

(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.

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Experimental Observation of Pentaatomic Tetracoordinate Planar Si- and Ge-Containing Molecules: MAI_4^- and MAI_4^{**}

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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.^[1–6] Tetracoordinate planar silicon molecules have also been studied theoretically^[7] and experimentally.^[8]

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 (CAI_4^-) which has a planar structure and represents the smallest species to contain a tetracoordinate planar carbon.^[9] Interestingly, however, its neutral CAI_4 parent molecule is tetrahedral. We showed that planarity in 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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third-row ligand atoms, these species should possess 17 or 18 valence electrons.^[9–11]

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_4^- and GeAl_4^- 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.^[12, 13] The SiAl_4^- and GeAl_4^- 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_4^- and GeAl_4^- are shown in Figure 1. The 532 nm spectrum of SiAl_4^- (Figure 1a) revealed a partially vibrationally resolved band with an

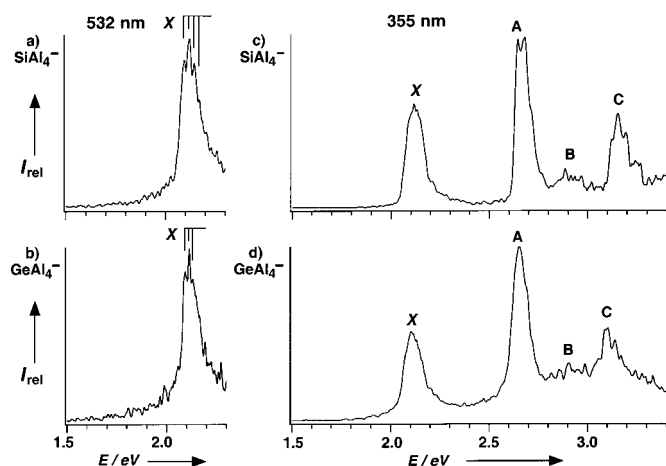


Figure 1. Photoelectron spectra of SiAl_4^- and GeAl_4^- at 532 nm (2.331 eV) and 355 nm (3.496 eV), plotted in increasing electron binding energy. The four observed detachment channels are labeled (X, A, B, and C). The vertical lines in (a) and (b) indicate vibrational structures.

average spacing of 220 cm^{-1} . The adiabatic electron detachment energy (ADE) of SiAl_4^- 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 $3b_2$ electron. A broad feature (B) was observed around 2.9 eV, followed by a feature (C) at 3.16 eV. The spectra of GeAl_4^- are nearly identical to those of SiAl_4^- , 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_4^- also revealed a partially vibrationally resolved band with a smaller vibrational spacing of 160 cm^{-1} . The ADE of GeAl_4^- is identical to that of SiAl_4^- within our experimental accuracy. The VDE of GeAl_4^- 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_4^- . All the observed ADEs and VDEs for SiAl_4^- and GeAl_4^- are given in Table 1.

Table 1. Experimental and theoretical VDE and ADE of SiAl_4^- and GeAl_4^- .

State	Experimental ADE [eV]	Experimental VDE [eV]	Detachment channel ^[a]	Theoretical VDE [eV] ^[b]	Theoretical ADE [eV] ^[b]
SiAl_4^-					
X	2.121 (0.020)	2.094 (0.020)	$5a_1 (^1A_1)$	2.00	2.00
A	2.65 (0.03)	2.65 (0.03)	$3b_2 (^3B_2)$	2.57	
B	≈ 2.9	≈ 2.8	$4a_1 (^3A_1)$	3.01	
C	3.16 (0.03)	3.11 (0.03)	$1b_1 (^3B_1)$	3.47	
GeAl_4^-					
X	2.114 (0.020)	2.094 (0.020)	$5a_1 (^1A_1)$	2.03	2.02
A	2.66 (0.06)	2.66 (0.06)	$3b_2 (^3B_2)$	2.56	
B	≈ 2.9	≈ 2.8	$4a_1 (^3A_1)$	3.00	
C	3.10 (0.03)	3.08 (0.04)	$1b_1 (^3B_1)$	3.35	

[a] $4a_1$ 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 $5a_1$ 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,^[14, 15] we considered in detail neutral SiAl_4 and GeAl_4 molecules and their anions. We performed a complete search for the global minimum of SiAl_4 and its anion. For GeAl_4 , we assumed that it would have a similar global minimum to that of SiAl_4 , 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_4^- and GeAl_4^- were found to be planar and contain tetracoordinate Si and Ge atoms (valence electronic configuration: $1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 1b_1^2 4a_1^2 3b_2^2 5a_1^1$). As expected, the small cavity formed by an Al_4 square was too small to accommodate Si or Ge atoms and the molecules are distorted into C_{2v} symmetry. Surprisingly and in contrast to

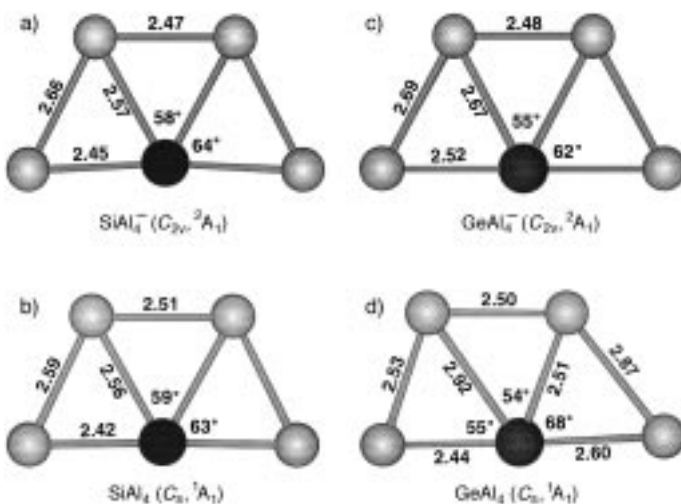


Figure 2. Ab initio structures of SiAl_4^- , SiAl_4 , GeAl_4^- , and GeAl_4 optimized at the MP2/6-311 + G* level of theory and showing the bond lengths [Å] and angles [°]. Note that SiAl_4 (b) is not planar, the two Al atoms appearing to be on the same line as Si are actually each 11° above the plane, giving a $158^\circ \angle \text{Al-Si-Al}$ angle, which cannot be seen in the two-dimensional plot.

CAI_4 , the neutral SiAl_4 and GeAl_4 molecules are not tetrahedral.^[9] The GeAl_4 molecule remains planar, whereas SiAl_4 is quasi-planar with the two Al units at the apices each being out of plane by 11° (Figure 2). However, the barrier to planarity for 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 SiAl_4 and GeAl_4 , but they are 27 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 SiAl_4^- and 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 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 CAI_4^- , whereas the neutral 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 CAI_4^- provided conclusive evidence for the large geometry changes from the planar square structure of CAI_4^- to the tetrahedral structure of CAI_4 .^[9] 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 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 CAI_4^- the corresponding neutral CAI_4 species becomes tetrahedral. In the case of SiAl_4^- and 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 SiAl_4 and

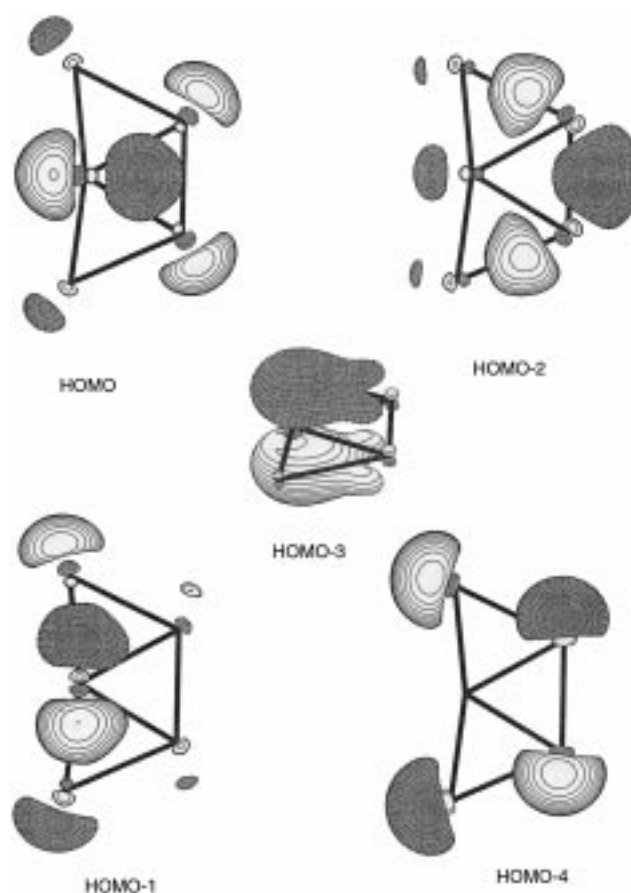


Figure 3. Molecular orbital diagram^[16] showing the HOMO ($5a_1$), HOMO-1 ($3b_2$), HOMO-2 ($4a_1$), HOMO-3 ($1b_1$), and HOMO-4 ($2b_2$) of SiAl_4^- . Note that the ligand–ligand bonding MO is the HOMO-2 ($4a_1$), and not the HOMO as in CAI_4^- .^[9]

GeAl_4 compounds remain planar, unlike their lighter congener, 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.

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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.^[1] 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.^[2, 3] 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,^[4] 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.^[5] The block-copolymer vesicles are robust^[3] and are very stable (samples have remained unchanged since 1997) in aqueous solution.^[5] Because the studies on block-copolymer vesicles are still in the early stages, only a few attempts at encapsulation have been made.^[3, 6]

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.^[5] 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.^[1]

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

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).^[1, 5, 13] 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.^[4, 9]

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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