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Observation of Triatomic Species with Conflicting Aromaticity: $AlSi_2^-$ and $AlGe_2^-$

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We created mixed triatomic clusters, $AlCGe^-$, $AlSi_2^-$, and $AlGe_2^-$, and studied their electronic structure and chemical bonding using photoelectron spectroscopy and ab initio calculations. Excellent agreement between theoretical and experimental photoelectron spectra confirmed the predicted global minimum structures for these species. Chemical bonding analysis revealed that the $AlSi_2^-$ and $AlGe_2^-$ anions can be described as species with conflicting (σ-antiaromatic and π-aromatic) aromaticity. The $AlCGe^-$ anion represents an interesting example of chemical species which is between classical and aromatic.

The heavier congeners of carbon with a formal triple bond (XMM′X, where M and M′ are Si, Ge, Sn, and Pb and X is a monovalent ligand) have remarkably rich potential energy surfaces with many local minima close in energy to the global minimum.[1,2] In contrast, C_2H_2 (acetylene) has the potential energy surface with the global minimum being significantly more stable than other local minima. Electropositive substitution of H in the HMM′H species can bring additional features to the chemical bonding in these species.[3] Previously, we have studied AlC_2^- and $AlCSi^-$, which can be viewed as Al^+ bonded to a C_2^{2-} or CSi^{2-} group.[3c] Chemical bonding in the two isomers of AlC_2^- with the π- (global minimum) and σ-coordination of Al to C_2 can be described as being rather ionic between Al^+ (with a lone pair) and C_2^{2-} which in turn can be described by a Lewis structure with a triple carbon−carbon bond (see the NBO analyses in the Supporting Information). Ionic bonding between Al^+ and C_2^{2-} favors a high symmetry (C_{2v}) structure. When both carbon atoms in AlC_2^- are substituted by Si or Ge, a significant electron delocalization between all three atoms occurs (the covalent character of bonding between Al and Si or Ge increases), and the chemical bonding in the resulting $AlSi_2^-$, $AlSiGe^-$, and $AlGe_2^-$ species cannot be described the same way as in AlC_2^- (see the Supporting Information). That delocalization results in the low symmetry C_s ($^1A'$) structures (Figure 1). Electron delocalization can be described in terms of aromaticity or antiaromaticity. The name "aromatic compound" was initially bestowed on benzene, its derivatives, and related compounds because of their aroma. Today, the terms "aromatic" and "aromaticity" (antiaromaticity) are used to describe cyclic, planar, and conjugated molecules possessing $4n + 2$ ($4n$) π-electrons and having specific chemical and structural stability. In addition to widely accepted π-aromaticity and π-antiaromaticity, σ-aromaticity and σ-antiaromaticity were also introduced in chemistry (see the detailed discussion in ref 4).

In the current communication, we present a photoelectron spectroscopy study of $AlCGe^-$, $AlSi_2^-$, and $AlGe_2^-$ and ab initio calculations at the B3LYP/6-311+G*, TD-B3LYP/6-311+G(2df), RCCSD(T)/6-311+G*, RCCSD(T)/6-311+G(2df), and ROVGF/6-311+G(2df) levels of theory.

The experiment was performed using a magnetic-bottle time-of-flight photoelectron spectroscopy apparatus equipped with a laser vaporization cluster source.[5] The $AlCGe^-$, $AlSi_2^-$, and $AlGe_2^-$ anion clusters were produced using Al/C/Ge, Al/Si, and Al/Ge mixed targets, respectively. The cluster anions of interest were mass-selected before photodetachment by one of two laser beams: 355 nm (3.496 eV) and 266 nm (4.661 eV). Photoelectron spectra were measured using the magnetic-bottle time-of-flight photoelectron analyzer with an electron kinetic energy resolution of $\Delta E_k/E_k \approx 2.5\%$, that is, 25 meV for 1 eV electrons. The spectrometer was calibrated with the known spectra of Cu^- and Rh^-.

Theoretically, we first performed the search for the global minima on the potential energy surfaces using the B3LYP method with the 6-311+G* basis sets. Geometries and frequencies for local minima were refined using the RCCSD(T) method with the same basis sets. Relative energies were evaluated at the RCCSD(T)/6-311+G(2df)//RCCSD(T)/6-311+G* level of theory. We also ran CASSCF(12,12)/6-311+G* calculations for $AlSi_2^-$ and $AlGe_2^-$ in order to probe the validity of the one-electron approximation. These calculations showed that the Hartree−Fock configurations were dominant ($C_{HF} = 0.914$ ($AlSi_2^-$) and $C_{HF} = 0.912$ ($AlGe_2^-$)) among 427 350 configurations. Thus, methods based on the one-electron approximation (B3LYP, CCSD(T), ROVGF) should perform adequately.

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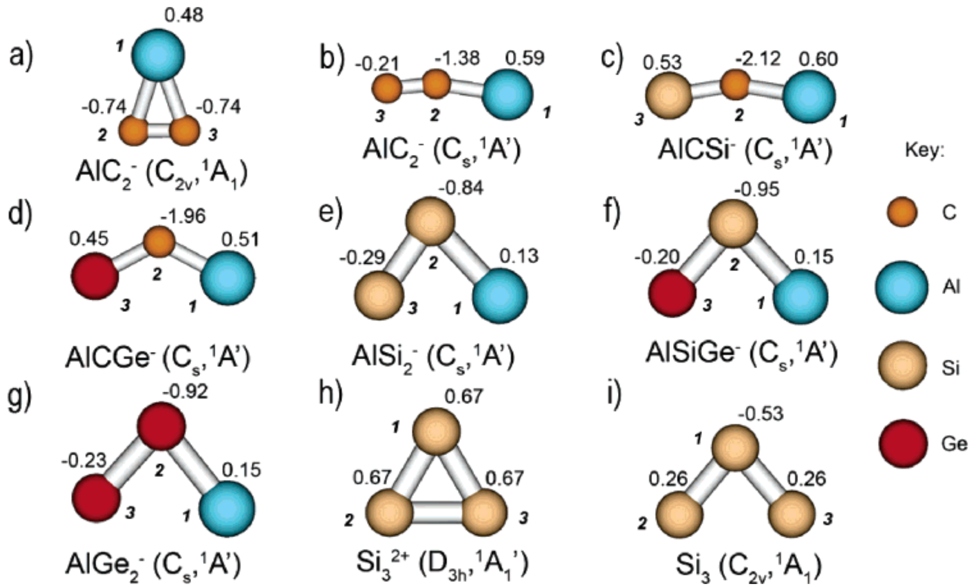

Figure 1. Computationally found isomers for AlC_2^-, $AlCSi^-$, $AlCGe^-$, $AlSi_2^-$, $AlSiGe^-$, $AlGe_2^-$, Si_3^{2+}, and Si_3. Effective atomic charges were calculated using NBO analysis.

TABLE 1: Experimental ADEs and VDEs of $AlCGe^-$, $AlSi_2^-$, and $AlGe_2^-$ Compared with Computed VDEs at Different Levels of Theory

	feature	ADE[a] (eV)	VDE (eV)	MO	ROVGF (eV)	TD-B3LYP (eV)	RCCSD(T) (eV)
$AlCGe^-$	X	2.41 ± 0.03	2.58 ± 0.03	5a′	2.688 (0.884)	2.430[b]	2.625
	A		3.07 ± 0.02	1a″	3.194 (0.877)	2.884[b]	3.105
				4a′	3.034 (0.879)	2.930[b]	
$AlSi_2^-$	X	2.19 ± 0.03	2.33 ± 0.03	5a′	2.308 (0.878)	2.285	2.323
	A		2.85 ± 0.02	1a″	2.913 (0.873)	2.725	2.955
				4a′	2.761 (0.863)	2.786	
$AlGe_2^-$	X	2.17 ± 0.03	2.32 ± 0.03	5a′	2.294 (0.877)	2.277	2.333
	A		2.76 ± 0.02	1a″	2.698 (0.877)	2.566	2.773
				4a′	2.746 (0.870)	2.672	

[a] Adiabatic detachment energy (ADE) also represents the electron affinity of the corresponding neutral molecule. [b] At the CCSD(T)/6-311+G* geometry.

Theoretical vertical detachment energies (VDEs) were calculated using the RCCSD(T)/6-311+G(2df), ROVGF/6-311+G(2df), and TD-B3LYP/6-311+G(2df) levels of theory. Natural bond orbital (NBO) analysis was employed for detailed chemical bonding examination. Molecular orbitals (MOs) were calculated at the RHF/6-311+G* level of theory. All HF, B3LYP, and RCCSD(T) (for closed shell species) calculations were performed using the Gaussian 03 program.[6] The ROVGF calculations were done using the Gaussian 98 package.[7] The RCCSD(T) (for open shell species) calculations were done using the MOLPRO-2000.1 package.[8] MO pictures were made using the MOLDEN3.4 program.[9]

The local minimum structures are presented in Figure 1. Their optimized geometries, harmonic vibrational frequencies, and total energies are summarized in the Supporting Information. For all of the anions, linear structures were found to be second-order saddle points. We found only one type of minimum structure, C_s ($1a'^2\, 2a'^2 3a'^2 4a'^2 1a''^2 5a'^2$), as shown in Figure 1. Surprisingly, the cyclic C_{2v} ($^1A_1$) structure, which was the global minimum for AlC_2^- (Figure 1a), was found to be a first-order saddle point for both $AlSi_2^-$ and $AlGe_2^-$, though the potential energy surfaces are rather flat.

To verify the obtained global minimum structures, we compared the calculated VDEs of $AlSi_2^-$, $AlGe_2^-$, and $AlCGe^-$ with the experimental data in Table 1. As shown in Figure 2, the photoelectron spectra for all three species are similar, each displaying two bands (X and A). The calculated VDEs at all three levels of theory are in excellent agreement with the experimental data, confirming the predicted global minimum structures. The VDEs calculated at B3LYP/6-311+G(2df) were found to be somewhat lower.

The unusual global minimum structures of $AlSi_2^-$, $AlSiGe^-$, and $AlGe_2^-$ suggest new modes of chemical bonding, different from that in AlC_2^-. Straightforward application of the NBO analysis to $AlSi_2^-$, $AlSiGe^-$, and $AlGe_2^-$ shows that there is deviation from the two-center two electron (2c−2e) picture for all three species. The occupation numbers (ONs) are just 1.80 e for the Si−Si, Si−Ge, and Ge−Ge bonds, and Al acquires three artificial lone pairs with ON = 0.54, 0.22, and 0.10 |e| (see the Supporting Information). In an ideal 2c−2e bond or an ideal lone pair, the ON should be 2.00 |e|. These deviations from the ideal 2c−2e bonding picture are manifestations of appreciable electron density delocalization, and in fact, these anions are π-aromatic and σ-antiaromatic systems. To prove this bonding description, let us first consider the D_{3h} Al_3^- anion, which has two electrons less than $AlSi_2^-$ and $AlGe_2^-$. It was recently shown[10] that Al_3^- is a doubly aromatic system with one completely delocalized σ-MO ($2a_1'$) and one completely delocalized π-MO ($1a_2''$). Dixon and co-workers[10b] have shown that Al_3^- has a very high resonance energy (between 56 and 79 kcal/mol), confirming the double aromaticity in Al_3^-. The various criteria of aromaticity for clusters of main group elements including metals have been recently reviewed.[11] In the present article, we will use only two criteria, MO analysis and geometry, because it is very difficult to find appropriate reference molecules for estimation of the resonance energy. We

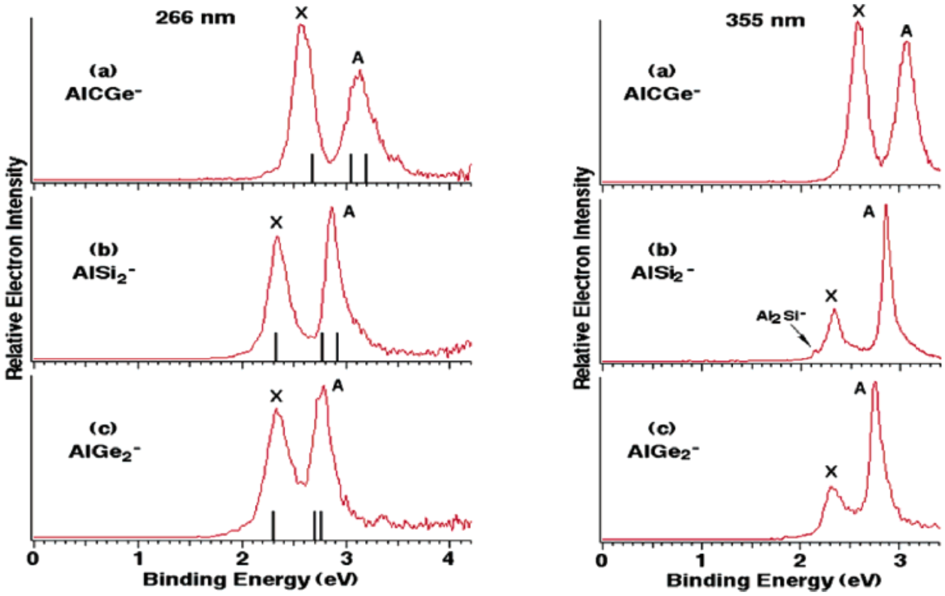

Figure 2. Photoelectron spectra of AlCGe$^-$ (a), AlSi$_2^-$ (b), and AlGe$_2^-$ (c) at 355 nm (3.496 eV) and 266 nm (4.661 eV). The vertical bars represent the calculated VDEs for the global minimum for each species at the ROVGF level of theory (Table 1).

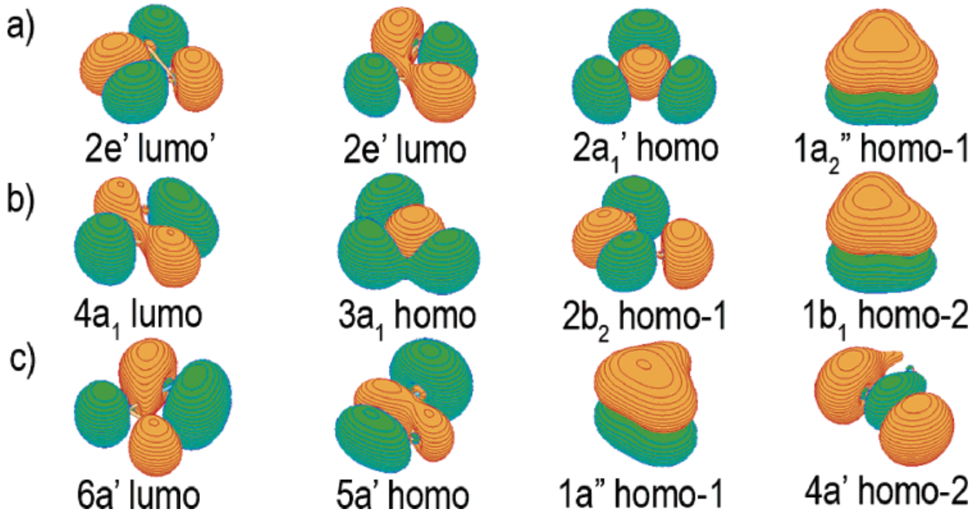

Figure 3. Molecular orbitals of Si$_3^{2+}$ (a), Si$_3$ (b), and AlSi$_2^-$ (c).

calculated an isoelectronic D_{3h} ($^1A_1'$) Si$_3^{2+}$ dication as another example of double aromaticity (Figure 1h). Its MOs are shown in Figure 3a. The two upper bonding MOs are the same as those in Al$_3^-$, and thus, Si$_3^{2+}$ is indeed doubly aromatic. When two additional electrons occupy the lowest unoccupied molecular orbital (LUMO) of Si$_3^{2+}$, forming the neutral Si$_3$ cluster, a Jahn−Teller distortion occurs because only one of the two doubly degenerate LUMOs is occupied (Figure 3b). In chemical language, the highest occupied molecular orbital (HOMO) of Si$_3$ adds antibonding character in the σ-framework, resulting in substantial elongation to one of the Si−Si bonds (Figure 1i). Four σ-electrons in Si$_3$ render its σ-antiaromaticity, which is resulting in the D_{3h}-to-C_{2v} structural distortion from Si$_3^{2+}$ to Si$_3$, similar to the transition from the aromatic C$_4$H$_4^{2+}$ to the antiaromatic C$_4$H$_4$. Antiaromaticity in C$_4$H$_4$ manifests itself as a localization of π-electrons. In Si$_3$, antiaromaticity leads to localization of σ-electrons. In the pure σ-antiaromatic triatomic Li$_3^-$ anion, four σ-electrons lead to a linear structure.[12] Though Si$_3$ is a σ-antiaromatic system with four σ-electrons, it is not linear because of the important influence from the π-electrons. The HOMO-2 of Si$_3$ is a completely delocalized π-orbital, making it π-aromatic. Thus, Si$_3$ is a system with conflicting aromaticity, that is, a system with σ-antiaromaticity and π-aromaticity. When one silicon atom in Si$_3$ is substituted by Al$^-$ (isoelectronic to a Si atom), the resulting AlSi$_2^-$ structure is very similar (Figure 1e). The isoelectronic AlSiGe$^-$ (Figure 1f) and AiGe$_2^-$ (Figure 1g) also have very similar structures to that of Si$_3$. Their valence molecular orbitals are also rather similar to those of Si$_3$ (Figure 3c). Thus, these hetero-triatomic species all should be considered to possess conflicting aromaticity, similar to Al$_4$,[4−13] which is σ-aromatic and π-antiaromatic. In systems with conflicting aromaticity, it is difficult to make a judgment about the net aromaticity or antiaromaticity.[14] However, we believe that geometric criteria should be considered to be paramount relative to other criteria of aromaticity or antiaromaticity. Thus, the structural distortion in AlSi$_2^-$, AlSiGe$^-$, and AlGe$_2^-$ makes them net antiaromatic, again similar to Al$_4$,[4−13] or they should be simply considered as π-aromatic and σ-antiaromatic.

The HCC$^-$ anion has a classical linear structure (with one 2c−2e H−C bond, three 2c−2e C−C bonds, and a lone pair on the terminal carbon atom), but its derivatives AlCC$^-$ (C_s, $^1A'$), AlCSi$^-$ (C_s, $^1A'$), and AlCGe$^-$ (C_s, $^1A'$) are not linear. That deviation from linearity indicates deviation from the classical structure toward a completely delocalized aromatic structure such as that in $\mathrm{Si_3}^{2+}$. The deviation from linearity increases from AlCC^- to AlCSi^- and to AlCGe^- when the electronegativity of the terminal atoms equalizes to allow electron delocalization. However, all three of these anions do not yet have conflicting aromaticity like in $\mathrm{AlSi_2}^-$, AlSiGe^-, and $\mathrm{AlGe_2}^-$, because there is no significant bonding interaction between the terminal atoms. Thus, the AlCC^-, AlCSi^-, and AlCGe^- anions are neither classical nor aromatic. They are somewhere in between.

In summary, we established the global minimum structures of AlCGe^-, $\mathrm{AlSi_2}^-$, and $\mathrm{AlGe_2}^-$ by comparing their experimental photoelectron spectra and computed VDEs. All three anions were found to have nonlinear structures (C_s, $^1A'$). Chemical bonding analysis revealed that the $\mathrm{AlSi_2}^-$ and $\mathrm{AlGe_2}^-$ anions can be described as species with conflicting (σ-antiaromatic and π-aromatic) aromaticity. The AlCGe^- anion represents an interesting example of a chemical species which is between classical and aromatic.

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Supporting Information Available: Calculated molecular properties of AlCGe^-, $\mathrm{AlSi_2}^-$, AlSiGe^-, and $\mathrm{AlGe_2}^-$. This material is available free of charge via the Internet at http://pubs.acs.org.

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