\(\pi-\) and \(\sigma\)-Coordinated Al in AlC\(_2^-\) and AlC\(_3^-\). A Combined Photoelectron Spectroscopy and ab Initio Study

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Abstract: Vibrationally resolved photoelectron spectroscopy is combined with ab initio calculations to investigate the structure and chemical bonding in AlC\(_2^-\) and AlC\(_3^-\). AlC\(_2^-\) was found to have a \(C_2v\) structure whereas AlC\(_3^-\) was found to be almost linear, thus establishing \(\pi\)-coordination of Al in AlC\(_2^-\) and \(\sigma\)-coordination in AlC\(_3^-\). The adiabatic electron affinities of AlC\(_2\) and AlC\(_3\) were measured to be 2.65(3) and 2.50(6) eV, respectively. The calculated vertical (2.87 eV) and adiabatic (2.60 eV) electron detachment energies for AlC\(_2^-\) agree well with the 2.73(0.03) and 2.65(0.03) eV experimental values, respectively. The calculated (2.86 eV) and experimental (2.64 \pm 0.04 eV) vertical detachment energies for AlC\(_3^-\) were also in good agreement. The calculated vibrational frequency for AlC\(_2\) and vertical detachment energies for other higher energy features in both AlC\(_2^-\) and AlC\(_3^-\) were also in good agreement with the experimental measurements. The combined experimental and theoretical effort allows us to elucidate the structures of AlC\(_2^-\) and AlC\(_3^-\) and the nature of their chemical bonding.

Introduction

The –CC– group is known to bond to a variety of atoms and functional groups, such as H, F, and CH\(_3\), using \(\sigma\)-coordination to produce linear X=C=CC=N X neutral and X=C=CC=N X anion structures. However, when X is an electropositive atom such as Li, Mg, Al, Ti, etc., \(\pi\)-coordination is known to be more favorable.\(^1\)–\(^8\) Simple electrostatic models based on charge transfer from X to C\(_2\) are used to explain why electropositive atoms prefer to form \(\pi\)-complexes. However, when one carbon atom is replaced by a more electropositive but isovalent atom such as silicon, it is not clear if the \(\sigma\)-complex of XCSi will be favored over the \(\pi\)-complex. In this work, we undertake a combined theoretical and experimental work on two anions AlC\(_2^-\) and AlC\(_3^-\) which help address the question of the relative stabilities of \(\sigma\)- and \(\pi\)-coordination of electropositive aluminum to C\(_2^-\) and CSi\(^-\). We found that indeed \(\sigma\)-coordination is favored in AlC\(_3^-\), in contrast to AlC\(_2^-\), where \(\pi\)-coordination occurs.

Experimental Methods

We used anion photoelectron spectroscopy (PES) to obtain electronic and vibrational information about AlC\(_2^-\), AlC\(_3^-\), and their respective neutral species. The experiments were carried out with a magnetic-bottle time-of-flight PES apparatus, equipped with a laser vaporization cluster source. Details of the experiment have been described previously.\(^9\)–\(^10\) AlC\(_2^-\) and AlC\(_3^-\) were produced by laser vaporization of a graphite/Al or graphite/Al/Si composite target, respectively, with a pure helium carrier gas, and detected by a time-of-flight mass spectrometer. The anion species of interest were selected, decelerated, and photodecomposed with two photon energies: 355 (3.496 eV) and 266 nm (4.661 eV). Photoelectron time-of-flight spectra were measured and converted to electron binding energy spectra calibrated with the known spectrum of Cu\(^+\). The electron kinetic energy resolution of the apparatus was typically 25 meV for 1 eV electrons.

Computational Methods

We initially optimized the geometries of AlC\(_2\), AlC\(_3^-\), AlC\(_3\), and AlC\(_3^-\) employing analytical gradients with polarized split-valence basis sets (6-311+G\(^d\))\(^13\)–\(^15\) using the hybrid method, which includes a mixture of Hartree–Fock exchange with density functional exchange-correlation (B3LYP).\(^14\)–\(^16\) Then, the geometries were refined using the CCSD(T)

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method\textsuperscript{17–19} and the same basis sets. Finally, the energies of the lowest-energy structures were refined using the CCSD(T) level of theory and the more extended 6-311+G(2df) basis sets. All core electrons were kept frozen in treating the electron correlation at the CCSD(T) levels of theory. Vertical electron detachment energies from the lowest-energy singlet structures of AlC\textsubscript{2}\textsuperscript{-} and AICSi\textsuperscript{-} were calculated using the outer valence Green function (OVGF) method\textsuperscript{20–24} incorporated in Gaussian-94. The 6-311+G(2df) basis sets were used in all OVGF calculations, and all calculations were performed using the Gaussian-94 program.\textsuperscript{25}

**Experimental Results**

Figure 1 shows the PES spectra of AlC\textsubscript{2} at two wavelengths, 355 and 266 nm. The 355-nm spectrum revealed one band (X) that contains a well-resolved vibrational progression with a 590 cm\textsuperscript{-1} spacing. The 0→0 transition yields an adiabatic electron affinity (ADE) of 2.65 eV for AlC\textsubscript{2} while the strongest vibrational feature yields a vertical detachment energy (VDE) of 2.73 eV. A second detachment feature (A) was observed at 3.71 eV VDE, also with a well-resolved vibrational progression of 590 cm\textsuperscript{-1} spacing, similar to that in the X band.

Figure 2 displays the PES spectra of AICSi at two detachment photon energies. The 355-nm spectrum shows two detachment features with VDEs at 2.64 (X) and 3.15 eV (A), respectively. However, no vibrational structures were resolved for either band of the AICSi\textsuperscript{-} spectrum. The 266-nm spectrum of AICSi\textsuperscript{-} revealed no additional detachment features. The adiabatic electron affinity of AICSi was estimated from the onset of the X feature to be 2.50 eV, which is slightly smaller than that for AlC\textsubscript{2}.

The spectra of AlC\textsubscript{2} and AICSi\textsuperscript{-} are similar, except that the A-feature of AICSi\textsuperscript{-} has a considerably lower binding energy compared to that of the AlC\textsubscript{2} spectrum. The measured electron detachment energies and spectroscopic constants for AlC\textsubscript{2} and AICSi are summarized in Table 1.

**Theoretical Results**

AlC\textsubscript{2}\textsuperscript{-}. At the B3LYP/6-311+G* level of theory, the global minimum of AlC\textsubscript{2} was found to have a linear singlet $\text{C}_{\text{ave}}$ ($\Sigma^+$, $1\sigma^22\sigma^21\pi^23\sigma^2$) structure (characterized in Table 2). The cyclic C\textsubscript{2v} ($^1A_1$, $1a_1^2b_2^2a_1^2b_1^23a_2^2$) was found to be a local minimum only 1.4 kcal/mol higher in energy. However, at the higher CCSD(T)/6-311+G* level of theory, the $C_{\text{ave}}$ ($\Sigma^+$) linear structure is a second-order saddle point with the cyclic C\textsubscript{2v} ($^1A_1$) structure being the global minimum (Table 2). The linear structure corresponds to a barrier on the intramolecular rotation of Al\textsuperscript{2+} around the C\textsubscript{2} group. The height of the internal rotation barrier is only 2.1 kcal/mol at the CCSD(T)/6-311+G(2df) level of theory.

AlC\textsubscript{2}. At the B3LYP/6-311+G* level of theory, the global minimum of AlC\textsubscript{2} was found to have a cyclic C\textsubscript{2v} ($^2A_1$, $1a_1^2b_2^2a_1^2b_1^23a_2^2$) structure (Table 2). A linear singlet $C_{\text{ave}}$ ($\Sigma^+$, $1\sigma^22\sigma^21\pi^23\sigma^2$) structure was found to be a local minimum, 8.7 kcal/mol higher in energy. At the CCSD(T)/6-311+G* level of theory, the $C_{\text{ave}}$ ($\Sigma^+$) linear structure becomes a second-order saddle point while the cyclic C\textsubscript{2v} ($^1A_1$)
structure remains the global minimum (Table 2). This structure was also found to be the global minimum in previous ab initio calculations.\(^6,^7\) As was established experimentally,\(^5\) the linear structure represents a barrier on the intermolecular rotation \(\text{Al}^+\) around the \(\text{C}_2^+\) group. The height of the internal rotation barrier is 12.3 kcal/mol at the CCSD(T)/6-311+G(2df) level of theory.

The calculated vertical and adiabatic electron detachment energies for \(\text{AlC}_2^-\) were found to be the following: \(\text{VDE} = 2.87\, \text{eV} \) (OVPG/6-311+G(2df) and \(\text{ADE} = 2.60\, \text{eV} \) (CCSD(T)/6-311+G(2df)). Both \(\text{AlC}_2^-\) and \(\text{AlC}_2^+\) are very stable thermodynamically with dissociation energies calculated to be the following: \(\Delta E = 4.52\, \text{eV} \) for \(\text{AlC}_2^-\) (\(C_2^-\), \(1\, \text{A}^+\)) \(\rightarrow \text{C}_2^- \pm \text{Al}\) (\(3\, \Sigma_g^+\)) and \(\Delta E = 5.06\, \text{eV} \) for \(\text{AlC}_2^+\) (\(C_2^+\), \(2\, \Sigma_g^+\)) \(\rightarrow \text{C}_2^+ \pm \text{Al}\) (\(2\, \Pi\)) at all the CCSD(T)/6-311+G(2df) level of theory.

\(\text{AlC}_2^-\). At the B3LYP/6-311+G* level of theory, the global minimum of \(\text{AlC}_2^-\) was found to have a linear singlet \(C_{\text{soc}}^0\) (\(1\, \Sigma^+\), \(1^2\sigma^2\sigma^3\pi^2\pi^1\pi^4\pi^2\)) structure (characterized in Table 3). The alternative linear singlet \(\text{AlSiC}_-^{-}\) \((1\, \Sigma^+)\), \(1^2\sigma^2\sigma^3\pi^2\pi^1\pi^4\pi^2\)) structure was also optimized at the B3LYP/6-311+G* level of theory, and it was found to be a second-order saddle point 60.8 kcal/mol higher in energy than the global minimum and it was excluded from further examination. The cyclic \(C_3\) (\(1\, \Lambda\^\prime\)) \((1^2\sigma^2\pi^3\pi^2\pi^1\pi^2\pi^2\pi^2\)) structure collapsed into the \(\text{AlC}_2^-\) \((1\, \Sigma^+)\) structure upon geometry optimization. However, at the CCSD(T)/6-311+G* level of theory, the \(C_{\text{soc}}^0\) \((1\, \Sigma^+)\) linear structure becomes a second-order saddle point, and a bent \(C_2\) \((1\, \Lambda\) structure becomes the global minimum (Table 3). The bent structure of \(\text{AlC}_2^-\) is very different from the global minimum cyclic structure of \(\text{AlC}_2^+\) because it does not have a \(\text{Al}^-\text{Si}\) bond and the 

| Table 3. Calculated Molecular Properties of \(\text{AlC}_2^-\) and \(\text{AlC}_2^+\) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| \(\text{AlC}_2^-\), \(1\, \text{A}^+\) | \(\text{B3LYP}\) | \(\text{CCSD(T)/6-311+G*}\) | \(\text{AlC}_2^+\), \(1\, \text{A}^+\) | \(\text{B3LYP}\) | \(\text{CCSD(T)/6-311+G*}\) |
| \(\text{R(C-Al)}\), Å | 1.934 | 1.943 | 1.720 | 1.720 | 1.720 |
| \(\text{R(C-C)}\), Å | 1.265 | 1.278 | 1.265 | 1.278 | 1.278 |
| \(\text{E_{iso}}\), au | 318.51216 | 318.49832 | 318.51216 | 318.49832 | 318.49832 |
| \(\omega(\pi),\) cm\(^{-1}\) | 1251 | 1251 | 1251 | 1251 | 1251 |
| \(\omega(\sigma),\) cm\(^{-1}\) | 509 | 509 | 509 | 509 | 509 |
| \(\omega(\alpha),\) cm\(^{-1}\) | 239 i | 239 i | 239 i | 239 i | 239 i |

Table 2. Calculated Molecular Properties of \(\text{AlC}_2^-\) and \(\text{AlC}_2^+\)

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<th>(\text{AlC}_2^-), (1, \text{A}^+)</th>
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<th>(\text{CCSD(T)/6-311+G*})</th>
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In all four species studied here, the B3LYP method predicted a minimum in the linear configuration that is not preserved in the CCSD(T) calculations. We believe that the artificial minima for the linear configuration are essentially due to one-configurational nature of the B3LYP method. One needs to use methods beyond the one-configurational approximation, such as CCSD(T) used here, to get reliable results for the species studied here.


stretching. However, the bending mode, which has a very low
in the neutral AlC₂. Therefore, one expects a vibrational
of the two major low-lying vertical one-electron detachment
0.04 eV is in reasonable agreement with
-1 spacing. According to our calcula-
the fact that AlC₂ has very closely spaced 1a⁻-MO or 4a⁻-MO (which are almost
degenerate because they originate from the 1π-HOMO in the
linear structure) occurs at 3.01 eV (OVGF/6-311+G(2df)). This value agrees well with the second detachment feature (A),
observed at 3.15 ± 0.06 eV. The 266-nm spectrum revealed a splitting in the second peak, which might derive from the
quasidegeneracy of the 1a⁻ and 4a⁻ MO found in our calculations.
We therefore conclude that both AlCIS⁻ and AlCISI have
quasilinear structures based on our calculations and the experimental
data.

**Discussion**

The overall agreement between the experimental PES spectra and the theoretical calculations is quite satisfying. In particular,
the excellent agreement between the calculations and the experimentally observed peak X in AlC₂⁻ provides strong
support for the quasilinear structure with 1a-coordination of aluminum
to C₂ in AlC₂⁻ and in AlC₂. The cyclic structure of AlC₂ was
previously found in ab initio calculations and in rare gas
matrix electron spin resonance studies by Knight and others. ⁵

The agreement between the calculations and observed PES spectral features of the AlCIS⁻ anion provides strong support
for the quasilinear structure with 1a-coordination in AlCIS⁻ and in AlCISI. The vertical and adiabatic electron
detachment energies are also very high for the AlCIS⁻ anion
(Table 1) and they can be explained in the same fashion as in the AlC₂⁻ anion. Surprisingly, both VDE and ADE of AlCIS⁻
are very close to the corresponding values in AlC₂⁻, despite the
fact that one carbon was substituted by a more electropositive
silicon atom. On the other hand, one should take into account
the fact that AlCIS⁻ has 1a-coordination, while AlC₂⁻ has
π-coordination. If we compare the 1a-complexes for both anions,
VDE(AlC₂⁻) = 3.54 eV and VDE(AlCIS⁻) = 2.86 eV, one
can see a substantial reduction in electron binding energy in
AlCIS⁻. Simple electrostatic considerations can also help to
understand why AlC₂⁻ has π-complex structure, while AlCIS⁻
has 1a-complex structure. Although the effective atomic charges
in both anions show a high degree of ionicity, the two carbon
atoms have the same charges in the cyclic AlC₂⁻, whereas in
AlCIS⁻ the carbon carries a larger negative charge than silicon,
which favors the 1a-complex configuration in the latter.

**Conclusions**

We report a combined experimental and theoretical investigation of AlC₂⁻ and AlCIS⁻ and their corresponding neutrals.
Photoelectron spectra of the anions were measured and the
electron detachment energies and vibrational frequencies were
obtained. The adiabatic electron affinities of AlC₂ and AlCISI
were determined to be 2.65(3) and 2.50(6) eV, respectively.
The first electronic excited state was also observed for each
species. Our theoretical calculations predicted that AlC₂⁻ and
AlC₂ both have a C₂ᵥ cyclic structure while AlCIS⁻ and AlCISI
have quasilinear structures. The agreement between the calcu-
lated and experimental spectroscopic parameters confirms the \( \pi \)-coordination of Al in AlC\( _2^- \) and \( \sigma \)-coordination of Al in AlCSi\( ^- \).

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