Физика твердого тела, 2002, том 44, вып. 4

Phosphorus clusters: Synthesis in the gas-phase and possible cage-like and chain structures

© A.V. Bulgakov, O.F. Bobrenok, V.I. Kosyakov*, I. Ozerov**, W. Marine**,
M. Hedén***, F. Rohmund***, E.E.B. Campbell***

Institute of Thermophysics Siberian Branch of Russian Academy of Sciences,
630090 Novosibirsk, Russia
* Institute of Inorganic Chemistry,
630090 Novosibirsk, Russia
** Université de la Méditerrancée, GPEC, UMR CNRS 6631,
Marseille, France
*** Göteborg University, Chalmers University of Technology,
Göteborg, Sweden
E-mail: bulgakov@itp.nsc.ru

The experimental results on gas-phase formation of neutral and cationic phosphorus clusters are presented. The clusters have been synthesized by visible (532 nm) or UV (193 nm) laser ablation of crystalline red phosphorus under high vacuum conditions and analyzed using TOF mass spectrometry. Neutral P_n clusters produced by 532-nm ablation are found to be even-numbered while P_n^+ cations are mainly odd-numbered with P_7^+ and P_{21}^+ being the most abundant ions. For UV laser ablation, stable compound clusters, neutral P_7H_3 and $P_{23}H_5$ as wellas cations $P_{23}H_6^+$, have been synthesized for the first time. Formation of P_n clusters by thermal vaporization of red phosphorus into a cold He gas has also been investigated, and only the small clusters ($n < 6$) have been discovered. Possible structures of the observed phosporus clusters as well as their formation mechanisms under different conditions are discussed.

This work was supported by the Russian Foundation for Basic Research (grant № 99-03-33372), by the Russian Scientific and Technical Program "Fullerenes and Atomic Clusters" (project N 5-4-99), and by the Royal Swedish Academy of Sciences.

The doscovery of fullerenes has naturally raised the question whether carbon is unique or other elements can also form stable closed cages. Recently there was renewed interest in the study of phosphorus clusters [1–3] which are expected to display a variety of structural forms. Two main structural families have been considered theoretically — chains and cages (polyhedra) [1,3–9]. A number of closed-shell structures for P_n clusters have been proposed as probably energetically more stable then tetrahedral P_4. Also, the viability of prosphorus nanotubes has been theoretically predicted [10].

The theoretical suggestions, however, are still not confivmed by experiment. Only a few experiments have been performed on clusters larger than P_4 [11–13]. Recently, a wide spectrum of neutral and cationic phosphorus clusters were synthesized in the gas phase by visible laser ablation of crystalline red phosphorus [2]. The cationic P_{21}^+ cluster was found to be the most abundant ion. Basing on topological analysis, it was suggested that dodecahedral fullerene-like P_{20}, stabilized with an additional phosphorus ion in the laser plasma, could be particularly stable. It was also speculated that the efficient generation of cage-like P_n clusters could be explained by the presence, in the laser plume, of their building blocks which were already formed in the target and ejected from its surface under irradiation.

In this paper we continue our investigations on the gas phase formation of phosphorus clusters. This work is focused mainly on the role of particles directly ejected (vaporized) from the red phosphorus. Three vaporization regimes, principally different from the viewpoint of the particle ejection mechanisms, have been studied: ablation by visible (532 nm) and UV (193 nm) laser ligth, and also thermal vaporization in a carrier gas. Possible structures of the observed P_n clusters as well as their formation mechanisms under different conditions are discussed.

1. Experimental

The apparatus used for laser ablation and cluster generation and detection was described earlier [14–16]. In brief, the target was placed in a rotating holder in a vacuum chamber (base pressure 10^{-5} Pa) and irradiated at normal incidence by a 13 ns FWHM laser pulse at 532 nm (the second harmonic of a Nd : YAG laser) or at incidence angle of 45° by a 15 ns FWHM ArF laser pulse at 193 nm. Crystalline red phosphorus (also called Hittorf's phosphorus) of 99.999% purity (with respect to metals) was used as the target. The laser fluence on the target was varied in the range $0.02-0.8\,\mathrm{J/cm^2}$ at a tixed spot area of about $0.4\,\mathrm{mm^2}$ with the Nd : YAG laser and about $6\,\mathrm{mm^2}$ with the ArF laser.

The relative abundance of neutral and positively charged particles in the laser-ablation plume was analyzed using a reflection time-of-fligth mass spectrometer (RETOF MS). When ions were studied, the plume was allowed to expand under field-free conditions while the neutral particles of the plume were analyzed using a simple plasma suppressor [14]. The latter consisted of a pair of deflection plates placed along the plume axis in front of the ion source of the MS, where neutral particles were pulse-ionized by 90 eV electrons. The 900 V/cm deflection field was sufficient to remove the plasma ions throughout the studied laser fluence range. At a distance of 6 cm (at 532-nm ablation) or 7 cm (at 193-nm ablation) from the target, the ions, either ablated or post-ionized, were sampled perpendicular (at 532 nm) or parallel (at 193 nm) to the plume axis by a 500 V repeller pulse after a time delay, t_d, following the laser pulse.

P_n cluster formation during thermal vaporization in a gas aggregation source [17,18] has also been investigated. In this source, phosphorus vapor was created in a oven at 570−620 K and quenched in an aggregation chamber in a cold He gas at a pressure of about 1 Torr. The outer mantel of the chamber was cooled with liquid nitrogen. The high efficiency of this type of cluster sources was demonstrated previously for a number of materials [11,17–19]. The cluster condensed out in the quenched vapor were transported by the gas stream through a nozzle at a temperature of 80−100 K. They crossed a differentially pumped region and were then pulse-ionized with 90 eV electrons and analyzed with a RETOF MS.

All spectra reported here represent an average over ~ 200 pulses.

2. Results and discussion

Fig. 1, *a* shows the TOF mass spectra of cations species in the plume at 532-nm ablation under "optimum" conditions corresponding to the maximum yield of large P_n^+ clusters ($n > 9$). Figs. 1, *b, c* illustrate typical mass spectra of P_n^+ cations obtained at 193-nm ablation. Clearly the spectra are quite different. At visible laser ablation, large P_n clusters are generated in abundance and their concentration in the plume is found to be comparable with that of molecules and small clusters. The mass distribution comprises mainly the odd-numbered P_n^+ clusters and is rather smooth with few magic numbers (Fig. 1, *a*). The strongest peaks correspond to P_7^+ and P_{21}^+ cations.

By contrast, at UV laser ablation, P_n clusters are presented in minor amounts in the plume. Even under "optimum" conditions the intensities of the strongest cluster peaks are less by about two orders of magnitude than those of molecular peaks ($n = 2-5$). The abundance spectra represent only few individual peaks corresponding presumably to the most stable clusters under these conditions. These stable species consist mainly of compound (oxidized and phosphane) clusters, again in contrast tp 532-nm ablation in which pure P_n clusters dominate. The O and H atoms appear to come from trace impurities in the red phosphorus. More efficient generation of compound clusters under UV light irradiation may be attributed to photodissociation and photodissociative ionization of the surface impurities in this case. The generated O and H atoms and ions react in the near-surface region with the ablated P_n clusters, which leads to formation of the stable structures.

The most intriguing feature of the mass spectra obtained with UV laser pulses is the strong dominance of the $P_{23}H_6^+$ cluster cation which was not observed with visible lasers. It is particularly abundant at a very low fluence of 0.06 J/cm^2 (Fig. 1, *b*) and is the only cluster to survive in the $n > 15$ range when the laser fluence is doubled (Fig. 1, *c*).

A study of the ablation plume dynamics by varying the time delay t_d also revealed different cluster expansion behavior for the two considered cases. At 532-nm ablation, large clusters ($n > 9$) are found to have approximately the same expansion velocity (about 1.6 km/s for the conditions shown in Fig. 1, *a*) in spite of the large difference in their masses. This implies a gas-phase condensation mechanism of cluster formation rather than their direct ejection. In the latter case one would expect the same kinetic energy of the plume particles rather than the same velocity. However, smaller P_n species ($n < 9$), and also oxidized clusters, are mainly ejected directly from the target [2]. At 193-nm ablation, the most probable velocities of the observed clusters (Figs. 1, *b, c*) are found to decrease gradually with increasing cluster size implying the direct ejection mechanism of cluster generation. The ejection of the "building blocks" ($P_7 - P_9$) of larger P_n clusters is much less efficient as compared to the case of 532-nm ablation and does not seem to be sufficient for the gas-phase cluster growth.

Fig. 2 shows mass spectra of neutral clusters obtained for the three experimental situations considered. Relatively large P_n clusters are generated in abundance during visible laser ablation (Fig. 2, *a*). The clusters are mainly even-numbered with "magic sizes" at $n = 10$, 14, and 40 (the latter is not shown in Fig. 2, *a*). In the $n = 16-26$ range, there is a prominent local minimum at $n = 22$. The analysis of cluster velocity distributions indicates again the gas-phase condensation mechanism of their formation. For UV laser ablation, the plume consists mostly of atoms and small molecules among which P_2 dominates (Fig. 2, *b*). In the larger mass region, only two neutral compound clusters P_7H_3 and $P_{23}H_5$ have been rigistered.

Fig. 2, *c* shows a mass spectrum of particles produced during thermal vaporization of red phosphorus in the gas aggregation source. Only atoms and small molecules have been registered with such a source where the initial vapor consists mainly of P_2 dimers [4]. The strongest peak corresponds to the P_4 molecule. Obviously the aggregation process in this case is terminated by the formation of the stable tetrahedral P_4. The key role of the ejection of small P_n clusters ($n = 7-9$) for the gas-phase growth of larger clusters is thus again demonstrated. It also seems likely that such a termination of the aggregation process can be avoided by adding a reactant gas into the chamber [11].

Of particular interest is the question about possible structures of the observed phosphorus clusters and specifically of the abundant P_{21}^+ and $P_{23}H_6$ cations, and P_7H_3 and $P_{23}H_5$ neutrals. Note that the availability of compound clusters, both neutral and ionized, can provide additional information about the structures of the phosphorus skeletons. In particular, the presence of an additional H atom is cationic $P_{23}H_6^+$ as compared to the corresponding neutral cluster

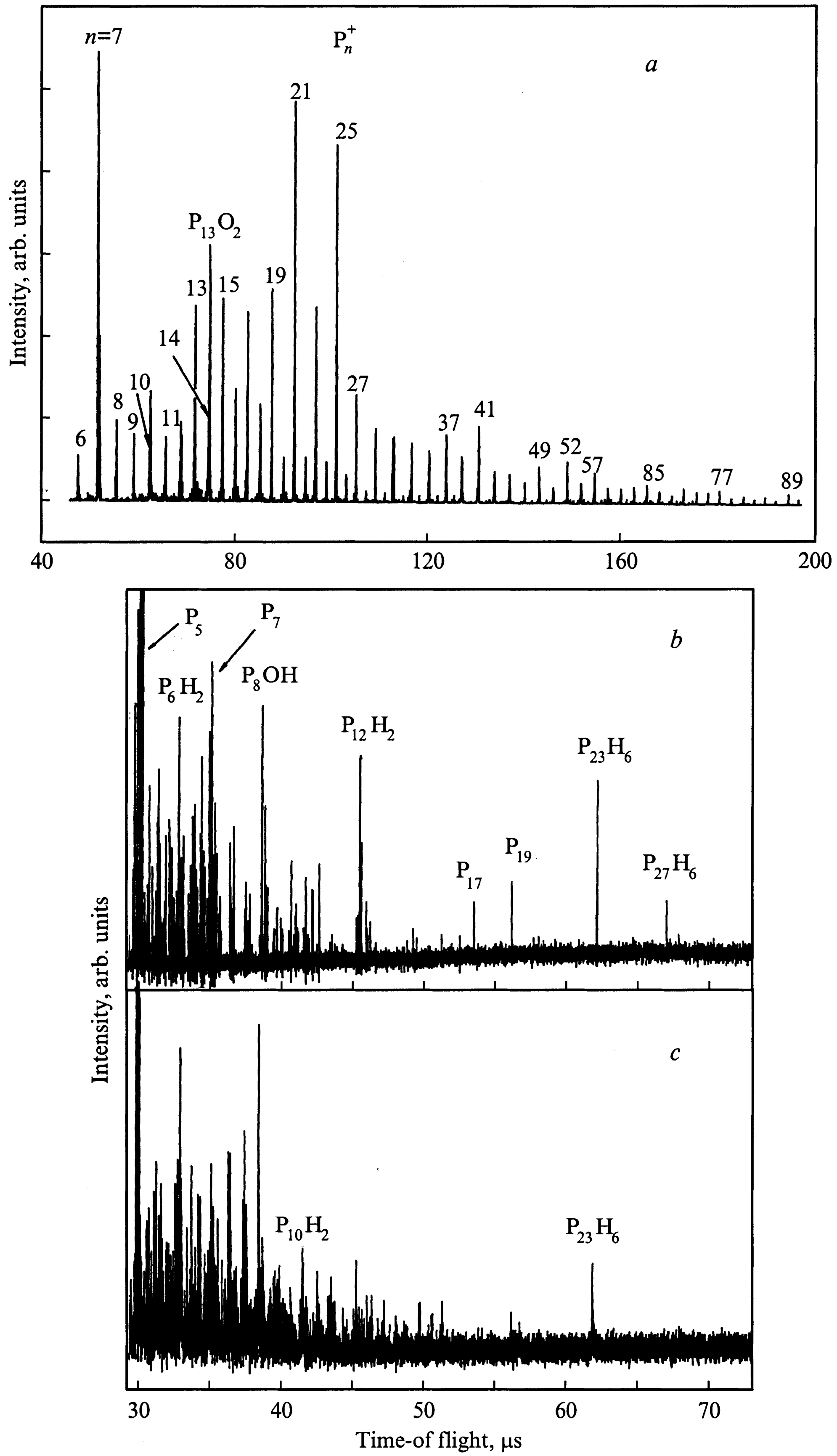

Figure 1. TOF mass spectra of phosphorus cluster cations produced by laser ablation: (*a*) 532-nm laser ablation, laser fluence $E = 0.3\,\mathrm{J/cm^2}$, time delay $t_d = 37\,\mu\mathrm{s}$; (*b*) 193-nm laser ablation, $E = 0.06\,\mathrm{J/cm^2}$, $t_d = 62\,\mu\mathrm{s}$; and (*c*) same as (*b*) but $E = 0.13\,\mathrm{J/cm^2}$.

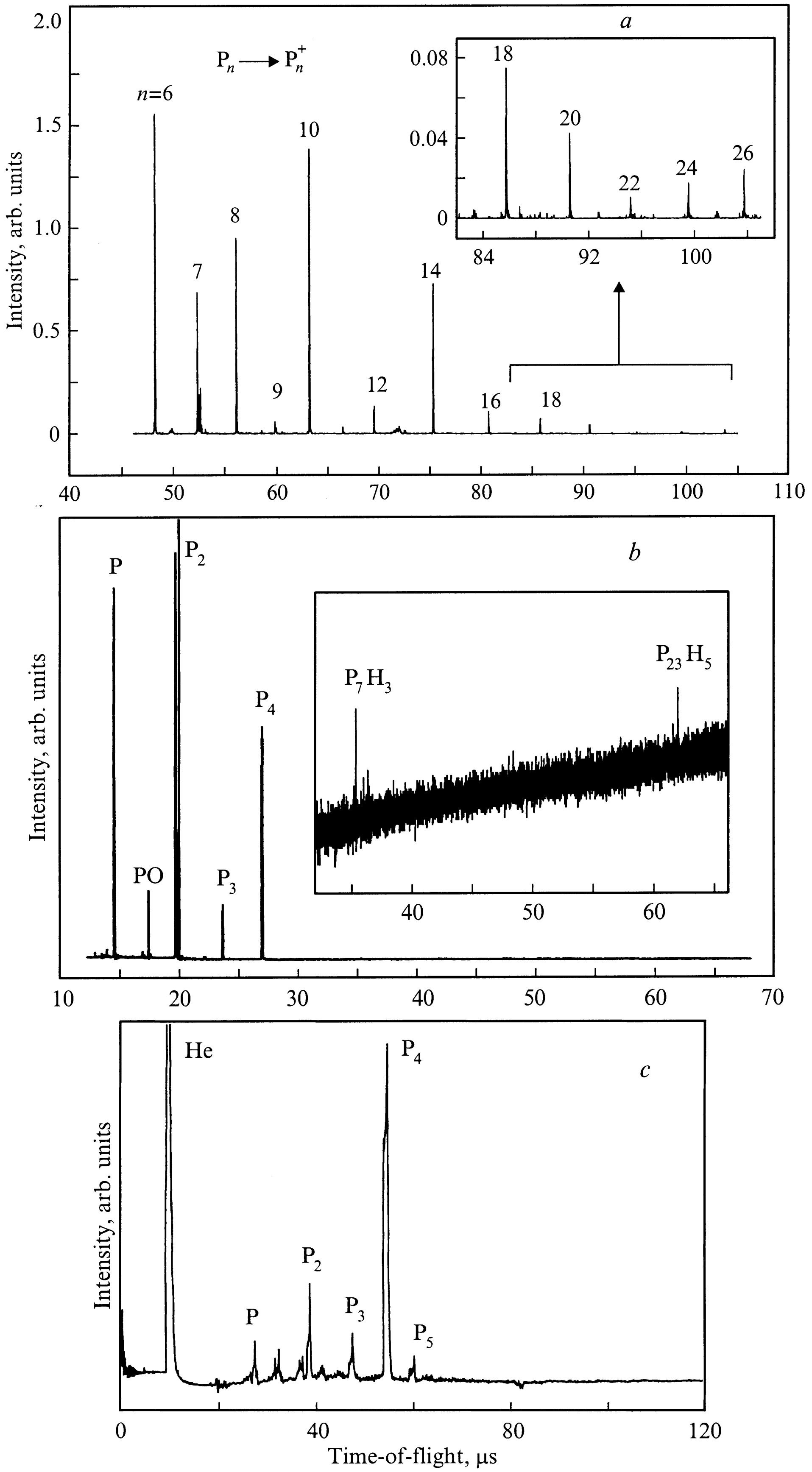

Figure 2. TOF mass spectra of neutral phosphorus cluster produced under different conditions: (*a*) 532-nm laser ablation, $E = 0.3\,\mathrm{J/cm^2}$, $t_d = 37\,\mu$s; (*b*) 193-nm laser ablation, $E = 0.06\,\mathrm{J/cm^2}$, $t_d = 62\,\mu$s; and (*c*) gas aggregation source, oven temperature is 590 K.

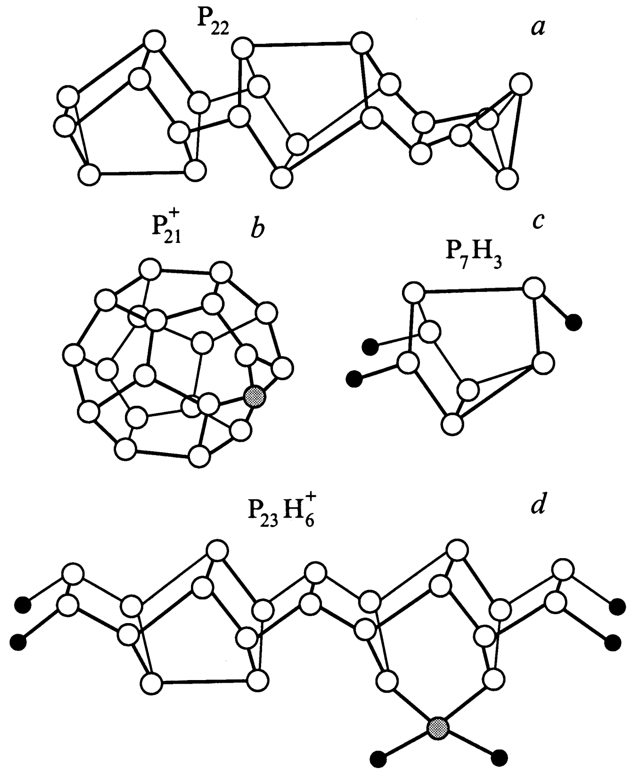

Figure 3. Possible structures of some phosphorus clusters observed in laser ablation plumes. Grey circles in (*b*) and (*d*) show a four-coordinated *P* atom. Closed circles in (*c*) and (*d*) stand for hydrogen atoms.

support recent calculations [1,3,12] which suggest that P_n^+ cations adopt structures with on four-coordinated atom.

The local abundance minimum at $n = 22$ for neutral phosphorus clusters (Fig. 2, *a*) provides convincing circumstantial evidence for the presence of fullerene-like P_n clusters in the plume induced by a 532-nm laser pulse. In fact, all the even-numbered polyhedra can be geometrically realized from P_{20} up to P_{60} (some in more than one form) except P_{22} [20]. The chain structure is still possible for P_{22} [7] (a plausible stable structure is shown in Fig. 3, *a*). One would thus speculate that dodecahedral fullerene-like P_{20}, stabilized in the plasma with an additional fourfold coordinated atom (as shown in Fig. 3, *b*), could be especially stable and explain the magic number of 21 in the cation spectra obtained from visible laser ablation (Fig. 1, *a*).

Since the observed compound clusters are ejected directly from the target, they should adopt structures with skeletons corresponding to structural groups of the red phosphorus. We believe that the stable P_7H_3 neutral is the cage-like cluster consisting of 3 five-membered rings and a triangle with three bridge P atoms and three H atoms satisfying the dangling bonds (Fig. 3, *c*). This structure has been identified by *X*-ray spectroscopy as the most stable P_7-based skeleton in polyphosphides [5]. Assuming a direct ejection mechanism one can also easily desing the structure of the magic clusters $P_{23}H_6^+$ and $P_{23}H_5$. Their phosphorus skeleton should represent the main unit of the infinite double "tube" of crystalline red phosphorus which is built by successive translation of the chain P_{23} cluster [21]. Fih. 3, *d* shows a plausible structure for the $P_{23}H_6^+$ ion, which needs six H atoms to satisfy the dangling bonds (assuming that one P atom is four-connected). In the neutral $P_{23}H_5$ cluster all P atoms are threefold.

References

[1] M.D. Chen, J.T. Li, R.B. Huang, L.S. Zheng, C.T. Au. Chem. Phys. Lett. **305**, 439 (1999).
[2] A.V. Bulgakov, O.F. Bobrekov, V.I. Kosyakov. Chem. Phys. Lett. **320**, 19 (2000).
[3] M.D. Chen, R.B. Huang, L.S. Zheng, Q.E. Zhang, C.T. Au. Chem. Phys. Lett. **325**, 22 (2000).
[4] D.E.C. Corbridge. The Structural Chemistry of Phosphorus. Elsevier, Amsterdam (1974).
[5] V.I. Kosyakov. Izv. SO AN SSSR. Ser. Khim. Nauk **9**, 96 (1982) [in Russian].
[6] R.O. Jones, G. Seifert. J. Chem. Phys. **96**, 7564 (1992).
[7] M. Häser, U. Schneider, R. Ahlrichs. J. Am. Chem. Soc. **114**, 9551 (1992).
[8] M. Häser, O. Treutler. J. Chem. Phys. **102**, 3703 (1995).
[9] C.-H. Hu, M. Shen. H.F. Schaefer III. Theor. Chim. Acta **88**, 29 (1994).
[10] G. Seifert, E. Hernández. Chem. Phys. Lett. **318**, 355 (2000).
[11] T.P. Martin. Z. Phys. **D3**, 211 (1986).
[12] R. Huang, H. Li, Z. Lin, S. Yang. J. Phys. Chem. **99**, 1418 (1995).
[13] Z. Liu, R. Huang, L. Zheng. Z. Phys. **D38**, 171 (1996).
[14] B.N. Kozlov, I.I. Pilyugin, V.G. Shchebelin, A.V. Bulgakov, A.P. Mayorov, M.R. Predtechensky. Tech. Phys. **39**, 944 (1994).
[15] A.V. Bulgakov, M.R. Predtechensky, A.P. Mayorov. Appl. Surf. Sci. **96–98**, 159 (1996).
[16] L. Patrone, D. Nelson, V.I. Safarov, S. Giorgio, M. Sentis, W. Marine. Appl. Phys. **A69** [Suppl.], S217 (1999).
[17] K. Hansen, H. Hohmann, R. Müller, E.E.B. Campbell. J. Chem. Phys. **105**, 6088 (1996).
[18] K. Hansen, R. Müller, H. Hohmann, E.E.B. Campbell. Z. Phys. **D40**, 361 (1997).
[19] T.P. Martin, U. Näher, H. Schaber, U. Zimmermann. Phys. Rev. Lett. **70**, 3079 (1993).
[20] A.F. Wells. Structural Inorganic Chemistry. 5th ed. Clarendon, Oxford (1984).
[21] H. Turn, H. Krebs. Acta Cryst. **B25**, 125 (1969).