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Structural and Bonding Properties of Al$_n$C$_4^{−/0}$ ($n=2–4$) Clusters: Anion Photoelectron Spectroscopy and Theoretical Calculations†

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We measured the photoelectron spectra of Al$_n$C$_4^{−}$ ($n=2–4$) clusters by using size-selected anion photoelectron spectroscopy. The structures of Al$_n$C$_4^{−/0}$ ($n=2–4$) clusters were explored with quantum chemistry calculations and were determined by comparing the theoretical results with the experimental spectra. It is found that the most stable structure of Al$_2$C$_4^{−}$ anion is a $C_{2v}$ symmetry planar structure with two Al atoms interacting with two C$_2$ units. In addition, Al$_2$C$_4^{−}$ anion also has a $D_{och}$ symmetry linear structure with two Al atoms located at the two ends of a C$_4$ chain, which is slightly higher in energy than the planar structure. The most stable structure of neutral Al$_2$C$_4$ has a $D_{oh}$ symmetry linear structure. The most stable structure of Al$_3$C$_4^{−}$ anion is a planar structure with three Al atoms interacting with two C$_2$ units. Whereas neutral Al$_3$C$_4$ cluster has a $C_{2h}$ symmetric V-shaped bent structure. The global minima structures of both Al$_4$C$_4^{−}$ and neutral Al$_4$C$_4$ are $C_{2h}$ symmetry planar structures with four Al atoms interacting with the ends of two C$_2$ units. Adaptive natural density partitioning analyses of Al$_n$C$_4^{−}$ ($n=2–4$) clusters show that the interactions between the Al atoms and C$_2$ units have both σ and π characters.

Key words: Anion photoelectron spectroscopy, Quantum chemistry calculations, Planar aluminum-carbon structures

I. INTRODUCTION

Aluminum-carbon clusters have potential application in synthesizing new two-dimensional materials and energetic materials [1–4]. Theoretical calculations on AlC, Al$_2$C, and Al$_3$C monolayer sheet-shape materials predicted that Al$_2$C sheets have a band gap of 1.05 eV, which could be deposited on the surface of PdO(100) substrate and has promising applications in solar-cell donor materials [5]. It is also intriguing that aluminum-carbon clusters can form some unusual structures such as planar tetracoordinate carbon (ptC) structures [6–12], planar pentacoordinate carbon (ppC) structures [13, 14], star-like structures [15], triangular structure [16], and endohedrally doped cage structures [17–21]. Quantum chemistry studies on small aluminum-carbon clusters predicted that the dominated structures of those clusters are flat and the aluminum-carbon bonds in those clusters are covalent bonds [22–26]. High-level ab initio computations and quantum molecular dynamics simulations suggested that CAI$_5^{+}$ has a ppC structure [27]. Theoretical studies on C$_2$E$_4$ (E=Al, Ga, In, and Tl) clusters suggested that C$_2$Al$_4$ is a double planar tetracoordinate carbon structure, and subsequent calculations predicted that structure could be used to design new molecular chains [28–30]. There are also many experimental studies on aluminum-carbon clusters. The structures of Al$_n$C$_{−/0}$ ($n=3–5$) and Al$_n$C$_2^{−/0}$ ($n=1–3$) clusters have been studied via combining anion photoelectron spectroscopy with ab initio calculations [31–36]. The structures of Al$_4$C$_2^{−/0}$ were also investigated in detail with photoelectron spectroscopy and theoretical calculations [37–40]. Photoelectron spec-
troscopy and theoretical study of $\text{Al}_n\text{C}_2^{-/0}$ ($n=5-13$) clusters suggested that those clusters can be classified into two types of structures distinguished by dissociation or undissociation of carbon-carbon bond [41]. The structures of $\text{Al}_n\text{C}_5^{-/0}$ ($n=1-5$) clusters were investigated with anion photoelectron spectroscopy and theoretical calculations [42]. The studies suggested that the most stable structures of $\text{Al}_2\text{C}_5^{-/0}$ clusters contain a $\text{ptC}$ unit and the star-like isomer of $\text{Al}_2\text{C}_5^-$ may also exist in the experiments. Mass spectrometry and theoretical calculations indicated that $\text{Al}_2\text{C}^-$ cluster is a stable cage-like structure with resistance to oxidation [43–45]. Mass spectrometry studies of $\text{Al}_n\text{C}_n\text{H}_x$ clusters suggested that those clusters may have potential application of hydrogen storage materials [46]. Understanding the structures and properties of aluminum-carbon clusters will be helpful for the designing of aluminum-based materials. To provide more information about the structures and bonding properties of small aluminum-carbon clusters, in this work, we investigate the structural evolution and chemical bonds of $\text{Al}_n\text{C}_4^{-/0}$ ($n=2-4$) clusters by utilizing anion photoelectron spectroscopy and theoretical calculations.

II. METHODS

A. Experimental methods

The experiments were conducted on a home-built apparatus which has been described elsewhere [47]. Briefly, the aluminum-carbon clusters were generated in a laser ablation source, in which a rotating and translating disk target containing a mixture of aluminum and carbon powder ($\text{Al}:\text{C}$ mole ratio 5:1) was ablated by the second harmonic (532 nm) light pulses from a nanosecond Nd:YAG laser (Continuum Surelite II-10). Simultaneously, helium carrier gas with ~0.4 MPa backing pressure was injected into the cluster source through a pulsed valve (General Valve Series 9) to cool the formed clusters after undergoing a supersonic expansion. Aluminum-carbon clusters were mass-analyzed by a time-of-flight mass spectrometer (TOF-MS). The $\text{Al}_n\text{C}_4^-$ ($n=2-4$) cluster anions were each size-selected by a mass-gate and decelerated by a momentum-decelerator before being photodetached by the fourth-harmonic light pulses (266 nm) from another nanosecond Nd:YAG laser (Continuum Surelite II-10). The detached photoelectrons were energy-analyzed by a magnetic-bottle photoelectron spectrometer. The photoelectron spectra of $\text{Al}_n\text{C}_4^-$ ($n=2-4$) cluster anions were calibrated with the spectra of $\text{Bi}^-$ and $\text{Pb}^-$ anions obtained under similar experimental conditions. The resolution of the magnetic-bottle photoelectron spectrometer is about 40 meV for photoelectrons with kinetic energy of 1 eV.

B. Theoretical methods

The initial structures of $\text{Al}_n\text{C}_4^{-/0}$ ($n=2-4$) clusters were obtained by the particle swarm optimization (CALYPSO) code [48, 49]. Full structural optimizations were carried out using the Gaussian 09 program package [50] employing the Lee-Yang-Parr’s gradient corrected correlation hybrid functional (B3LYP) [51, 52] with the 6-311+G(d) basis set [53, 54]. Different spin multiplicities were considered during the calculations. No symmetry constraint was imposed during the full geometry optimizations. Harmonic vibrational frequency analyses were also carried out to confirm that the optimized structures were true local minima on the potential energy surfaces. To obtain more accurate relative energies of the low-lying isomers for $\text{Al}_n\text{C}_4^{-/0}$ ($n=2-4$) clusters, the single-point energies were calculated by using the coupled-cluster methods including single, double, and perturbative contributions of connected triple excitations [CCSD(T)] [55, 56] methods with the aug-cc-pVTZ basis set [57–59]. It is necessary to mention that we used the restricted open-shell [ROCCSD(T)] methods to avoid spin contamination. The zero-point energies (ZPEs) obtained at the B3LYP/6-311+G(d) level were used for the corrections of total energies. The charge distributions of $\text{Al}_n\text{C}_4^-$ ($n=2-4$) clusters were studied by employing the natural bond orbital (NBO) (Version 3.1) [60] implemented in the Gaussian 09 program. The chemical bonds of $\text{Al}_n\text{C}_4^-$ ($n=2-4$) clusters were studied via the adaptive natural density partitioning (AdNDP) [61] methods by using the Multiwfn soft (Version 3.6) [62].

III. RESULTS

A. Photoelectron spectra of $\text{Al}_n\text{C}_4^-$ ($n=2-4$) clusters

The photoelectron spectra of $\text{Al}_n\text{C}_4^-$ ($n=2-4$) clusters measured at 266 nm wavelength are presented in FIG. 1. The experimental vertical detachment energies (VDEs) of $\text{Al}_n\text{C}_4^-$ ($n=2-4$) are obtained from the maxima of the first peaks in their photoelectron spectra, while the experimental adiabatic detachment energies
(ADEs) are assigned by drawing a straight line along the leading edge of the first peaks to intersect with the baseline of the photoelectron spectra and adding the instrumental resolution to the electron binding energies (EBEs) at the crossing points.

As shown in FIG. 1, the spectrum of Al$_2$C$_4^-$ cluster has a low intensity peak at 1.05 eV, a broad peak centered at 2.99 eV, two sharp peaks at 3.34 and 3.39 eV. The spectrum of Al$_3$C$_4^-$ cluster has two major peaks at 2.96 and 3.49 eV. The spectrum of Al$_4$C$_4^-$ has a low intensity peak at 1.87 eV, a broad peak at 3.31 eV with a shoulder peak at 3.08 eV, and a low signal-to-noise ratio band centered at ~4.15 eV. Some weak signals extending from 2.08 eV to 2.67 eV can also be observed in the spectrum of Al$_4$C$_4^-$. The theoretical VDE of isomer 2B is calculated to be 1.39 eV at the B3LYP level and 1.05 eV at the ROCCSD(T) theoretical level, in agreement with the broad experimental spectrum. From FIG. 4, one can see that the combination of the theoretical spectra for isomers 2A and 2B can reproduce the peak positions and patterns of the experimental spectrum very well. Isomers 2C and 2D are much higher in energy than isomer 2A by 0.24 and 0.76 eV, respectively. Hence, we suggested that isomers 2A and 2B coexist in our experiments. For neutral Al$_2$C$_4$, the most stable isomer (2a) is a $C_{2v}$ symmetry planar structure similar to the second isomer of Al$_2$C$_4^-$ anion. The energies of isomers 2b, 2c, and 2d are much higher than that of isomer 2a by 1.11, 1.34, and 1.43 eV, respectively. Based on the peaks contributed by the $D_{\infty h}$ symmetry linear structure (isomer 2B) in the experimental spectrum of Al$_2$C$_4^-$ anion, we can evaluate that the HOMO–LUMO gap (the gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital) for the $D_{\infty h}$ symmetry linear structure of neutral Al$_2$C$_4$ (isomer 2a) is approximately 2.3 eV, suggesting that the neutral Al$_2$C$_4$ linear structure is very stable.

The most stable isomer of Al$_4$C$_4^-$ anion (2A) has a $C_{2v}$ symmetry planar structure that two C$_2$ units are connected by two Al atoms. In that structure, the C–C bond lengths are 1.26 Å, and the Al–C bond lengths are 2.00, 2.08, and 2.20 Å, respectively. Isomer 2B has a $D_{\infty h}$ symmetry linear structure that two Al atoms locate at the two ends of a C$_4$ chain. The energy of isomer 2B is slightly higher than isomer 2A by only 0.05 eV. The theoretical VDE of isomer 2A is calculated to be 2.94 eV at the B3LYP level and 3.00 eV at the ROCCSD(T) level, in agreement with the broad peak at 2.99 eV in the experimental spectrum. The theoretical VDE of isomer 2B is calculated to be 1.39 eV at the B3LYP level and 1.05 eV at the ROCCSD(T) level, consistent with the peak at 1.05 eV in the experimental spectrum. From FIG. 4, one can see that the combination of the theoretical spectra for isomers 2A and 2B can reproduce the peak positions and patterns of the experimental spectrum very well. Isomers 2C and 2D are much higher in energy than isomer 2A by 0.24 and 0.76 eV, respectively. Hence, we suggested that isomers 2A and 2B coexist in our experiments. For neutral Al$_2$C$_4$, the most stable isomer (2a) is a $D_{\infty h}$ symmetry linear structure similar to the second isomer of Al$_2$C$_4^-$ anion. The energies of isomers 2b, 2c, and 2d are much higher than that of isomer 2a by 1.11, 1.34, and 1.43 eV, respectively. Based on the peaks contributed by the $D_{\infty h}$ symmetry linear structure (isomer 2B) in the experimental spectrum of Al$_2$C$_4^-$ anion, we can evaluate that the HOMO–LUMO gap (the gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital) for the $D_{\infty h}$ symmetry linear structure of neutral Al$_2$C$_4$ (isomer 2a) is approximately 2.3 eV, suggesting that the neutral Al$_2$C$_4$ linear structure is very stable.

The most stable structure of Al$_3$C$_4^-$ (3A) can be viewed as one Al atom is attached to the end of one C$_2$ unit of isomer 2A. In that structure, the Al–Al bond length is 2.75 Å, the C–C bond lengths are 1.26 Å, and the Al–C bond lengths are in the range of 1.98–2.52 Å.
FIG. 2 Low-lying isomers of $\text{Al}_n\text{C}_4^-$ ($n=2-4$) anions. The relative energies are calculated at the ROCCSD(T)/aug-cc-pVTZ//B3LYP/6-311+G(d) level. The yellow and red balls stand for the aluminum and carbon atoms, respectively. The unit of bond length is Å.

FIG. 3 Low-lying isomers of neutral $\text{Al}_n\text{C}_4$ ($n=2-4$) clusters. The relative energies are calculated at the ROCCSD(T)/aug-cc-pVTZ//B3LYP/6-311+G(d) level. The yellow and red balls stand for the aluminum and carbon atoms, respectively. The unit of bond length is Å.
TABLE I Relative energies, theoretical (B3LYP and ROCCSD(T)) VDEs and ADEs of the low-lying isomers of Al\textsubscript{2}C\textsubscript{4}\textsuperscript{−} (n=2–4) clusters, as well as the experimental VDEs and ADEs estimated from their photoelectron spectra.

| Isomer | Symmetry | State | ∆E/eV | VDE/eV | ADE/eV |
|--------|----------|-------|-------|--------|--------|
|        |          |       | B3LYP | ROCCSD(T) | Expt. | B3LYP | ROCCSD(T) | Expt. |
| Al\textsubscript{2}C\textsubscript{4}\textsuperscript{−} | 2A | C\textsubscript{2v} | 2A\textsubscript{1} | 0 | 2.94 | 3.00 | 2.99 | 2.51 | 2.44 | 2.75 |
|        | 2B | D\textsubscript{2h} | 2I\textsubscript{g} | 0.05 | 1.39 | 1.05 | 1.05 | 1.32 | 0.99 | 0.97 |
|        | 2C | C\textsubscript{s} | 2A\textsuperscript{′} | 0.24 | 2.74 |       |       |       |       |       |
|        | 2D | C\textsubscript{s} | 2A\textsuperscript{′} | 0.76 | 2.37 |       |       |       |       | 1.60 |
| Al\textsubscript{3}C\textsubscript{4}\textsuperscript{−} | 3A | C\textsubscript{s} | 1A\textsuperscript{′} | 0 | 2.80 | 3.08 | 2.99 | 2.51 | 2.65 | 2.97 |
|        | 3B | C\textsubscript{s} | 1A\textsuperscript{′} | 0.23 | 2.69 |       |       |       |       |       |
|        | 3C | C\textsubscript{s} | 1A\textsuperscript{′} | 0.51 | 2.50 |       |       |       |       |       |
|        | 3D | C\textsubscript{2v} | 1A\textsuperscript{1} | 0.59 | 2.44 |       |       |       |       | 2.01 |
| Al\textsubscript{4}C\textsubscript{4}\textsuperscript{−} | 4A | C\textsubscript{2h} | 2B\textsubscript{g} | 0 | 1.92 | 1.81 | 1.87 | 1.77 | 1.67 | 1.75 |
|        | 4B | C\textsubscript{2v} | 2B\textsubscript{1} | 0.07 | 2.24 |       |       |       |       | 2.06 |
|        | 4C | C\textsubscript{s} | 2A\textsuperscript{″} | 0.08 | 2.34 |       |       |       |       | 2.15 |
|        | 4D | C\textsubscript{1} | 2A | 0.10 | 2.52 |       |       |       |       | 2.24 |

The theoretical VDE of isomer 3A is calculated to be 2.80 eV at the B3LYP level and 3.08 eV at the ROCCSD(T) level, in agreement with the experimental value (2.99 eV). The simulated spectrum of isomer 3A matches the experimental spectrum very well. The existence of isomers 3B, 3C, and 3D can be ruled out because they are much higher in energy than isomer 3A by 0.23, 0.51, and 0.59 eV, respectively. Therefore, it is suggested that isomer 3A is the most probable one observed in our experiments. The most stable structure of neutral Al\textsubscript{3}C\textsubscript{4} cluster (3a) is a bent structure, which can be viewed as two linear Al–C≡C–Al units sharing an Al atom. Isomer 3b is slightly higher in energy than 3a by only 0.02 eV, which has a planar structure similar to the second structure of Al\textsubscript{3}C\textsubscript{4}\textsuperscript{−} anion. Isomers 3c and 3d are higher than 3a in energy by 0.13 and 0.22 eV, respectively.

For Al\textsubscript{4}C\textsubscript{4}\textsuperscript{−} cluster, isomers 4A, 4B, 4C, and 4D are close in energy with 4B, 4C, and 4D higher than 4A by 0.07, 0.08, and 0.10 eV, respectively. Isomer 4A is a C\textsubscript{2h} symmetry planar structure composed of two Al–C≡C–Al chains. In that structure, the Al–Al bond lengths are 2.71 Å, the C–C bond lengths are 1.26 Å, and the Al–C bond lengths are 1.97, 2.04, 2.17, and 2.52 Å. Isomer 4B has two Al atoms attached to one side of an Al–C≡C–C≡C–Al chain. Isomer 4C and 4D can be viewed as one Al atom caps different positions of isomer 3A. The VDE of isomer 4A is calculated to be 1.92 eV at the B3LYP level and 1.81 eV at the ROCCSD(T) level, in good agreement with the experimental value (1.87 eV). The simulated spectrum of isomer 4A fits the experimental spectrum very well. The theoretical VDEs of isomers 4B, 4C, and 4D are calculated to be 2.24, 2.34, and 2.52 eV, respectively. Thus, we suggest that isomer 4A is the most probable one detected in our experiments. Isomers 4B, 4C, and 4D may contribute to the weak signals in the range of 2.08–2.67 eV and some of the high electron binding energy peaks. The most sable structure of neutral Al\textsubscript{4}C\textsubscript{4} cluster (4a) is a C\textsubscript{2h} symmetry planar structure similar to that of Al\textsubscript{3}C\textsubscript{4}\textsuperscript{−} anion. The energies of isomers 4b, 4c, and 4d are higher than 4a by 0.22, 0.31, and 0.59 eV, respectively.
0.46 eV, respectively. It is worth mentioning that the structures of neutral Al$_n$C$_4$ ($n=2-4$) found in this work are in agreement with those reported in the literature [25, 26].

**IV. DISCUSSION**

To probe the electron distribution and bond strength of Al$_n$C$_4^-$ ($n=2-4$) clusters, the natural population analysis (NPA) [65] and Mayer bond index (MBI) [66] of those clusters were calculated and presented in FIG. 5. It is found that the NPA charges on the Al atoms are all positive in the range of +0.33 $|e|$ to +1.16 $|e|$, suggesting some electrons are transferred from Al atoms to C atoms. The MBIs of the Al–C bonds are in the range of 0.33 to 1.10, indicating that the Al–C bonds in these clusters have different characters. The MBIs of the C–C bonds are in the range of 1.97–2.28, indicating that the C–C bonds in those clusters are weaker than C≡C triple bond.

FIG. 6 Adaptive natural density partitioning molecular orbitals of Al$_n$C$_4^-$ ($n=2-4$) clusters.

To further understand the chemical bonds of Al$_n$C$_4^-$ ($n=2-4$) clusters, the AdNDP analyses of those clusters were conducted and shown in FIG. 6. It is found that Al$_3$C$_4^-$ and Al$_4$C$_4^-$ clusters have two-center two-electron (2c-2e) Al–Al $\sigma$ bonds with occupation numbers (ONs) equal to 1.71 $|e|$ and 1.73 $|e|$, indicating that those bonds are weak. For the interactions between the Al atoms and C atoms, Al$_n$C$_4^-$ ($n=2-4$) clusters have 2c-2e Al–C $\sigma$ bonds with ONs=1.90–1.97 $|e|$. Additionally, two 3c-2e $\pi$ bonds and two 3c-2e bonds with ONs=1.96–2.00 $|e|$ between the Al atoms and C$_2$ units of each cluster can be found. For the 3c-2e bond, the C–C interaction has $\pi$ character while the Al–C interaction has $\sigma$ character. Observation of different chem-
ical bonds between the Al atoms and the C atoms is consistent with the Mayer bond index analyses. Each C$_2$ unit has a 2c-2e C–C σ bond and participates a 3c-2e bond and a 3c-2e π bond, leading to the C–C bond length (1.26 Å) of those clusters are longer than the C≡C bond length (1.20 Å) in acetylene and shorter than the C=C bond length (1.33 Å) in ethylene.

V. CONCLUSION

The electronic and geometric structures of Al$_n$C$_4$\(^{-/0}\) (n=2–4) were studied by using size-selected anion photoelectron spectroscopy and theoretical calculations. The most stable structure of Al$_2$C$_4$\(^{-}\) has a planar structure with two Al atoms interacting with two C$_2$ units. A linear structure with two Al atoms attached to two ends of one C$_4$ chain can also be detected in our experiments. Neutral Al$_2$C$_4$ cluster has a linear structure. Al$_3$C$_4$\(^{-}\) is a planar structure with neutral Al$_3$C$_4$ is a V-shaped bent structure. Al$_4$C$_4$\(^{-/0}\) clusters have C$_{2h}$ symmetry planar structures with two Al–C≡C–Al units interacted by two 3c-2e π bonds and two 3c-2e bonds. The confirmation of planar Al$_n$C$_4$\(^{-/0}\) structures may be useful for designing of new two-dimensional functional materials.

Supplementary materials: The Cartesian coordinates of low-lying isomers of Al$_n$C$_4$\(^{-}\) (n=2–4) clusters and the molecular orbital of neutral Al$_2$C$_4$ cluster are available.

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