

# Structures and electron affinities of triatomic molecules consisting of Al, P and X (X = B, Al, Ga; C, Si, Ge; N, P, As; O, S and Se)

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**Abstract** The structures and electronic properties of the triatomic molecules containing Al, P, X atoms (X = B, Al, Ga; C, Si, Ge; N, P, As; O, S and Se) and their anions are investigated at the B3LYP/cc-PVTZ and the B3LYP/aug-cc-PVTZ levels. The results show that the most stable structures of the anions are  $\text{AlXP}^-$  (X = B, C, N) and  $\text{PAIX}^-$  (X = S, Se), while for the neutral molecules, the most stable structures are  $\text{PXAl}$  (X = C, N and O). The order of the VDEs of the anions molecules and the AEAs of the neutral species are  $\text{C} < \text{N} < \text{O} < \text{Si} \approx \text{Ge} < \text{P} \approx \text{As} < \text{Al} = \text{Ga} < \text{B} < \text{S} \approx \text{Se}$  and  $\text{C} < \text{O} < \text{N} < \text{Si} \approx \text{Ge} < \text{P} \approx \text{As} < \text{B} < \text{Al} \approx \text{Ga} < \text{S} \approx \text{Se}$ , respectively.

**Keywords** AEAs · Stability · Structure · VDEs

## Introduction

The structures and electronic properties of IIIA-VA clusters have been attracting considerable attention [1–14] arising from the extensive applications of the related compounds in the field of semiconductor materials. The first work of

aluminum phosphide (AlP) was carried out theoretically by Meier and co-workers [4] to study the ground state structures using the multi-reference double excitation configuration interaction (MRD CI) method. And then, the structures and stabilities of larger stoichiometric  $(\text{AlP})_n$  ( $n=1-6$ ) clusters were carried out by *ab initio* and density functional theory (DFT) [2, 5, 6]. Recently, the properties of small aluminum phosphide species  $\text{Al}_m\text{P}_n$  ( $m+n=2-6$ ) and  $\text{Al}_m\text{P}_n$  ( $m=1-2$  and  $n=1-7$ ) as well as their ions were studied using DFT and *ab initio* methods [5–17], including the complete active-space self-consistent field (CASSCF), the multi-reference configuration interaction (MRCI), CCSD (T) and the B3LYP. More recently, the photoelectron spectra of  $\text{Al}_x\text{P}_y^-$  ( $x, y \leq 4$ ) were observed experimentally by Gomez and co-workers [11]. However, for the gallium arsenide clusters, only the work of Jenkins et al. is known to date [1].

Generally, the properties of semiconductor compounds are influenced significantly by the presence of small amounts of various impurities or dopants, such as the gallium phosphide semiconductor [17–19], doped with sulfur, zinc, tin, tellurium, etc. Previous studies on  $\text{GaPX}^-$  (X = C, Si, Ge; O, S; P and Ga) show that the X can influence the vertical detachment energy (VDE) and adiabatic electron affinity (AEA) of gallium phosphide molecules [20]. In this paper, we report the theoretical results of the triatomic molecules containing Al, P, X atoms (X = B, Al, Ga; C, Si, Ge; N, P, As; O, S and Se). The aim is to explore their electronic structures, stability, bonding characters and electron affinities.

## Computational methods

In our previous study of the anions containing Ga, P, X (X = C, Si, Ge; O, S; P and Ga) atoms, we examined the

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performance of a variety of computational methods. The results showed that the geometries and energy order of the anions obtained by the B3LYP/cc-PVTZ were well consistent with those treated by the B3LYP/aug-cc-PVTZ [20]. Thus, all the structures of triatomic AIPX<sup>-</sup> and AIPX (X = B, Al, Ga; C, Si, Ge; N, P, As; O, S and Se) in the present work are optimized based on the hybrid density functional theory (B3LYP) with the cc-PVTZ basis set, and the doublet and triplet states are computed with an unrestricted open-shell method. The vibrational frequencies are calculated at the same level of theory in order to characterize the properties on the potential energy surface. The VDEs and AEAs of AIPX<sup>-</sup> are obtained at the B3LYP/cc-PVTZ and the B3LYP/aug-cc-PVTZ levels. The bonding properties of all the ground state structures are computed with natural bond orbital (NBO) analysis carried out by NBO 5.0 program package [21]. All the calculations have been performed using Gaussian03 program [22].

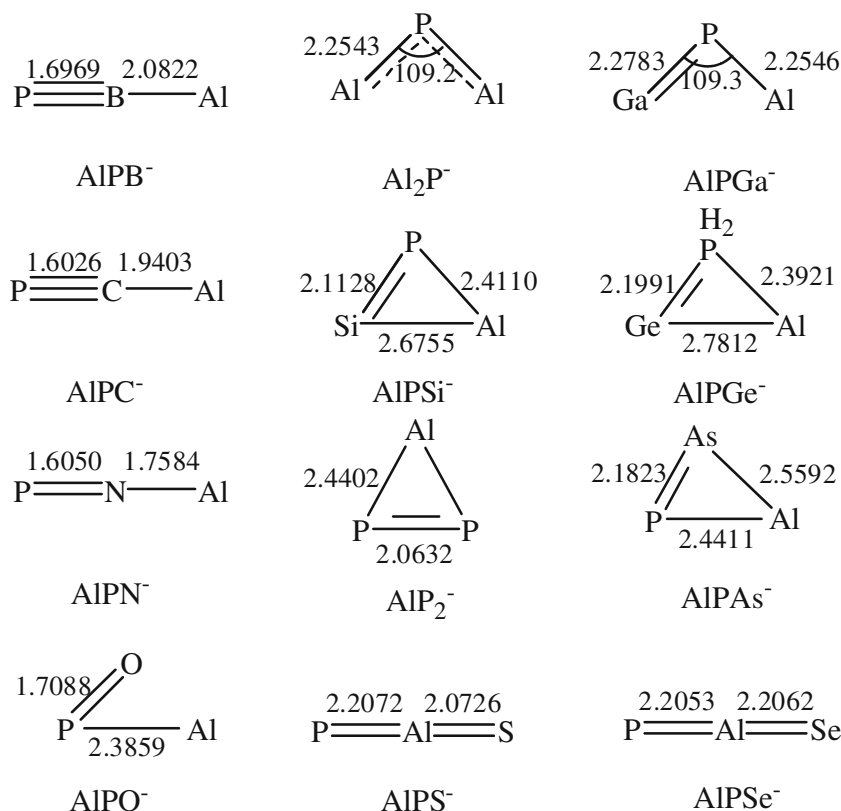
### The stability and vibrational frequencies of AIPX<sup>-</sup>

All the ground state structures of AIPX<sup>-</sup> (X = B, Al, Ga; C, Si, Ge; N, P, As; O, S and Se) obtained at the B3LYP/cc-PVTZ level are shown in Fig. 1. The symmetries, electronic states, total energies and zero point energies (ZPEs) are

listed in Table 1. The vibrational frequencies and the natural bond orders are presented in Tables 2 and 3, respectively.

As seen from Fig. 1, the ground state of AIPB<sup>-</sup> (<sup>1</sup>Σ<sup>+</sup>) is linear structure, in which the B atom locates at the middle position. NBO analysis shows that the P–B is triple covalent bond (see Table 3) with the bond length of 1.697 Å, while the Al–B is a mixed covalent and ionic single bond with a bond length of 2.082 Å. Differently, both the Al<sub>2</sub>P<sup>-</sup> and AIPGa<sup>-</sup> are bent structures with the electronic states of <sup>1</sup>A<sub>1</sub> and <sup>1</sup>A', respectively. Natural population analysis shows that the center P carries the entire excessive electron with the bond angle Al–P–X (X = Al and Ga) of 109.5°, which indicates that the P is sp<sup>3</sup> hybridized. It can be expected that the bonding property of Al–P in the Al<sub>2</sub>P<sup>-</sup> is very similar to that in AIPGa<sup>-</sup>, for example, the very near bond length (2.254 vs. 2.255 Å) agrees well with the previous theoretical results [10, 11]. The natural bond orders of Ga–P and Al–P in AIPGa<sup>-</sup> are 1.92 and 1.16, respectively, indicating that the Ga–P is stronger than the Al–P bond. Different from the anions AIPX<sup>-</sup> with X = Al, P and Ga, all of the ground states of the AIPX<sup>-</sup> (X = C, Si and Ge) are doublets with the electronic states of <sup>2</sup>Π, <sup>2</sup>A' and <sup>2</sup>A', respectively. AIPC<sup>-</sup> is a linear structure consisting of a triple P–C bond (1.603 Å) and a single Al–C (1.940 Å). In contrast, the Al–X (X = Si and Ge) in the bent AIPX<sup>-</sup> structure is a very weak bond

**Fig. 1** The geometries of AIPX<sup>-</sup>



**Table 1** The symmetry, electronic states, total energies and ZPE (in Kcal/mol) of AIPX<sup>-</sup>

X	Symm.	State	Energy	ZPE
B	C <sub>∞v</sub>	<sup>1</sup> Σ <sup>+</sup>	-608.67893	2.45
Al	C <sub>2v</sub>	<sup>1</sup> A <sub>1</sub>	-826.34630	1.43
Ga	C <sub>s</sub>	<sup>1</sup> A'	-2508.84551	1.28
C	C <sub>∞v</sub>	<sup>2</sup> Π	-621.91732	2.87
Si	C <sub>s</sub>	<sup>2</sup> A'	-873.38156	1.56
Ge	C <sub>s</sub>	<sup>2</sup> A'	-2660.97700	1.31
N	C <sub>∞v</sub>	<sup>3</sup> Σ <sup>-</sup>	-638.63085	2.94
P	C <sub>2v</sub>	<sup>1</sup> A <sub>1</sub>	-925.26644	1.78
As	C <sub>s</sub>	<sup>1</sup> A'	-2819.85674	1.49
O	C <sub>s</sub>	<sup>2</sup> A''	-659.13642	2.33
S	C <sub>∞v</sub>	<sup>2</sup> Π	-982.14879	1.95
Se	C <sub>∞v</sub>	<sup>2</sup> Π	-2985.56598	1.70

(bond order of 0.52) which contains both covalent and ionic components. Similarly, among the AIPX<sup>-</sup> (X = N, P and As) species, the AIPN<sup>-</sup> is a linear structure with electronic state of <sup>3</sup>Σ while the other two anions are bent structures with <sup>1</sup>A<sub>1</sub> and <sup>1</sup>A' for X = P and As, respectively. The electronic structure of AIPN<sup>-</sup> is ...3π<sup>4</sup>11σ<sup>2</sup>4π<sup>2</sup>, in which the bonding 3π and anti-bonding 4π MOs are the linear combinations of atomic orbitals p<sub>x</sub> and p<sub>y</sub> of P and N atoms. Considering that the σ bond between the P and N atoms is formed by the p<sub>z</sub> orbitals, the nature of the P–N is a double bond, which can be confirmed by the natural bond order of 2.04 (Table 3). For the AIPX<sup>-</sup> (X = O, S and Se) species, all the ground states are doublets with the electronic states of <sup>2</sup>A', <sup>2</sup>Π and <sup>2</sup>Π for X = O, S and Se, respectively. As shown in Fig. 1, the AIPO<sup>-</sup> is a bent structure while the AIPs<sup>-</sup> and AIPse<sup>-</sup> are linear structures in which Al always locates at the middle position. The natural population data shows that the positive Al carries 0.92e while the negative P and S carry -0.86e and -1.06e in the AIPs<sup>-</sup>, respectively. More detailed NBO analysis indicates that the Al–P and Al–S are double bonds (bond

**Table 2** The vibrational frequencies (in cm<sup>-1</sup>), vibrational mode and IR intensity (in km/mole) of AIPX<sup>-</sup>

X	frequencies (mode and IR intensity)
B	73(π, 1), 387(σ, 64), 1183(σ, 92)
Al	77(a <sub>1</sub> , 0), 428(a <sub>1</sub> , 15), 498(b <sub>2</sub> , 173)
Ga	69(a', 1), 354(a', 43), 476(a', 143)
C	148(π, 1), 215(π, 4), 425(σ, 5), 1217(σ, 177)
Si	201(a', 2), 326(a', 18), 567(a', 12)
Ge	155(a', 0), 321(a', 14), 444(a', 20)
N	196(π, 3), 534(σ, 12), 1128(σ, 7)
P	292(b <sub>2</sub> , 7), 362(a <sub>1</sub> , 22), 590(a <sub>1</sub> , 9)
As	237(a', 2), 338(a', 15), 466(a', 11)
O	332(a', 32), 546(a', 14), 746(a', 45)
S	146(π, 17), 157(π, 9), 374(σ, 1), 684(σ, 102)
Se	134(π, 10), 143(π, 5), 298(σ, 0), 612(σ, 71)

**Table 3** The natural bond orders of AIPX<sup>-</sup> and AIPX

X	Bond <sup>a)</sup>	Al–P	Al–X	P–X	
B	t	0.00 <sup>b)</sup>	<b>0.01</b> <sup>c)</sup>	1.07 <b>1.11</b> 2.93 <b>2.79</b>	
	c		<b>0.00</b>	0.50 <b>0.42</b> 2.55 <b>2.37</b>	
	i		<b>0.01</b>	0.57 <b>0.59</b> 0.38 <b>0.42</b>	
Al	t	1.92	<b>1.41</b>	<b>0.14</b>	
	c	0.57	<b>0.44</b>	<b>0.04</b>	
	i	1.35	<b>0.97</b>	<b>0.10</b>	
G	t	1.16	<b>2.02</b>	1.92 <b>1.04</b>	
	a	c	0.39	<b>0.82</b>	0.63 <b>0.32</b>
	i	0.77	<b>1.20</b>	1.28 <b>0.72</b>	
C	t	0.00	<b>0.00</b>	0.51 <b>1.02</b> 2.49 <b>2.98</b>	
	c			0.12 <b>0.18</b> 2.03 <b>2.42</b>	
	i			0.39 <b>0.84</b> 0.46 <b>0.56</b>	
Si	t	0.99	<b>1.05</b>	0.52 <b>0.00</b> 2.01 <b>2.84</b>	
	c	0.38	<b>0.21</b>	0.31 1.32 <b>1.43</b>	
	i	0.61	<b>0.83</b>	0.20 0.69 <b>1.41</b>	
G	t	1.02	<b>1.06</b>	0.52 <b>0.00</b> 1.98 <b>2.83</b>	
	e	c	0.39	<b>0.22</b>	0.30 1.30 <b>1.40</b>
	i	0.63	<b>0.84</b>	0.22 0.68 <b>1.43</b>	
N	t	0.03	<b>0.01</b>	1.02 <b>0.55</b> 2.04 <b>2.50</b>	
	c	0.00	<b>0.00</b>	0.36 <b>0.06</b> 0.93 <b>1.26</b>	
	i	0.03	<b>0.01</b>	0.76 <b>0.49</b> 1.11 <b>1.24</b>	
P	t	1.03	<b>0.54</b>	1.95 <b>2.43</b>	
	c	0.40	<b>0.15</b>	1.04 <b>2.43</b>	
	i	0.63	<b>0.39</b>	0.01 <b>0.01</b>	
A	t	1.03	<b>0.53</b>	1.03 <b>0.58</b> 1.94 <b>2.41</b>	
	s	c	0.39	<b>0.15</b>	0.41 <b>0.15</b> 1.87 <b>2.24</b>
	i	0.64	<b>0.38</b>	0.62 <b>0.43</b> 0.08 <b>0.17</b>	
O	t	1.05		0.09 <b>1.05</b> 1.47 <b>1.08</b>	
	c	0.43		0.01 <b>0.07</b> 0.59 <b>0.34</b>	
	i	0.62		0.08 <b>0.98</b> 0.89 <b>0.74</b>	
S	t	2.15	<b>1.02</b>	1.79 <b>1.00</b> 0.00 <b>1.98</b>	
	c	1.02	<b>0.30</b>	0.67 <b>0.18</b> <b>1.34</b>	
	i	1.13	<b>0.72</b>	1.12 <b>0.82</b> <b>0.64</b>	
Se	t	2.16	<b>1.02</b>	1.78 <b>1.00</b> 0.00 <b>1.98</b>	
	c	1.03	<b>0.29</b>	0.72 <b>0.20</b> <b>1.47</b>	
	i	1.13	<b>0.73</b>	1.05 <b>0.80</b> <b>0.51</b>	

a) t, c and i denote the total, covalent, ionic bond orders, respectively.  
 b) The natural bond orders of AIPX<sup>-</sup> (in plain)  
 c) The natural bond orders of AIPX (in bold)

order of 2.15 and 1.79, respectively) which contain one half covalent and one half ionic parts. Therefore, the properties of AIPse<sup>-</sup> are similar to that of AIPs<sup>-</sup>.

As listed in Table 2, the vibrational frequencies with strong IR activity of AIPX<sup>-</sup> (X = B, Al and Ga) situated at 1183, 498 and 476 cm<sup>-1</sup> corresponded to the asymmetrical stretch of bonds. And the data of the Al<sub>2</sub>P<sup>-</sup> obtained in this work is consistent with a previous study [11]. Interestingly, the two bent vibrations for the AIPC<sup>-</sup> (148 and 215 cm<sup>-1</sup>) are nondegenerate π vibrational modes which will lead to a Renner-Teller effect. As described in detail in [23–28], the Renner-Teller parameter *e* is a dimensionless constant which is used to describe the Renner-Teller splitting of a bending potential, where  $e = \frac{[(\omega^+)^2 - (\omega^-)^2]}{[(\omega^+)^2 + (\omega^-)^2]}$ .

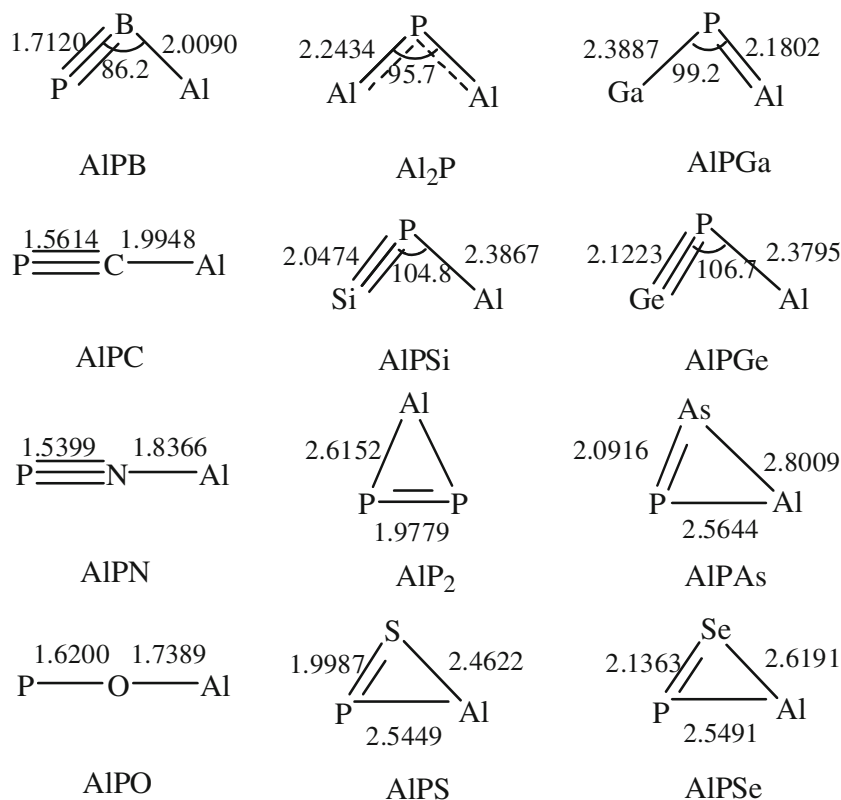
The actual experimental bend frequency is an averaged value obtained from  $\omega = \sqrt{(\omega^+)^2 + (\omega^-)^2} / 2$ , where  $\omega^+$  and  $\omega^-$  are the two nondegenerate bending vibrational frequencies determined theoretically. From Table 2, the Renner-Teller parameter  $e$  and the average vibrational frequency  $\omega$  of AIPC are 0.36 and  $185 \text{ cm}^{-1}$ , respectively, which indicates that the anion has high average bending frequency. In comparison, the IR activities of AIPX ( $X = \text{Si, Ge, N, P, As}$ ) are very weak, in good agreement with the CCSD(T) method for  $\text{AIP}_2^-$  [9]. Among the AIPX ( $X = \text{O, S and Se}$ ) species, there are three IR active vibrational modes for the AIPO (Table 2), the AIPS and  $\text{AIPSe}_1^-$  with the strongest IR peaks situated at  $612$  and  $684 \text{ cm}^{-1}$ , respectively. The Renner-Teller parameters  $e$  of the AIPS and  $\text{AIPSe}_1^-$  are very small (0.07 and 0.06), which show that the average bending frequencies  $\omega$  are  $152$  and  $139 \text{ cm}^{-1}$ , respectively.

### The stability and vibrational frequencies of AIPX

The geometries of the ground state structures of AIPX obtained by the B3LYP/cc-PVTZ method are showed in Fig. 2. All the AIPX ( $X = \text{B, Al and Ga}$ ) are bent structures with doublet ground states,  $^2A'$ ,  $^2B_2$  and  $^2A'$  (Table 4) for  $X = \text{B, Al and Ga}$ , respectively. In  $\text{Al}_2\text{P}$  the bond length of Al–P is  $2.243 \text{ \AA}$  and the bond angle of Al–P–Al is  $95.7^\circ$ , which are in good agreement with the results obtained from

the B3LYP/aug-cc-PVTZ [11]. The structures of AIPX ( $X = \text{C, Si and Ge}$ ) are analogous to their corresponding anions, in which all the P–X are typically triple bonds with orders of  $2.83\sim 2.98$ . The AIPC is stabilized by an ionic-typed Al–C bond and triple P–C bond, which can be reformulated as  $[\text{P}=\text{C}]^-\text{Al}^+$ . Removing an electron from the  $\text{AIPSi}^-$  and  $\text{AIPGe}^-$ , the P–Si and P–Ge bonds change to triple bonds accompanied by the breaking of the Al–Si and Al–Ge bond. In contrast, removing the single electron of the highest antibonding orbital in  $\text{AIPN}^-$  yields the ground state of AIPN, accompanied by the shortening of the P–N bond length ( $0.065 \text{ \AA}$ ) and increasing of the bond order (0.46). The bond distances of the P–P and Al–P in  $\text{AIP}_2$  are  $2.615$  and  $1.978 \text{ \AA}$ , respectively, and are consistent with those obtained at the B3LYP/aug-cc-PVTZ level [11]. Compared to those in the corresponding anions, the P–P and P–As bonds in the  $\text{AIP}_2$  and AIPAs are shorter while the Al–P and Al–As are longer. The AIPO is a linear structure ( $^3\Sigma$ ), in which the O atom locates in the middle position. The Al–O bond is a typical ionic bond with an ionic component of 93.3% and a bond order of 1.05. The electron charges on the Al and P atoms of the AIPO decrease from 0.33 to 0.83e and from 1.14 to 0.51e, respectively, and the electronegativity of the O atom is greater than that of the P atom, and the charge on the O atom increases from  $-1.19$  to  $-1.35e$ . The Al and the O form a typical ionic bond, which is in good agreement with the calculation of NBO as described above.

Fig. 2 The geometries of AIPX



**Table 4** The symmetry, electronic states, total energies and ZPEs (in Kcal/mol) of AIPX

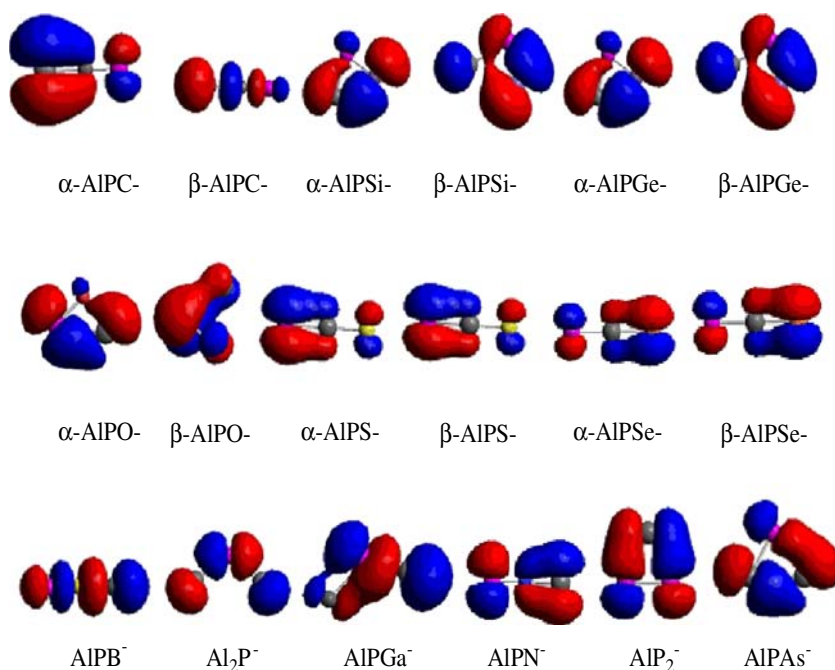
X	Symm.	State	Energy	ZPE
B	C <sub>S</sub>	<sup>2</sup> A'	-608.59843	2.47
Al	C <sub>2v</sub>	<sup>2</sup> B <sub>2</sub>	-826.26113	1.04
Ga	C <sub>S</sub>	<sup>2</sup> A'	-2508.76141	1.16
C	C <sub>∞v</sub>	<sup>1</sup> Σ <sup>+</sup>	-621.89192	2.88
Si	C <sub>S</sub>	<sup>1</sup> A'	-873.32865	1.57
Ge	C <sub>S</sub>	<sup>1</sup> A'	-2660.92504	1.35
N	C <sub>∞v</sub>	<sup>2</sup> Π	-638.58869	2.92
P	C <sub>2v</sub>	<sup>2</sup> B <sub>2</sub>	-925.20082	1.61
As	C <sub>S</sub>	<sup>2</sup> A'	-2819.78829	1.35
O	C <sub>∞v</sub>	<sup>3</sup> Σ <sup>-</sup>	-659.09952	2.48
S	C <sub>S</sub>	<sup>1</sup> A'	-982.06111	1.72
Se	C <sub>S</sub>	<sup>1</sup> A'	-2985.47318	1.42

As shown in Figs. 1 and 2, the bond lengths and bond angles of the AIPX differ significantly from those in the corresponding anions, for example, the most stable bent AlPO<sup>-</sup> turns to a linear structure after losing an electron. It is well known that the HOMO plays an important role in relaxing the structure after the system obtains/loses electrons; that is, the variation in the HOMO with respect to its bonding or anti-bonding nature influences the overall structure significantly, in contrast to the slight influence for a HOMO with non-bonding or weak-bonding nature. Thus, we show the pictures of the HOMOs of AIPX<sup>-</sup> (X = B, Al, Ga; C, Si, Ge; N, P, As; O, S and Se) clusters in Fig. 3 in order to explore the changes of the structures after losing an electron from the HOMO of the AIPX<sup>-</sup> clusters.

As shown in Fig. 3 and Tables 1 and 4, the ground states of the AIPX<sup>-</sup> (X = C, Si and Ge) are open-shell doublets, and the ground states of their neutral clusters are closed-shell singlets. Similarly, the β-HOMOs of the AIPX<sup>-</sup> (X = O, S and Se) are also conjugated π orbitals. The β-HOMO orbital is made of the Al and P atomic orbitals in AlPO<sup>-</sup>, thus the <sup>3</sup>Σ state of the AlPO results from losing an electron from the β-HOMO orbital. For the AIPX<sup>-</sup> (X = S, Se), the β-HOMO orbitals are made of the Al and S or the Al and Se atomic orbitals, and the bond distances of Al–S and Al–Se in the AIPX (X = S, Se) clusters are lengthened when an electron is removed from the β-HOMO orbital.

For the AIPX<sup>-</sup> (X = B, Al, Ga; N, P and As), the most stable structures of the closed-shell singlets lose an electron from the HOMO to form open-shell doublet structures. Obviously, when one of the electrons in the HOMO of the AIPX<sup>-</sup> (X = B, N, P and As) is detached, the bond length of the Al–X will increase and the bond angle of P–B–Al will change, which is consistent with the variation frequency calculated with the B3LYP/aug-cc-PVTZ method.

Unlike the AIPB<sup>-</sup> and AIPGa<sup>-</sup>, the IR activities of all of the vibrational modes of their neutral molecules are weak (see Table 5). The three vibrational frequencies of the Al<sub>2</sub>P are 70, 227 and 431 cm<sup>-1</sup> and are almost the same as those from the B3LYP/aug-cc-PVTZ method [11]. The vibrational frequency of the Al<sub>2</sub>P with a strong IR intensity situates at 227 cm<sup>-1</sup>. For the AIPX (X = C, Si and Ge), there are the two kinds of stretch vibrations for each species with strong IR activities. The two types of bend vibrational frequencies of the linear ground state AIPN are nondegenerate and will undergo the Renner-Teller effect. The Renner-Teller pa-

**Fig. 3** The HOMO of the most stable structures of AIPX<sup>-</sup>

**Table 5** The vibrational frequencies (in  $\text{cm}^{-1}$ ), vibrational mode and IR intensity (in  $\text{km/mole}$ ) of AIPX

X	Frequencies (mode and IR intensity)
B	212(a', 18), 534(a', 2), 980(a', 3)
Al	70(a <sub>1</sub> , 1), 227(b <sub>2</sub> , 235), 431(a <sub>1</sub> , 11)
Ga	76(a', 0), 254(a', 17), 483(a', 16)
C	99( $\pi$ , 0), 413( $\sigma$ , 123), 1403( $\sigma$ , 142)
Si	95(a', 1), 360(a', 99), 645(a', 70)
Ge	83(a', 1), 358(a', 84), 503(a', 83)
N	115( $\pi$ , 0), 143( $\pi$ , 6), 479( $\sigma$ , 77), 1305( $\sigma$ , 144)
P	155(b <sub>2</sub> , 2), 285(a <sub>1</sub> , 63), 687(a <sub>1</sub> , 1)
As	127(a', 2), 278(a', 55), 539(a', 1)
O	111( $\pi$ , 3), 500( $\sigma$ , 21), 1009( $\sigma$ , 464)
S	246(a', 9), 326(a', 62), 629(a', 12)
Se	198(a', 8), 309(a', 51), 490(a', 6)

parameter  $e$  and the average bending frequency  $\omega$  of the AIPN are 0.21 and  $130 \text{ cm}^{-1}$ , respectively, which shows that it has high averaged bending frequency. The three vibrational frequencies of the  $\text{Al}_2\text{P}$  are in good agreement with the results of the B3LYP/aug-cc-PVTZ study [11]; the biggest difference is only  $3 \text{ cm}^{-1}$ . For the  $\text{AlP}_2$  and AIPAs, the vibrational frequencies with strong IR intensity situate at about  $280 \text{ cm}^{-1}$ . The asymmetrical stretch vibration of AIPo, located at  $1009 \text{ cm}^{-1}$ , also has a very strong IR intensity. For the AIPs and AIPSe, the vibrational frequency with strong IR activity corresponds to the symmetrical stretch of the Al–P and Al–X (X = S and Se) bonds and situates at 326 and  $309 \text{ cm}^{-1}$ , respectively.

## The VDEs and AEAs

The VDEs of  $\text{AIPX}^-$  (X = B, Al, Ga; C, Si, Ge; N, P, As; O, S and Se) are obtained with the B3LYP and OVGf levels and the cc-PVTZ basis set, while the AEAs of the AIPX are performed at the B3LYP/cc-PVTZ level. Moreover, the VDEs and AEAs were obtained by the B3LYP/aug-cc-PVTZ//B3LYP/cc-PVTZ for the most stable structures of the  $\text{AIPX}^-$  and AIPX. The calculated data according to the following formulae are provided in Table 6.

$$\text{VDE} = E(\text{neutral at optimized anion geometry}) - E(\text{optimized anion}).$$

$$\text{AEA} = E(\text{optimized neutral}) - E(\text{optimized anion})$$

In Table 6, the first VDEs of the  $\text{AIPX}^-$  obtained by the B3LYP method are in good agreement with those of OVGf, and the VDEs of the  $\text{AlP}_2^-$  and  $\text{Al}_2\text{P}^-$  calculated by the OVGf method agree well with the experimental values (1.93 and 2.51 eV, respectively). For the  $\text{AIPX}^-$ , the VDE obtained from the B3LYP/cc-PVTZ method are 0.10–0.18 eV greater than that from the B3LYP/aug-cc-PVTZ. Despite the differences induced by the basis sets, the orders of the VDEs of the  $\text{AIPX}^-$  and AEAs of AIPX molecules at the B3LYP/cc-PVTZ and the B3LYP/aug-cc-PVTZ levels are consistent with each other:  $\text{C} < \text{N} < \text{O} < \text{Si} \approx \text{Ge} < \text{P} \approx \text{As} < \text{Al} = \text{Ga} < \text{B} < \text{S} \approx \text{Se}$  and  $\text{C} < \text{O} < \text{N} < \text{Si} \approx \text{Ge} < \text{P} \approx \text{As} < \text{B} < \text{Al} \approx \text{Ga} < \text{S} \approx \text{Se}$ , respectively. Similar to the

**Table 6** The VDEs and AEAs of  $\text{AIPX}^-$ 

X	VDE (eV)			AEA (eV)		
	X <sup>e)</sup>	A <sup>e)</sup>	B <sup>e)</sup>			
B	2.59 <sup>a)</sup> , 2.75 <sup>b)</sup>	<b>2.72<sup>e)</sup></b>	3.07	5.78	2.19	<b>2.32<sup>e)</sup></b>
Al	2.32, 2.55, 2.55 <sup>d)</sup>	<b>2.41</b>	2.81, 2.83 <sup>d)</sup>	3.03, 2.98 <sup>d)</sup>	2.30, 2.51 <sup>d)</sup> , 2.39 <sup>e)</sup>	<b>2.39</b>
Ga	2.32, 2.54	<b>2.41</b>	2.78	2.94	2.28	<b>2.37</b>
C	0.76	<b>0.91</b>			0.69	<b>0.84</b>
Si	1.83, 2.14	<b>1.95</b>			1.44	<b>1.56</b>
Ge	1.84, 2.14	<b>1.94</b>			1.42	<b>1.52</b>
N	1.30, 1.82	<b>1.46</b>			1.15	<b>1.31</b>
P	2.01, 2.21, 2.21 <sup>d)</sup>	<b>2.14</b>	2.45, 2.65 <sup>d)</sup>	4.93	1.78, 1.93 <sup>d)</sup> , 1.90 <sup>e)</sup>	<b>1.90</b>
As	2.08, 2.25	<b>2.20</b>	2.48	4.11	1.86	<b>1.97</b>
O	1.65, 1.65	<b>1.82</b>			1.01	<b>1.20</b>
S	3.82, 3.46	<b>3.95</b>			2.38	<b>2.52</b>
Se	3.79, 3.51	<b>3.89</b>			2.51	<b>2.63</b>

<sup>a)</sup> Results using B3LYP with the cc-PVTZ basis set (in plain).

<sup>b)</sup> Results using OVGf with the cc-PVTZ basis set (in italic).

<sup>c)</sup> Results using B3LYP with the aug-cc-PVTZ basis set (in bold)

<sup>d)</sup> Experimental values in Ref. [11].

<sup>e)</sup> Theoretical values in Ref. [11].

<sup>f)</sup> X, A and B are the first, second and third VDE, respectively.

GaPC<sup>-</sup> [20], the lowest AEA for the AlPC<sup>-</sup> exhibits that the AlPC is more stable than the other neutral molecules.

## Summary

The structures and electronic properties of the AlPX<sup>-</sup> and AlPX (X = B, Al, Ga; C, Si, Ge; N, P, As; O, S and Se) have been investigated by means of the B3LYP/cc-PVTZ and the B3LYP/cc-PVTZ methods. We find that the most stable neutral structures are linear: the PXAl for X = B, C and N and the PAIX for X = S and Se, while the most stable structures of the AlPX<sup>-</sup> (X = Al, Ga, Si, Ge, P, As and O) are bent. In addition, the geometries of the AlPX (X = C, N and O) are linear PXAl structures, while others are bent. The electronic states of both AlPN<sup>-</sup> and AlPO are  $3\sum^-$ . The P and the X atoms easily form strong P–X bonds except for the AlPS<sup>-</sup> and AlPSe<sup>-</sup>. The VDEs calculated by the OVGf method agree well with the results of the B3LYP method and experiments. The orders of the VDEs and AEAs of the AlPX<sup>-</sup> are C < N < O < Si ≈ Ge < P ≈ As < Al = Ga < B < S ≈ Se and C < O < N < Si ≈ Ge < P < As < B < Al ≈ Ga < S ≈ Se, respectively.

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