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An *ab initio* investigation on the vertical electron detachment energies of semiconductor-alkali binary anions E_nA^- ($A=K, Na, Li$; $E=Ge, Si$; $n=1-10$)

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Ground-state structures of semiconductor-alkali binary anions E_nA^- ($E=Ge, Si$; $A=K, Na, Li$; $n=1-10$) have been optimized using the second-order Møller–Plesset perturbation (MP2) method and their vertical detachment energies predicted employing the outer valence Green's function (OVGF) procedure. The calculated lowest detachment energies of E_nA^- anions composed of E_n^{2-} semiconductor Zintl anions and face-capping or edge-bridging A^+ alkali cations exhibit maximums around $n=2, 5, 9$, and 10 and minimums at $n=3$ and 7 , in overall agreement with the magic numbers observed for Ge_nK^- in time-of-flight mass spectroscopy. The lowest detachment energies of E_nA^- series increase from $A=K, Na$, to Li with increasing electronegativities of the alkali atoms and decreased $E-A$ ionic bond lengths. Small ternary $Ge_mSi_nK^-$ ($m+n\leq 6$) exhibit similar behavior to binary E_sK^- at the same sizes ($s=m+n$). © 2003 American Institute of Physics. [DOI: 10.1063/1.1617972]

Zintl anions E_n^{x-} composed of group-14 elements ($E=Ge, Sn, Pb$; $n=5, 9, 10$; $x=2, 3, 4$), with most of which stabilized in $[A-(2,2,2)-\text{ceypt}]_6^+$ ($A=K, Na$) complexes,¹⁻⁴ have been characterized in the past two decades, while the existence of their analogies in gaseous phases remain to be confirmed in experiments. Predicting the structural and stability relationship between Zintl anions in solids and corresponding gas-phase clusters has received considerable attention in recent years. Fassler *et al.*⁵ recently measured the time-of-flight (TOF) mass spectroscopies of binary Ge_nK^- anions and observed their magic number distributions at $n=5, 9$, and 10 and weaker peaks at $n=8, 11$, and 13 in the laser desorption of a K_4Ge_9 binary phase. In a recent paper,⁶ our group investigated the geometries and electron properties of Ge_n^{m-} and Ge_nK^- ($n=2-10$; $m=2-4$) in gaseous phases with the Becke's three parameter hybrid density functional with the Perdew/Wang expression (B3PW91) and confirmed that the Zintl–Klemm–Busmann (ZKB) principle is applicable to Ge_nK^- anions, implying that, by transferring the valence s electrons of K atoms to the Ge_n cores in Ge_nK^- , the Ge_n^{2-} Zintl dianions result. There have been no data available on silicon Zintl dianions Si_n^{2-} .

Anion photoelectron spectroscopies (PES) resulting from the vertical detachments of electrons from the ground states of anions to the ground and excited states of corresponding neutrals at the same geometries has proven to be very useful in probing the geometrical and electronic structures of both anions and neutrals and combining PES experiments with *ab initio* calculations offered a particular powerful approach in interpreting the spectra and characterizing structures of gas-phase clusters. The outer valence Green's

function procedure (OVGF) (Refs. 7, 8) was confirmed to be fairly accurate in interpreting the PES spectra of anions such as Al_4K^- ,⁹ Al_4C^- ,¹⁰ and XAl_3^- ($X=Si, Ge, Sn, Pb$).¹¹ To the best of our knowledge, there have been neither PES experimental nor theoretical studies reported to date on applying this approach to semiconductor-alkali binary anions E_nA^- ($E=Ge, Si$; $A=K, Na, Li$) which contain an important class of E_n^{2-} Zintl anions. It is our view that a systematic theoretical investigation on the electron detachment energies of E_nA^- and their ternary and quaternary analogies based on reliable *ab initio* structures is desirable at this stage.

In this work, we present an *ab initio* investigation on the ground-state structures and vertical detachment energies (VDEs) of E_nA^- binary cluster anions containing semiconductor cores ($E=Si, Ge$; $A=K, Na, Li$; $n=1-10$). Comparative studies on small ternary $Ge_mSi_nK^-$ ($m+n\leq 6$) and quaternary $GeSi_mC_nK^-$ ($m, n=1, 2$) anions are also performed. Initial geometries are taken from our earlier optimized structures obtained for Ge_nK^- at B3PW91/6-311G(d) (Ref. 6) or arbitrarily constructed to explore the configuration space more extensively. Various initial structures are optimized at B3PW91/6-311+G(d) including both the polarization and diffuse functions and the normal vibration frequencies at the optimized geometries checked for imaginary frequencies at the same theoretical level. The lowest-energy structures are further refined at MP2(FULL)/6-311+G(d) level with all electrons included (FULL) in electron correlation calculation for the whole Si_nK^- series with $n=1-10$, Ge_nK^- with $n=1-4$, ternary $Ge_mSi_nK^-$ with $m+n\leq 6$, and small quaternary systems $GeSi_mC_nK^-$ ($m, n=1, 2$). The MP2(FC)/6-31+G(d)

TABLE I. The calculated restricted OVGF vertical electron detachment energies (eV) of $E_n K^-$ ($E=Ge$ and Si), $Ge_m Si_n K^-$ ($m+n \leq 6$), and $GeSi_m C_n K^-$ ($m, n=1,2$) at MP2 structures. Orbital assignments are provided and pole strengths over 0.85 indicated in parentheses. Basis sets used are 6-311+G(d) and all electrons are included in OVGF correlation calculations except specifically noticed.

	$C_{2v} Ge_2 K^-$		$C_{2v} Si_2 K^-$		$C_s GeSiK^-$	
b_1	1.54(0.91)		1.48(0.91)		a''	1.51(0.91)
a_1	1.73(0.88)		1.65(0.89)		a'	1.70(0.89)
a_1	1.54(0.89)		1.34(0.89)		a'	1.45(0.89)
	$C_{2v} Ge_3 K^-$	$C_{2v} Si_3 K^-$	$C_{2v} GeSi_2 K^-$		$C_{3v} Ge_3 K^-$	$C_{3v} Si_3 K^-$
a_1	1.35(0.88)	1.01(0.89)	1.16(0.89)	e	1.23(0.88)	1.08(0.88)
b_2	1.84(0.89)	1.48(0.89)	1.42(0.89)	a_1	2.61(0.89)	2.67(0.88)
b_1	2.42(0.96)	2.45(0.90)	2.37(0.90)	a_1	2.29(0.87)	2.36(0.87)
a_1	2.50(0.88)	2.89(0.88)	2.31(0.88)			
	$C_s Ge_4 K^-$ (FC/6-311+G(d))		$C_s Si_4 K^-$		$C_s GeSiC_2 K^-$	$C_s Ge_2 Si_2 K^-$ (FC/6-311+G(d))
a'	1.61(0.88)		1.50(0.88)	a'	1.08(0.88)	1.63(0.88)
a''	1.82(0.88)		1.70(0.89)	a''	1.91(0.89)	1.66(0.88)
a'	2.55(0.88)		2.49(0.88)	a'	2.21(0.89)	2.50(0.88)
a''	2.56(0.88)		2.68(0.88)	a'	3.03(0.88)	2.60(0.88)
a'	2.95(0.87)		3.03(0.87)	a''	3.48(0.88)	2.99(0.87)
	$C_s Ge_5 K^-$ (FC/6-31+G(d))		$C_s Si_5 K^-$ (FC/6-311+G(d))		$C_s GeSi_2 C_2 K^-$ (FC/6-31+G(d))	
a'	2.30(0.89)		2.19(0.89)	a'	2.21(0.89)	
a''	2.38(0.89)		2.31(0.89)	a''	1.84(0.89)	
a'	2.27(0.89)		2.24(0.89)	a'	2.88(0.89)	
a'	2.79(0.89)		3.05(0.89)	a'	2.67(0.88)	
a''	2.94(0.89)		3.08(0.89)	a'	3.44(0.88)	
a'	3.45(0.88)		3.48(0.87)	a''	3.92(0.89)	
	$C_{3v} Ge_6 K^-$ (FC/6-31+G(d))		$C_{3v} Si_6 K^-$ (FC/6-311+G(d))		$C_{3v} Ge_3 Si_3 K^-$ (FC/6-31+G(d))	
a_1	2.03(0.89)		2.04(0.89)		2.03(0.89)	
e	2.17(0.89)		2.18(0.89)		2.17(0.89)	
e	3.80(0.89)		4.19(0.88)		3.97(0.88)	
a_1	3.83(0.89)		4.18(0.88)		3.96(0.88)	
a_1	4.41(0.87)		4.73(0.86)		4.59(0.87)	
	$C_s Ge_7 K^-$ (FC/6-31+G(d))		$C_s Si_7 K^-$ (FC/6-311G(d))			
a'	1.72(0.89)	a'	1.45(0.90)			
a''	2.83(0.89)	a'	2.76(0.89)			
a'	2.92(0.89)	a''	2.81(0.89)			
a'	2.82(0.89)	a'	2.90(0.89)			
a''	2.88(0.89)	a''	2.91(0.89)			
a''	4.10(0.89)	a''	4.41(0.89)			
a'	4.18(0.90)	a'	4.43(0.89)			
a'	4.50(0.85)	a'	4.54(0.87)			
	$C_1 Ge_8 K^-$ (FC/6-31G(d))		$C_1 Si_8 K^-$ (FC/6-31G(d))			
a	2.27(0.91)		2.23(0.90)			
a	2.59(0.89)		2.67(0.89)			
a	2.72(0.90)		2.68(0.89)			
a	2.90(0.90)		2.86(0.90)			
a	3.34(0.90)		3.30(0.90)			
a	3.41(0.90)		3.61(0.90)			
a	3.92(0.89)		3.95(0.89)			
a	4.16(0.89)		4.43(0.89)			
a	4.53(0.87)		4.87(0.87)			
	$C_{3v} Ge_9 K^-$ (FC/6-31G(d))		$C_{3v} Si_9 K^-$ (FC/6-31G(d))			
a_1	2.42(0.91)	a_1	2.60(0.91)			
e	2.75(0.91)	e	2.83(0.90)			
e	3.35(0.90)	e	3.39(0.89)			
a_2	3.41(0.91)	a_1	3.59(0.90)			
a_1	3.72(0.91)	e	3.60(0.91)			
e	3.60(0.91)	a_2	3.75(0.90)			
a_1	5.08(0.94)	a_1	5.42(0.90)			

TABLE I. (Continued.)

	C_s Ge ₁₀ K ⁻ (FC/6-31G(d))		C_s Si ₁₀ K ⁻ (FC/6-31G(d))
a'	2.72(0.91)	a'	2.75(0.91)
a'	2.74(0.91)	a'	2.85(0.91)
a''	2.87(0.91)	a''	2.94(0.91)
a'	3.20(0.91)	a'	3.12(0.91)
a'	3.72(0.91)	a''	3.64(0.90)
a'	3.88(0.91)	a'	3.69(0.90)
a''	3.92(0.92)	a'	3.73(0.90)
a''	3.97(0.91)	a''	3.88(0.91)
a''	4.25(0.92)	a'	4.48(0.91)
a'	4.57(0.92)	a''	4.58(0.91)
		a'	5.85(0.92)

method with the frozen core approximation (FC) and a smaller bases is employed for Ge_{*n*}K⁻ with *n* = 5–10. The optimized structures at various theoretical levels follow the ZKB principle and agree well with one another. Vertical electron detachment energies at the MP2 structures are calculated using the OVGf approach with basis sets indicated in Table I. It is confirmed that, for small clusters containing only Si and K atoms, the OVGf(FULL) method and the OVGf(FC) procedure produce essentially the same VDEs. It is also checked that the derivations produced for small Ge_{*n*}K⁻ clusters with the frozen core approximation relative to that with all electrons included are also within an acceptable range. The frozen core approximation, which is much less computationally demanding and commonly accepted in electron correlation calculations,^{9–11} is utilized for big anions in this work as indicated in Table I. Limited by available computation resources, diffuse functions are excluded in OVGf calculations for clusters with more than 7 Ge and Si atoms. All calculations in this work are performed utilizing the GAUSSIAN 03 package.¹²

The optimized MP2 ground-state structures are depicted in Fig. 1 with necessary bond parameters indicated for Si_{*n*}K⁻ in Fig. 1(a) and small ternary Ge_{*m*}Si_{*n*}K⁻ and quaternary GeSi_{*m*}C_{*n*}K⁻ anions in Fig. 1(b). The MP2 geometries and bond parameters of Ge_{*n*}K⁻ (not shown in Fig. 1) agree well with our earlier B3PW91 results⁶ in most cases, except Ge₃K⁻, for which the distorted planar C_{2*v*} rhombus structure is found to be 0.307 eV lower in energy than the C_{3*v*} trigonal prism reported before.⁶ Similarly, C_{2*v*} Si₃K⁻ lies 0.339 eV lower in energy than C_{3*v*} Si₃K⁻. As will be discussed below, the peripheral σ bonds play a critical role in providing extra stability to planar C_{2*v*} E₃A⁻ over the C_{3*v*} prism. It can be seen from Fig. 1 that the E_{*n*}²⁻ Zintl dianion structural units are well maintained in E_{*n*}K⁻ with alkali cations A⁺ located at the face-capping or edge-bridging positions. Mulliken charge distributions indicate that the valence electrons of alkali atoms have been partially transferred to E_{*n*} cores and the E_{*n*}-A interactions are basically ionic. For example, the Si₅²⁻ and Ge₅²⁻ trigonal-bipyramid structures are kept in C_{*s*} Si₅K⁻ and Ge₅K⁻ in which the face-capping K atoms possess the positive charges of +0.735*e* and +0.762*e*, respectively. Similarly, the capping K atoms of C_{*s*} Ge₇K⁻ and Si₇K⁻ carry the positive charges of +0.951 and

+0.564*e*. Ternary Ge_{*m*}Si_{*n*}K⁻ take capped or bridged structures similar to corresponding E_{*s*}K⁻ with the same sizes (*s* = *m* + *n*) with K atoms bonded with neighboring Si. Typical situations are shown for GeSi₂K⁻, Ge₂Si₂K⁻, and Ge₃Si₃K⁻ in Fig. 1(b). The Ge–C–Si bond angle in quaternary GeSiC₂K⁻ is reduced to 89° from 113° in neutral GeSiC at MP2 and 126° at a configuration interaction with all single and double substitutions method (CISD(full)).¹³ GeSiC₂K⁻ is an edge-bridged butterfly with the bridging K connected to the two transannular C atoms while GeSi₂C₂K⁻ takes a capped trigonal bipyramid structure (C_{*s*}) with the capping K bonded to the two equatorial C atoms and the two axial Si.

The calculated detachment energies with pole strengths greater than 0.85 for E_{*n*}K⁻ (E = Ge and Si), Ge_{*m*}Si_{*n*}K⁻, and GeSi_{*m*}C_{*n*}K⁻ are tabulated in Table I with corresponding orbital assignments indicated. For E₃K⁻, the results for both the planar C_{2*v*} and trigonal pyramid C_{3*v*} are presented with the former having four separated detachment energies while the latter has three. The other difference is that the highest VDEs of the planar structures are higher than that of corresponding trigonal pyramids. These differences provide strong theoretical evidence in characterizing the two isomers in future PES experiments. We discuss the bonding feature of C_{2*v*} Ge₃K⁻ below in details. The frontier molecular orbitals (MOs) of Ge₃K⁻ involve, in a qualitative view, the outer valence *s* orbital of K atom, the converted *sp*² (in this case *sp_xp_y*) hybrid orbitals of the two transannular Ge atoms, and the *sp* (*sp_x*) hybrid and nearly pure *p_y* orbitals of the Ge atom in diagonal with K. The left three *p_z* atomic orbitals of the three Ge atoms form a delocalized three-centered π MO perpendicular to the molecular plane. Orbital analyses show that the four separated VDEs of Ge₃K⁻ correspond to the four doubly occupied frontier MOs of the system depicted in Fig. 2(a): the lowest detachment energy at 1.35 eV arises from the vertical detachment of an electron from the σ -typed HOMO (*a*₁) composed of mainly the *sp*² of transannular Ge atoms and *sp* of diagonal Ge and partially the *s* valence orbital of K, the second lowest at 1.84 eV from the weak σ -typed HOMO-1 (*b*₂) composed of the *sp*² of transannular Ge and *p_y* of diagonal Ge, the third at 2.42 eV from the delocalized π -typed HOMO-2 (*b*₁) which is an effective delocalized orbital purely composed of contributions from the

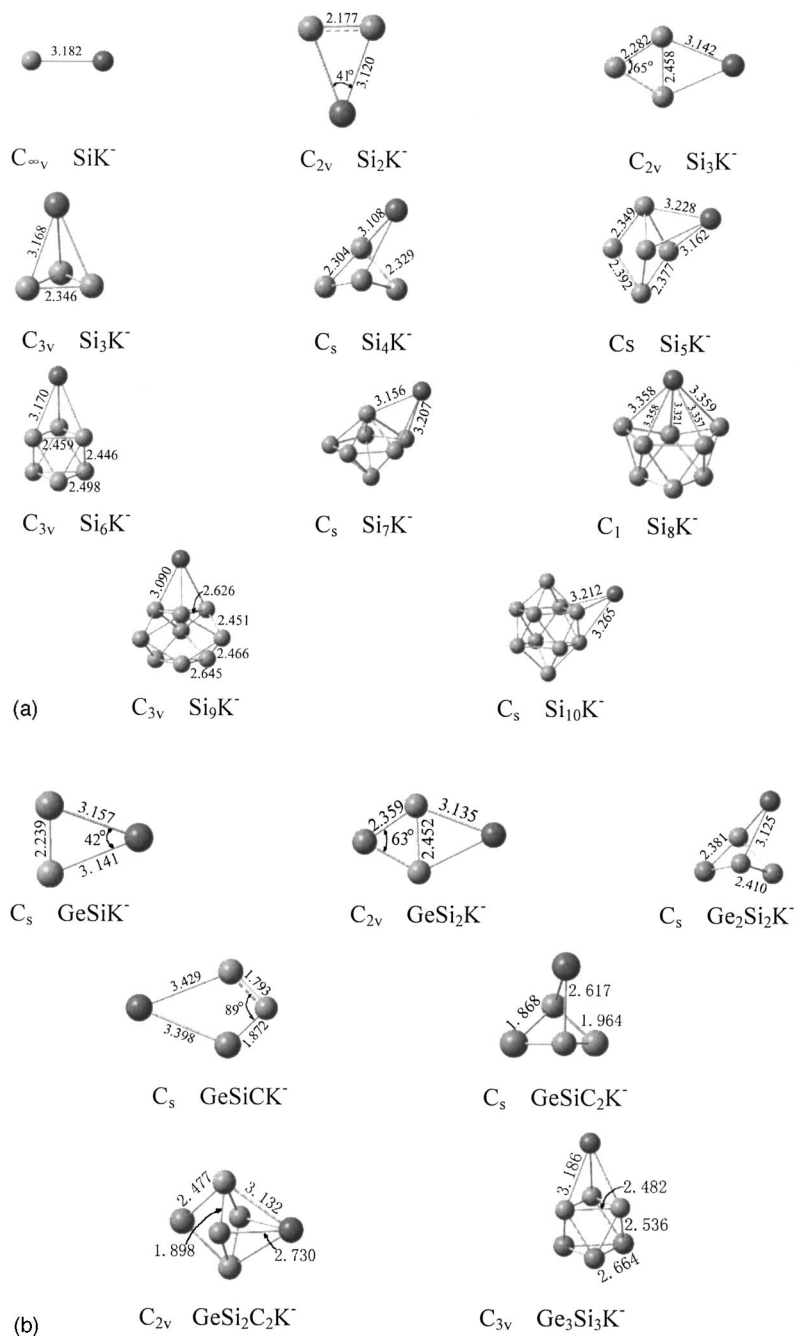


FIG. 1. (a) Optimized structures of E_nK^- anions at the MP2 level ($E=Ge, Si$) with necessary bond parameters indicated for Si_nK^- at MP2(full)/6-311+G(d) level. (b) Optimized structures of ternary $Ge_mSi_nK^-$ ($m+n \leq 6$) and quaternary $GeSi_mC_nK^-$ ($m, n=1, 2$) at the MP2(full)/6-311+G(d) level with necessary bond parameters indicated.

three p_z orbitals of Ge atoms, and the fourth at 2.50 eV from HOMO-3 (a_1) purely composed of the sp^2 of two transannular Ge atoms and sp of diagonal Ge. The two equivalent Ge–K peripheral bond lengths (3.225 Å) in C_{2v} Ge_3K^- are shorter than the three equivalent Ge–K bonds (3.237 Å) in C_{3v} Ge_3K^- and the two Ge–Ge peripheral interactions (2.424 Å) in the former are much stronger than that (2.513 Å) in the latter. It should be noticed that a weaker Ge–Ge transannular interaction (2.665 Å) also exists in planar Ge_3K^- , similar to the Si–Si transannular bond shown for Si_3K^- in Fig. 1(a). All together with the effective π bond perpendicular to the molecular plane, this bonding pattern provides an extra stability to the planar arrangement of Ge_3K^- over the C_{3v} prism. Similar bonding features exist in other E_3A^- anions. Generally speaking, the predicted de-

tachment energies listed in Table I lie within the range of 1.0–5.0 eV, covered by the energies of conventional detachment laser wavelengths 266 nm (4.661 eV) and 355 nm (3.496 eV). The lowest two calculated VDEs of GeK^- , SiK^- , and $GeSiCK^-$, which possess the values lower than 1.0 eV, are not included in Table I, considering that fact that the pole strengths of these detachment processes are too low (below 0.81) in the OVGf calculation. No improvement was achieved utilizing a bigger basis 6-311+G(3df). For clusters with bigger sizes and lower symmetries, more detachment energy lines with considerable pole strengths are found to lie close to one another as can be seen from Table I and their PES spectra expected to overlap heavily in experiments.

Figure 3 shows the lowest vertical detachment energies (LVDEs) of Ge_nK^- and Si_nK^- in the size range of n

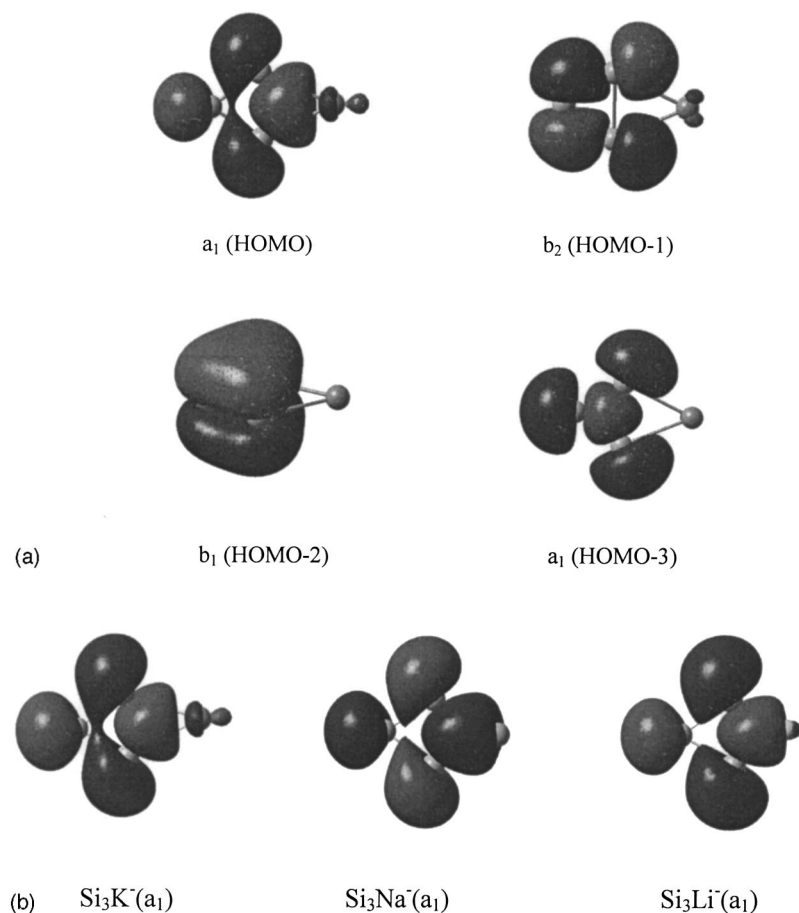


FIG. 2. The molecular orbital pictures of E_3K^- : (a) the HOMO, HOMO-1, HOMO-2, and HOMO-3 of Ge_3K^- and (b) the HOMOs (a_1) of Si_3K^- , Si_3Na^- , and Si_3Li^- .

$=1-10$. LVDEs arise from the vertical detachment processes with the lowest energies required. Figure 3 clearly shows that the LVDEs of both Ge_nK^- and Si_nK^- vary in the same trend with maximums around $n=2, 5, 9$, and 10 and minimums at $n=3$, and 7 . The predicted high VDE values at $n=5, 9$, and 10 and the relatively higher VDE values at $n=8$ generally agree well with the magic numbers observed for Ge_3K^- in TOF mass spectroscopy at $n=5, 9$, and 10 and the weaker peak at $n=8$.⁵ Figure 4 compares the variation trend of the calculated LVDEs of Si_nK^- , Si_nNa^- , and Si_nLi^- with the same Si_n^{2-} cores and clearly shows that the LVDEs of these anions vary in parallel curves and possess maximums and minimums at the same positions. The LVDEs of Si_nA^- increase systematically from $A=\text{K}, \text{Na}$, to Li , in line with the chemical expectation that, the more electronegative the alkali atoms, the more difficult to detach electrons from the systems. The fact that the calculated positive Mulliken charges decrease from K, Na , to Li in Si_nA^- series also supports this conclusion. Si_nA^- anions contain similar Si_n^{2-} cores, but their $\text{Si}_n\text{-A}$ bonding distances decrease dramatically from $A=\text{K}, \text{Na}$, to Li , with the typical $\text{Si}_n\text{-K}$ bond lengths being around 3.2 , $\text{Si}_n\text{-Na}$ around 2.8 , and $\text{Si}_n\text{-Li}$ around 2.4 Å. The bonding difference in the HOMOs of $E_n\text{A}^-$ series mainly comes from the difference in the bonding abilities of the alkali atoms A . Figure 2(b) compares the HOMO orbital pictures of Si_3A^- series ($A=\text{K}, \text{Na}, \text{Li}$). The $\text{Si}_n\text{-A}$ interactions in $E_n\text{A}^-$ are all basically ionic bonds, but with alkali atoms changing from K, Na , to Li and the decreasing of

$E_n\text{-A}$ bond lengths, the outer valence s orbitals of alkali atoms participate in the formation of HOMOs at increasing levels.

It can be seen from Table I that small ternary $\text{Ge}_m\text{Si}_n\text{K}^-$ anions possess detachment energies close to corresponding $E_s\text{K}^-$ ($s=m+n$) and their VDE values vary in similar patterns, a phenomenon resulting from the fact that $\text{Ge}_m\text{Si}_n\text{K}^-$ are structurally very close to $E_s\text{K}^-$ because Ge and Si have only 4% difference in atomic radii. But the highest VDEs of small $\text{GeSi}_m\text{C}_n\text{K}^-$ ($m=1,2; n=1,2$) quaternary systems are significantly higher than that of corresponding

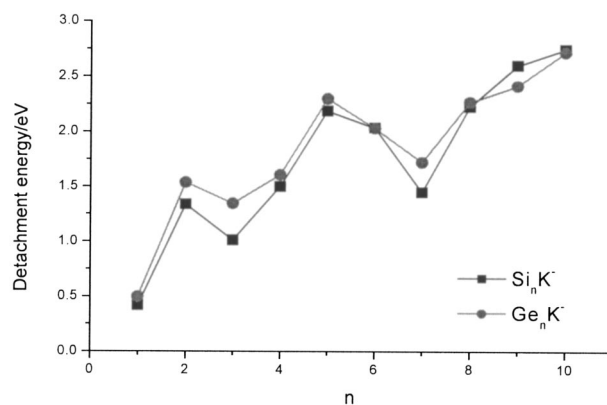


FIG. 3. Variation of the lowest detachment energies of Ge_nK^- (circles) and Si_nK^- (squares) with cluster size n .

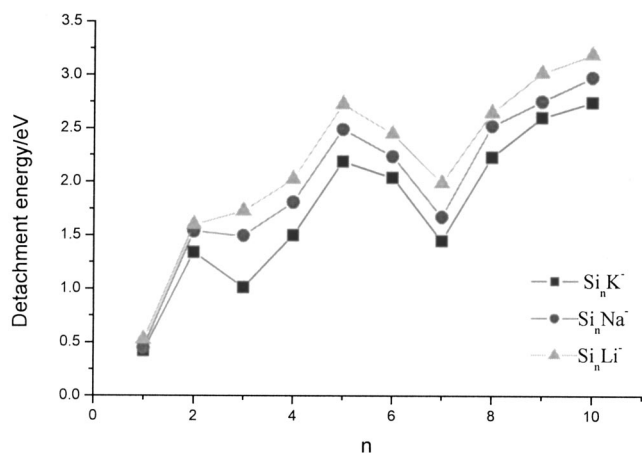


FIG. 4. Comparison of the lowest detachment energies of Si_nK^- (squares), Si_nNa^- (circles), and Si_nLi^- (triangles) with clusters size n .

$E_s\text{K}^-$ of the same size and their irreducible orbital representations are different from that of the latter. Introduction of the highly electronegative C atoms into semiconductor-alkali mixed anions causes dramatic changes to the energy distribution of their frontier MOs.

In the current work, we have presented an *ab initio* investigation on the structural properties and vertical detachment energies of small semiconductor-alkali mixed anions and revealed the detachment energy variation trend with both cluster sizes and capping alkali atoms. Further work on big-

ger binary E_nA^- ($n \geq 11$) anions is on the way. Most of the calculated *ab initio* VDEs are within the energy range of the conventional detachment laser wavelengths and therefore possible to be observed in conventional PES. We believe that Zintl anions E_n^{2-} existing in E_nA^- could be synthesized in materials such as E_nA_2 or E_nAA' and a combination of reliable theoretical predictions and future PES experiments may produce complete spectral assignments and structural characterizations of these anions in gas phase at the *ab initio* level.

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