does not affect the parity of the cluster electron number. But the valence electron number of the phosphorus atom is 3. Therefore, the binary cluster anions with odd phosphorus atoms have all valence electrons paired (considering one additional electron for anions) and have no dangling bonds.

The experiment shows that most of bare $Si^+_n$ and bare $P^+_m$ with even $m$ are hydrogenated with one hydrogen atom (the hydrogen atoms may come from trace impurities in red phosphorus), such as $HSi^+_4$, $HP^+_2$, $HP^+_4$, and $HP^+_6$ in cations and $HSi^-_4$, $HP^-_6$, and $HP^-_8$ in anions. In particular, $P^-_4$ is hydrogenated with three hydrogen atoms to form $H_3P^-_5$. However, for bare $P^+_m$ with odd $m$, there are intense signals observed for the bare clusters (i.e. not hydrogenated) or clusters hydrogenated only with even number of hydrogen atoms, such as $H_2P^-_5$. In Fig. 1(a) and (b), we use a prime to indicate hydrogen atoms in cluster ions, i.e. (0,2’) in Fig. 1(a) corresponds to $HP^+_2$, and (0,3’) in Fig. 1(b) corresponds to $H_2P^-_5$. This phenomenon again supports the idea that Si/P cluster ions prefer the even number electron system where all electrons can be paired up.

Fig. 1(b) reveals some intense peaks assigned to $P^-_{5+4n}$ $(n = 0–3)$, $Si^-_{3+4n}$ $(n = 0–3)$, $Si^-_{5+4n}$ $(n = 0–2)$, $Si^-_{3+4n}$ $(n = 0–2)$, and $Si^-_{5+4n}$.
We note that these cluster anions all have paired valence electrons and their intensities are less affected by the molar ratio of Si/P in the targets, indicating they are thermodynamically stable. The fact that these anions grow by P4 unit implies the possibility of attaching P4 unit to the cluster skeletons during formation. Among these cluster anions, P52 has plane ring structure (D5h) and compares to an aromatic 6π system [26]. SiP32 is isoelectronic to P4 and should have a structure of tetrahedron [27]. SiP72 is isoelectronic to P8 and may have a structure consisting of two tetrahedrons as P8 [28]. In addition, we observed some cations isoelectronic to these cluster anions, i.e. P5+ and Si1P3+, P7+ and Si2P5−, SiP5+ and Si3P3+, SiP7+ and Si3P5−. These analogues all have intense peaks in the mass spectra. Thus, it can be inferred that isoelectronic cluster species have similar stabilities. On the other hand, some positive and negative cluster ions with same isostoichiometries differ greatly in stabilities. It is conceivable, therefore, that the electron structure plays a more important role in determining the stability of Si/P cluster ions.

Due to the similarities in the chemical properties of silicon and germanium, the mass spectra of Ge/P binary cluster ions are expected to be similar with those of Si/P binary cluster ions. The fact that this is the case can be seen in Fig. 2(a) and (b). For n + m ≤ 5, GePn+m− have composition distributions similar to SinPn+m− and contain all possible binary clusters with every n and m. However, for n + m ≥ 6, the number of germanium atoms in binary cluster ions is larger than that of phosphorus atoms. Thus, the atom-clustering ability of germanium is a bit more intense than that of phosphorus. We note here that Ge/P binary cluster ions have magic numbers that are 2/3, 5/1, 6/1, and 9/1 for cations, and 1/3 and 4/1 for anions, which will be discussed in detail later.

3.1.2. Sn/P and Pb/P binary cluster ions

The mass spectra of Sn/P and Pb/P binary cluster ions are depicted in Figs. 3 and 4, which are very similar to each other. As shown in mass spectra, SnnPm+ and PbPm+ can be divided into several groups according to the number of metal atoms contained in the clusters, and each group includes species with the same number of metal atoms and various numbers of phosphorus atoms. For the group of SnPm+ (or PbPm+), SnHPm+ (or PbHPm+) rather than SnP2m+ (or PbP2m+) is produced because the presence of a hydrogen atom helps the cluster to meet the condition of paired valence electrons in the cation. For the clusters of SnnPm+ and PbPm+, only when m is odd, are the valence electrons in the cluster ions paired. So mass peaks of cluster ion with odd m are generally more intense than those with even m. When the size of clusters increases, the number of phosphorus atoms in
clusters \( \text{Sn}_n \text{P}_m^+ \) and \( \text{Pb}_n \text{P}_m^+ \) decreases greatly. For example, for \( n \geq 10 \) the cluster ions only exist as \( \text{Sn}_n^- \) and \( \text{Pb}_n^- \). Such distribution is not influenced by the composition of the targets but appear to be the intrinsic attributes of the binary clusters.

We also observed some magic numbers for \( \text{Sn}/\text{P} \) and \( \text{Pb}/\text{P} \) cluster ions, which are 2/3 (M = Ge, Sn, Pb), 5/1 (M = Sn, Pb), 6/1 (M = Sn, Pb), and 9/1 (M = Sn) for cations, and 1/3 (M = Sn, Pb) and 4/1 (M = Sn) for anions.

3.2. Photodissociation of group 14/P binary cluster cations

The photodissociation of cluster cations \( \text{Ge}_n \text{P}_m^+ \), \( \text{Sn}_n \text{P}_m^+ \), and \( \text{Pb}_n \text{P}_m^+ \) was carried out with a 248 nm excimer laser. Fig. 5 is typical mass spectra obtained from the photodissociation of \( \text{Ge}_n \text{P}_m^+ \), \( \text{Sn}_n \text{P}_m^+ \), and \( \text{Pb}_n \text{P}_m^+ \), respectively. As shown, there exist several photodissociation channels leading to \( \text{M}_n \text{P}_m^+ \), \( \text{M}_n \text{P}_m^+ \), \( \text{M}_n \text{P}_m^+ \) (M = Ge, Sn, Pb), etc. From the relative intensities of the fragment ions, we can estimate the efficiency \( R_i \% \) of each photodissociation channel according to

\[
R_i = \left( \frac{I_i}{\sum_j I_j} \right) \times 100\%
\]

where \( I_i \) is the intensity of the studied fragment ions and \( \sum_j I_j \) is the intensities of all fragment ions including the remaining parent ions. We note that the photodissociation behavior of cluster cations is less sensitive to the power density of the photodissociation laser in the range of 200—400 mJ/cm\(^2\). Table 1 summarizes the photodissociation channels and the corresponding efficiencies for each cation obtained with laser power of 400 mJ/cm\(^2\).

It can be seen that \( \text{Ge}/\text{P} \), \( \text{Sn}/\text{P} \), and \( \text{Pb}/\text{P} \) binary cluster cations have a similar pattern of photodissociation, which implies similarities in their structures. For small cluster cations \( \text{M}_n \text{P}_m^+ \) the main photodissociation channel is the detachment of neutral phosphorus atom, indicating that the metal/metal bond is stronger than metal/phosphorus bond. For the same reason \( \text{M}_n \text{P}_m^+ \) has the main photodissociation channel of \( \text{M}_n \text{P}_m^+ + \text{P}_2 \). However, the main photodissociation channels of the larger cluster cations \( n > 3 \) are
different from those of small cluster cations, i.e. the metal atoms rather than the phosphorus atoms are stripped from the clusters in the photodissociation process. The cations \( \text{M}_4 \text{P}^+ \), \( \text{M}_5 \text{P}^+ \), and \( \text{M}_6 \text{P}^+ \) have the dissociation channels of \( \text{M}_3 \text{P} + \text{M} \), \( \text{M}_4 \text{P} + \text{M} \), and \( \text{M}_5 \text{P} + \text{M} \), respectively, where one metal atom is stripped. The fragment cations \( \text{M}_3 \text{P}^+ \), \( \text{M}_4 \text{P}^+ \), and \( \text{M}_5 \text{P}^+ \) are also found as intensive peaks in the laser ablation mass spectra, which indicates that these fragments have stable structures.

### 3.3. Structures and bonding of magic numbered group 14/P binary cluster ions

As shown from above discussion, cluster magic numbers of 2/3 (\( \text{M}_2 \text{P}^+ \), \( \text{M} = \text{Ge, Sn, Pb} \)), 5/1 (\( \text{M} = \text{Ge, Sn, Pb} \)), 6/1 (\( \text{M} = \text{Ge, Sn, Pb} \)), and 9/1 (\( \text{M} = \text{Ge, Sn} \)) are observed for the binary cluster cations, and 1/3 (\( \text{M} = \text{Ge, Sn, Pb} \)) and 4/1 (\( \text{M} = \text{Ge, Sn} \)) for the binary cluster anions. These magic numbers indicate the particular stable electronic and/or geometric structures. Here, the possible structures of these magic numbers are predicted based on Wade’s rule and further confirmed by B3LYP calculations using the LANL2DZ basis set for metals and 6-31G(d) basis set for P. Structures, which are local minima on potential surface from B3LYP calculations, are characterized rigorously by the presence of all positive eigenvalues of the force constant matrix, i.e. no imaginary frequencies.

#### 3.3.1. Binary cluster cations 5/1 and 9/1

The binary cluster cations \( \text{M}_5 \text{P}^+ \) and \( \text{M}_9 \text{P}^+ \) have valence electrons 12 and 20, respectively (each group 14 metal atom contributes two \( p \) electrons and phosphorus atom contributes three \( p \) electrons). If a phosphorus atom attaches itself as an electron-donating ligand to the cluster skeletons, then \( \text{M}_5 \text{P}^+ \) and \( \text{M}_9 \text{P}^+ \) are, respectively, isoelectronic to \( \text{M}_5^2^+ \) and \( \text{M}_9^2^+ \) Zintl anions.

By Wade’s rule, \( \text{M}_5^2^+ \) has a structure of trigonal bipyramid, and thus \( \text{M}_9^2^+ \) may have a similar trigonal

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**Table 1**

Photodissociation channels and photodissociation efficiencies of group 14/P binary cluster cations

<table>
<thead>
<tr>
<th>Parent ion Channel</th>
<th>( R )%</th>
<th>Parent ion Channel</th>
<th>( R )%</th>
<th>Parent ion Channel</th>
<th>( R )%</th>
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<td>( \text{Sn}_2 \text{P}^+ )</td>
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<td>( \text{Sn}_2^+ \text{P} )</td>
<td>9</td>
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<tr>
<td>( \text{Ge}_2 \text{P}^+ )</td>
<td>( \text{Ge}_2^+ \text{P} )</td>
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<td>( \text{Sn}_3 \text{P}^+ )</td>
<td>( \text{Sn}_3^+ \text{P} )</td>
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<td>( \text{Sn}_2^+ \text{P} )</td>
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<td>15</td>
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<td>( \text{Sn}_2^+ \text{P} )</td>
<td>6</td>
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bipyrimid skeleton attached by a phosphorous atom additionally. In order to confirm this prediction, the possible structures of Ge₅P⁺ and Sn₅P⁺ were studied with B3LYP calculations. The optimized structures of Ge₅P⁺ and Sn₅P⁺ are shown as (I) in Fig. 6. The calculation results are listed in Table 2. In structure (I), five metal atoms construct trigonal bipyrimid skeleton, and three metal atoms M₁, M₂, and M₄ are connected to a phosphorus atom. With this configuration M₃ and M₅ are relatively bonded weakly compared with the remaining three metal atoms and thus are easily stripped on photodissociation, which is consistent with the photodissociation results. As noted already, for M₅P⁺ the most efficient fragmentation is the neutral loss of one or two metal atoms.

The bonding scheme in M₅P⁺ can be rationalized in terms of multicenter bonds. Each metal atom contributes three $p$ orbitals and two $p$ valence electrons to the cluster skeleton, and each phosphorus atom contributes three $p$ orbitals and three $p$ valence electrons, thus total eighteen $p$ orbitals and twelve $p$ electrons are included in the M₅P⁺ skeleton. Supposing that M₅P⁺ is constructed by “$d$” pairs of two-center two-electron M–M bonds and “$t$” pairs of three-center two-electron M–M–M bonds, and a phosphorus atom is connected to the skeleton by three pairs of two-center two-electron M–P bonds, then we

![Fig. 6. Proposed structures of I, M₅P⁺; II(a), II(b), and II(c), M₃P⁺; III(a) and III(b) M₄P⁺; IV(a) and IV(b), M₆P⁺.](image)

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Atomic distance (Å)</th>
<th>Atomic charge</th>
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<td></td>
</tr>
<tr>
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<td>Ge1 0.370</td>
</tr>
<tr>
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<td>4.398</td>
<td>Ge2 0.370</td>
</tr>
<tr>
<td>Ge₄–Ge₁</td>
<td>3.258</td>
<td>Ge3 0.378</td>
</tr>
<tr>
<td>Ge₅–Ge₁</td>
<td>2.655</td>
<td>Ge4 0.206</td>
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<tr>
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<td>Ge5 –0.103</td>
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<tr>
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<td>Sn3 0.378</td>
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</tr>
</tbody>
</table>
have $d = -3$ and $t = 6$. This result is, of course, impossible. Alternatively, if $M_3P_5^+$ is constructed by $d$ pairs of two-center two-electron M–M and M–P bonds, and $t$ pairs of three-center two-electron M–M–M and M–P–M bonds (i.e. phosphorus is involved in multicenter bonding), then we have $d = 0$ and $t = 6$. It means that $M_3P_5^+$ is constructed by multicenter bonds exclusively, which includes three pairs of M–M–M bonds and three pairs of M–P–M bonds. In this picture, stable polyhedral clusters are formed when multicenter bonds delocalize throughout the cluster and achieve various resonant configurations. This delocalized picture of cluster bonding in three dimensions is analogous to aromacity in two dimension structures (e.g. benzene).

Likewise, the structure and bonding of $M_2P_5^+$ can be predicted by Wade’s rule. Nine metal atoms in $M_9P_5^+$ build up a tricapped trigonal prism polyhedron as $Ge_5^2$ [11,12], to which a phosphorus atom as an electron donor is attached.

3.3.2. Binary cluster cations 2/3 and anions 1/3

The stabilities of cations $M_2P_3^+$ and anions $M_3P^-$ can be expected by the Wade’s rule. However, unlike $M_2P^+$ in $M_6P_3^+$ and $M_3P$–P the phosphorus atoms join directly to the polyhedral skeletons rather than attach to the skeletons as ligands. Wade’s rule is satisfied for $M_2P_3^+$ and $M_3P^-$ as $12$(electrons) = $2N$(atoms) + 2, and their structures should be trigonal bipyramid by Wade’s rule. In both $M_2P_3^+$ and $M_3P^-$, there should be three pairs of two-center two-electron bonds and three pairs of three-center two-electron bonds.

There are three possible trigonal bipyramid structures of $M_2P_3^+$ shown as II(a), II(b), and II(c) in Fig. 6, corresponding to $D_{3h}$, $C_{2v}$, and $C_s$ symmetry respectively. In structure II(a), both two phosphorus atoms are located at the vertices of the trigonal bipyramid, while in structure II(b) and II(c), either one or two phosphorus atoms are located on the plane of the trigonal bipyramid. The B3LYP calculations for $Ge_2P_3^+$ and $Sn_2P_3^+$ give the stability sequence as II(a) > II(c) > II(b), the structure II(a) with the highest symmetry is the most stable one. The energy difference between these structural isomers is listed in Table 3.

For $Ge_4P^-$ and $Sn_4P^-$, B3LYP calculations have been done on two possible structures III(a) and III(b), shown in Fig. 6. Since III(a) and III(b) are similar and can convert to each other, the energy difference between III(a) and III(b) is quite small. The structure III(a) with higher symmetry ($C_{3v}$) is a bit more stable than III(b) ($C_{2v}$) (see Table 3).

3.3.3. Binary cluster cations 6/1 and anions 1/3

The cation $M_6P^+$ and anion $MP_3^-$ are, respectively, isoelectronic to neutral $M_7$ ($M = Ge$, Sn, Pb) and $P_4$. 7 is a magic number of neutral clusters of group 14 elements, which has a structure of pentagonal bipyramid [4,9,29,30], while 4 is a magic number of the neutral phosphorus cluster which has a structure of tetrahedron [27]. $M_6P^+$ and $MP_3^-$ may have structures of pentagonal bipyramid like $M_7$ and tetrahedron like $P_4$, respectively. Based on these guesses, two possible pentagonal bipyramid structures of $Ge_6P^+$ and $Sn_6P^+$, IV(a) ($C_{3v}$) and IV(b) ($C_{2v}$), have been calculated by B3LYP. In structure IV(a) the phosphorus atom is located at one vertex of the pentagonal bipyramid, while in structure IV(b) it is located on the pentagonal plane. As expected, the energy of structure IV(a) with a higher symmetry is at a local minimum.

4. Conclusions

Both positive and negative group 14 (Si, Ge, Sn, Pb)/phosphorus binary cluster ions were produced by laser ablation. The composition and intensity distributions of these binary cluster ions vary with each different group 14 element. The Si/P binary cluster ions display the most abundant compositions. The formation process of $Si_nP^+_{m}$ can be viewed as substitution of phosphorus atoms by silicon atoms from pure $P_n^+$ where the numbers of $n$ and $m$ change continuously. The relative intensity of $Si_nP^+_{m}$ correlates with the relative stability of $P^+_{n+m}$. It is known that $P^+_{7}$ is the most stable among $P^+_{n+m}$ [28], then in the series of $Si_nP^+_{m}$ with $n + m = 7$, the signal of $P^+_{7}$ is the most intense one. For $Ge_nP^+_{m}$, $Sn_nP^+_{m}$, and $Pb_nP^+_{m}$, the binary cluster ions of small sizes ($n \leq 5$) are composed of metal atoms and phosphorus atoms
with nearly all possible compositions, while those of larger sizes (n > 5) mainly contain metal atoms. In summary, from silicon to lead the atomic clustering ability of group 14 elements increases and is preferred to binary clustering with phosphorus.

The stabilities of group 14/phosphorus cluster ions depend on both electronic and geometric structures. The cluster ions prefer to have all valence electrons paired up, and some clusters pick up hydrogen atoms to achieve this result. The close packing structures are much favored for these binary cluster ions, and most isoelectronic cluster species have similar structures and stabilities.

Zintl type binary cluster ions have been observed

Table 3
Calculation results for different structures of M₂P³⁺, M₄P²⁺, and M₆P¹⁺ (M = Ge, Sn) by B3LYP/LANAL2DZ for M, 6031G(d) for P

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Structure</th>
<th>ΔE (eV)</th>
<th>Atomic distance (Å)</th>
<th>Atomic charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge₂P³⁺</td>
<td>II(a)</td>
<td>0.0</td>
<td>P2–P1 2.301</td>
<td>P1 -0.056</td>
</tr>
<tr>
<td></td>
<td>II(b)</td>
<td>0.616</td>
<td>P3–P2 2.301</td>
<td>Ge4 P5–P3 2.493</td>
</tr>
<tr>
<td></td>
<td>II(c)</td>
<td>0.471</td>
<td>Ge1 P3–P2 2.493</td>
<td>Ge5 P2 -0.056</td>
</tr>
<tr>
<td></td>
<td>Ge4P²⁺</td>
<td>0.0</td>
<td>II(a) 2.956 Ge3–Ge2</td>
<td>Ge1 P5–Ge3 2.442</td>
</tr>
<tr>
<td></td>
<td>II(b)</td>
<td>0.866</td>
<td>II(c) 3.813 P5–Ge4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sn₂P¹⁺</td>
<td>0.0</td>
<td>II(a) 3.288 Sn3–Sn2</td>
<td>Sn1 P5–Sn3 2.621</td>
</tr>
<tr>
<td></td>
<td>II(b)</td>
<td>0.027</td>
<td>II(c) 4.185 Sn2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ge₆P¹⁺</td>
<td>0.0</td>
<td>IV(a) 2.791 Ge6–Ge2</td>
<td>Ge1 P7–Ge3 2.634</td>
</tr>
<tr>
<td></td>
<td>IV(b)</td>
<td>0.265</td>
<td>IV(c) 2.875 Sn6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sn₆P⁰⁺</td>
<td>0.0</td>
<td>IV(a) 3.081 Sn6–Sn3</td>
<td>Sn1 P7–Sn3 2.807</td>
</tr>
<tr>
<td></td>
<td>IV(b)</td>
<td>0.470</td>
<td>IV(c) 3.285 Sn6</td>
<td></td>
</tr>
</tbody>
</table>

for Ge/P, Sn/P, and Pb/P binary cluster ions. The bonding and structures for these cluster ions can be predicted by Wade’s rule. This prediction, together with the results of DFT calculations, further confirms that isoelectronic clusters exhibit similar structures and stabilities. One feature observed in these clusters is that group 14 metals are still liable to form closo polyhedron in the gas phase as they are in condensed phases. These studies provide further connection between cluster studies in the gas and in condensed phases.

References