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Density-functional global optimization of \((\text{La}_2\text{O}_3)_n\) clusters

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Structures of stoichiometric \((\text{La}_2\text{O}_3)_n\) \((n = 1–6)\) clusters have been systematically studied by theoretical calculations. Global minimum structures for these clusters are determined by genetic algorithm based global optimizations at density functional level. The ground state structure for \(\text{La}_6\text{O}_9\) was found to be highly symmetric with point group \(O_h\) and the centered oxygen atom has the coordination number as large as six, which is the same as the highest coordination number of oxygen atoms in bulk \(\text{La}_2\text{O}_3\). Analysis of the binding energies shows that \(\text{La}_6\text{O}_9\) has a high stability among the studied clusters. The energies of the highest occupied/lowest unoccupied molecular orbitals, vertical ionization energy, and vertical electron affinity of each cluster are provided. Electronic structure of \(\text{La}_6\text{O}_9\) is discussed by analysis of the frontier molecular orbitals and unpaired spin density distributions of charged clusters. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4769282]

I. INTRODUCTION

Lanthanum oxide \((\text{La}_2\text{O}_3)\) is widely used as heterogeneous catalysts or catalyst-supports for many reactions such as methane oxidative coupling,1, 2 reduction of NO,3, 4 and water-gas shift reaction.5 Due to the complexity of condensed phase systems, the structure-property relationship in the reactions is far from clear. Atomic clusters are an intermediate state of matter situated between isolated atoms and condensed phase materials, and can be studied under isolated, controlled, and reproducible conditions.6 To reveal the mechanisms of reactions involving lanthanum oxide at a molecular level, an important method is to study the structural and reactivity properties of lanthanum oxide clusters.

There have been several experimental studies on the formation, dissociation, and reactivity of lanthanum oxide clusters.7–11 The ground state structures of mono-lanthanum oxide clusters were extensively studied experimentally and theoretically,10–19 while for those containing more than one La atom, only \(\text{La}_2\text{O}_3\), \(\text{La}_3\text{O}_5\), and \(\text{La}_5\text{O}_7\) have been studied.8, 20 Recently, we performed a mass spectrometry study combined with theoretical calculations on the reactivities of lanthanum oxide cluster anions with butane.21 The ground state structures of \(\text{La}_2\text{O}_4^-\), \(\text{La}_3\text{O}_7^-\), and \(\text{La}_4\text{O}_7^{2-}\) were obtained and the calculated reaction paths interpreted the experimental findings well. However, when using the cluster model to mimic the properties of bulk material, a problem is often encountered that the highest coordination number of a certain type of atom in the cluster cannot reach that in the bulk material. For example, seven-atom \([\text{La}_3\text{O}_4]^+\) cluster was used to model the \{001\} surface of \(\text{La}_2\text{O}_3\) in studying the reaction mechanisms of methane on \(\text{La}_2\text{O}_3\) surface.1, 22 In this model cluster, there are one threefold and three twofold coordinated O atoms, while in the crystalline \(\text{La}_2\text{O}_3\) with \(\text{A-M}_2\text{O}_3\) hexagonal structure O atoms have the highest coordination number of six. In all of the above mentioned studies on lanthanum oxide clusters, the highest coordination number of oxygen atoms is three, far below the highest coordination number in the bulk material. To better understand the bulk \(\text{La}_2\text{O}_3\) material with the cluster approach, it is important to find the smallest size of lanthanum oxide clusters, at which the O or La atom has the same highest coordination number as the bulk material does.

To address the above issue of coordination number, as well as to investigate other properties and establish the structure-property relationship, it is desirable to perform a systematic study on the structures of lanthanum oxide clusters, and this study focuses on the stoichiometric clusters \((\text{La}_2\text{O}_3)_n\). However, it is quite difficult to determine the ground state structure of a metal oxide cluster because there are numerous local minima (structural isomers) in the high dimensional potential energy surface. To have an unbiased search for global minimum structures, various global optimization methods23 may be used, such as genetic algorithm (GA),24–28 basin-hopping method,29, 30 molecular dynamics simulated annealing approach,31, 32 and many others such as the method based on systematical listing of the topological structures.33, 34

The GA method has been widely used in global optimization of cluster structures by many research groups and the details of the implementation are quite different because in each step of GA various schemes may be chosen according to the inherent properties of the studied clusters.35–45 Due to very high computational costs, most implementations of GA are based on parametrized interatomic potentials or semi-empirical methods, which have been successfully applied to many homonuclear clusters (e.g., Si46–52 and Au clusters53–55) and also some binary clusters especially bimetallic alloys.56–63 Recently, attempts have been made

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to perform GA techniques on metal oxide clusters, including \((\text{MgO})_{10-35}, \text{(Mg}_3\text{O}_3)_{2-10}, \text{(Mg}_2\text{O})_{2-7}, \text{Al}_8\text{O}_{12}, \text{Al}_4\text{O}_7, (\text{Al}_2\text{O}_3)_{1-4}\text{AlO}^+, \text{V}_4\text{O}_{11-69}, (\text{Ti}_2\text{O})_{1-70}, \text{and (ZnO)}_{2-18}. \)

For these oxide clusters, the bonding cannot be described just by geometric parameters (lengths, angles, etc), and the quantum electronic structures must be calculated to obtain the reliable total energy, so a high level of theory is often required to describe the interactions within the clusters more accurately. Here we report the low-lying energy isomers of \((\text{La}_2\text{O}_3)_n\) \((n = 1–6)\) clusters found by our own implementation of GA approach. Quantum chemistry calculations at density functional theory (DFT) level are adopted in each local minimization step of GA, following closely the idea of hybrid \textit{ab initio} genetic algorithm,\(^2\) which makes the results more reliable.

**II. METHOD**

To conduct an unbiased search of the global minimum (GM) structures of lanthanum oxide clusters, we used our implementation of GA to perform the global optimization at DFT level (goDFT). The general routine of GA is quite similar to those in previous works such as in Ref. 28. Here we only give some details in our calculations that ensure our program to be suitable for oxide clusters. The GA routine includes four steps as discussed below.

Step 1: Generating the initial population. Various methods are used to generate the initial population in goDFT: total randomization of atomic positions, cutting from crystal structures, adding or removing several atoms from other \(\text{La}_n\text{O}_m\) clusters, or a group of optimized structures obtained by low level calculations, such as semi-empirical methods (such as PM6)\(^72\) or molecular dynamics simulated annealing approach.\(^73\) A checking subroutine is performed on each structure in the initial population to ensure that all bond lengths and coordination numbers of each atom are reasonable. For the metal oxide clusters, the electrostatic energy of a structure is calculated by Coulomb interactions between charged pairs: \(\text{La}^{3+} - \text{La}^{3+}, \text{O}^{2-} - \text{O}^{2-},\) and \(\text{La}^{3+} - \text{O}^{2-}\). Structures with high electrostatic energy are excluded in the initial population. By the checking subroutine unreasonable structures are not included in the initial population, thus further expensive calculations on rubbishy structures are avoided.

Step 2: Local optimization. Each structure in the initial population is optimized at DFT level (B3LYP) by an external program such as \textsc{gaussian 09}.\(^8\) Small basis sets (LanL2DZ for both \text{La} and \text{O})\(^75,76\) and coarse thresholds in both self-consistent field and optimization steps are chosen to reduce the computational costs.

Step 3: Assigning the fitness. Relative energies are used in the assigning of fitness and structures with lower relative energy have a higher chance to be maintained in the population. Relative energies and sorted distance matrices are used to judge whether two structures are the same and it is important to remove isomers with the same structure from the population.\(^77\)

Step 4: Generating new population by crossover and mutation. Crossover operation is the key search operator for GA approach. After centering (set the geometrical center of a cluster at the origin of Cartesian coordinates) and rotating of the structures of two selected father clusters, the child cluster takes atoms from one father cluster with \(z < 0\) and the rest of the atoms from the other father cluster with \(z\) values as large as possible \((z\) is a Cartesian coordinate). This method is a simple way to ensure that the child cluster has the correct number of atoms for each element type. In goDFT, mutation is implemented by randomly exchanging two atoms or randomly moving of several atoms. The checking subroutine mentioned in Step 1 is also applied to the newly generated populations.

Steps 2–4 are cycled to optimize and generate more and more populations. The cycle is stopped when more than 200 structures have been obtained totally or no new structures are obtained for 20 cycles. The last population is used as the initial population to perform the GA approach for more times with different crossing and mutation parameters to further ensure that we have found the GM structure. Our implementation of GA can well reproduce the results of other studies such as the GM structure of \(\text{Al}_3\text{O}_{12}^+\)\(^67\).

Both singlet and triplet states are tested in separated GA optimizations. The candidate structures obtained from GA calculations are then re-optimized at a relatively higher theoretical level. B3LYP functional is chosen because it has been used to investigate the structural and energetic properties of lanthanum oxide clusters and the results were found to agree well with experiments and high level theoretical calculations.\(^8,11,15,17-21\) The newly designed Minnesota M06-class functionals\(^78\) and \textsc{ccsdt}(T) (coupled-cluster method with single, double, and perturbative triple excitations) are also employed for comparison. Polarized triple-\(\zeta\) basis set (Def2-TZVP)\(^79\) for valence electrons with the corresponding effective core potential\(^80\) is used for \text{La} to take into account the scalar relativistic effects, while the all electron Def2-TZVP basis set is used for \text{O}. In the GA step, a pruned \((75,302)\) grid (default grid in \textsc{gaussian 09}) is used for numerical integrations, while in the following re-optimization steps, a pruned \((99,590)\) grid (“ultrafine” grid in \textsc{gaussian 09}) is used to avoid problems both in geometry optimizations and single-point energy calculations.\(^8\) When using the default integration grid, the optimizations of \(\text{La}_2\text{O}_3\) with \(D_{3h}\) symmetry by B3LYP/LanL2DZ or B3LYP/Def2-TZVP cannot converge. Only the lower symmetry (\(C_{3v}\)) structures can be obtained. This indicates that undensed grid may cause optimization problem not only for the Minnesota classes of functionals but also for ordinary functionals such as B3LYP, especially in optimizations of structures with high symmetry. Vibrational frequency calculations are performed to check that all stable structures have no imaginary frequency. The calculated energies reported herein are all with zero-point vibrational energy correction.

**III. RESULTS AND DISCUSSION**

**A. Low-lying energy isomers of \((\text{La}_2\text{O}_3)_n\) \((n = 1–6)\)**

The five most stable structures for each of \((\text{La}_2\text{O}_3)_n\) \((n = 1–6)\) clusters are given in Fig. 1 denoted as \(n-i\) \((i = 1–5)\). Closed shell singlet states are found to be more stable than electronic states with other spin multiplicities for all structures shown in Fig. 1, with the only exceptions for \(\text{La}_2\text{O}_3\)
FIG. 1. (a-g) DFT optimized structures of \((\text{La}_2\text{O}_3)_n\) \((n = 1-6)\) and \(\text{La}_4\text{O}_6\) clusters. Five most stable isomers are shown for each cluster, denoted as \(n-i\) for \((\text{La}_2\text{O}_3)_n\) \((n = 1-6)\) and \((3-O)-i\) for \(\text{La}_6\text{O}_8\) with \(i = 1-5\). Bond lengths in pm are given and a dashed line denotes a La–O bond between 250 and 280 pm. The symmetry and relative energy (in eV) with respect to the most stable isomer are given below each geometry. Relative energies obtained by M062X, M06, and M06L are listed in the parentheses and the values by CCSD(T) are in square brackets for \(\text{La}_4\text{O}_6\).
(Fig. 1(a)) that the triplet states of isomers 1-2, 1-3, and 1-5 are more stable than the corresponding singlet states. 1-1 with $D_{3h}$ symmetry is the GM structure for La$_2$O$_3$ and all the three O atoms are bridgingly bonded. Other than 1-1, terminally bonded oxygen atom (denoted as O, as in 1-2) or O–O moiety (as in 1-3 to 1-5) has to be included in the structures for La$_2$O$_3$. Isomers with O, or O–O moiety are all with high relative energies, which is also true for other studied clusters and the five most stable structures for each $n > 1$ cluster are all without O$_3$ or O–O moieties (except 3-2), as shown in Fig. 1. Note that the GM structure at a theoretical level is not definitely the true ground state of a cluster, especially for the cluster with more than one low-lying energy isomers with very close relative energies. Here 1-1 is much lower in energy than its competitors, so it is quite safe to conclude that 1-1 is actually the ground state of La$_2$O$_3$.

The GM structure (2-1) for La$_4$O$_6$ (Fig. 1(b)) is found to be a regular tetrahedron with $T_d$ symmetry. However, the relative energies of other low-lying energy isomers (2-2 to 2-5) are not very high. To check the precision of the B3LYP calculations, single point CCSD(T) calculations (including zero-point vibrational energy corrections at B3LYP level) and full optimizations by M062X, M06, and M06L functionals are performed on the five isomers. All the M06-class functionals predict that 2-1 is the GM structure and give quite close relative energies to those by B3LYP. The only differences are that M06-class functionals predict 2-5 is slightly more stable than 2-4 by about 0.05 eV and 2-3 is unstable and can be optimized to 2-2 when using M062X and M06L functionals. The order of stability by CCSD(T) calculations is generally accordant with those by B3LYP. However, the relative energies at CCSD(T) level are generally lower than the corresponding B3LYP values by about 0.3 eV and CCSD(T) calculations predict that 2-2 is more stable than 2-1 (but the difference is only 0.05 eV). This indicates that the precision of B3LYP level of calculations on the relative energies may not be better than 0.3 eV. So in this work, isomers with relative energies within 0.4 eV (at B3LYP) are all rechecked by M06-class functionals. Based on the relative energies of low-lying energy isomers by B3LYP calculations, and also considering the results by M06-class functionals and CCSD(T) calculations, 2-1 and 2-2 are suggested as the candidates for the ground state structure of La$_4$O$_6$.

A highly symmetric structure (3-1 in Fig. 1(c)) with point group $O_h$ is found to be the GM structure of La$_6$O$_9$. 3-1 is much more stable than other isomers by more than 1.7 eV, so it is quite safe to assign 3-1 as the ground state of La$_6$O$_9$. The structure of 3-1 can be viewed as a hollow cage-like structure of La$_6$O$_9$ [(3–O)–1 in Fig. 1(g)] plus a centered O atom and the second most stable structure 3-2 can be viewed as (3–O)–1 with a terminally bonded O atom. This suggests that the (3–O)–1 structure also has high stability and may be the ground state structure of La$_6$O$_9$, which is further confirmed by global optimization calculations (Fig. 1(g)). It is clear that other structures of La$_6$O$_9$ (3-3, 3-4, and 3-5) without moieties similar to 3-1 or (3–O)–1 have very high relative energies with respect to 3-1.

For larger clusters (La$_{2n}$O$_{3n}$)$_n$ ($n = 4–6$), all the five most stable structures of each cluster (Figs. 1(d)–1(f)) have moieties similar to 3-1 or (3–O)–1, and the GM structure of La$_{2n}$O$_{3n}$ at B3LYP is even just the combination of two 3-1 structures connected through four La–O bonds. The structures of large (La$_2$O$_{12}$)$_n$ clusters further support that the 3-1 and (3–O)–1 structures have very high stability. 4-1 and 5-1 are suggested as the ground state structures of La$_2$O$_{12}$ and La$_2$O$_{15}$, respectively, which is further supported by M06-class functionals calculations. As the largest cluster we study here, La$_2$O$_{15}$ has many isomers with low relative energies. Isomers with the relative energies within 0.4 eV are all recalculated by M06-class functionals. Accordant results are obtained except that M062X and M06L give too high relative energy for 6-2 and M06 predicts that 6-3 is the GM structure of La$_2$O$_{15}$. So we suggest that 6-1 and 6-3 as the two candidates for the ground state structure of La$_{12}$O$_{18}$, while higher level of theories or experimental works are needed to determine the true ground state. Note that for the three types of M06-class functionals, M06 gives generally more consistent results with B3LYP for the calculated clusters, which may come from the similar percentages of Hartree-Fock exchange in B3LYP (20%) and M06 (27%) while in M062X and M06L the percentages are 54% and 0%, respectively.

The coordination number of oxygen atoms is an important property of an oxide cluster, which has a close relationship with the structural compactness and bonding character. It is also a clue to study the microstructure of bulk oxide materials by methods such as NMR. In the following, the oxygen atom with coordination number $n$ is denoted as O($n$). In metal oxide clusters, O(1) and O(2) atoms are the most common ones corresponding to the terminally and bridgingly bonded oxygen, respectively. For example, (V$_2$O$_5$)$_n$ ($n = 1–5$, 8, 10, 12) clusters prefer to have cage-like stable structures, and in this type of a structure all the O atoms are one- or twofold coordinated with V atoms even in the very large cluster (V$_2$O$_{12}$)$_12$. O(3) atoms are also quite common in oxide clusters, such as in (In$_2$O$_3$)$_n$ ($n = 3–10$) and (Fe$_2$O$_3$)$_n$ ($n = 2–6$, 10) clusters. O(4) atoms can be found in large oxide clusters such as in (Ga$_2$O$_3$)$_n$ ($n = 6–10$) and (Al$_2$O$_3$)$_n$ ($n = 7–9$). Coordination numbers of O atoms larger than five have rarely reported in the stable structures of oxide clusters. For example, the cube structure of (MgO)$_{18}$ has two O(5) atoms and one O(6) atom and each of the doubly charged clusters MoO$_{19}^{2–}$ and W$_2$O$_{19}^{2–}$ contains one O(6) atom. To the best of our knowledge, La$_6$O$_9$ reported in this work is the smallest metal oxide cluster that has O(6) atom. O(6) atoms also exist in the studied larger lanthanum oxide clusters, such as in the low-lying energy isomers of La$_6$O$_{18}$ (6-1, 6-3, and 6-4). It is quite interesting to note that O(6) begins to appear from very small lanthanum oxide clusters. Different situations are found for other trivalent metals. The coordination number of each oxygen atom in metal sesquioxides $\alpha$-Al$_2$O$_3$, $\alpha$-Ga$_2$O$_3$, cubic-In$_2$O$_3$, $\alpha$-Ga$_2$O$_3$, $\alpha$-Fe$_2$O$_3$, $\alpha$-$\beta$-Fe$_2$O$_3$, cubic-Y$_2$O$_3$, and $\alpha$-$\beta$-Fe$_2$O$_3$, all equal four and in the most stable structures of studied (M$_2$O$_3$)$_n$ clusters (M = Al, Ga, In, and Fe) the highest coordination number of oxygen atoms is usually less than four, especially for small clusters ($n < 6$). The difference between La and other trivalent metals may be derived from the higher metallic character of La than others: La has the lowest first, second, and third ionization energies.
TABLE I. Energetic properties of (La$_2$O$_3$)$_n$ ($n=1–6$) clusters. Listed values (all in eV) are binding energies ($E_b$), average binding energies ($E_{b, ave}$), the first and second differences of binding energies ($\Delta E_b$ and $\Delta^2 E_b$), energies of HOMO and LUMO, HOMO-LUMO gaps, vertical ionization energies (VIE), and vertical electron affinities (VEA). See text for details. NA denotes not available.

<table>
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<th>(La$_2$O$_3$)$_n$</th>
<th>$n$</th>
<th>$E_b$</th>
<th>$E_{b, ave}$</th>
<th>$\Delta E_b$</th>
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<th>HOMO</th>
<th>LUMO</th>
<th>Gap</th>
<th>VIE</th>
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among all these mentioned trivalent metals and it is even the one with the lowest third ionization energy among all chemical elements. So in these (M$_2$O$_3$)$_n$ clusters and related bulk M$_2$O$_3$ materials, the La–O bond has more ionic character than other M–O bonds, thus with the least restriction of orientation and saturation for bonding with covalent character. As a result, in both lanthanum oxide clusters and bulk material, La and O atoms can have a higher coordination number compared with other trivalent-metal oxides.

B. Relative stabilities

The binding energy of (La$_2$O$_3$)$_n$ is defined as $E_b(n) \equiv [n \times E(1)] - E(n)$, where $E(n)$ is the energy of (La$_2$O$_3$)$_n$ cluster for $n=1–6$. The average binding energy of (La$_2$O$_3$)$_n$ is defined as $E_{b, ave}(n) \equiv E_b(n)/n$ and listed in Table I. It is clear that the $E_{b, ave}$ values increase strictly monotonically with $n$ for (La$_2$O$_3$)$_n$ including those for the meta-stable isomers, indicating that all these structures are stable with respect to fragmentation into smaller (La$_2$O$_3$)$_m$ clusters. The fragmentation energy can also be illustrated by the first-order difference of $E_b$ which is defined as $\Delta E_b(n) \equiv E_b(n) - E_b(n-1) = E(n) - [E(n-1) + E(1)]$ (for $n = 2–6$). $\Delta E_b(n)$ can be viewed as the fragmentation energy of (La$_2$O$_3$)$_n$ into (La$_2$O$_3$)$_{n-1}$ and La$_3$O$_5$, or the energy release from the growing of (La$_2$O$_3$)$_{n-1}$ to (La$_2$O$_3$)$_n$ by adding a La$_2$O$_3$. From Table I, it is clear that $\Delta E_b(3) (= 6.20$ eV) is the largest among all the $\Delta E_b$ values, which is consistent with the high stability of La$_6$O$_9$. For (La$_4$O$_6$)$_n$ $(n = 4–6)$ clusters, the fragmentation into stoichiometric (La$_2$O$_3$)$_m$ $(m < n)$ clusters may take place through different channels and the fragmentation energies for the channel (La$_2$O$_3$)$_n$ $\rightarrow$ (La$_2$O$_3$)$_m$ + (La$_2$O$_3$)$_{n-m}$ can be calculated by $E_b(n) - E_b(m) - E_b(n-m)$. By comparing the fragmentation energy for each channel, it is found that the fragmentation with La$_4$O$_6$ as one fragment is the most favorable channel. The fragmentation of La$_6$O$_9$ into La$_4$O$_6$ and La$_2$O$_3$ is with lower energy by 0.89 eV than that into two La$_6$O$_9$ fragments. The fragmentation energies of La$_{10}$O$_{15}$ (5-1) and La$_{12}$O$_{18}$ (6-1) through the channel with La$_4$O$_6$ fragments are 5.28 and 4.28 eV, respectively, which are much lower than the values listed in Table I (5.91 and 5.20 eV) for fragmentation with La$_2$O$_3$ as one fragment. The fragmentation energy of the channel La$_{12}$O$_{18}$ $\rightarrow$ La$_6$O$_9$ + La$_6$O$_9$ is calculated to be 5.80 eV, which is higher than those of other channels for La$_{12}$O$_{18}$. Note that only the fragmentation channels with stoichiometric clusters are considered in this work to compare the relative stabilities among (La$_2$O$_3$)$_n$ clusters, while other channels such as La$_4$O$_6$ $\rightarrow$ LaO + La$_3$O$_3$ are not considered.

The second-order difference of binding energy ($\Delta^2 E_b$) is another useful quantity for determining the stability of clusters, which is defined as $\Delta^2 E_b(n) \equiv \Delta E_b(n) - \Delta E_b(n+1)$ from the definition, a positive value of $\Delta^2 E_b(n)$ reflects that the energy release for the formation of $n$-sized cluster is larger than that for the growing to $(n+1)$-sized cluster. So $\Delta^2 E_b$ values can be used to interpret the relative abundances in experimental cluster distribution and a large positive $\Delta^2 E_b(n)$ value indicates a high relative stability of a certain cluster. From Table I, La$_4$O$_6$ and La$_{10}$O$_{15}$ have positive $\Delta^2 E_b(n)$ values while La$_6$O$_9$ and La$_{12}$O$_{18}$ have negative ones. The highest $\Delta^2 E_b(n)$ value of La$_6$O$_9$ and the negative values of the two neighbors (La$_4$O$_6$ and La$_{12}$O$_{18}$) demonstrate that La$_6$O$_9$ is very stable among (La$_2$O$_3$)$_n$ clusters. Note that $\Delta^2 E_b$ can also be written as $\Delta^2 E_b(n) = 2 \times E_b(n) - E_b(n-1) - E_b(n+1)$ and the values of $\Delta^2 E_b$ in Table I are calculated by this equation.

C. Molecular orbital analysis

The frontier molecule orbitals (MOs) are the most reactive MOs of a cluster. Initial interactions between the cluster and other molecules are dominated by the relative energies and the distributions of their frontier MOs. So the frontier MOs have a close relationship with the chemical reactivity and stability of a cluster. The ionization potential and electron affinity of a cluster also reflect its ability to lose or obtain an electron. In Table I we list the energies of the highest occupied MO (HOMO), the lowest unoccupied MO (LUMO), and the gaps of HOMO and LUMO of the studied clusters, accompanying with the vertical ionization energies (VIE) and vertical electron affinities (VEA). The most stable structures of La$_4$O$_6$, La$_6$O$_9$, and La$_{12}$O$_{18}$ have quite large gaps above 4.0 eV, which is close to the band gap of bulk La$_2$O$_3$ (4.3–5.5 eV).
orbitals. When La6O9 loses an electron in HOMO to become LUMO (a1g) of La6O9 is mainly composed of La 6 symmetry due to the Jahn-Teller effect and the unpaired spin level. The ground state structure of La6O9 (and also La6O8) is highly symmetric with point group Oh. Moeities with similar structures to La6O9 or La6O8 are also found in all of the stable isomers of larger (La2O3)n (n = 4–6) clusters, which further indicates that the structures of La6O9 and La6O8 have a very high stability. Analysis of the binding energies of the (La2O3)n clusters also confirms that La6O9 is very stable. The oxygen atom in La6O9 can have the same highest coordination number (six) as in the bulk La2O3. So far, La6O8 reported in this work is the smallest metal oxide cluster that has sixfold coordinated oxygen atom. It can be postulated that molecular level mechanisms of reactions over bulk La2O3 may be reasonably understood by study of (La2O3)n (n ≥ 3) clusters.

Some magic clusters with novel structures, such as C60 (Ih),102 Al13 (Ih),103 and Au20 (Td),104 have relatively high symmetry and high stability. These magic clusters may be used as building blocks to synthesize cluster assembled materials105, 106 or even act as superatoms107, 108 which can mimic the chemical behavior of certain atoms. Here, based on unbiased global search with GA method, highly symmetric structures with point group Oh are found to be the ground state structures of La6O9 and La6O8. It is interesting to study bonding and reactivity issues involved with the high symmetry nature of La6O9 and La6O8 in future.

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IV. CONCLUSIONS AND REMARKS

Global minimum structures for lanthanum oxide clusters (La2O3)n (n = 1–6) and La6O8 are determined by genetic algorithm based global optimizations at density functional level. The profiles of the frontier molecule orbitals of La6O9, the symmetries of molecule orbitals of neutral clusters and the symmetries of the structures for optimized cluster ions are given.

FIG. 2. Profiles of the frontier molecule orbitals of La6O9 (a) and unpaired spin density distributions of La6O9+/− (b). The symmetries of molecule orbitals of neutral clusters and the symmetries of the structures for optimized cluster ions are given.

The VIE values generally decrease when the sizes of clusters increase, but still much larger than the electronic work function of bulk La2O3 materials (2.5 eV).101 La6O8 has the highest LUMO (~0.90 eV) and lowest VEA (0.07 eV) among all the studied clusters, indicating that it is the least favorable for La6O9 to obtain extra electrons.

To better understand the electronic structure of La6O9, the profiles of the frontier molecule orbitals are plotted in Fig. 2. The HOMOs of La6O9 and other (La2O3)n clusters are all mainly composed of O 2p orbitals. The HOMO (t1g) of La6O9 shown in Fig. 2(a) is one of the three triply degenerated orbitals. When La6O9 loses an electron in HOMO to become La6O9+, the optimized structure of La6O9+ is distorted to C3v symmetry due to the Jahn-Teller effect and the unpaired spin density distribution is mainly localized on three O atoms. The LUMO (a1g) of La6O9 is mainly composed of La 6s orbitals. Because the LUMO of La6O9 is a non-degenerated orbital, the optimized structure of the anionic cluster La6O9− can still maintain the Oh symmetry. The spin density distribution of La6O9− is similar to the LUMO shape of neutral La6O9. The LUMO of La6O9 (or spin density of La6O9−) is symmetrically delocalized on six La atoms and distributed quite far away from the La atomic cores, which may have a close relationship with the high LUMO and low VEA of La6O9. The obtained distributions of frontier MOs/spin densities of neutral/charged La6O9 are important clues to predict their chemical reactivities.