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Communication: A density functional investigation of structure-property evolution in the tetrakis hexahedral $\text{C}_4\text{Al}_{14}$ nanocluster

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Nanoclusters are prime objects of study in modern nanotechnology and offer a variety of applications promoted by their properties tunable by size, shape, and composition. DFT calculations are employed to analyze structure, stability, and selected electronic properties of a core-shell $\text{C}_4\text{Al}_{14}$ species. With insertion of the carbon core, the original low-symmetry aluminum cluster is predicted to undergo a considerable reshaping and acquire a striking $D_{4h}$ tetrakis-hexahedral geometry, with proportions controlled by a near-degenerate spin state or charge. The system also becomes more stable to dissociation. Surprisingly, other properties such as ionisation energy and electron affinity do not change significantly, although still exhibit some interesting features including opposite variations for vertical and adiabatic values. The stability and property evolutions are analyzed in terms of contributions from reshaping of the shell and its further interaction with the core. The system thus has potential applications as a symmetric building unit and a molecular device for nano-electronics/spintronics.

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I. INTRODUCTION

Interest in nanoparticle design has shown unwavering growth throughout the past half-century.\textsuperscript{1,2} This is primarily due to the fascinating properties exhibited by nanoparticles, distinct from those shown at the bulk and molecular level.\textsuperscript{3-5} Although chemical composition naturally plays a crucial role in determining nanoparticle properties, size-manipulation is also of paramount importance in this regard, with perhaps the best known examples of size-dependent phenomena arising in quantum dots.\textsuperscript{6,7} Different shapes\textsuperscript{8} can also be exploited in tuning nanoparticle properties. The conventional image tends to be that of a (roughly) spherical core-shell ensemble, although alternative shapes are now known to be important, particularly in light of their potential applications in diverse areas such as nanoelectronics and biomedical sensors.\textsuperscript{8-11}

In our previous studies on core-shell $\text{C}_n\text{Al}_{12}$ species, the $n=4$ system has exhibited a unique behaviour. The original $\text{Al}_{12}$ shell generally preserved its near-icosahedral structure for $n=1$ to $3$, but, apparently due to an “oversized” carbon core, acquired a tetracapped-cube-like geometry for $\text{C}_4\text{Al}_{12}$. In light of its unique structure, completing the shell of Al atoms that surround the $\text{C}_4$ core, by capping the two remaining faces of the $\text{Al}_8$ cage, is a tempting prospect as this allows us to verify if such a highly symmetric system could be stable and to investigate its properties. In addition, $\text{C}_4\text{Al}_{14}$ has 58 valence electrons which is a “magic” number, suggesting an increased stability.\textsuperscript{12}

Since the $\text{C}_4\text{Al}_{14}$ system represents $\text{Al}_{14}$ doped with $\text{C}_4$, it is interesting to check how different are its properties relative to those of $\text{Al}_{14}^+$, and to follow their evolution starting from the pure aluminum cluster. Previous \textit{ab initio}\textsuperscript{13} and mass spectral\textsuperscript{14} studies have shown $\text{Al}_{14}^+$ to exhibit magic behaviour. That is, upon adopting a capped-icosahedral geometry, the 3$s$ electrons of the capping aluminum induce an electronic shell-closing effect, as in commonplace in metal clusters with 40 valence electrons (a “magic number” electron count coinciding with completion of the $2p$ electronic shell).

II. RESULTS

Initial calculations were aimed at identifying the (global) minimum of the neutral $\text{C}_4\text{Al}_{14}$ nanocluster, as well as determining its electronic properties, namely, the (vertical and adiabatic) first ionisation potential, $(V/A)\text{IE}_{1}$, and electron affinity, $(V/A)\text{EA}_{1}$. Accordingly, the minimum energy geometries of the neutral, cationic, and anionic forms of the cluster have been calculated. Optimised conformations of the neutral cluster, for both the ground triplet state and near-degenerate singlet state, are presented in Figure 1, with key properties and parameters (of triplet) provided in Table I.

The central portion of the $\text{C}_4\text{Al}_{14}$ cluster resembles a cyclic $\text{C}_4$ core, enclosed within an 8-membered aluminum “cuboid.” Adjacent to each of the six faces of the cuboid sit the six remaining aluminum atoms. All C-C bonds are optimised to $\sim 1.50$ Å, and the C-Al bond lengths (considering immediate interactions only) lie within the range 2.19−2.28 Å (2.10−2.23 Å for the singlet state). The six “apical” aluminum atoms sit between 2.64 and 2.86 Å (cf. $\sim 2.80$ Å for short contacts and $\sim 3.00$ Å for long contacts of the singlet cluster) away from the four Al atoms comprising associated face of the $\text{Al}_8$ cuboid. All Al-Al bonds comprising the $\text{Al}_8$ structure are optimised to between 2.91 and 3.39 Å (2.76 and 3.40 for singlet).

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In the cationic form, [C\textsubscript{4}Al\textsubscript{14}]\textsuperscript{+}, the Al\textsubscript{8} cuboid is slightly more compact, now essentially consisting of two 4-membered rings of aluminum atoms, and slightly elongated perpendicular to the plane in which the C\textsubscript{4} ring resides. Both of the “Al\textsubscript{4}” rings have all bonds optimised at \(\sim\)2.84 Å, with the longer edges optimised at \(\sim\)3.30 Å. As with the neutral cluster, all C-C bonds are optimised to \(\sim\)1.50 Å. Regarding the apical aluminum atoms, the shorter contact lengths are now \(\sim\)2.83 Å, with the longer ones \(\sim\)2.90 Å. The anionic form, [C\textsubscript{4}Al\textsubscript{14}]\textsuperscript{-}, has an even more distorted Al\textsubscript{8} cuboid at its core: two Al\textsubscript{4} rings with bonds optimised to an alternating pattern of \(\sim\)2.70 and \(\sim\)2.80 Å and an elongation (again perpendicular to the C\textsubscript{4} plane) of the longer cuboid edges to 3.50 Å. In this instance, the apical aluminum atoms are now somewhat more evenly dispersed, each lying between 2.80 and 2.90 Å away from their nearest neighbours.

Comparison of the \(D_e\) and \(D'_e\) values (defined in Sec. IV) shows that the overall interaction between the core and the shell contributes only \(\sim\)10% to the total stability of the system relative to C\textsubscript{4} + 14 Al. This is apparently due to a considerable restructuring of the aluminum shell. The singlet (S=0) and triplet (S=1) states of C\textsubscript{4}Al\textsubscript{14} are near-degenerate, with the triplet lying only \(\sim\)4 meV lower in energy than the singlet. Interestingly, the singlet state corresponds to a more “stretched” structure, as is evident in Figure 1. Besides, both \(D_e\) and \(D'_e\) values are lower than those for C\textsubscript{2}Al\textsubscript{12} studied by us previously, even though the latter species is not “magic.” This is in accord with a similar situation for “magic” CAl\textsubscript{12}\textsuperscript{+} and supports limited validity of the jellium model for clusters of mixed composition.

Additional calculations aimed at evaluating the comparative stabilities of the cationic and anionic forms of C\textsubscript{4}Al\textsubscript{14} have also been performed. Assuming, based on the relative IE and EA of the components,\textsuperscript{15} we observe the following decomposition pathways: [C\textsubscript{4}Al\textsubscript{14}]\textsuperscript{+} \(\rightarrow\) C\textsubscript{4} + Al\textsubscript{14}\textsuperscript{+} and [C\textsubscript{4}Al\textsubscript{14}]\textsuperscript{-} \(\rightarrow\) C\textsubscript{4} + Al\textsubscript{14}\textsuperscript{-}. [C\textsubscript{4}Al\textsubscript{14}]\textsuperscript{+} is apparently less stable than C\textsubscript{4}Al\textsubscript{14}, with a calculated \(D_e\) of 3.88 eV (0.24 eV less than C\textsubscript{4}Al\textsubscript{14}). On the other hand, a negatively charged cluster is marginally more stable than its neutral counterpart, with [C\textsubscript{4}Al\textsubscript{14}]\textsuperscript{-} having a \(D_e\) of 4.15 eV (0.03 eV greater than C\textsubscript{4}Al\textsubscript{14}).

In previous calculations exploring the C\textsubscript{n}Al\textsubscript{12} (n = 1–4) series, for n = 4 we calculated a vertical first ionisation energy and electron affinity of 6.66 and 2.35 eV, respectively. The symmetrization of the cluster, as achieved via the addition of two aluminum atoms to form C\textsubscript{4}Al\textsubscript{14}, has not dramatically altered its electronic properties. We observe a 0.45 eV reduction (to 6.21 eV) in VIE\textsubscript{1}, alongside a 0.18 eV increase (to 2.53 eV) in VEA\textsubscript{1}. The adiabatic energies for C\textsubscript{4}Al\textsubscript{14} are similar to the vertical ones, suggesting that shape-change (or lack thereof) upon primary ionisation is not a defining factor in this instance.

In order to contextualize the properties of C\textsubscript{4}Al\textsubscript{14}, extensive calculations were performed on the “pure” Al\textsubscript{14} cluster whose global minimum (denoted Al\textsubscript{14}\textsuperscript{*}) alongside its ionic variants, are shown in Figure 2. Its structure is a capped, centrally occupied Al\textsubscript{12} icosahedron, in which the core aluminum sits roughly 2.70 Å away from its surrounding atoms. The fourteenth Al atom assumes a position on the periphery of the cluster, equidistant (at 2.89 Å) from each of the three nearest Al atoms. This Al-Al contact length is only marginally longer than those found within the main body of the cluster, each of

![FIG. 2. L-R: Global minimum, Al\textsubscript{14}\textsuperscript{*}; optimised minima of [Al\textsubscript{14}\textsuperscript{+}] and [Al\textsubscript{14}\textsuperscript{-}].](Image 85x553 to 265x741)

<table>
<thead>
<tr>
<th>Cluster</th>
<th>(D_e)</th>
<th>(D'_e/m\text{Al})</th>
<th>VIE\textsubscript{1}</th>
<th>VEA\textsubscript{1}</th>
<th>AIE\textsubscript{1}</th>
<th>AEA\textsubscript{1}</th>
<th>(R_e(\text{Al – Al}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{4}Al\textsubscript{14}\textsuperscript{a}</td>
<td>39.46</td>
<td>2.82</td>
<td>6.21</td>
<td>2.53</td>
<td>5.95</td>
<td>2.55</td>
<td>2.64–3.39</td>
</tr>
<tr>
<td>Al\textsubscript{14}\textsuperscript{+}</td>
<td>35.35</td>
<td>2.53</td>
<td>6.33</td>
<td>2.30</td>
<td>5.70</td>
<td>2.53</td>
<td>2.62–2.89</td>
</tr>
<tr>
<td>Al\textsubscript{14}\textsuperscript{-}</td>
<td>30.45</td>
<td>2.18</td>
<td>5.98 (5.91)</td>
<td>2.72 (2.52)</td>
<td>n/a</td>
<td>n/a</td>
<td>2.76–3.00</td>
</tr>
<tr>
<td>Al\textsubscript{14}\textsuperscript{*}</td>
<td>35.32</td>
<td>2.52</td>
<td>6.18</td>
<td>2.33</td>
<td>5.67</td>
<td>2.55</td>
<td>2.56–2.95</td>
</tr>
</tbody>
</table>

\textsuperscript{a}For the C\textsubscript{4}Al\textsubscript{14} cluster, C-C bonds are all optimised to \(\sim\)1.50 Å; all C-Al interactions fall within the range 2.19–2.28 Å; \(D'_e = 4.12\) eV.

\textsuperscript{b}For each of the Al\textsubscript{14} clusters, \(D_e\) essentially represents cluster binding energy in terms of the simple decomposition process: Al\textsubscript{14} \(\rightarrow\) 14Al. Values in parentheses are for the singlet C\textsubscript{4}Al\textsubscript{14} case.
which are approximately 2.75 Å. This is in good agreement with the previous investigations of Kumar.13

To complement the calculations performed on Al14+, we also studied the frozen Al14 shell of C4Al14 (i.e., abstracting the Al coordinates from the neutral ground triplet state cluster shown in Figure 1 and performing single-point energy calculations for its neutral, cationic, and anionic forms) as well as the cluster obtained having (re)optimised the shell. The frozen shell and its optimised analogue will henceforth be denoted as Al14+ and Al14, respectively. The Al14+ shell is shown in Figure 3 (top left), along with the optimised neutral groundstate structure (Al14+) and its (subsequently optimised) cationic and anionic forms.

Comparison of De values in Table I allows us to assign 9 eV (0.64 eV per Al atom) to the attractive interaction between the carbon core and aluminum shell in C4Al14 (i.e., Dc(C4Al14) - Dc(Al14)). The binding in the shell is ∼5 eV (0.35 eV/atom) weaker than in the relaxed aluminum cluster, consistent with longer Al-Al bonds.

Similar comparisons indicate the following differences in the property evolution. The VIE+ value is slightly reduced when the aluminum cluster transforms into the shell, but then recovered with the further interaction (including charge transfer) with the core. By contrast, the VEA1 value is first increased with inflating shell and then decreases by half as much (or remains, for the singlet state). Curiously, the corresponding AIE+ and AEA1 values exhibit opposite overall variations slightly increasing in the core-shell system relative to the pure aluminum cluster or staying same, respectively.

To gain further insight into the electronic structure of C4Al14, charge distribution within the cluster has also been studied. This entailed calculating Mulliken16,17 and Löwdin18 charges of C4Al14 (triplet and near-degenerate singlet state) and its ions; the results are summarised in Table II. In general, it would appear that the C4 core is insensitive to changes in cluster charge, with the comparatively electropositive formal charge borne by the Al14 shell exhibiting fluctuations in accord with charge and spin perturbations.

III. CONCLUSIONS

Density functional calculations predict a highly symmetric (D4h) tetrakis-hexahedral geometry for the core-shell C4Al14 nano-cluster, very different from the original Al14 cluster (resembling an Al13 icosahedron with an additional “cupping” Al atom). The C4 core stabilizes the Al14 shell relative to dissociation, with the reduction of stability due to inflation of the shell more than compensated by the further core-shell interaction, including charge-transfer. When going from Al14 to C4Al14, the systems exhibit a considerable alteration of geometry but relatively weak variations of electronic properties such as vertical/adiabatic ionisation energies and electron affinities. Insertion of the carbon core dramatically symmetrizes the aluminum shell. The weak evolution of these electronic properties in the sequence Al14+ - Al14 - Al14 - C4Al14 indicates their low sensitivities to the Al14 geometry as well as the presence of C4 inside. This illustrates the possibility of selective parameter variation, namely shaping the aluminum shell without affecting its electronic properties. Even though relatively weak, the variation in VEA1 can be assigned predominantly to the inflation of the aluminum shell in the system. For VIE+, however, the corresponding alteration is compensated for by the further interaction with the carbon core. Interestingly, upon relaxation of the ions, the net variations, for AEA1 and AIE+, interchange. In addition, the system exhibits a significant elongation upon transition into an ionic (both −/+ ) or near-degenerate singlet state. This exhibits a significant (inverted) property-structure relationship (property being charge- or spin-state) and might allow a nano-electronic/spintronic application as a charge- or spin-controlled switch.

IV. COMPUTATIONAL DETAILS

Calculations were performed at the DFT level employing the PBE0 functional and the 6-311g** basis set19,20 on all atoms, as implemented in the NWChem ab initio software package.21 Our benchmarking showed this combination of basis set and density functional to reproduce experimental parameters with suitable accuracy.15,22 An overview of the performance of our method vs previous calculations and

TABLE II. Mulliken charges (χM) and Löwdin charges (χL) for the C4Al14 cluster and its ions.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>χM C</th>
<th>χM Al</th>
<th>χL C</th>
<th>χL Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4Al14+</td>
<td>−0.77</td>
<td>−0.02 to +0.36</td>
<td>−0.31 to −0.30</td>
<td>−0.05 to +0.18</td>
</tr>
<tr>
<td>C4Al14</td>
<td>−0.74</td>
<td>+0.11 to +0.24</td>
<td>−0.31</td>
<td>+0.06 to +0.13</td>
</tr>
<tr>
<td>[C4Al14]+</td>
<td>−0.75</td>
<td>+0.21 to +0.30</td>
<td>−0.33</td>
<td>+0.14 to +0.22</td>
</tr>
<tr>
<td>[C4Al14]−</td>
<td>−0.74 to −0.72</td>
<td>−0.01 to +0.17</td>
<td>−0.30</td>
<td>−0.07 to +0.04</td>
</tr>
</tbody>
</table>

S = 1.  
S = 0.  

experiment can be found in previous work.23 Reasonable starting structures were generated using Avogadro.24,25 All calculations were run on the requin node of the SHARCNET cluster.26 For each system, the optimisation has been performed in a low symmetry, \( C_1 \), and energy minima confirmed via analysis of vibrational frequencies.

Both vertical and adiabatic first ionisation energies, \((V/A)IE_1\), and first electron affinities, \((V/A)EA_1\), are reported. Dissociation energies take into consideration the appropriate bond strengths (at 298 K): \( \text{Al-Al} \sim 167 \text{ kJ mol}^{-1} \) (1.73 eV) < \( \text{C-Al} \sim 286 \text{ kJ mol}^{-1} \) (2.96 eV) < \( \text{C-C} \sim 607 \text{ kJ mol}^{-1} \) (6.29 eV).15,27,28 Upon dissociation one may reasonably expect the carbon fragment to retain its structural integrity, whereas the partner aluminum cluster is atomized:

\[
C_n\text{Al}_m \rightarrow C_n + m\text{Al}.
\]  

Alternatively, one is also likely to observe the less energetic scenario of the cluster being broken down into two separate clusters or “whole” constituent parts:

\[
C_n\text{Al}_m \rightarrow C_n + m\text{Al}.
\]

This approach is in conformity with previous investigations.29 All dissociation energies referring to Eqs. (1) and (2) are denoted as \( D_e \) and \( D_v \) respectively. We also report \( D_e/m\text{Al} \) values, i.e., the dissociation energy obtained via Eq. (1) per Al atom (in this instance, \( m = 14 \)). Furthermore, all energies used for the calculations pertain to the lowest energy isomer obtained via our calculations (see the supplementary material).30

**ACKNOWLEDGMENTS**

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\[\text{C}_n\text{Al}_m \rightarrow C_n + m\text{Al}.\]

\[\text{C}_n\text{Al}_m \rightarrow C_n + m\text{Al}.\]

26. SHARCNET, see [https://www.sharcnet.ca/](https://www.sharcnet.ca/) for an overview of the high performance computing facilities provided by the SHARCNET consortium.
30. See supplementary material at [http://dx.doi.org/10.1063/1.4897259](http://dx.doi.org/10.1063/1.4897259) for Cartesian coordinates and energies of the optimised geometries.