Tetracoordinated Planar Carbon in the $\text{Al}_4\text{C}^-$ Anion. A Combined Photoelectron Spectroscopy and ab Initio Study

Xi Li,$^1$ Lai-Sheng Wang,$^{*,1}$ Alexander I. Boldyrev,$^{*,1,3}$ and Jack Simons$^{*,3}$

Contribution from the Department of Physics, Washington State University, Richland, Washington 99352, the Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, MS K8-88, P.O. Box 999, Richland, Washington 99352, and the Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112

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Introduction

The basis of the most successful stereochemical concept in organic chemistry, that of the tetravalent tetrahedral carbon atom, was published in 1874 independently by van’t Hoff$^1$ and LeBel.$^2$ The possibility of designing molecules containing a planar tetracoordinated carbon atom, a task that requires overcoming the inherent preference for tetrahedral bonding, has been pursued for some considerable time.$^3$–$^10$ Two approaches to achieving this goal have been employed. The electronic approach involves selecting substituents that will preferentially stabilize a planar arrangement. 4–10 The alternative approach is based on using mechanical forces exerted by the surrounding ligands bound to the carbon atom.$^{11,15}$ In the present efforts we consider a species for which the electronic effects are most important. Recently, a set of pentaatomic molecules, cis-CSi$_2$Al$_2$, trans-CSi$_2$Al$_2$, cis-CSi$_2$Ga$_2$, trans-CSi$_2$Ga$_2$, cis-CGe$_2$Al$_2$, and trans-CGe$_2$Al$_2$, was studied by photoelectron spectroscopy.$^{10}$

$^1$ Washington State University and Pacific Northwest National Laboratory.
$^2$ Present address: Department of Chemistry and Biochemistry, Utah State University, Logan. UT 84322-0300.


$^{*3}$ The University of Utah.

$^3$ For some considerable time. 3


$^5$ A Combined Photoelectron Spectroscopy and ab Initio Study

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clusters. IV

We believe that understanding the bonding in such molecules is crucial to future progress in designing novel molecules and compounds with tetracoordinated planar carbon.

It is shown in ref 6 that the stability of the predicted planar tetracoordinated carbon species is related to the occurrence of 18 valence electrons, which produce three σ and one π bonds to the central carbon atom plus one four-center ligand-π bond, and four ligand-centered lone pairs. According to the model of ref 6, 16-valence-electron species such as Al₄C will not be stable at D₄h symmetry because they lack the ligand-π bond. Indeed for such species, the planar structure has been found to be less stable than the tetrahedral. Although the situations for 18 and 16 electrons have been resolved, the 17-electron case remains to be addressed.

In the current work, we present a combined experimental and theoretical study on a 17-valence-electron pentaaatomic species, Al₄C⁻. We demonstrate that the combination of anion photoelectron spectroscopy (PES) and high-level ab initio calculations can completely elucidate the structures of both Al₄C⁻ and the neutral Al₄C. Our findings confirm that the 16-electron Al₄C is indeed tetrahedral, and show that the 17-electron Al₄C⁻ is actually planar. To the best of our knowledge, there are no other experimental data available on Al₄C⁻ and Al₄C, although a number of other hyperaluminum molecules, Al₂O, Al₄O, 16 Al₄N (n = 3, 4), 21,22 Al₃S (n = 3–9), 23 have been studied in the literature. The substantial stability of the later molecules is due to the high degree of ionic character in the bonding between the central atom and its ligands, as well as the bonding interactions among the ligand aluminum atoms. 17

**Experimental Methods**

The experiments were performed with a magnetic-bottle time-of-flight PES apparatus. Details of the experiment have been described previously. 24,25 Briefly, Al₄C⁻ was produced by a laser vaporization cluster source. An intense laser pulse (532 nm) from a Q-switched Nd:YAG laser was focused onto a pure Al target. Sufficient Al₄C⁻ signals were produced due to carbon impurity in the Al target. A mixed Al/C target was also used, but it favored clusters with high C content.

The PES spectra of Al₄C⁻ are shown in Figure 1 at three photon energies. The 355-nm spectrum (Figure 1a) shows a broad low-energy tail (X) and two intense and sharp features with 2.86 (A) and 3.00 eV (B) vertical (inferrred from peak energies) binding energies (VDEs), respectively. A weak feature (C) at 3.3 eV VDE is also discernible. At 266 nm (Figure 1b), the broad low-energy tail (X) was enhanced and became a well-defined feature with a VDE at 2.65 eV. The C feature was also observed more clearly in the 266-nm spectrum. Additional higher energy broad features were observed at 266 nm. Two features (D and E) could be roughly identified at ~3.7 and 4.2 eV VDEs. The 193-nm spectrum (Figure 1c) seems to reveal more transitions at high binding energies beyond 4.4 eV, but they are broad and congested.

The PES spectra of Al₄C⁻ are rather complicated. The broad low-energy feature (X) was unusual and could be due to several sources. It could be due to hot band transitions, excited states of anions, or minor isomers, all of which should depend on the cluster source conditions to some degree. However, this broad tail always existed even when source conditions were changed slightly to produce colder clusters. Therefore, we concluded that, even though there could be contributions due to hot bands to the broad feature (X), the main intensity of this feature was due to the transition from the ground state of the anion to that of the neutral ground state. This suggests a large geometry.
change between the anion and the neutral ground state. There are additional factors causing the complicated PES spectra of Al₄C⁻ which possess an odd number of valence electrons and can lead to states with more complicated spin multiplicities as discussed below.

**Theoretical Results**

**Al₄C⁻.** At all three levels of theory, B3LYP/6-311+G*, MP2/6-311+G*, and CCSD(T)/6-311+G*, the global minimum of Al₄C was found to have a singlet \( Tₐ \) (\(^1A₁\)) structure (characterized in Table 1 and shown in Figure 2) in agreement with the previous MP2(full)/6-31G* calculations. The optimal geometries and harmonic frequencies are consistent at all levels of theory. The tetrahedral structure of Al₄C is to be expected based on the occupations of the valence MOs in the 32-valence-electron \( \text{tetrahedral} \) CF₄ molecule, \( 1a_{1g}^2 1t_{2g}^2 2a_{1g}^2 2t_{2g}^2 e^3 t_{1u}^3 t_{2u}^6 \). The first four \( (1a_{1g}^2 \) and \( 1t_{2g}^2 \)) orbitals are the C–F σ bonds and the remaining 12 orbitals are lone-pair orbitals localized on F atoms, lying perpendicular and parallel to the C–F bond axes. The above orbital occupancy clearly describes a situation with four σ bonds and no net bonding or antibonding interactions among the ligands. If we assume that this order of MOs remains valid for other tetrahedral molecules, for example, for a species with 16 valence electrons such as Al₄C, the tetrahedral structure should have a \( 1a_{1g}^2 1t_{2g}^2 2a_{1g}^2 2t_{2g}^2 e^3 t_{1u}^3 t_{2u}^6 \) electronic configuration, which describes four σ bonds (\( 1a_{1g}^2 \) and \( 1t_{2g}^2 \)) and four lone-pair bonds (\( 2a_{1g}^2 \) and \( 2t_{2g}^2 \)). This result suggests that each Al in Al₄C can be viewed as monovalent with a 3s lone pair.

Al₄C⁻. Addition of an electron to the 1e LUMO of \( Tₐ \) Al₄C, which consists of Al 3p orbitals lying perpendicular to the Al–C bond axes, leads to a \( 1a_{1g}^2 1t_{2g}^2 2a_{1g}^2 2t_{2g}^2 e^5 t_{1u}^3 t_{2u}^6 \) electronic configuration with a \( 3e \) state for Al₄C⁻ which is expected to undergo Jahn–Teller distortion toward a \( D_{4h} \) (\( B_{2g} \)) geometry (Figure 2). We optimized the \( D_{4h} \) structure \( (B_{2g}^2 \) \( 1a_{1g}^2 e^2 1t_{2g}^2 2a_{1g}^2 1b_{2g}^2 2e_{u}^4 1b_{2g}^4 e_{u}^2 \)) at the above three levels of theory (Table 2 for final geometry parameters) and found the \( D_{4h} \) (\( B_{2g} \)) state to be a minimum at the B3LYP/6-311+G* and MP2/6-311+G* levels of theory, but a second-order saddle point at the CCSD(T)/6-311+G* level of theory. Distortion along the \( a_{2u} \) mode of imaginary frequency leads to a \( C_{6v} \) (\( B_{1g} \)) pyramidal (but almost planar) structure with the carbon atom lying just 0.005 Å above the Al₄ plane and with an inversion barrier of only 0.002 kcal/mol. Distortion along the \( b_{2u} \) mode of imaginary frequency leads to a butterfly type \( D_{2d} \) (\( B_{1u} \)) structure (Figure 2 and Table 3), which turns out to be the global minimum at the CCSD(T)/6-311+G* level of theory. However, the deviation from planarity in the butterfly structure is also rather small with the energy difference between \( D_{2d} \) (\( B_{1u} \)) and \( D_{4h} \) (\( B_{2g} \)) being 0.14 kcal/mol. Therefore, when zero-point vibrational motion is considered, the vibrationally averaged structure is actually planar.

The propensity of 17- and 18-valence-electron pentaatomic systems to achieve planarity can be understood by considering of the \( 1b_{2g} \) HOMO (Figure 3), which is clearly bonding with
Table 3. Calculated Molecular Properties of the \( {C}_{6} (^{2}B_{1}) \) Saddle Point and the \( \Delta D_{2d} (^{2}B_{1}) \) Global Minimum of the \( {A}_{1}C^{-} \) Anion

<table>
<thead>
<tr>
<th>property</th>
<th>( \Delta D_{2d} )</th>
<th>( C_{n} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \bar{R}(C^{-}−{A}_{1}^{3}S,3S) ), Å</td>
<td>1.990</td>
<td>1.992</td>
</tr>
<tr>
<td>( \bar{R}(Al−{A}_{1}^{3}S) ), Å</td>
<td>2.827</td>
<td>2.816</td>
</tr>
<tr>
<td>( \bar{Z}(Al−{A}_{1}^{3}S) )</td>
<td>169.2</td>
<td>176.2</td>
</tr>
<tr>
<td>( E_{\text{total}}, \text{au} )</td>
<td>−1005.971512</td>
<td>−1005.671286</td>
</tr>
</tbody>
</table>

With respect to ligand–ligand interactions and plays a key role in maintaining planarity. Why the \( {A}_{1}C^{-} \) anion is not exactly planar most likely has to do with the size of the “cavity” in the planar \( Al_{4} \) cluster; a similar observation was made in the \( CsI_{2}Al_{3} \) case.\(^6\) To achieve perfect planarity one could use iso-electronic but larger ligands such as \( Ga \) or \( In \) in place of \( Al \).

Thus, we expect that planar (or quasiplanar) structures will also occur in \( CaI_{2}Ga_{4}^{-}, CGa_{4}^{-}, \) and neutral 17-valence-electron species such as \( CaI_{5}Si, CaI_{5}GaSi, CaIGaSi_{2}, CGa_{5}Si, CaI_{5}Ge, \) etc.

**Alternative Structures.** For both the neutral \( Al_{4}C^{-} \) and \( Al_{4}C^{2-} \) we also considered other structures with different spin multiplicities and geometries.

For the triplet state of \( Al_{4}C^{-} \), we do not expect a tetrahedral structure because the \( 1a_{1}^{2}1e_{g}^{2}2a_{1}^{2}2e_{g}^{2}1e_{u}^{2} \) electronic configuration is not stable toward Jahn–Teller distortion. We performed geometry optimization for this triplet state of \( Al_{4}C^{-} \) without any symmetry restriction which generated a local minimum planar structure \( C_{2h}, 2B_{2g} (1a_{1}^{2}2a_{1}^{2}1b_{1}^{1}3a_{1}^{1}1b_{1}^{1}4a_{2}^{1}2b_{2}^{1}3a_{1}^{1}3b_{1}^{1}) \) 1.01 eV (MP2/6-311+G*) higher in energy than the singlet tetrahedral structure.

Next, we considered structures with one \( Al \) atom coordinated outside a \( CaI_{2} \) cluster. Geometry optimization of the \( AlCa_{2}Al^{-} \) (\( C_{2v}, 1A_{1} \)) structure within \( C_{2v} \) symmetry converged to a \( D_{4h}, 1A_{1g} \) structure which is a saddle point 0.85 eV (MP2/6-311+G*) higher in energy than the singlet tetrahedral structure. Geometry optimization of the \( AlCaAl \) (\( C_{3v}, 1A_{1} \)) structure with the carbon atom coordinated to a face of a tetrahedral \( Al \) cluster within \( C_{3v} \) symmetry converged to the \( T_{d}, 1A_{1} \) structure. Therefore, all alternative structures were found to be higher in energy than the \( T_{d}, 1A_{1} \) structure from which we conclude that the \( T_{d}, 1A_{1} \) structure detailed in Table 1 and Figure 2 is the global minimum of the \( AlC^{-} \) anion.

For the quartet state of \( Al_{4}C^{-} \) we do not expect a tetrahedral structure because the \( 1a_{1}^{2}1e_{g}^{2}2a_{1}^{2}1a_{1}^{2}2e_{g}^{2}2e_{g}^{2}1e_{u}^{2}1a_{1}^{2} \) electronic configuration is not stable toward Jahn–Teller distortion. We performed geometry optimization for this quartet state of \( Al_{4}C^{-} \) without any symmetry restriction which converged to a \( C_{3v}, 1A_{1} \) (\( 1a_{1}^{2}2a_{2}^{1}1e_{g}^{3}2e_{u}^{2}4a_{2}^{1}3e_{g}^{2} \)) local minimum structure, which is 1.72 eV (MP2/6-311+G*) higher in energy than the doublet \( D_{2d} (^{2}B_{2g}) \) structure.

Next, we considered anion structures with one \( Al \) atom coordinated outside the \( CaI_{3} \) cluster. Geometry optimization of the \( AlCa_{2}Al^{-} \) (\( C_{2v}, 2B_{2g} \)) structure within \( C_{2v} \) symmetry converged to the \( D_{4h}, 2B_{2g} \) structure. Geometry optimization of the \( AlCa_{2}Al^{-} \) (\( C_{2v}, 2B_{1} \)) structure within \( C_{2v} \) symmetry converged to a structure, which is a second-order saddle point, 2.05 eV higher in energy than the \( D_{2h} (^{2}B_{2g}) \) structure. Therefore, all alternative structures were found to be higher in energy than the \( D_{2h} (^{2}B_{2g}) \) structure, and we conclude that the \( D_{2d} (^{2}B_{1}) \) structure detailed in Table 3 and Figure 2 is the global minimum for the \( AlC^{-} \) anion.

Both the \( D_{2d} AlC^{-} \) anion and the \( T_{d} AlC \) neutral molecule are very stable toward dissociation. Representative dissociation energies were calculated to be as follows: \( \Delta E = 2.41 \) eV for \( Al_{4}C^{-} (D_{2d}, ^{2}B_{1}) \rightarrow Al_{3}C^{-} (C_{3v}, ^{1}A_{1}), Al (^{2}P) \) and \( \Delta E = 3.05 \) eV for \( AlC \) (\( T_{d}, ^{1}A_{1} \) → \( Al_{3}C^{-} (C_{3v}, ^{2}B_{2}), Al (^{2}P) \) (all at the CCSD(T)/6-311+G(2df) level of theory).

**Interpretation of the Experimental Spectra**

The deviation from planarity in \( AlC^{-} \) is below the ZPE corrections and therefore we consider that electron detachment occurs from the \( D_{4h} (^{2}B_{2g}) \) planar structure in our interpretation of the experimental photoelectron spectra. In Table 4 we present the results of our calculations of the four major low-lying vertical one-electron detachment processes from the \( D_{4h} (^{2}B_{2g}) \) state of \( AlC^{-} \). The four calculated detachment channels are also shown in Figure 1b as vertical bars.

**Feature X.** The lowest vertical electron detachment should occur by electron removal from the \( 1b_{2g}^{-}HOMO \). The broad feature X (Figure 1) peaking at 2.65 ± 0.06 eV agrees well with the calculated VDE of 2.71 eV (CCSD(T)/6-311+G(2df)) from the \( 1b_{2g}^{-}HOMO \). The \( 1b_{2g}^{-} \) orbital (Figure 3) is a ligand–ligand bonding MO composed primarily of 3s and 3p atomic orbitals (AOs) of the aluminum atoms. Therefore, we assign feature X to the \( (X, Al_{4}C^{-}) \rightarrow (X, AlC) \) transition. The broad nature of this transition is consistent with the fact that neutral \( AlC \) is tetrahedral while \( AlC^{-} \) is planar, so the adiabatic transition requires a large geometry deformation. Indeed, according to our calculations, the adiabatic detachment energy (ADE) is 1.93 eV [CCSD(T)/6-311+G(2df)], which is substantially smaller than the 2.71 eV VDE. Feature X was observed as a structureless band in the PES spectra (Figure 1) because the experimental resolution was not sufficient to resolve the low-frequency vibrations in this band. Thus, the ADE could not be reliably obtained experimentally, as is clear from the long tail of the PES spectra at the low binding energy side (Figure 1). The calculated ADE of 1.93 eV is consistent with the onset of the PES signal around 2 eV, as seen from Figure 1.

**Features A, B, and C.** Removal of an electron from the \( 2e_{u} \) MO (HOMO-1) of \( AlC^{-} \) leads to a \( (1a_{1}^{2}1e_{g}^{2}2a_{1}^{2}1a_{1}^{2}1b_{1}^{2}2e_{g}^{2}1e_{u}^{2}) \) electronic configuration for the \( AlC \) neutral, which can result in both a triplet and a singlet state. The theoretical methods employed in this work do not allow us to rigorously calculate the singlet state (because of the multiconfigurational character of the reference wave function), but the triplet state can be treated with more reasonable accuracy. According to our CCSD(T)/6-311+G(2df) calculations, the VDE leading to the triplet state is 2.88 eV, which is in excellent agreement with experimental feature A (Figure 1) at 2.86 eV. We therefore assign this peak to removal of an electron from the \( 2e_{u} \) orbital (HOMO-1) to produce triplet \( AlC \). This \( 2e_{u} \) orbital is a primarily nonbonding MO (Figure 3) and is composed of a 2p AO of carbon and 3s–3p hybridized AOs of the aluminum atoms. The removal of the \( 2e_{u} \) electron results in a triplet state, which is Jahn–Teller unstable and splits into two components as the \( Al \) square distort into a diamond shape. We therefore assign feature B at 3.00 eV to be the second component of this Jahn–Teller splitting of the triplet state.

The fourth detachment feature (peak C, Figure 1), observed at 3.3 eV VDE (Table 4), is assigned to the singlet state resulting from removing an electron from the same \( 2e_{u} \) MO. This feature and features A and B are all considerably sharper than the ground-state feature X. The relative sharpness of these three detachment channels suggests that the geometry changes are smaller upon removal of a \( 2e_{u} \) electron from \( AlC^{-} \) and that the corresponding neutral states may possess similar quasiplanar structures as that of the anion. This is understandable because removing an electron from the \( 2e_{u} \) orbital only weakly disturbs the quasiplanar geometry, although it may induce some excita-
tion of Al—C stretching modes because of its small antibonding nature. More importantly, the 1b₂g MO, which is important for planarity, is still occupied in all three detachment channels.

**Feature D.** According to the 1a₁g₂1e_u 2a₁g 1a₂u 2e_u 21b₁g 22e_u 41b₂g 1e_g 0 ground-state configuration of Al₄C⁻, the next detachment channel should involve removal of a 1b₁g electron, resulting in two states 3 A₂g and 1 A₂g (1a₁g₂1e_u 2a₁g 1a₂u 2e_u 21b₁g 22e_u 41b₂g 1e_g 0). Our CCSD(T)/6-311+G(2df) calculations yielded a VDE for the 3 A₂g final state of 3.77 eV, which is in excellent agreement with feature D at 3.7 eV (Figure 1b). The 1b₁g orbital is a nonbonding MO composed primarily of the 3s AO of aluminum atoms with some hybridization with the 3p AO (Figure 3). For the reason we discussed earlier, we could not calculate the singlet open-shell 1 A₂g state, which might correspond to the weak feature observed near 3.9 eV.

**Feature E.** The next detachment channel should be due to the removal of an electron from the 1a₂u MO, which is weakly C—Al π-bonding and mainly composed of the out-of-plane p_G AO from the central C with some π-bonding from the p_G AOs of the ligands (Figure 3). Again, removing an electron from this MO results in two states, 3 B₁u and 1 B₁u. According to our CCSD(T)/6-311+G(2df) calculations, the VDE for the 3 B₁u final state is found to be 4.30 eV, which is in good agreement with the experimental value obtained for feature E (Figure 1). The PES features at higher binding energies were especially complicated and less well resolved. Nevertheless, the qualitative agreement between the calculation and the experiment lends strong support for this assignment for feature E.

**Discussion**

The overall agreement between the experimental PES spectra and the theoretical calculations is quite satisfying. Despite the apparent complexity of the PES spectra of Al₄C⁻, the calculations allowed us to make semiquantitative assignments of all the major spectral features. In particular, the excellent agreement between the calculations and the experiment on the energy and broadness of the transition to the ground state of Al₄C provides strong support for the planar structure of the Al₄C⁻ anion and the tetrahedral structure for the Al₄C neutral. The quasiplanarity of Al₄C⁻ indicates that occupation of the ligand—ligand bonding MO, 1b₂g, is critical to achieving planar geometry. As a result, excited states of Al₄C involving occupation of the 1b₂g MO are also likely to be planar or quasiplanar. The relative sharpness of the photodetachment features corresponding to the A, B, C, and D (Figure 1) features is consistent with this observation and suggests that these neutral states may in fact be planar.

The high vertical and adiabatic electron detachment energies of Al₄C⁻ (2.65 and 1.93 eV, Table 4) show the strong ligand—ligand bonding in the 1b₂g HOMO which is composed of electronegative aluminum orbitals (Figure 3). We can estimate the strength of this bonding by comparing the electron affinity

Figure 3. Molecular orbital pictures for D₄h Al₄C⁻, showing the HOMO (1b₂g), HOMO-1 (2e_u), HOMO-2 (1b₁g), and HOMO-3 (1a₂u).

<table>
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<th>State</th>
<th>Experimental VDE (eV)</th>
<th>Electron Detachment from MO</th>
<th>Theoretical VDE (eV)</th>
<th>ADE (eV)</th>
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<tr>
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<td>2.65(6)</td>
<td>1b₂g</td>
<td>2.71</td>
<td>1.93</td>
</tr>
<tr>
<td>A</td>
<td>2.86(6)</td>
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<tr>
<td>B</td>
<td>3.00(6)</td>
<td>2e_u</td>
<td>3.00</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>3.30(6)</td>
<td>2e_u</td>
<td>3.30</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>3.7</td>
<td>1b₁g</td>
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</tr>
<tr>
<td>E</td>
<td>4.2</td>
<td>1a₂u</td>
<td>4.30</td>
<td></td>
</tr>
</tbody>
</table>

*At the CCSD(T)/6-311+G(2df) level of theory with CCSD(T)/6-311+G* geometry. *Final singlet state. *Final triplet state. *Due to Jahn–Teller splitting of the triplet state.
of atomic Al (0.441 ± 0.10 eV\textsuperscript{38}) with the 1.93 eV adiabatic EA of Al\textsubscript{4}C. The difference between 1.93 and 0.44 eV represents the strong stabilization arising when the aluminum ligand atoms interact to form the Ib\textsubscript{2} HOMO and then produce the 1-electron, four-center chemical bond.

We calculated the vertical electron attachment energy (VEAE) of an electron into the 1e LUMO at the T\textsubscript{d} structure of neutral Al\textsubscript{4}C using the OVGF/6-311+G(2df) level of theory. This VEAЕ (0.93 eV) obtained is much smaller than the 1.93 eV adiabatic electron attachment energy (AEAE), showing the importance of planarization upon formation of Al\textsubscript{4}C\textsuperscript{−} to achieving maximum stabilization in the bonding.

These findings suggest that a wide variety of planar molecules with 17 or 18 valence electrons can be designed. Several such planar molecules have already been predicted theoretically by replacing two of the ligand Al atoms with Si or Ge.\textsuperscript{6} The central C can also be replaced to achieve planarity. We noted that Al\textsubscript{4}N and Al\textsubscript{4}N\textsuperscript{−}, which have been studied previously, are both planar.\textsuperscript{21,22} The latter is particularly interesting because the anion Al\textsubscript{4}N\textsuperscript{−} has 18 valence electrons with a closed shell electron configuration, which should result in simple PES spectra because only doublet final states can be accessed. That was indeed born out in our previous PES study.\textsuperscript{22} Planar molecules involving other central atoms, such as Si, P, or Ge, are likely to exist and would be extremely interesting to investigate.

Conclusions

The pentaatomic Al\textsubscript{4}C\textsuperscript{−} molecule with a tetracoordinated planar carbon (averaged over the zero-point energies) was experimentally observed for the first time. Planarity in Al\textsubscript{4}C\textsuperscript{−} is achieved through ligand–ligand bonding interactions in the HOMO. While the central cavity in the Al\textsubscript{4}C\textsuperscript{−} anion is a bit too small to accommodate the carbon atom at the potential energy surface minimum, vibrational averaging results in an essentially planar structure. To achieve perfect planarity at the potential energy surface minimum, one can use larger ligands such as Ga, Ge, In, or Sn to better accommodate the carbon atom in the center of the cavity. We also expect that neutral pentaatomic molecules, such as CAl\textsubscript{3}Si, CAl\textsubscript{2}GaSi, CAlGa\textsubscript{2}Si, CGa\textsubscript{3}Si, or CAl\textsubscript{3}Ge, should be good candidates for further search for pentaatomic species with planar carbon.

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\textsuperscript{(37)} MO pictures were made with MOLDEN3.4 program. G. Schaftenaar, MOLDEN3.4; CAOS/CAMM Center, The Netherlands, 1998.