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Bare phosphorus and binary phosphide cluster ions generated by laser ablation

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Abstract. Both positive and negative phosphorus cluster ions were generated from the laser ablation of a red phosphorus sample. The mass distribution of phosphorus cluster ions was found to be very sensitive to the power density of the ablation laser. The P_7^+ species exhibits the highest signal intensity in the recorded mass spectra of bare phosphorus cluster cations, as does P_5^- among the anions. Their special structural stability can be attributed to their planar configuration and their aromatic character. As the phosphorus cluster size increases, the odd/even alternation of the signal intensity becomes more pronounced. For the P_n^+ species with $n > 24$, the relative abundance varies in the order of 8 and P_n^+ with $n = 8k + 1$ ($k = 3$–11) are more intense than their neighbors. For comparison, some binary phosphide cluster ions, including $C_nP_m^-$, $Si_nP_m^-$, $B_nP_m^+$ and $Al_nP_m^{\pm}$, were produced as well. The mass distribution of binary phosphide cluster ions changes with different components. From analysis of the recorded mass spectra of the phosphide cluster ions, the larger clusters may be in a polyhedral configuration and tend to have all valence electrons paired.

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1 Introduction

The geometry of carbon clusters, from linear to cyclic, to spherical, and further to tubular, have been well studied [1–3]. Phosphorus is the diagonal element of carbon in the Periodic Table, so its structural chemistry is also of interest. In fact, phosphorus, in its elemental crystalline state, does exhibit structural variety [4], such as red, white, yellow and black phosphorus. A cluster is an intermediate state between the isolated atom and its crystal, so it is very interesting to examine the structures of phosphorus clusters with different sizes. Due to the difficulty in performing the experiment, most studies carried out on phosphorus clusters use the quantum chemistry method [5–9]. The largest phosphorus cluster calculated is P_{28} [5]. Some small phosphide clusters have been studied both theoretically and experimentally [10–11]. In inorganic chemistry, compounds containing a small naked phosphorus cluster have been synthesized and characterized [12–13] and some interesting structures have been revealed. For example, both cyclic and tetrahedral P_4 units were found in those compounds by single crystal X-ray diffraction. The bare phosphorus cluster cations were studied experimentally by Martin et al. [14] for the first time, where P_n^+ with $n < 25$ were generated by quenching phosphorus vapor and ionized by laser beam. The recorded mass spectrum showed an odd/even alternation of the signal intensity.

The main difficulty in producing phosphorus clusters is the purification of the sample, because elemental phosphorus is very reactive and easily oxidized. After solving this problem, we were able to generate P_n^+ with n up to 89 on a homemade apparatus. In order to generate the binary cluster ions, we mixed the powder of red phosphorus with the powder of the other elements, carbon, silicon, boron, or aluminium, as the sample. Thus, with the standard laser-ablation technique and special handling of the samples, binary phosphide cluster ions with different compositions have been produced for the first time.

2 Experimental methods

The experiments were performed on a homebuilt time-of-flight mass spectrometer with a mass resolution of about 150. The important feature of the apparatus is its capability of detecting both positive and negative ions simultaneously. The apparatus has been described in detail elsewhere [15]. In brief, the sample holder is 8 cm away from the acceleration region. The laser generated plasma diffuses into the accelerating region with its initial kinetic energy, and then positive and negative ions are separated by the accelerating field and fly in opposite directions down to the detectors, respectively. The pulsed laser beam, which is the second harmonic output of a Q-switched Nd: YAG laser, with wave length 532 nm and pulse width 7 ns, is gently focused by a long focus-length lens. The power density of the laser beam ablating on the sample surface can be adjusted in two ways: (1) by varying the output of the laser, (2) by changing the distance between the focusing lens and the sample, i.e. by changing the spot size where the laser beam ablated. In general, the power density is in the range of 5×10^6–5×10^8 W/cm^2. The whole system was running under a vacuum of 10^{-4} Pa, and no buffer gas was introduced during the experiments.

Red phosphorus was purified before the experiments by being washed several times in high purity water and then dried in inert atmosphere. Carbon, silicon, aluminium and boron are all high purity agents. To produce binary clusters, powders of red phosphorus and powder of C, Si, B or Al were ground together and pressed into a specially designed sample holder. It was found that variation of the mixed molar ratio from 1:4 to 4:1 does not affect the mass distribution of the phosphide cluster ions generated from the sample.

3 Results and discussion

3.1 Bare phosphorus cluster cations and anions, $P_n^\pm$

It is known that the crystalline phosphorus of different allotropes can be converted into each other under certain temperatures and pressures [4]. Variation of the power density of the ablating laser beam will certainly change both the surface temperature and the amount of the material vaporized. Since the vaporization only takes a very short time, the vaporized species will be confined to a very small volume, so variation of the power density will also affect the pressure on the sample. It is therefore not surprising that mass distribution of bare phosphorus clusters is very sensitive to the ablating laser fluency. In the case of high laser fluency, mass distribution of the observed phosphorus cluster ions is very complicated and not reproducible. The cluster size increases as the power density decreases. When the power density is lowered to less than 1×10^7 W/cm^2, mass distribution of the phosphorus cluster ions becomes reproducible and appears in a nice order, but their signal intensities are weaker. Figures 1 and 2 display the typical TOF mass spectra of positive and negative phosphorus cluster ions, respectively. Both of them were averaged results from 250 continuous laser shots and were recorded under identical experimental conditions.

The most outstanding mass peaks in Figs. 1 and 2 are P_7^+ and P_5^- respectively. If all clustering phosphorus atoms adopted sp^2 hybridization, they would form a planar single ring like benzene with each lone-pair of electrons occupying a hybrid orbital. When the charge of the cluster ions is taken into account, the total number of π electrons of both P_7^+ and P_5^- is 6, so both ions are aromatic according to the Hückle rule and are very stable. In fact, phosphorus is not the first element in the VA group that has been found to form aromatic clusters. Pentamer anions of other elements in the VA group, such as Bi_5^- and Sb_5^-, have been proved to possess aromaticity both experimentally and theoretically [16]. When Fig. 1 is compared with Fig. 2, it can be found that, although mass distributions of positive and negative ions are very different, cluster ions composed of 13 and 23 phosphorus atoms show higher signal intensity in the mass spectra of both positive and negative ions. The same phenomenon has also been observed in the mass spectra of aluminium cluster cations and anions [17]. Note that both phosphorus and aluminium are in the same row of the Periodic Table, but the former belongs to the VA group and the later belongs to the IIIA group. M_{13} is just a icosahedron with an atom in the center, and the added ten atoms of M_{23} may bind to half of its plane.

The odd/even alternation of signal intensity is the feature of the mass distributions of both positive and

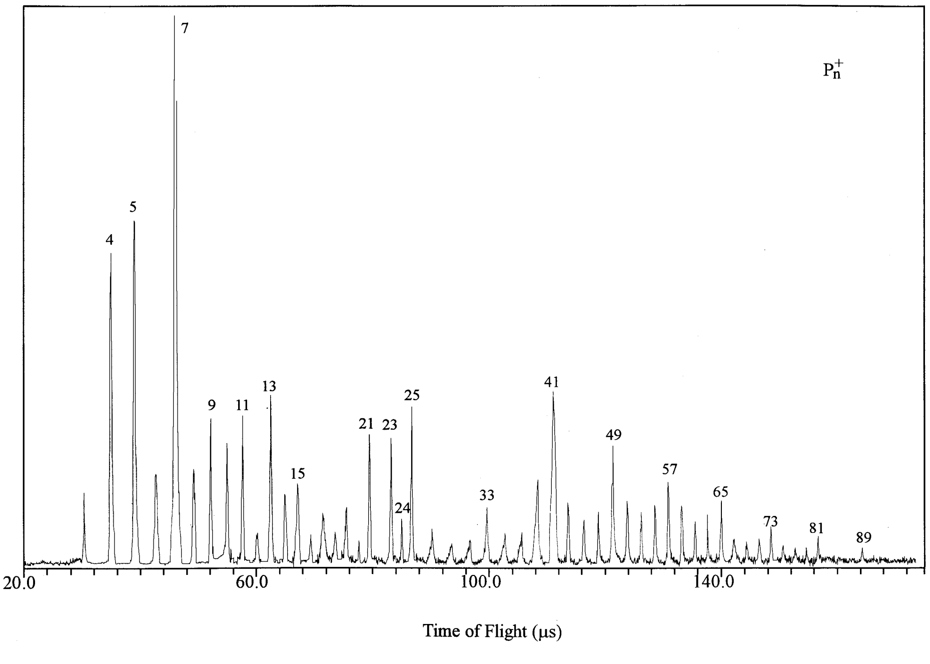

Fig. 1. Mass spectrum of laser generated P_n^+. The number marked on each peak represents the number of phosphorus atoms. For n larger than 24, P_n^+ with $n = 8 \times k + 1$ is more intense than its neighbors, and when n reaches 41, the intensities of $P_{8\times k+1}^+$ ($k > 5$) fit the statistical distribution model

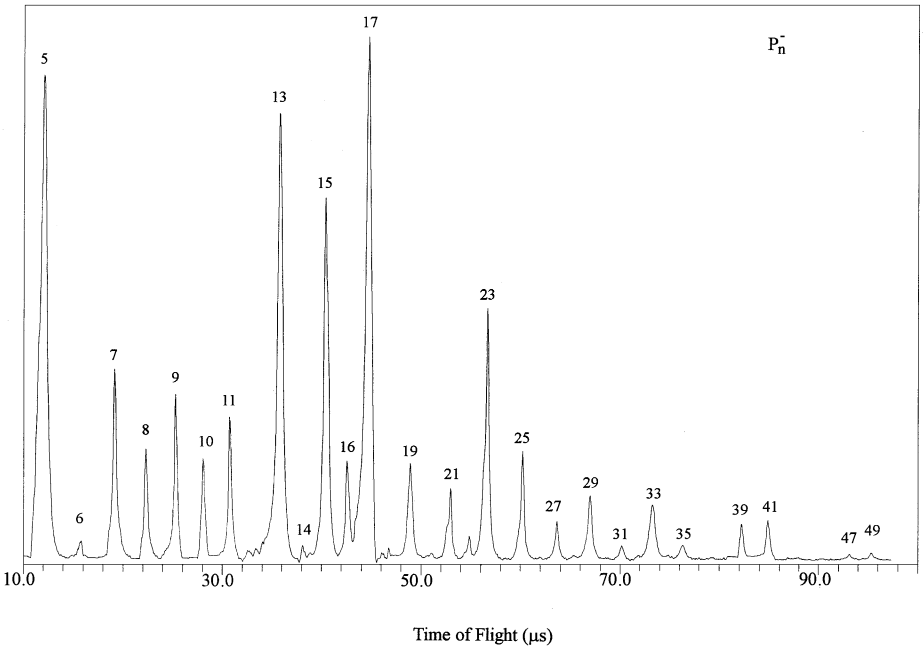

Fig. 2. Mass spectrum of P_n^- produced from laser ablation of red phosphorus powders. The number marked on each peak represents the number of clustering phosphorus atoms. An odd/even alternation occurs, and with the cluster size increasing, only the cluster with odd size exists

negative phosphorus cluster ions. The difference between odd size and even size cluster ions becomes more and more significant with the increase in cluster size. Furthermore, as is shown in Figs 1 and 2, no even size cluster ions are detected for P_n^+ with $n > 20$ except for P_{24}^+ and for P_n^- with $n > 12$ except for P_{16}^-. If high mass carbon cluster (fullerene) is the only observed cluster composed of only an even number of atoms, the high mass phosphorus cluster ion detected in this experiment is the only cluster composed of odd atoms. The alternation effect is the result of the structure of phosphorus cluster ions. Phosphorus is an odd-electron atom. Since all observed cluster ions in the experiment are singly charged, phosphorus cluster ions with odd size will have even number of electrons. Obviously, large phosphorus cluster ions have a strong tendency to have all their electrons paired and there is no dangling bond. The odd/even alternation has also been observed in the binary cluster ions composed of IIIA–VA group elements [18], such $Ga_xAs_y^{\pm}$, $Ga_xP_y^{\pm}$, and $In_xP_y^{\pm}$. Smaller phosphorus clusters may have different structures, so they do not show this effect.

In the case of $n \geq 25$, P_n^+ with even n is no longer observed and its signal intensity oscillates in a period of 8, i.e., P_n^+ with $n = 8k + 1$, ($k = 3, 4, 5, \cdots$) exhibits a relatively higher signal intensity. Among the observed phosphorus cluster cations, P_{41}^+ is the highest and P_{89}^+ is the largest. In addition, relative abundance of these cluster ions starting from P_{41}^+ can be fitted by a lognormal curve. According to the statistical distribution model for laser generated clusters [19], if the observed clusters have analogous structural configurations and similar structural stability, their mass distribution can be described by a lognormal curve. Obviously, P_8 is the structural unit of phosphorus cluster ions and the addition of each P_8 unit to P_{41}^+ does not change the structural framework of the cluster ion. In addition, the "magic number", $8k + 1$, suggests that there should be a single phosphorus atom in the center of the cluster ions. From this structural information, the geometry of these cluster ions can be pictured: P_{25}^+ is the smallest cluster in this series and it may be triangular with three P_8 units. For the same reason, geometry of P_{41}^+ may be a bipyramid, and all valence electrons of the centered phosphorus atom participate in the chemical bonding, making it the most stable cluster in this series. The signal intensity of the larger phosphorus cluster ion decreases with the cluster size and follows the same distribution curve, so that all of them have to grow from P_{41}^+. Their added P_8 units may not be bonded to the central atom, but may combine with each plane of the bipyramid. There are six planes on a pyramid, so a P_{41}^+ cluster can combine up to six P_8 units to form P_{89}^+, which is just the largest phosphorus cation observed in the experiment. P_4 may be another structural unit of phosphorus clusters. P_{13}^+ and P_{21}^+ therefore may have the same geometry as P_{25}^+ and P_{41}^+, respectively, so as to have a relatively high structural stability, as shown in Fig. 1. In fact, both P_4^+ and P_8^+ are also quite stable, although they are cluster ions of even size.

The magic number, 8, is also shown in the mass spectrum of negative phosphorus cluster ions. As can be observed in Fig. 2, the signal intensity of P_n^- decreases with the cluster size, and P_{37}^- is not observed. But mass peaks of two pairs of cluster anions, P_{39}^-, P_{41}^- and P_{47}^-, P_{49}^-, show up again. The size differences for the two pairs are all 8. Furthermore, the magic number is also shown in the correlation between the positive and negative phosphorus cluster ions: among positive ions, P_{21}^+, P_{23}^+ and P_{25}^+ are three high peaks with similar signal intensity; there are also three neighboring high peaks in the mass spectrum of negative ions, but they are P_{13}^-, P_{15}^-, P_{17}^-. Notice that their difference is 8 between P_{21}^+ and P_{13}^-, P_{23}^- and P_{15}^-, as well as P_{25}^+ and P_{17}^-. As is mentioned above, P_{24}^+ and P_{16}^- are the largest cluster cation and anion, respectively. Their sizes are a multiple of 8 and their difference is still 8. Since the mass spectra of both positive and negative ions were recorded at the same time in the experiment, the correlation is more significant.

The ring and cage geometry of carbon clusters is well known. Since the small phosphorus clusters, such as P_5^- and P_7^+, may adopt the planar ring configuration, is it possible for larger phosphorus clusters to have a cage-like structure like fullerene? In order to test the possibility, we made the mixture of red phosphorus and NaCl, KCl or NaBr as a sample, but no $MP_n^{\pm}$ was detected in the laser ablation experiment. Hence, although the possible dodecahedron structure of P_{20} has been studied in theory [20], the results of our experiment do not support the hypothesis.

3.2 Binary phosphide cluster ions

3.2.1 $C_nP_m^-$. Carbon and phosphorus elements are diagonal neighbors in the Periodic Table, so structures of carbon and phosphorus clusters may have some similarities and differences. It is, therefore, very interesting to examine the binary clusters composed of both carbon and phosphorus. Figure 3 shows the negative ion mass spectrum recorded from the laser ablating the mixture of carbon and purified red phosphorus powders. The spectrum was averaged result from 200 continuous laser shots. The mass spectrum of positive ions was recorded at same time. No binary cluster cation was observed.

In Fig. 3, one can find abundant $C_nP_m^-$ binary cluster anions as expected, as well as some bare cluster anions of carbon or phosphorus. It is notable that bare clusters of certain sizes are missing in the mass spectrum. For example, C_n^- with $n > 9$ cannot be observed, and some P_m^- are also missing when we compare Fig. 3 with Fig. 2, such as P_m^- with $n < 5$ and P_6^-, P_{12}^-, etc. The result reflects the relative structural stability of C_n^- and P_m^- for different cluster sizes. Previous work on carbon clusters [21], either experimentally or theoretically, confirmed that the configuration of carbon clusters with smaller sizes are linear and become cyclic as size increases. In the case of linear carbon cluster anions, clustering carbon atoms adopt sp hybridization and the remaining p_x and p_y orbitals form two delocalized π orbitals (the direction of p_z is towards the direction of bond axial), so there is no dangling bond except one on a terminal carbon atom (the carbon atom on the other end of the chain is satisfied with the negative charge). If the carbon clusters are cyclic, clustering carbon atoms around the ring would have an unpaired electron, so they are more reactive than the linear carbon clusters and harder to survive from the laser plasma reaction. Polyhedron geometry is dominant in the structure of phosphorus clusters, so larger clusters are generally more stable. In fact, the surviving bare phosphorus cluster anions such as P_5^- and P_{13}^- also exhibit high signal intensity, as can be seen in Fig. 2.

By examining the composition of $C_nP_m^-$, it can be found that the number of the clustering carbon atoms, n, is generally larger than that of phosphorus, m. The difference reflects the difference of the aggregation ability between carbon and phosphorus. In fact, only those binary cluster anions $C_nP_m^-$ with $m = 1, 2, 3, 5$ can be observed in Fig. 3. The absence of $C_nP_4^-$ is a very striking feature but can be explained by the special structural stability of the P_4 unit. P_4 is known as the molecule of yellow phosphorus and as the most predominant species of phosphorus in gas phase [4]. The neutral P_4 cluster produced in our experiment must be a tetrahedron so that it has no dangling bond and cannot react with carbon atom or clusters. Some other isomers of P_4 such as cyclic or butterfly-shaped, which have been characterized in crystal [13, 22], would be more reactive.

The binary cluster anions containing only a single phosphorus atom, C_nP^-, show an odd/even alternation in

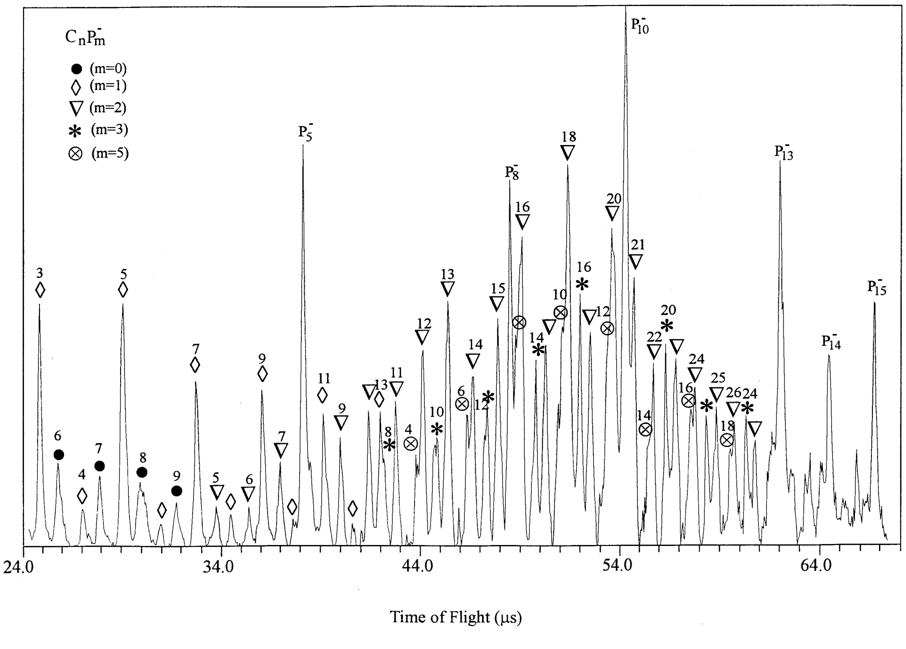

Fig. 3. Mass spectrum of $C_nP_m^-$ binary cluster anions. Each series of cluster anions (with same m) were marked with a different symbol, and the number on each symbol represents the number of clustering carbon atoms. The intensity of C_nP^- with odd n is more intense than that of even n; for $C_nP_2^-$, no odd/even alternate exists; the intensity of $C_nP_3^-$ and $C_nP_5^-$ with even n is more intense than that of odd n, in contrast to odd n in C_nP^-, and it fits the lognormal distribution. It is remarkable the no $C_nP_4^-$ is observed

signal intensity, and those with odd n are more stable. The series of cluster anions have been observed in our previous work [15], where triphenylphosphine instead of the mixture of phosphorus and carbon powders was selected as the sample. The alternation effect has also been observed in other C_nX^- cluster anions where X is a IIIA or VA group element, and was attributed to their linear configuration and electronic structure [15]. When compared with C_nP^-, mass distribution of $C_nP_2^-$ is broader, covering from $n = 4$ to $n = 28$. Their signal intensity changes gradually with n, except for clusters with n from 13 to 20, and no magic number or periodic alternation can be distinguished. In fact, among the binary cluster ions containing different number of phosphorus atoms, $C_nP_2^-$ are the only ions that do not show the alternation effect. For $C_nP_3^-$ and $C_nP_5^-$, the odd/even alternation appears again. In contrast to C_nP^-, however, signal intensities of $C_nP_3^-$ and $C_nP_5^-$ with even n are higher than those with odd n. In fact, $C_nP_3^-$ and $C_nP_5^-$ with odd n are even absent from the mass spectrum. Moreover, relative abundance of either $C_nP_3^-$ or $C_nP_5^-$ with even n can be fitted to a lognormal distribution curve. The distribution suggests that each series of cluster anions have similar structural configuration and stability. Another interesting observation for $C_nP_3^-$ is that only those cluster ions with $n \geq 8$ can be produced and detected. In other words, if a carbon phosphide cluster anion contains three phosphorus atoms, it can be stabilized only when its clustering carbon atom number is equal to or exceeds 8.

3.2.2 Si_nP_m. Although silicon is in the same group as carbon in the Periodic Table, their chemical properties differ significantly. On the other hand, silicon and phosphorus are neighbors, and there are many similarities in their structural chemistry. These behaviors involved are reflected by the compositions of the observed silicon phosphide cluster anions. Figure 4 is the TOF mass spectrum of laser generated Si-P cluster anions, which is averaged by 250 continuous records. No Si-P cluster cations were detected at the same time.

Mass distribution of the observed Si-P cluster anions possesses the following characteristics:

(1) In addition to the binary cluster ions, some bare phosphorus cluster ions are also observed, but no bare silicon cluster ion has been detected. Again, some P_m^- ions, such as P_{12}^- and P_{14}^-, are absent in the recorded mass spectrum.

(2) Though the observed $Si_nP_m^-$ cluster anions are very abundant, not all possible compositions are presented. Except for the clusters with the size $(n + m)$ equal to 3, 5 or 9, the number of the clustering silicon atoms cannot exceed that of phosphorus atoms. Besides, $Si_nP_4^-$ cluster ions, such as SiP_4^- and $Si_2P_4^-$, are also missing, as in the case of C_nP_m.

(3) The odd/even alternation can also be observed in the mass distribution of $Si_nP_m^-$ as well, but it appears in a different manner. Except for $Si_2P_8^-$, signal intensities of the cluster anions with an odd number of the clustering phosphorus atoms are stronger, and the parity of the clustering silicon atoms does not affect the relative abundance of the cluster ions. The difference is apparently related to the number of valence electrons of the two component elements. The valence electron number of silicon is 4, an even number, and thus the number of the clustering silicon atoms does not affect the parity of the cluster electron number. On the other hand, the valence electron number of phosphorus is 5, an odd number. In order to have all the valence electrons of the cluster anions paired, the number of the clustering phosphorus atoms must be odd (taking account of the negative charge of the cluster anions). This indicates that all valence electrons in the Si-P cluster anions tend to be paired and the cluster has no dangling bond, as was observed in the bare

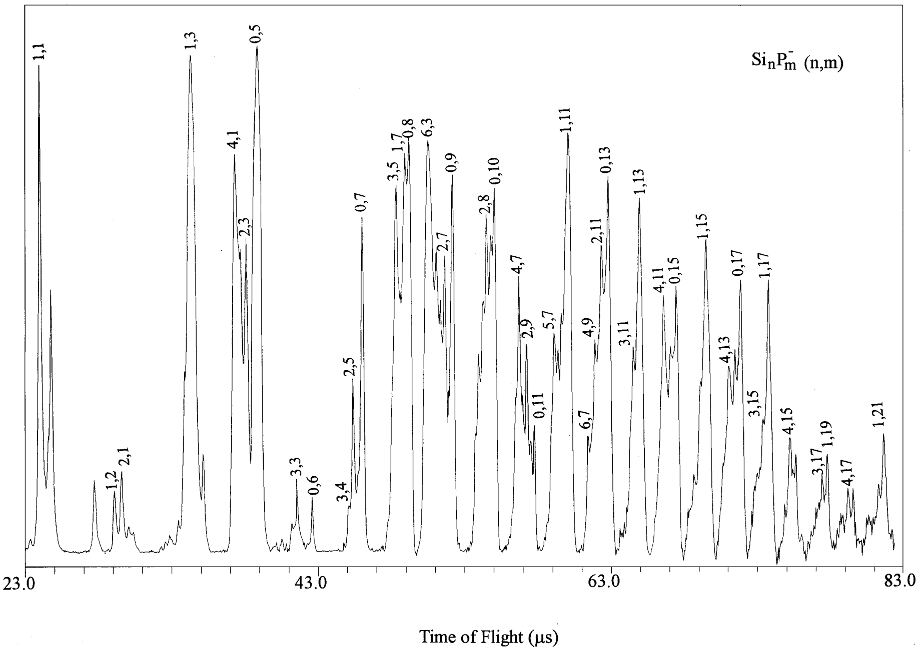

Fig. 4. Mass spectrum of $Si_nP_m^-$ cluster ions generated by laser ablation of the mixture of red phosphorus and silicon powders. The marked number (n, m) on each peak represents the number of clustering silicon and phosphorus atoms, respectively. Both abundant binary cluster ions and pure phosphorus cluster ions were observed and the mass distribution confirms that phosphorus cluster ions take a polyhedral configuration

Table 1. List of boron-phosphorus binary cluster cations observed by laser ablation. The changes of signal intensity of $B_nP_m^+$ can be seen from the context

BP_m^+	$m = 2$–22
$B_2P_m^+$	$m = 2$–7
$B_3P_m^+$	$m = 3$–6

phosphorus cluster ions. The structural character results from the fact that silicon and phosphorus are neighbors in the Periodic Table.

(4) Among $Si_nP_m^-$ with odd m, the cluster anions with $n = 4$ or $m = 3$ generally exhibit relative high signal intensity, such as Si_4P^-, $Si_4P_7^-$, $Si_4P_{11}^-$, $Si_4P_{15}^-$, $Si_3P_3^-$, $Si_6P_3^-$, etc. In fact, 4 and 3 are just the predominant oxidation states of silicon and phosphorus, respectively.

3.3.3 $B_nP_m^+$. Boron-phosphorus binary cluster ions were also generated from laser ablation. Mass spectrum of negative ions is not informative because there are too many oxides. Phosphorus cluster cations of various sizes can be observed in the mass spectrum, but no bare boron cluster cations were detected. The generated cations are presented in Table 1.

As displayed in Table 1, only three series of binary cluster cations, BP_m^+, $B_2P_m^+$, $B_3P_m^+$ were detected. The signal intensity of BP_m^+ or $B_3P_m^+$ alternates with odd/even m too, but in reverse pattern. The BP_m^+ species with even m are more stable than those with odd m. Instead of the odd/even alternation, the signal intensity of $B_2P_m^+$ can generally be fitted to a distribution curve, indicating their analogous structural configuration and stability, based on the statistical distribution model [19]. The variation in signal intensity is somewhat similar to that observed in the $C_nP_m^-$ cluster ions, but the variable in the latter is the number of clustering phosphorus atoms. Furthermore, when m increased only BP_m^+ with even m were observed. As discussed above, the larger phosphorus cluster ions may possess the structures with one phosphorus atom lying in the center of the clusters. The larger $B_nP_m^+$ can contain only one boron atom and their relative abundance also shows odd/even alternation. Therefore, the larger boron phosphide cluster ions may adopt the same geometry as the bare phosphorus cluster ions, but the core atom is boron instead of phosphorus.

3.3.4 $Al_nP_m^{\pm}$. Among the four elements, C, Si, B, Al, only aluminum is a typical metal element. All binary cluster cations with significant signal intensity contain only one aluminum atom. They are actually aluminum complexes coordinated with phosphorus atoms and/or phosphorus clusters. Products generated from laser ablation of the mixture of phosphorus and different metal elements were studied in the previous experiments, and their mass distributions are similar [23]. For instance, among the observed $Ag_nP_m^+$ species, AgP_4^+, AgP_8^+, AgP_{14}^+ exhibit special signal intensity [23]. The coordinated phosphorus atoms may be bound as stable clusters such as P_4 so there will not be too many dangling bonds. The remarkable feature is the existence of a series of cluster cations that is composed of only one phosphorus atom but several aluminum atoms. Configuration of the Al_nP^+ ions may be similar to that of AlP_m^+, but the positions of Al and P are just interchanged. Similar structure was also found in Al_nS^- species [24]. In general, it is difficult for bare metal clusters to survive the laser plasma without colliding with the buffering gas. The central phosphorus atom may be bound with the surrounding aluminium atoms so as to stabilize the clusters.

Compared with the positive ions, observed negative ions of the binary clusters detected simultaneously are more abundant, but their clustering aluminum atom number n is still generally less than that of the phosphorus atom number m. For instance, signal intensity of $Al_4P_4^-$ is still significant, but $Al_5P_3^-$ does not appear at all. Exceptions are the clusters of odd sizes, such as $Al_3P_2^-$ and $Al_5P_4^-$, but their intensities are very weak and n can only be as large as $m + 1$. On the other hand, no "magic number" can be distinguished from the mass spectrum and the observed $Al_nP_m^-$ anions do not show the odd/even oscillation of signal intensity, as in the case of some other IIIA-VA binary cluster ions such as $Ga_xAs_y^-$, $Ga_xP_y^-$ and $In_xP_y^-$ [18]. As the result of the above characteristics of the composition distribution, a steep step always follows on the left side of the mass peak belonging to $Al_nP_m^-$ with $n = m$ for even m or $n = m - 1$ for odd m. Although the binary cluster anions do not exhibit special high signal intensity, their relative abundance are still quite different, and some cluster anions such as $Al_3P_8^-$, $Al_3P_9^-$ are not observed at all. If the binary clusters can be regarded as the substituted phosphorus clusters, relative abundance between the bare phosphorus cluster anion and its left neighbor in the mass spectrum, $Al_nP_m^-$ with same size, can reflect the relative stability of the phosphorus cluster ions. From the comparison, P_5^-, P_7^-, P_8^- and P_{10}^- should be more stable than P_4^-, P_6^-, P_{11}^- and P_{12}^-.

4 Summary

(1) Both positive and negative phosphorus cluster ions were produced by laser ablation. The size of the observed phosphorus cluster ions in the experiment was up to 89, much greater than ever before observed. In addition, some phosphide cluster ions, $X_nP_m^{\pm}$ (X = C, Si, B, Al), were generated for the first time from laser ablation of proper samples.

(2) Mass distribution of the binary phosphide clusters changes with different components. The number of the clustering phosphorus atoms in $Si_nP_m^-$, $B_nP_m^+$ and $Al_nP_m^{\pm}$ is generally greater than the number of the other components. P_4 cannot be combined with carbon to form binary clusters.

(3) The large phosphorus cluster ions exhibit remarkable odd/even alteration of signal intensity. P_n^+ with $n > 24$ and P_n^- with $n > 16$ are the only observed elemental cluster ions which are solely composed of an odd number of atoms. Binary phosphide cluster ions $Si_nP_m^-$ and $B_nP_m^+$ also show the parity effect, but for $Si_nP_m^-$ this effect is only related to the number of the clustering phosphorus atoms and not to the cluster size ($n + m$). The parity effect shows that these cluster ions tend to have all their electrons paired. The cluster ions C_nP^-, $C_nP_3^-$ and $C_nP_5^-$ exhibit the

parity effect as well, but their signal intensity is varied with the number of clustering carbon atoms, n.

(4) In addition to the well-known P_4 unit, P_8 is also found to be a structural unit of the bare phosphorus cluster ions. For instance, P_n^+ with $n = 8k + 1$ ($k = 3$–11) has a relatively high abundance.

(5) Though cluster ions $B_nP_m^+$ and $Al_nP_m^\pm$ are composed of IIIA and VA group elements, they do not show the odd/even alternation effect which is found for $Ga_xAs_y^\pm$, $Ga_xP_y^\pm$ and $In_xP_y^\pm$. Since the latter compounds in solid state are good semiconductors, the parity effect may be an indication of the semiconductivity.

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