Hydrogen binding effect on charged P_{2n} ($n = 1-7$) clusters

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Abstract. An all-electron (AE) calculation of the hydrogen binding effect on charged phosphorus clusters has been performed under the framework of density functional theory (DFT). Compared with the $P_{2n}^{\pm}$ ($n = 1-7$) clusters, the $HP_{2n}^{\pm}$ ($n = 1-7$), cluster has shorter average P–P bond length, larger binding energy and HOMO–LUMO gap (HLG), higher chemical hardness and frequency of P–P mode. After binding with one hydrogen atom, the electronic structure is changed from open electronic shell to closed electronic shell. Geometrical stability, chemical stability and electronic stability are strengthened. These stability enhancements may be simply understood considering the electron pairing effect.

Keywords. Charged phosphorus clusters; hydrogen binding effect; electron pairing effect.

1. Introduction

Phosphorus with three unpaired electrons in $3p$ orbital that are available for bonding is known to form a wide range of homo-atomic clusters is the highlight of this study. With the development of laser vaporization technology and time-of-flight mass spectroscopy, pure phosphorus clusters have been studied well experimentally.¹⁻⁷ The P_4 cluster has been generated experimentally in the vapour phase of white phosphorus early in 1935¹ and the P_n^+ (n up to 24) clusters can be observed after quenching the vapour of red phosphorus in a helium beam.² Laser ablation of pure red phosphorus leads to formation of singly charged P_n^+ ($n = 1-189$) and P_n^- ($n = 1-225$) clusters.³ Much higher n values than those known in literature were proved. Neutral phosphorus clusters P_n (up to $n = 40$) and their cations P_n^+ (up to $n = 91$) had been synthesized in the gas phase by laser ablation of crystalline red phosphorus.⁴ Neutral P_n clusters were found to be even-numbered with local n abundance maxima at $n = 8, 10, 14$, and 40 . An abundance minimum at $n = 22$ indicated the possibility of stable cage-like structures of clusters. In contrast, cationic clusters are preferentially odd-numbered with P_{21}^+ being the most abundant ion. It is suggested that dodecahedral fullerene-like P_{20} , stabilized with an additional phosphorus ion in the laser plasma, can be parti-

cularly stable. Formation and photodissociation of phosphorus cluster ions, produced by laser ablation, were studied with a tandem time-of-flight mass spectrometer.⁵ Stability of these cluster ions is influenced by their electronic and geometric structures. Meanwhile, a few theoretical research reports were also found.⁸⁻¹⁴ Energetic and thermodynamic stability of selected phosphorus clusters containing 18 to 168 atoms were studied by employing DFT.⁸ The series P_{18+12n} is definitely more stable than the series P_{18+10n} , the most stable compounds are the D_{nd} structures P_{120} , P_{144} , and P_{168} . Geometrical and electronic properties of P_n ($n = 2-15$) neutrals, cations and anions were investigated using the density functional method of B3LYP.⁹ Stability of clusters exhibits strong even–odd alternations with several magic numbers. Neutral P_n clusters were found to be even-numbered with local maxima at $n = 2, 4$ and 14 , while the cationic and anionic clusters are preferentially odd-numbered with P_2^+ , P_3^+ , P_2^- , P_5^- and P_{15}^- being the most stable ions. A total of 50 isomers of P_5 , P_7 , P_9 and their cations and anions which exhibit intensities of significance on the mass spectra had been acquired by means of the B3LYP, DFT method.¹⁰ A cationic cluster prefers to adopt structures with an atom which is four-fold coordinated. The planar pentagon structure is a frequent sub-unit in the phosphorus clusters. Both tetrahedral P_4 and P_8 are common components of the clusters and can be considered as important units for the construction of large clusters.

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Among all these earlier studies, we are most interested in the study by Liu *et al.*⁵ Analysis results of tandem time-of-flight mass spectrometer indicated that the even-numbered charged $P_n^\pm$ cluster produced by laser ablation has one unpaired electron and is unstable relatively. These charged clusters prefer to bind with one hydrogen atom additionally and then their stabilities may be improved expectedly.⁵ However, experimental studies cannot provide a complete picture of these clusters. In order to explain and verify the experimental conclusions, and also to predict the lowest possible energy geometries which are very difficult to obtain from experiments, we shall conduct a DFT study on the hydrogen binding effect on the stabilities of $P_{2n}^\pm$ ($n = 1-7$) clusters with the generalized gradient approximation (GGA) at PW91 level.

2. Computational method

With the inter-atomic interaction approximated by Gupta-like tight-binding¹⁵ and Sutton–Chen¹⁶ empirical many-body potentials, the initial structures of $P_{2n}^\pm$ ($n = 1-7$) and $HP_{2n}^\pm$ ($n = 1-7$) clusters were generated using genetic algorithm (GA). All these initial structures were then fully DFT-optimized based on the DMOL 3 program package.^{17,18} During optimization, the double-numerical basis set, together with *d*-polarization functions (DNP), were chosen to describe the electronic wave functions. Within the generalized gradient approximation (GGA), the Perdew–Wang 91 exchange–correlation (XC) functional (PW91),¹⁹ combined with the DFT-basis all-electron treatment were adopted in the calculations.

3. Results and discussion

3.1 Geometrical structures

The lowest energy geometries of $P_{2n}^\pm$ and $HP_{2n}^\pm$ ($n = 1-7$) clusters are depicted in figure 1, the P–P and P–H bond lengths in Å are shown in these figures. Meanwhile, the symmetry, electronic state and total energy corresponding to these geometries are listed in table 1. Electronic states corresponding to the cation and anion P_2 clusters are $^2\Sigma_g$ and $^2\Pi$, respectively. The optimized P–P bond lengths of 1.999 Å and 1.989 Å for cationic and anion P_2 clusters compare favourably with the measured values.²⁰ Different from the neutral phosphorus tetramer with tetrahedral (T_d) structure, the loss or gain of one additional electron results in a Jahn–Teller distortion in cation and anion phosphorus tetramer to some extent. The symmetry is changed from

T_d to D_{2d} and C_{2v} , respectively. The most stable geometry for charged P_4 clusters is the tetrahedral structure displaying T_d symmetry and 2A_1 electronic state. This structure is proved to be the dominant form of elemental phosphorus in the vapour phase.¹¹ The average P–P bond-length in charged P_4 clusters is longer than the P–P distance of 2.209 ± 0.005 Å in neutral P_4 cluster inferred from a low-temperature X-ray structure analysis in crystalline white phosphorus.²¹ Similar to the neutral P_6 cluster, the cation and anion P_6 clusters are constructed by binding the linear P_2 structure and tetrahedral P_4 structure together, and these two structures are regarded as the relatively stable units in phosphorus clusters. The C_{2v} symmetry of the cation and anion P_6 clusters is also same as the neutral P_6 cluster. The lowest energy geometry of cation P_8 cluster is a cuneane structure with the symmetry of C_{2v} (2A_1). It is similar to the geometry of neutral P_8 cluster.⁹ Assembling the stable structure of P_3^- and P_5 , we can obtain the lowest-energy structure of anion P_8 cluster with Cs ($^2A'$) symmetry, which is different from its neutral and cation clusters. The lowest energy geometry of cation P_{10} cluster is constructed by connecting two tetrahedral P_4 units with linear P_2 unit. The anion P_{10} cluster is formed by binding cuneane P_8 with two P atoms on one side, which was also proposed to be the ground-state structure of anion P_{10} cluster by Chen *et al.*¹⁰ Both cation and anion P_{12} clusters have the same C_{2h} symmetry and 2A_1 electronic state, which can be seen as the cuneane P_8 structure binding with four P atoms on two sides. The most stable structure of cation P_{14} cluster is the Cs ($^2A'$) form which can be seen as the combination of P_8 and P_6 units, and has the same geometry as its neutral cluster.¹⁰ The anionic P_{14} cluster, however, has a different structure as its neutral and cationic clusters, and is constructed by connecting the cuneane P_8 structure with two P_3 units on two sides. When H atom approaches $P_{2n}^\pm$ ($n = 1-7$) clusters, the hydrogen atom prefers to be bonded with cationic P_2 clusters and charged P_4 clusters by two-fold bond, and prefers to occupy the single-fold coordination site for other $P_{2n}^\pm$ ($n = 1-7$) clusters. After binding with H atom, the structures of $P_{2n}^\pm$ ($n = 1-7$) clusters are perturbed and distorted slightly, the average P–P bond length for $HP_{2n}^\pm$ cluster is obviously shorter than the average P–P bond length in corresponding charged P_{2n} cluster, it is inferred that the geometrical stabilities of these charged P_{2n} clusters are strengthened to some extent after binding with one hydrogen atom. This situation can be explained in terms of electron exchange between the hybridized orbital of $P_{2n}^\pm$ ($n = 1-7$) cluster and the hybridized orbital of H atom, which results in better overlap of these orbitals and the enhancement of P–P interaction in $P_{2n}^\pm$ ($n = 1-7$) clusters.

3.2 Energy and electronic structures

An unambiguous insight into the stability of clusters can be gained by analysing their energy and electronic structures. We first calculate the binding energy/atom of $P_{2n}^{\pm}$ and $HP_{2n}^{\pm}$ ($n = 1-7$) clusters. This is defined by:

$$E_b(P_{2n}^{\pm}) = [(2n-1)E(P) + E(P^{\pm}) - E(P_{2n}^{\pm})] / (2n)$$

$$E_b(HP_{2n}^{\pm}) = [(2n-1)E(P) + E(P^{\pm}) + E(H) - E(HP_{2n}^{\pm})] / (2n+1).$$

The results are plotted as a function of cluster size in figures 2 and 3. With increasing size of $P_{2n}^{\pm}$ ($n = 1-7$) clusters, binding energy decreases gradually for cation phosphorus clusters and increases gradually for anion phosphorus clusters. After binding with one hydrogen atom, although the variation tendency is almost not changed, binding energy of $HP_{2n}^{\pm}$ ($n = 1-7$) cluster is obviously larger than that of corresponding $P_{2n}^{\pm}$ ($n = 1-7$) cluster, indicating that the total thermodynamic stability of $P_{2n}^{\pm}$ ($n = 1-7$) cluster may be strengthened after binding with one hydrogen atom.

Figure 1. Lowest energy geometries of $P_{2n}^{\pm}$ and $HP_{2n}^{\pm}$ ($n = 1-7$) clusters.

Table 1. Symmetry, electronic state and total energy (eV) of the lowest energy geometries of $P_{2n}^{\pm}$ and $HP_{2n}^{\pm}$ ($n = 1-7$) clusters.

Cluster	Symmetry	Electronic state	Total energy	Cluster	Symmetry	Electronic state	Total energy
P_2^+	$D_{\infty h}$	$2\Sigma_g$	-18567.309	HP_2^+	C_{2v}	$1A_1$	-18584.564
P_4^+	T_d	$2A_1$	-37148.490	HP_4^+	C_{2v}	$1A_1$	-37165.403
P_6^+	C_{2v}	$2A_1$	-55727.459	HP_6^+	C_s	$1A'$	-55744.377
P_8^+	C_{2v}	$2A_1$	-74307.215	HP_8^+	C_s	$1A''$	-74323.837
P_{10}^+	C_{2v}	$2A_1$	-92886.478	HP_{10}^+	C_s	$1A'$	-92903.417
P_{12}^+	C_{2h}	$2A_1$	-111464.979	HP_{12}^+	C_1	$1A'_1$	-111481.924
P_{14}^+	C_s	$2A'$	-130044.825	HP_{14}^+	C_1	$1A'_1$	-130061.223
P_2^-	$D_{\infty h}$	2Π	-18577.991	HP_2^-	C_s	$1A''$	-18593.985
P_4^-	T_d	$2A_1$	-37157.551	HP_4^-	C_{2v}	$1A_1$	-37173.391
P_6^-	C_{2v}	$2A_1$	-55737.538	HP_6^-	C_1	$1A''_1$	-55753.833
P_8^-	C_s	$2A'$	-74316.272	HP_8^-	C_1	$1A'_1$	-74333.268
P_{10}^-	C_s	$2A'$	-92896.578	HP_{10}^-	C_1	$1A'_1$	-92912.908
P_{12}^-	C_{2h}	$2A_1$	-111475.755	HP_{12}^-	C_1	$1A'_1$	-111491.939
P_{14}^-	C_s	$2A'$	-130054.821	HP_{14}^-	C_s	$1A'$	-130071.362

Vertical ionization potential (VIP) and vertical electron affinity (VEA) are often used as the measurements of chemical stability of small clusters. From the calculated results shown in figures 4–7, it is easily found that the variation tendency of VIP for $P_{2n}^{\pm}$ and $HP_{2n}^{\pm}$ ($n = 1-7$) cluster is consistent with the corresponding variation tendency of binding energy. The VIP for $HP_{2n}^{\pm}$ ($n = 1-7$) cluster is larger than that of corresponding $P_{2n}^{\pm}$ ($n = 1-7$) cluster, and the VEA for $HP_{2n}^{\pm}$ ($n = 1-7$) cluster is smaller than that of corresponding $P_{2n}^{\pm}$ ($n = 1-7$) cluster, it is suggested that more energy is needed for vertical ionization of one electron and less energy is released when an electron is added in $HP_{2n}^{\pm}$ ($n = 1-7$) clusters, the production of the corresponding cation and anion is not relatively easy. In addition to the VIP and VEA, the maximum hardness principle (MHP) can also be used to characterize the chemical stability of small

clusters.^{22,23} Using the finite difference approximation and the Koopmans' theorem, the chemical hardness η can be approximated as $\eta = (VIP - VEA)/2$.^{24–28} Combining the results of VIP and VEA, chemical hardness for the lowest energy structures of $P_{2n}^{\pm}$ and $HP_{2n}^{\pm}$ ($n = 1-7$) clusters is calculated and shown in figures 8 and 9. Obviously, the chemical hardness η of $HP_{2n}^{\pm}$ ($n = 1-7$) clusters is larger than that of corresponding $P_{2n}^{\pm}$ ($n = 1-7$) clusters, the enhancement of chemical stability after binding with hydrogen atom can be observed clearly.

The HOMO (LUMO) (HOMO - highest occupied molecular orbital, LUMO - lowest unoccupied molecular orbital) energy level and HOMO–LUMO gap (HLG) are adopted to investigate the electronic structure of small clusters. From the results depicted in figures 10–15, we can find that the HOMO (LUMO) energy level of $HP_{2n}^{\pm}$ ($n = 1-7$) clusters is lower (higher) than that

Figure 2. Size dependence of binding energy for P_{2n}^{+} and HP_{2n}^{+} clusters. **Figure 3.** Size dependence of binding energy for P_{2n}^{-} and HP_{2n}^{-} clusters.

Figure 4. Size dependence of VIP for P_{2n}^+ and HP_{2n}^+ clusters.

Figure 7. Size dependence of VEA for P_{2n}^- and HP_{2n}^- clusters.

Figure 5. Size dependence of VEA for P_{2n}^+ and HP_{2n}^+ clusters.

Figure 8. Size dependence of chemical hardness for P_{2n}^+ and HP_{2n}^+ clusters.

Figure 6. Size dependence of VIP for P_{2n}^- and HP_{2n}^- clusters.

Figure 9. Size dependence of chemical hardness for P_{2n}^- and HP_{2n}^- clusters.

Figure 10. Size dependence of HOMO for P_{2n}^+ and HP_{2n}^+ clusters.

Figure 13. Size dependence of HOMO for P_{2n}^- and HP_{2n}^- clusters.

Figure 11. Size dependence of LUMO for P_{2n}^+ and HP_{2n}^+ clusters.

Figure 14. Size dependence of LUMO for P_{2n}^- and HP_{2n}^- clusters.

Figure 12. Size dependence of HLG for P_{2n}^+ and HP_{2n}^+ clusters.

Figure 15. Size dependence of HLG for P_{2n}^- and HP_{2n}^- clusters.

Figure 16. Electron densities in the best fit plane obtained using same parameters for the lowest energy geometries of $P_{2n}^{\pm}$ and $HP_{2n}^{\pm}$ ($n = 1-7$) clusters.

of corresponding $P_{2n}^{\pm}$ ($n = 1-7$) clusters, the HLG of $HP_{2n}^{\pm}$ ($n = 1-7$) clusters is obviously larger than that of corresponding $P_{2n}^{\pm}$ ($n = 1-7$) clusters. More energy is required to excite electron from valence band to conduction band in $HP_{2n}^{\pm}$ ($n = 1-7$) clusters. Meanwhile, from figure 1, we find that the $HP_{2n}^{\pm}$ and $P_{2n}^{\pm}$ ($n = 1-7$) clusters prefer low spin multiplicity ($M = 1$ for $HP_{2n}^{\pm}$ clusters and $M = 2$ for $P_{2n}^{\pm}$ clusters). The HOMO

of $P_{2n}^{\pm}$ clusters with odd number of valence electrons is occupied partially only by majority spin electrons or minority spin electrons and have open electronic shell. According to the Jahn–Teller theorem,²⁹ these $P_{2n}^{\pm}$ ($n = 1-7$) clusters with open electronic shell have a tendency to distort further towards lower symmetry in order to reduce or to remove the degeneracy and lower the energy, the electronic structure of these clusters is

Figure 17. Spatial orientations of HOMO and LUMO for the lowest energy geometries of $P_{2n}^{\pm}$ and $HP_{2n}^{\pm}$ ($n = 12, 14$) clusters.

unstable relatively. After binding with one hydrogen atom, the HOMO of $HP_{2n}^{\pm}$ ($n = 1-7$) clusters with even number of valence electrons are fully occupied by the majority spin and minority spin electrons, which leads to the ground state of these clusters with closed electronic shell and the electronic structure stability of these clusters is improved remarkably. This situation can be simply understood by considering the electron pairing effect and is also observed in the H binding onto small copper clusters³⁰ and small gold clusters.³¹

In order to understand the nature of chemical bonding in these systems, electron densities in the best fit plane for the lowest energy geometries of $P_{2n}^{\pm}$ and $HP_{2n}^{\pm}$ ($n = 1-7$) clusters were plotted in figure 16. Compared with electron cloud distribution in corresponding $P_{2n}^{\pm}$ ($n = 1-7$) clusters, more electron cloud overlap between phosphorus atom in $HP_{2n}^{\pm}$ ($n = 1-7$) clusters can be found. This picture tells us that P–P bonding is strengthened after introduction of one hydrogen atom. Moreover, from the spatial orientations of HOMO and LUMO for representative $P_{2n}^{\pm}$ ($n = 12, 14$) clusters and $HP_{2n}^{\pm}$ ($n = 12, 14$) clusters shown in figure 17, we can see that almost all phosphorus atoms contribute to HOMO and LUMO in $P_{2n}^{\pm}$ ($n = 12, 14$) clusters, the delocalization of frontier orbital is obvious. After binding with one hydrogen atom, the degree of delocalization is decreased. The contribution of hydrogen seldom appears in the HOMO and LUMO of $HP_{2n}^{\pm}$ clusters due to the low orbital energy of hydrogen. Hydrogen binding with small cluster often can be seen as partly involving an excitation to a formerly unoccupied orbital in the

cluster, since the open shell has to be ‘pushed up’ when the cluster-hydrogen bond is formed.^{32,33}

3.3 Frequency analysis

Vibrational frequency is another important parameter to check the interaction between bonded atoms, higher vibrational frequency often corresponds to stronger interaction between the specified bonded atoms. By frequency analysis, the highest vibrational frequencies of P–P mode for the lowest energy geometries of $P_{2n}^{\pm}$ and $HP_{2n}^{\pm}$ ($n = 1-7$) clusters are given in table 2. It is easily found that the highest frequency of P–P mode in $HP_{2n}^{\pm}$ ($n = 1-7$) clusters is higher than that of corresponding $P_{2n}^{\pm}$ ($n = 1-7$) clusters. It is believed that P–P interaction is strengthened after binding to the hydrogen atom, appearing as the shorter average P–P bond-length in $HP_{2n}^{\pm}$ ($n = 1-7$) clusters observed clearly in figure 1.

4. Conclusions

In this study, an all-electron (AE) calculation of the hydrogen binding effect on $P_{2n}^{\pm}$ ($n = 1-7$) clusters has been performed. After binding with one hydrogen atom, the geometrical structures of $P_{2n}^{\pm}$ ($n = 1-7$) clusters are perturbed and distorted slightly, the average P–P bond length becomes shorter obviously. The binding energy, chemical hardness, HLG and the highest frequency of P–P mode for $HP_{2n}^{\pm}$ ($n = 1-7$) clusters are larger than those for $P_{2n}^{\pm}$ ($n = 1-7$) clusters. Electronic

Table 2. Highest vibrational frequencies of P–P mode for the lowest energy geometries of $P_{2n}^{\pm}$ and $HP_{2n}^{\pm}$ ($n = 1-7$) clusters.

n	P_{2n}^{+} V_{P-P} (cm^{-1})	HP_{2n}^{+} V_{P-P} (cm^{-1})	P_{2n}^{-} V_{P-P} (cm^{-1})	HP_{2n}^{-} V_{P-P} (cm^{-1})
1	638.4	718.0	647.8	772.4
2	567.5	728.9	546.6	628.1
3	534.0	766.5	500.8	757.2
4	476.8	721.5	511.2	746.2
5	516.3	757.7	451.0	734.9
6	559.3	753.3	509.4	703.3
7	455.0	733.7	506.8	737.0

structure changes from open electronic shell to closed electronic shell. Geometrical stability, chemical stability and electronic stability are strengthened and these stability enhancements are the reflection of electron pairing effect.

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