

(Quantum Design) in the temperature range 5 to 300 K. The output data were corrected for the diamagnetism of the sample holder and of the samples, calculated from their Pascal's constants.

Received: January 26, 2000  
Revised: June 6, 2000 [Z14603]

## Experimental Observation of Pentaatomic Tetracoordinate Planar Si- and Ge-Containing Molecules: $\text{MAI}_4^-$ and $\text{MAI}_4^{*2-}$

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The chemistry of silicon and germanium is dominated by their tendency to form tetracoordinate tetrahedral structures, just as their more famous congener, the tetracoordinate tetrahedral carbon atom. The tetrahedral carbon idea, proposed by van't Hoff and Le Bel 125 years ago, has been the most important stereochemistry concept in understanding organic and biomolecules. The tetracoordinate tetrahedral structure of C, Si, and Ge atoms is rationalized elegantly by the concept of  $sp^3$  hybridization. However, in the last 30 years chemists have attempted to make unusual compounds that contain *planar* tetracoordinate C, Si, and Ge atoms. In particular, substantial efforts and progress have been made in the design and synthesis of tetracoordinate planar carbon molecules by overcoming the inherent preference for tetrahedral bonding.<sup>[1-6]</sup> Tetracoordinate planar silicon molecules have also been studied theoretically<sup>[7]</sup> and experimentally.<sup>[8]</sup>

We are interested in the generation of planar carbon, silicon, germanium, tin, and lead species in the gas phase and the investigation of their electronic structure and chemical bonding by using a combined experimental and theoretical approach. We recently reported the first observation of a *pentaatomic* tetracoordinate planar carbon molecule ( $\text{CAI}_4^-$ ) which has a planar structure and represents the smallest species to contain a tetracoordinate planar carbon.<sup>[9]</sup> Interestingly, however, its neutral  $\text{CAI}_4$  parent molecule is tetrahedral. We showed that planarity in  $\text{CAI}_4^-$  is achieved through ligand–ligand bonding interactions in its HOMO. We also found a general rule, that to achieve planarity in pentaatomic species composed of a first-row central atom and second- or

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[\*\*] The theoretical work was done at Utah State University and supported by the donors of The Petroleum Research Fund (ACS-PRF no. 35255-AC6), administered by the American Chemical Society. The experimental work was supported by the National Science Foundation (DMR-9622733) and was performed at the W. R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory, which is operated for DOE by Battelle Memorial Institute. L.S.W. is an Alfred P. Sloan Foundation Research Fellow. M = Si, Ge.

third-row ligand atoms, these species should possess 17 or 18 valence electrons.<sup>[9–11]</sup>

It is, however, not clear if the planar structure will be preserved when the first-row central atom is substituted by a second- or third-row atom. These molecules would be isoelectronic with the species that contain a first-row central atom, but the central cavity may be too small to accommodate the second- or third-row atom in the planar square structure. Herein we address this question by investigating SiAl<sub>4</sub><sup>-</sup> and GeAl<sub>4</sub><sup>-</sup> and their corresponding neutral molecules.

The experiments were performed with a magnetic-bottle time-of-flight photoelectron spectroscopy apparatus with a laser vaporization cluster source.<sup>[12, 13]</sup> The SiAl<sub>4</sub><sup>-</sup> and GeAl<sub>4</sub><sup>-</sup> ions were produced by laser vaporization of the corresponding mixed targets (Si/Al and Ge/Al) with pure helium carrier gas. The 532 and 355 nm spectra of SiAl<sub>4</sub><sup>-</sup> and GeAl<sub>4</sub><sup>-</sup> are shown in Figure 1. The 532 nm spectrum of SiAl<sub>4</sub><sup>-</sup> (Figure 1a) revealed a partially vibrationally resolved band with an

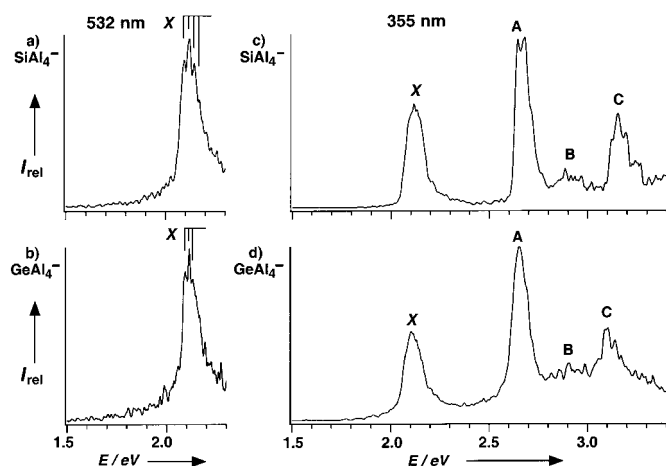


Figure 1. Photoelectron spectra of SiAl<sub>4</sub><sup>-</sup> and GeAl<sub>4</sub><sup>-</sup> at 532 nm (2.331 eV) and 355 nm (3.496 eV), plotted in increasing electron binding energy. The four observed detachment channels are labeled (X, A, B, and C). The vertical lines in (a) and (b) indicate vibrational structures.

average spacing of 220 cm<sup>-1</sup>. The adiabatic electron detachment energy (ADE) of SiAl<sub>4</sub><sup>-</sup> was determined from the 0-0 transition to be 2.094 eV and its vertical electron detachment energy (VDE) was measured to be 2.121 eV. At 355 nm (Figure 1c), several more features were observed. The feature at 2.7 eV (labeled A) shows a splitting which does not seem to be a vibrational progression. According to our theoretical result (see below), this splitting corresponds to a possible triplet–singlet splitting caused by detachment of a 3b<sub>2</sub> electron. A broad feature (B) was observed around 2.9 eV, followed by a feature (C) at 3.16 eV. The spectra of GeAl<sub>4</sub><sup>-</sup> are nearly identical to those of SiAl<sub>4</sub><sup>-</sup>, which indicates that the anions were correctly selected, as these two isoelectronic species are expected to have similar electronic and molecular structures. The 532 nm spectrum (Figure 1b) of GeAl<sub>4</sub><sup>-</sup> also revealed a partially vibrationally resolved band with a smaller vibrational spacing of 160 cm<sup>-1</sup>. The ADE of GeAl<sub>4</sub><sup>-</sup> is identical to that of SiAl<sub>4</sub><sup>-</sup> within our experimental accuracy. The VDE of GeAl<sub>4</sub><sup>-</sup> was measured to be 2.114 eV. At 355 nm

(Figure 1d), again several more features (A–C) were observed, similar to those of SiAl<sub>4</sub><sup>-</sup>. All the observed ADEs and VDEs for SiAl<sub>4</sub><sup>-</sup> and GeAl<sub>4</sub><sup>-</sup> are given in Table 1.

Table 1. Experimental and theoretical VDE and ADE of SiAl<sub>4</sub><sup>-</sup> and GeAl<sub>4</sub><sup>-</sup>.

State	Experimental		Detachment channel <sup>[a]</sup>	Theoretical	
	ADE [eV]	VDE [eV]		VDE [eV] <sup>[b]</sup>	ADE [eV] <sup>[b]</sup>
SiAl <sub>4</sub> <sup>-</sup>					
X	2.121 (0.020)	2.094 (0.020)	5a <sub>1</sub> ( <sup>1</sup> A <sub>1</sub> )	2.00	2.00
A	2.65 (0.03)	2.65 (0.03)	3b <sub>2</sub> ( <sup>3</sup> B <sub>2</sub> )	2.57	
B	≈ 2.9	≈ 2.8	4a <sub>1</sub> ( <sup>3</sup> A <sub>1</sub> )	3.01	
C	3.16 (0.03)	3.11 (0.03)	1b <sub>1</sub> ( <sup>3</sup> B <sub>1</sub> )	3.47	
GeAl <sub>4</sub> <sup>-</sup>					
X	2.114 (0.020)	2.094 (0.020)	5a <sub>1</sub> ( <sup>1</sup> A <sub>1</sub> )	2.03	2.02
A	2.66 (0.06)	2.66 (0.06)	3b <sub>2</sub> ( <sup>3</sup> B <sub>2</sub> )	2.56	
B	≈ 2.9	≈ 2.8	4a <sub>1</sub> ( <sup>3</sup> A <sub>1</sub> )	3.00	
C	3.10 (0.03)	3.08 (0.04)	1b <sub>1</sub> ( <sup>3</sup> B <sub>1</sub> )	3.35	

[a] 4a<sub>1</sub> is the ligand–ligand bonding MO; the other three orbitals are ligand-centered nonbonding lone-pair MOs (see Figure 3). The final state is given in parentheses. [b] The 5a<sub>1</sub> MO is singly occupied in the anions. Thus, the first detachment channel corresponds to a singlet final state (ground state of the neutral) and all the other detachment channels correspond to triplet final states. All data are at the CCSD(T)/6-311 + G(2df)//MP2/6-311 + G\* level of theory.

In our ab initio calculations,<sup>[14, 15]</sup> we considered in detail neutral SiAl<sub>4</sub> and GeAl<sub>4</sub> molecules and their anions. We performed a complete search for the global minimum of SiAl<sub>4</sub> and its anion. For GeAl<sub>4</sub>, we assumed that it would have a similar global minimum to that of SiAl<sub>4</sub>, based on their nearly identical photoelectron spectra (Figure 1). The lowest energy anion structures for each cluster are shown in Figure 2. Indeed, both SiAl<sub>4</sub><sup>-</sup> and GeAl<sub>4</sub><sup>-</sup> were found to be planar and contain tetracoordinate Si and Ge atoms (valence electronic configuration: 1a<sub>1</sub><sup>2</sup> 1b<sub>2</sub><sup>2</sup> 2a<sub>1</sub><sup>2</sup> 3a<sub>1</sub><sup>2</sup> 2b<sub>2</sub><sup>2</sup> 1b<sub>1</sub><sup>2</sup> 4a<sub>1</sub><sup>2</sup> 3b<sub>2</sub><sup>2</sup> 5a<sub>1</sub><sup>1</sup>). As expected, the small cavity formed by an Al<sub>4</sub> square was too small to accommodate Si or Ge atoms and the molecules are distorted into C<sub>2v</sub> symmetry. Surprisingly and in contrast to

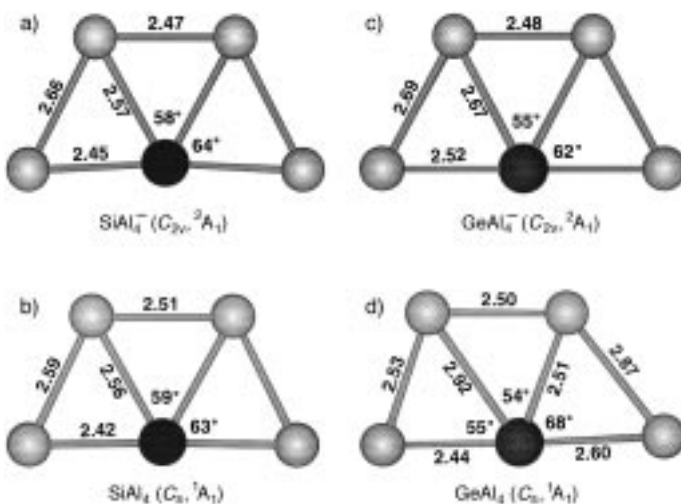


Figure 2. Ab initio structures of SiAl<sub>4</sub><sup>-</sup>, SiAl<sub>4</sub>, GeAl<sub>4</sub><sup>-</sup>, and GeAl<sub>4</sub> optimized at the MP2/6-311 + G\* level of theory and showing the bond lengths [Å] and angles [°]. Note that SiAl<sub>4</sub> (b) is not planar, the two Al atoms appearing to be on the same line as Si are actually each 11° above the plane, giving a 158° ∠Al–Si–Al angle, which cannot be seen in the two-dimensional plot.

$\text{CAI}_4$ , the neutral  $\text{SiAl}_4$  and  $\text{GeAl}_4$  molecules are not tetrahedral.<sup>[9]</sup> The  $\text{GeAl}_4$  molecule remains planar, whereas  $\text{SiAl}_4$  is quasi-planar with the two Al units at the apices each being out of plane by  $11^\circ$  (Figure 2). However, the barrier to planarity for  $\text{SiAl}_4$  after the zero-point energy (ZPE) corrections was found to be just  $0.26 \text{ kcal mol}^{-1}$  (MP2). We did find  $T_d$  local minima for  $\text{SiAl}_4$  and  $\text{GeAl}_4$ , but they are  $27 \text{ kcal mol}^{-1}$  (MP2) higher in energy than the structures shown in Figure 2.

In Table 1 we present results of our calculations of the four lowest-lying vertical one-electron detachment processes from the tetracoordinate planar global-minimum structures of  $\text{SiAl}_4^-$  and  $\text{GeAl}_4^-$  (that is from the  $5a_1$ ,  $3b_2$ ,  $4a_1$ , and  $1b_1$  orbitals, respectively) and compare them with the experimental data. Removal of the single electron from the  $5a_1$  orbital results in the  $^1A_1$  ground state for the neutral species. The calculated ADE and VDE of this detachment channel agree well with the experimental values (Table 1). Detachment from the  $3b_2$ ,  $4a_1$ , and  $1b_1$  orbitals will each result in both triplet and singlet excited states for the neutral species. Only the triplet final states are considered here, because the final singlet excited states require multiconfigurational references and cannot be treated by the CCSD(T) method used here. The calculated VDEs for the triplet excited states agree well with the major experimental features (A–C). The singlet excited states are likely to be close in energy to the corresponding triplet states. The splitting observed for the feature A in the 355 nm spectrum of  $\text{SiAl}_4^-$  is probably because of the singlet state. Both the features B and C are relatively broad and may conceivably contain the singlet states as well. The overall excellent agreement between the theoretical and experimental results of the global-minimum tetracoordinate planar structures provide solid evidence that we have indeed identified the first *pentaatomic* tetracoordinate planar silicon and germanium molecules in their anion states.

Our previous work provided the tetracoordinate planar carbon anion in  $\text{CAI}_4^-$ , whereas the neutral  $\text{CAI}_4$  has a tetrahedral structure. Our previous experimental observation of an extremely broad  $(X, \text{CAI}_4^-) \rightarrow (X, \text{CAI}_4)$  transition in the photoelectron spectra of  $\text{CAI}_4^-$  provided conclusive evidence for the large geometry changes from the planar square structure of  $\text{CAI}_4^-$  to the tetrahedral structure of  $\text{CAI}_4$ .<sup>[9]</sup> Interestingly, in the current work both the  $(X, \text{SiAl}_4^-) \rightarrow (X, \text{SiAl}_4)$  and the  $(X, \text{GeAl}_4^-) \rightarrow (X, \text{GeAl}_4)$  transitions are relatively sharp. These observations agree well with the relatively small geometry changes between the anionic and neutral molecules that contain Si and Ge centers. The planar structure of  $\text{CAI}_4^-$  was attributed to the occupation of the peripheral ligand–ligand bonding orbital (HOMO) by a single electron. When this electron is removed from the HOMO of  $\text{CAI}_4^-$  the corresponding neutral  $\text{CAI}_4$  species becomes tetrahedral. In the case of  $\text{SiAl}_4^-$  and  $\text{GeAl}_4^-$ , the peripheral ligand–ligand bond is no longer the HOMO, but the HOMO-2 ( $4a_1$ ), which remains doubly occupied in both the anion and neutral ground states (Figure 3). Feature B in the photoelectron spectra corresponds to the removal of an electron from this peripheral bond, and the broad nature of feature B is consistent with the bonding nature of this orbital. Therefore, it is understandable that the neutral  $\text{SiAl}_4$  and

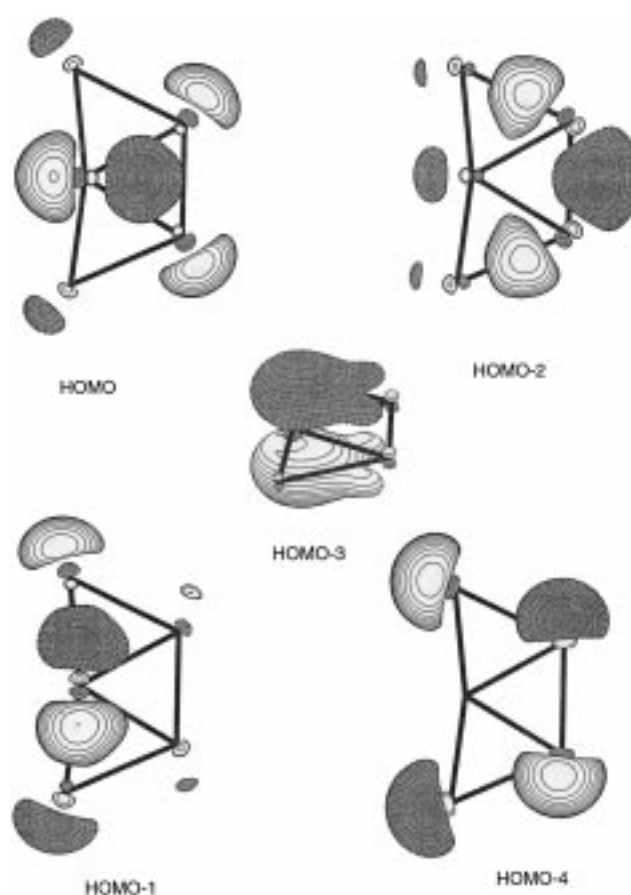


Figure 3. Molecular orbital diagram<sup>[16]</sup> showing the HOMO ( $5a_1$ ), HOMO-1 ( $3b_2$ ), HOMO-2 ( $4a_1$ ), HOMO-3 ( $1b_1$ ), and HOMO-4 ( $2b_2$ ) of  $\text{SiAl}_4^-$ . Note that the ligand–ligand bonding MO is the HOMO-2 ( $4a_1$ ), and not the HOMO as in  $\text{CAI}_4^-$ .<sup>[9]</sup>

$\text{GeAl}_4$  compounds remain planar, unlike their lighter congener,  $\text{CAI}_4$ , which is tetrahedral. These results again reinforce the concept and importance of the ligand–ligand bonding in the stabilization of the planar structures in tetracoordinate C, Si, and Ge species.

Received: March 2, 2000 [Z14797]

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## Control of Architecture in Block-Copolymer Vesicles\*\*

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It has been known for some years that highly asymmetric amphiphilic block copolymers can self-assemble in solution to form crew-cut aggregates of an extremely wide range of morphologies.<sup>[1]</sup> The various morphologies include spheres, rods, bicontinuous structures, lamellae, vesicles, tubes, large compound vesicles (LCVs), hexagonally packed hollow hoops (HHHs), large compound micelles (LCMs), and many others. In such aggregates, the relatively long block forms the core, while the short one forms the corona. A number of other groups have also studied block-copolymer aggregates of various morphologies in recent years.<sup>[2, 3]</sup> The appeal of this field is, in part, because of the many potential applications of

these nano-sized structures with their different morphologies, and in part academic curiosity.

Among the various morphologies, vesicles, including liposomes,<sup>[4]</sup> are of special interest because of their potential application as encapsulation agents. However the stability of liposomes has been a concern because of the high mobility of the component molecules under ambient conditions; therefore, many attempts have been made to stabilize these liposomes. As polymers have higher stability and lower mobility than small-molecule amphiphiles most of these stabilization strategies consist of the polymerization of the liposomes or the addition of polymeric materials to the liposomes.

Block-copolymer vesicles can be equilibrium structures under some conditions, but can also be kinetically frozen during preparation.<sup>[5]</sup> The block-copolymer vesicles are robust<sup>[3]</sup> and are very stable (samples have remained unchanged since 1997) in aqueous solution.<sup>[5]</sup> Because the studies on block-copolymer vesicles are still in the early stages, only a few attempts at encapsulation have been made.<sup>[3, 6]</sup>

To utilize block-copolymer vesicles in any given application, the precise control of vesicular parameters, such as vesicle size, wall thickness, number of walls, and space between the walls, is crucial. In our previous studies on the phase diagrams of block-copolymer systems we found that under some conditions the vesicles can be under thermodynamic control.<sup>[5]</sup> It is believed that the parameters which control the aggregate morphologies, that is the core chain stretching, interfacial tension, and corona repulsion, are also responsible for the control of the vesicular architecture. Thus, variation of these factors allows the properties of the vesicles to be tuned.<sup>[1]</sup>

A special type of vesicle, the so-called dense “onions”, which are found in bulk block-copolymer blends were reported over a decade ago.<sup>[7]</sup> In block-copolymer solutions, onionlike micelles have been prepared by the stepwise aggregation of two diblocks, first AB and then BC.<sup>[8]</sup> Onionlike structures have also been reported in small molecule surfactant systems.<sup>[9]</sup> Recently, it was found that shear can induce the formation of onions from a lamella phase in surfactant systems.<sup>[10]</sup> By the same strategy, onionlike structures could also be formed in Pluronic systems,<sup>[11]</sup> and, very recently, onions were prepared from block-copolymer solutions.<sup>[12]</sup>

Herein we report a new morphology for block copolymers in solution, this consists of concentric vesicles with uniform spacing between the walls; we also describe the preparation in solution of multi-lamella onions in which there is no spacing between the walls, and discuss the control of these morphologies in the context of the other observed vesicular architectures (see Table 1),<sup>[1, 5, 13]</sup> Our understanding of this subject is still qualitative, but the evidence obtained suggests that one can exercise control over a variety of vesicular morphologies. Noteworthy is that equally spaced concentric vesicles have been observed in small molecule amphiphiles.<sup>[4, 9]</sup>

Figure 1 shows concentric vesicles with uniform spaces between the walls, which we refer to as “onions with spaces”. From the shadow of the vesicular structures seen by transition electron microscopy (TEM) observation (not shown here),

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\*\*] We thank the Petroleum Research Fund, administered by the American Chemical Society, for the support of this work.