Density-Functional Study of Structural and Electronic Properties of the Zr$_n$Al$^{\pm m}$ Clusters

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Abstract

The geometries, stabilities, and electronic properties of Zr$_n$Al$^{\pm m}$ ($n = 1 – 7$ and $m = 0, 1$) clusters were investigated at the UB3LYP/LANL2DZ level. The variations of structural and electronic properties with the changes of $n$ and $m$ were probed. Several possible multiplicities of each cluster were tested. The multiplicity of the most stable neutral clusters is 4 instead of 2. For all the three differently charged of Zr$_n$Al clusters, the lowest-energy geometry is in favor of three-dimensional structure when $n \geq 3$. The Zr$_3$Al$,^+$, Zr$_4$Al$,^-$, Zr$_5$Al$^+$, Zr$_6$Al$^-$ and Zr$_7$Al clusters are more stable than their corresponding differently charged species of the same size. Moreover, the odd-even oscillations are found in the fragmentation energy and the second-order difference of total energies for Zr$_n$Al$^\pm$ clusters. The Zr$_2$Al$^+$ cluster is more inert to chemical reaction than others judged by the HOMO-LUMO gaps. NBO analysis was done to analysis the electronic properties.

Keywords: Zr$_n$Al$^{\pm m}$ clusters, UB3LYP/LANL2DZ, odd-even oscillations, NBO, three-dimensional structures

1. Introduction

Recently, a large number of experimental and theoretical studies of clusters were performed (Alexandrova et al, 2004), (Zhai et al, 2003), (Lei, 2011), (Hua et al, 2013), (Addicoat et al, 2007), because they have many unique physical and chemical properties in the terms of the geometry and electronic properties (Schmidt et al, 1998), (Herry, 2012), but also have potential applications in catalysis (Yamazoe et al, 2014), (Tang et al, 2014), hydrogen storage (Ramos-Castillo et al, 2015), (Wu et al, 2015) etc. Moreover, the study of clusters plays a key role in understanding the growth behavior of microscopic particles of their bulk.

As we all know, zirconium atom is a rare metal, a 4$d$ transition-metal (TM), and has an electronic configuration of $4d^25s^2$. The Zr material used in the nuclear industry for cladding fuel elements, and own to a lower absorption cross section for neutrons. It is very resistant to corrosion by many common acids, alkalis, and sea water. Therefore, the metal, which is utilized as an alloying agent in steel and for making surgical appliances, is developed extensively by the chemical industry where corrosive agents are employed (Zhao et al, 2009), (Wang, 2006). Due to these special properties of TM Zr clusters, a number of research groups have been striving to investigate the geometrical structures and electronic properties for X-doped ($X$ = metals) zirconium and the pure zirconium clusters recently. (Zhao et al, 2009), (Wang, 2006), (Sengupta et al, 2016), (Yang et al, 2008). (Lekka, 2010) investigated the bonding characteristics and mechanical properties of Cu–Zr and Cu–Zr–Al clusters by density functional theory (DFT), they found the most abundant microstructural units on the Cu$_{60}$Zr$_{40}$ cluster. Zhao and co-workers studied the structural, electronic, and magnetic properties of the Zr$_n$Cr ($n = 2–14$) clusters, showed that the Zr$_2$Cr, Zr$_3$Cr and Zr$_5$Cr clusters are more stable than their neighbors. (Zhao et al, 2009). The chemisorption of molecular hydrogen on small Zr$_n$ clusters ($n = 2–15$) was performed by (Sheng et al, 2008). The preferred adsorption sites for H$_2$ reacting with the Zr$_n$ clusters are the bridge sites. As for Al-doped Zr clusters, (Du et al, 2010) studied the geometrical and electronic properties of neutral Zr$_{n-1}$Al clusters and the pure Zr$_n$ clusters ($n = 2–8$) with hybrid HF/DFT functional. From the above reports, although there are a lot of researches for X-doped Zr clusters, but few researches are systematically performed for the neutral and...
positively/negatively charged Al-doped zirconium clusters. What is the difference between the neutral Zr\textsubscript{n}Al and Zr\textsubscript{n}Al\textsuperscript{m} clusters? Can we find the “odd-even alteration” phenomenon in Zr\textsubscript{n}Al\textsuperscript{m} clusters as in MgB\textsubscript{6} clusters (Wu et al, 2014) for some properties? To explore these, we investigated the geometric structures, stabilities and electronic properties of Zr\textsubscript{n}Al\textsuperscript{m} (n = 1–7 and m = 0, 1) clusters.

2. Computational Methods

All the clusters were optimized by the B3LYP method (Lee et al, 1988), (Becke, 1993) in combination with the LANL2DZ basis set (Hay & Wadt, 1985). This basis set is modified by the relativistic effective core potential, therefore, suitable for the transition metals (TM) Zr clusters (Yao et al, 2008), (Ge et al, 2012). In order to check the correctness of this method used for the investigation of the Zr\textsubscript{n}Al clusters, we first accomplished the calculation on Al\textsubscript{2} and Zr\textsubscript{2} dimers. The bond length of the Al\textsubscript{2} (2.64 Å) and Zr\textsubscript{2} (2.33 Å) dimers are in nice accordance with experimental value of 2.70 Å (Fu et al, 1990) and 2.24 Å (Doverstål et al, 1998), respectively.

We have also considered the spin multiplicities for the initial configurations of Zr\textsubscript{n}Al\textsuperscript{m} clusters (n = 1–7 and m = 0, 1). To investigate the relative stability of differently charged Zr\textsubscript{n}Al clusters, we calculated the average binding energy, fragmentation energy and the second-order difference in total energies. The average binding energy (E\textsubscript{b}) for Al\textsubscript{13}B\textsubscript{n} clusters can be defined by the following formula:

\[ E_b(n) = \frac{nE(Zr)+E(Al)}{n+1} \]

The fragmentation energy (E\textsubscript{f}) can be defined by the following formula:

\[ E_f(n) = E(Zr) + E(Zr_{n-1}Al) - E(ZrAl) \]

The second-order difference of total energies (\( \Delta^2 E \)) can be defined by the following formula:

\[ \Delta^2 E(n) = E(Zr_{n+1}Al) - E(Zr_{n}Al) - 2E(ZrAl) \]

where \( E(Zr_{n+1}Al) \) and \( E(Zr_{n}Al) \) represent the energies of the most stable of Zr\textsubscript{m}Al\textsuperscript{m} and Zr\textsubscript{m-1}Al\textsuperscript{m} clusters, respectively. For the electronic properties, we calculated HOMO-LUMO (highest occupied molecular orbital-lowest unoccupied molecular orbital) gaps energies and the chemical hardness for the most stable Zr\textsubscript{n}Al\textsuperscript{m} clusters. Chemical hardness is defined as the resistance of chemical potential to a change in the number of electrons: (Pearson, 2005), (Suh et al, 2015)

\[ \eta = (I - A)/2 \]

where \( I \) and \( A \) are the ionization potential and electron affinity, respectively.

The natural bond orbital (NBO) (Carpenter & Weinhold, 1988), (Reed et al, 1988) analysis was carried out for the most stable structures in order to study the chemical bonding characteristics. All the computations were performed through Gaussian 09 package (Frisch et al, 2010).

3. Results and Discussion

3.1 Stable Geometric Structure

The fully optimized structures with lowest-energy and low-lying metastable isomers of Zr\textsubscript{n}Al\textsuperscript{m} clusters were shown in Figure 1. Through this figure we can fully understand the characteristics of different charged Zr\textsubscript{n}Al clusters enough. For \( n = 2 \), the lowest-energy structures of AlZr\textsubscript{2} and AlZr\textsubscript{2} are isosceles triangle (C\textsubscript{2v}), whose apex angle (Zr-Al-Zr) are 50.26\(^{\circ}\) and 53.75\(^{\circ}\), respectively, and the Al–Zr bond length are slightly different (See Table 1). While the most stable structure of Zr\textsubscript{2}Al\textsuperscript{1} cluster is a chain, the energy of Zr\textsubscript{2}Al\textsuperscript{1} cluster is 0.09 eV lower than its isosceles triangle structure. This phenomenon of structures for Zr\textsubscript{2}Al\textsuperscript{m} clusters is similar to B\textsubscript{2}Mg\textsuperscript{m} clusters (Wu et al, 2014). As for Zr\textsubscript{2}Al\textsuperscript{m} clusters, we got the distorted tetrahedron geometry (3a) with C\textsubscript{1} symmetry for Zr\textsubscript{2}Al cluster, but the lowest-energy structures of Zr\textsubscript{2}Al\textsuperscript{m} clusters are trigonal pyramid with C\textsubscript{2v} symmetry. The second most stable structure for the cation Zr\textsubscript{2}Al\textsuperscript{1} cluster is a quadrilateral structure with C\textsubscript{2h} symmetry whose total energy is 1.04 eV higher than the lowest-energy structure. We also tried to construct some planar and quasi-planar structures as initial configuration, but these initial configurations change to the three-dimensional (3D) structures for Zr\textsubscript{2}Al and Zr\textsubscript{2}Al\textsuperscript{1} clusters during the geometrical optimization. The V-like structures appear in Zr\textsubscript{2}Al and Zr\textsubscript{2}Al\textsuperscript{1} clusters, whose energy are 0.11 eV and 0.36 eV larger than the most stable ones, respectively.
Figure 1. Lowest-energy and low-lying structures of Zr$_n$Al$_m^{\pm}(n = 1 – 7$ and $m = 0, 1)$ clusters. (The first digit denotes the number of zirconium, the letter (a, b, c, d) is the structure label (from lower to higher energy), superscript + or - denotes a positive/negative charge, and the 0.00 represents the relative energy in eV. Others are similar)
Table 1. Shortest Zr-Al bond lengths ($R_{Zr-Al_{min}}$), shortest Zr-Zr bond lengths ($R_{Zr-Zr_{min}}$), average Zr-Zr bond lengths ($R_{Zr-Zr_{ave}}$), multiplicity, symmetry and electronic state of the Zr$_n$Al$^{1m}$ ($n = 1 – 7, m = 0, 1$) clusters for the lowest-energy structures $^a$

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Multi.</th>
<th>Symmetry</th>
<th>$R_{Al-Zr_{min}}$</th>
<th>$R_{Zr-Zr_{min}}$</th>
<th>$R_{Zr-Zr_{ave}}$</th>
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<tr>
<td>AlZr</td>
<td>4</td>
<td>D$_{4h}$</td>
<td>2.58</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>AlZr$_2$</td>
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<td>C$_{2v}$</td>
<td>2.88</td>
<td>2.45</td>
<td>2.45</td>
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<tr>
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<td>C$_1$</td>
<td>2.73</td>
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<td>2.76</td>
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<td>4</td>
<td>C$_{3v}$</td>
<td>2.83</td>
<td>2.79</td>
<td>2.82</td>
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<tr>
<td>AlZr$_5$</td>
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<td>C$_1$</td>
<td>2.74</td>
<td>2.76</td>
<td>2.87</td>
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<td>2.84</td>
</tr>
<tr>
<td>AlZr$_7$</td>
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<td>C$_1$</td>
<td>2.85</td>
<td>2.74</td>
<td>2.87</td>
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<tr>
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<td>2.79</td>
<td>2.85</td>
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<td>2.74</td>
<td>2.87</td>
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<tr>
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<td>C$_1$</td>
<td>2.85</td>
<td>2.66</td>
<td>2.86</td>
</tr>
</tbody>
</table>

$^a$ Bond lengths in Å.

The Zr$_4$Al$^{1m}$ clusters favor trigonal bipyramid (TBP) structures with $C_{3v}$ symmetry ($4a$, $4a^*$, $4a^+$) as the lowest-energy structures. It is noteworthy that there is a tetragonal pyramid isomer ($4b^+$) with high $C_{4v}$ symmetry, but the relative energy ($\Delta E$) is 1.56 eV. The most stable structures for Zr$_5$Al and Zr$_5$Al$^+$ clusters are in 3D configurations (similar to Al-caped add the top right of TBP structure), and with high spin multiplicity and $C_1$ symmetry. Meanwhile, the minimum Al–Zr bond lengths are 2.74 Å and 2.79 Å for Zr$_5$Al and Zr$_5$Al$^+$ clusters, respectively. For Zr$_6$Al$^+$ cluster, the most stable structures is a rectangular bipyramid with the Al atom located at an apex of the bipyramid ($5a^*$, $C_{4v}$). As for $n = 6$ and 7, we have optimized the isomers for Zr$_6$Al$^{1m}$ and Zr$_7$Al$^{1m}$ clusters, all the stable structures are 3D geometry. This phenomenon has also been found for AlB$_n$ clusters. (Feng & Luo, 2007)

3.2 Relative Stability

We plotted the binding energies ($E_b$) for the most stable structures of Zr$_n$Al$^{1m}$ clusters in Figure 2. The $E_b$ generally increases with increasing cluster size. No odd-even oscillations are exhibited. As a whole, the average binding energies of the Zr$_n$Al clusters are smaller than those of the Zr$_n$Al$^+$ and Zr$_n$Al$^-$ clusters from $n \geq 2$, indicating that the Zr$_n$Al clusters gain stability after the gain or loss of one electron, this phenomenon is similar to MgB$_n$$^{1m}$ clusters (Wu et al, 2014). It can be observed that the $E_b$ essentially increases sharply when $n$ goes from 1 to 4, but increasing smoothly when $n \geq 4$.

![Figure 2. Clusters size ($n$) dependence of the average binding energy ($E_b$) of Zr$_n$Al$^{1m}$ clusters](image-url)
As shown in Figure 3, the fragmentation energies ($E_f$) for the anionic Zr$_n$Al clusters have an obvious odd-even oscillation with increasing size of clusters. The local maximum fragmentation energies appear at $n = 4$ and 6 for the anionic Zr$_n$Al clusters, indicating that AlZr$_4$ and AlZr$_6$ clusters are more stable than their neighbors of Zr$_n$Al$^+$ clusters. The local minimum $E_f$ appears at Zr$_5$Al, Zr$_5$Al$^+$ and Zr$_7$Al$^+$ clusters, it means that these clusters are less stable than their neighbors.

![Figure 3. Cluster size ($n$) dependence of the fragmentation energy ($E_f$) for Zr$_n$Al$^{m}$ clusters](image)

There is a sensitive quantity that can reflect the relative stability of clusters (Wang et al., 2010), this parameter is the second-order difference of total energies ($\Delta^2 E$) in Figure 4 and it was calculated with Eq. (3). The values of $\Delta^2 E$ are the largest at $n = 4$ for all three kinds of clusters, indicating that these clusters present the highest stabilities with respect to the clusters with the same charge. This is probably due to the Zr$_4$Al$^{m}$ clusters having high symmetry ($C_{4v}$) and more charge transfer from Zr atoms to Al atom (Table 2). This viewpoint could be partially supported by Ref (Feng & Luo, 2007). Additionally, we analyzed the relationship among different charged clusters in Figure 4. The second-order difference of total energies of Zr$_3$Al$^+$, Zr$_4$Al$^+$, Zr$_5$Al$^+$, Zr$_6$Al$^+$ and Zr$_7$Al$^+$ clusters are larger than their corresponding species, this phenomenon also appears in Figure 3.

![Figure 4. Cluster size ($n$) dependence of the second-order difference energy ($\Delta^2 E$) for Zr$_n$Al$^{m}$ clusters](image)

3.3 Electronic Property

The HOMO-LUMO gap ($G_{\text{HLL}}$) is the prototypical electronic property and is an invaluable parameter in clusters electronic property analysis. (Du et al., 2010). Therefore, we have calculated the $G_{\text{HLL}}$ of Zr$_n$Al$^{m}$ clusters in Figure 5. The $G_{\text{HLL}}$ values of the cationic Zr$_n$Al clusters are usually larger than those of neutral and anionic Zr$_n$Al clusters except at $n = 4$ and 7, and the gaps are close to each other at $n = 5$ and 7 within 0.072 eV and 0.030 eV. It should be pointed out that the gaps of all clusters have minimum and maximum values for ZrAl and Zr$_2$Al$^+$, respectively, indicating that the ZrAl cluster has the highest chemical activities, but the Zr$_2$Al$^+$ cluster is the most inert in Zr$_n$Al$^{m}$ clusters. In this figure, we found no correlation between the HOMO-LUMO gaps and the energetic stability of these clusters. (Feng & Luo, 2007)
Table 2. The natural electron configuration of Al atom in Zr₄Alₓ⁺⁺⁺ clusters

<table>
<thead>
<tr>
<th>n</th>
<th>neutral</th>
<th>cation</th>
<th>anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3s0.833p⁰.42</td>
<td>3s0.833p⁰.37</td>
<td>3s0.833p⁰.67</td>
</tr>
<tr>
<td>2</td>
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<td>3s0.863p⁰.23</td>
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</tr>
<tr>
<td>3</td>
<td>3s0.763p⁰.69</td>
<td>3s0.763p⁰.63</td>
<td>3s0.763p⁰.78</td>
</tr>
<tr>
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<td>3s0.763p⁰.61</td>
<td>3s0.763p⁰.57</td>
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<tr>
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</tr>
<tr>
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<td>3s0.523p⁰.80</td>
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<tr>
<td>7</td>
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<td>3s0.623p⁰.69</td>
<td>3s0.623p⁰.70</td>
</tr>
</tbody>
</table>
Figure 7. Cluster size (n) dependence of average atomic charges (Q_AL) of Al in Zr_nAl^m clusters

4. Conclusions

The geometries, relative stability and electronic property of the Zr_nAl^m clusters were investigated at the B3LYP/LANL2DZ level. For Zr_nAl^m clusters and Zr_nAl^m clusters, all stable structures are three-dimensional. The average binding energies of Zr_nAl^m clusters increase as the size n increases. It is noticeable that the Zr_2Al^+, Zr_4Al^-, Zr_3Al^+, Zr_5Al and Zr_7Al clusters are more stable than their corresponding differently charged species judged by the fragmentation energies and the second-order difference energies. The HOMO-LUMO energy gaps indicate that the AlZr cluster has the highest chemical activity, while the AlZr_2^- cluster is the most inert in Zr_nAl^m clusters. Natural electron populations show that the electrons transfer from the Zr atoms to Al atom only in Zr_4Al^m clusters.

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References


117


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