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Structure and stability of neutral and cationic Al_nO clusters*

Yang Peng(杨 鹏)[a], Ge Jian-Hua(葛建华)[a], and Jiang Zhen-Yi(姜振益)[b,c,†]

[a] *ISN National Key Laboratory, Xidian University, Xi'an* 710071, *China*
[b] *State Key Laboratory of Electrical Insulation for Power Equipment, Xi'an Jiaotong University, Xi'an* 710049, *China*
[c] *Multidisciplinary Materials Research Center, Xi'an Jiaotong University, Xi'an* 710049, *China*

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In this paper various structural possibilities for Al_nO neutral and cationic isomers were investigated by using the B3LYP/6-311G(3df) method. Calculations of this paper predicted the existence of a number of previously unknown isomers. The stabilities of the Al_nO ($n = 2-7$) clusters with even n are greater than those with odd n, however the stabilities of cationic ions have the opposite odd–even alternation. The mass spectra observations of $Al_{17}O^+$ and $Al_{19}O^+$ ions support our theoretical predictions on their stabilities.

Keywords: Al_nO clusters, geometric configuration, ionization potentials, stability
PACC: 3640B, 3640C, 7115M

1. Introduction

Aluminium oxide (Al_2O_3) not only forms the basis of an important class of ceramic materials, but also is important in many minerals. There has been a great deal of interest in the study of various oxide surfaces to understand the role of the defect sites in their properties. Small clusters of these oxide materials provide useful models to understand the physics and chemistry of the surfaces. The small sizes of the clusters make it possible to obtain detailed electronic, geometric, and bonding information which can also be used to benchmark theoretical calculations.

The reaction of metal atoms with oxygen is also of major importance because of the use of oxides as catalysts and substrate materials. Most commercial catalysts consist of microscopic metal particles supported on oxide surfaces such as Al_2O_3. Clusters of these materials have consequently been studied both experimentally[1,2] and theoretically[3–6] to better understand the structure and bonding between aluminium and oxygen. The experimental technique used to study the neutral clusters has been mainly low-temperature matrix isolation, while other methods have been used to study the negative cluster ions.[7] However the geometries of cationic ions have remained unknown. Previous experimental observations[1,2] have not yet been well understood due to the lack of direct information about the cationic geometrical and electronic structures.

The goal of this paper is to present a systematic study of neutral and cationic aluminium oxide species containing one oxide atoms. We performed density functional calculations at the standard B3LYP/6-311G(3df) level so as to improve our comprehension on experimental observations and magic number. The rest of the paper is organized as follows. In Section 2, we give a brief description of the computational method used in this work. Results, discussion and stability will be presented in Section 3 for aluminium-oxygen species. Finally, our conclusions will be summarized in Section 4.

2. Computational methods

The initial geometrical optimizations were carried out at the B3LYP/6-31G(d) and then B3LYP/6-311G(d) level. Finally higher level geometrical optimizations were performed at B3LYP/6-311+G(3df). The geometry optimization of the Al_nO configurations considered here was achieved by searching constraints without symmetry. Frequency analyses were also performed at the same theoretical level to check

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†Corresponding author. E-mail: jiang_mater@yahoo.com

whether the optimized structures are transition states or true minima on the potential energy surfaces of corresponding clusters. The first electron ionization potentials of various clusters were calculated with adiabatic approximation. All calculations were carried out by using the GAUSSIAN 03 program[8] on a Dell workstation.

3. Results and discussion

3.1. Geometry

The geometric figures of the ground states and low-lying states of Al_nO ($n = 2 - 7$) are shown in Figs.1–3. Al and O atoms are shown with big and small balls respectively. The 'bonds' are shown for internuclear separations less than 3.1 Å (Al-Al) and 2.0 Å (Al-O), respectively. Geometric parameters are listed in Table 1.

3.1.1. . AlO

The electronic structure of AlO is well understood.[9] Our calculations support the results obtained by Ref.[9] that the ground state of AlO is a doublet state ($^2\sum^+$) [$\pi^4\sigma^1$] with a bond length of 1.6276 Å. A comparison between our bond length and experimental value[10] shows that the difference is 0.4%. When forming bonds with the oxygen atom, the aluminium atom tends to donate its valence electrons to the oxygen atom and then form a σ bond as well as two π bonds. In the case of the diatomic AlO, a single electron occupies a σ-type molecular orbital. Since the O atom is of valence -2, this electron may be viewed as an excess electron. The binding energies per atom of Al–O and Al–Al are 2.60 and 0.67 eV respectively. This large difference in binding energy leads to preference of Al–O bonding over Al–Al bonding in Al–O mixed clusters.

Loss of an electron to the AlO yields a $^1\sum^+$ ground state of AlO^+ [π^4], with a 9.90 eV higher. The ionic equilibrium separation calculated (1.7468 Å) is smaller than that of the corresponding neutral molecule. This reduction can be explained with rather nonbonding 2σ MO in molecule.

3.1.2. . Al_2O

Theoretical and experimental studies[5,11−13] on the Al_2O molecule indicate that the Al_2O molecule is linear Al–O–Al configuration at equilibrium in its ground electronic state, which is in well agreement on our predictions. The Al_2O trimer has C_{2v} and $D_{\infty h}$ structures with comparable energies, the $^1\sum_g^+$ state of the linear isomer Fig.1(a) being 2.87 eV more stable than the $^3B_2$ state of the C_{2v} isomer Fig.1(b). It is worth noting that our predicted equilibrium AlO bond length of 1.712 Å is in satisfactory agreement on that determined at 2350 K by electron diffraction (Ref.[14], 1.72 Å). The third most stable isomer is a linear ($C_{\infty v}$, $^1\sum$) Fig.1(c), which locates at 3.49 eV higher in energy above the Fig.1(a). We should notice that the strong Al-O bonds are favoured over Al–Al bonds, and Al–Al bonds are of small importance for the geometrical arrangement of the mixed clusters.

The energy ordering is preserved in the cationic species. The (C_{2v},$^4B_2$) triangular Fig.1(b) and linear ($C_{\infty v}$,$^2\sum$) Fig.1(c) lie at 3.40 and 3.62 eV which are less stable relative to the global minimum ($D_{\infty h}$,$^2\sum_u$) Fig.1(a) respectively.

3.1.3. . Al_3O

Previous calculations have theoretically and experimentally investigated on Al_3O molecules.[3,4,7,11−13] We support the prediction that the global minimum is a T-shaped C_{2v} ($^2B_2$ state) structure Fig.1(d), which can be viewed as capping an Al atom over atom (1) in Al_2O Fig.1(a). This is followed by a Y-shaped C_{2v} ($^2A_1$ state) isomer Fig.1(e) with imaginary frequency, lying only 0.11 eV higher in energy. The next structure in the energetic ordering is a $C_{\infty v}$($^2\sum$ state) linear Fig.1(f) lying 0.33 eV higher in energy relative to the Fig.1(d).

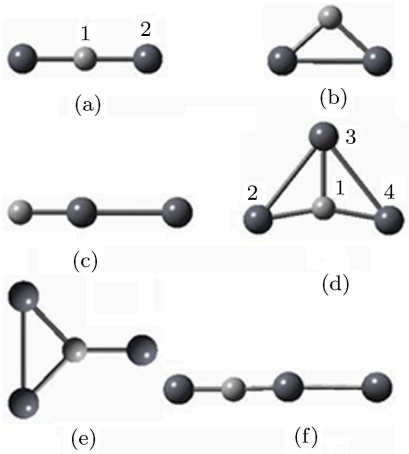


Fig.1. Low-lying isomers of (a, b, c) Al_2O and (d, e, f) Al_3O clusters.

The energy ordering is partially changed in the cationic species. There exists symmetry enhancing

($C_{2v} \rightarrow D_{3h}$) as the ground state of neutral cluster loses an electron. The linear ($C_{\infty v}$,$^1\sum$) Fig.1(f) and planar (C_{2v},$^3B_2$) Fig.1(e) lie 0.32 and 2.07 eV respectively, which are less stable than that D_{3h} ($^1A'$) isomer similar to Fig.1(d).

Table 1. Geometric parameters (L) of neutral and cationic Al_nO clusters.

clusters	Type	L/nm	clusters	Type	L/nm
Al_2O ($D_{\infty h}$) Fig.1(a)	1–2	0.1712	Al_3O^+(D_{3h}) Fig.1(d)	1–3	0.1894
Al_3O (C_{2v}) Fig.1(d)	1–2	0.1813	Al_4O^+ (C_{2v}) Fig.2(c)	1–2	0.1853
	1–3	0.1981		1–3	0.1879
	2–3	0.2879		3–5	0.2927
Al_4O (D_{4h}) Fig.2(a)	1–2	0.1963		3–4	0.3080
Al_5O (C_{2v}) Fig.2(d)	1–2	0.1770	Al_5O^+ (C_{2v}) Fig.2(d)	1–2	0.1842
	2–3	0.1899		2–3	0.1866
	3–4	0.2724		3–4	0.2720
	3–5	0.2797		3–5	0.2811
	5–6	0.2550		5–6	0.2547
Al_6O (C_s) Fig.3(a)	1–2	0.1713	Al_6O^+ (C_s) Fig.3(a)	1–2	0.1747
	2–3	0.1694		2–3	0.1667
	3–4	0.2423		3–4	0.2519
	3–5	0.2920		3–5	0.2992
	4–5	0.2620		4–5	0.2640
	5–6	0.3762		5–6	0.3411
	5–7	0.2650		5–7	0.2714
Al_7O (C_{2v}) Fig.3(d)	1–2	0.1728	Al_7O^+ (C_{2v}) Fig.3(e)	1–2	0.1833
	2–7	0.2740		1–3	0.1876
	2–3	0.2676		3–4	0.2773
	3–4	0.2934		3–7	0.2907
	3–6	0.2596		7–8	0.3728
	3–5	0.2671		3–5	0.2544
Al_2O^+ ($D_{\infty h}$) Fig.1(a)	1–2	0.1703		5–7	0.2767

3.1.4. . Al_4O

Boldyrev and Schleyer[11] and Patzer *et al*[15] predicted that the most stable configuration is a D_{4h} structure ($^1A_{1g}$) Fig.2(a), which can be viewed as capping an Al atom over the atom (1) in Al_3O Fig.1(d). The present calculations reach the same conclusion. The strong Al–O bonds are preference over Al–Al bonds and four Al–O bonds were formed. The planar (C_{2v},$^3B_1$) isomer Fig.2(b) is less stable than the Fig.2(a) (by 0.11 eV) and 0.19 eV below the planar (C_{2v},$^3B_1$) Fig.2(c).

The energy ordering differs significantly in the cationic isomers. Loss of an electron stabilizes the C_{2v} ($^2A_1$) isomer Fig.2(c) with respect to the other forms. The Al–O bonds are less important for the geometrical arrangement of the cationic mixed clusters. Next low-lying isomer is predicted to be the C_{2v} ($^2B_1$) form Fig.2(b) located at 0.23 eV higher in energy. Next Al_4O isomer in the energy ordering (0.33 eVabove the ground state) possesses C_{2v} ($^2B_2$) geometry with an imaginary radial mode frequency, which can be viewed as an aluminium atom capping over atom (3) in the structure Fig.1(d). Its imaginary frequency corresponds to a relative vibration of middle Al atom along the radial direction which ultimately leads to forming Fig.2(c).

3.1.5. . Al_5O

The global minimum of Al_5O was predicted to be a C_{2v} ($^2A_1$) structure, Fig.2(d). This geometrical configuration Fig.2(d) can be viewed as a distortion of capping an Al atom over the atom (4) in Al_4O Fig.2(c). This is followed by spacial C_s ($^2A''$) isomer, Fig.2(e), located at only 0.02 eV above the Fig.2(d). The energy difference between Fig.2(d) and Fig.2(e) is much smaller than the zero-point energies (ZPEs) (0.18 eV), hence they may coexist experimentally. The next structure in the energetic ordering is a

planar C_{2v} ($^2B_1$) rearrangement, Fig.2(f), lying 0.36 eV higher in energy.

The energy ordering of the cationic species is partially changed. The C_{2v} ($^1A_1$) form Fig.2(d) is also stabilized with respect to other forms. It is more stable than a planar C_{2v} ($^1A_1$) conformer Fig.2(f) by 0.16 eV. The third is a planar C_{2v} ($^1A_1$) geometrical configuration (0.19 eV above the cationic lowest energy state), which can be considered as two triangles bridging with vertex Al–O atoms.

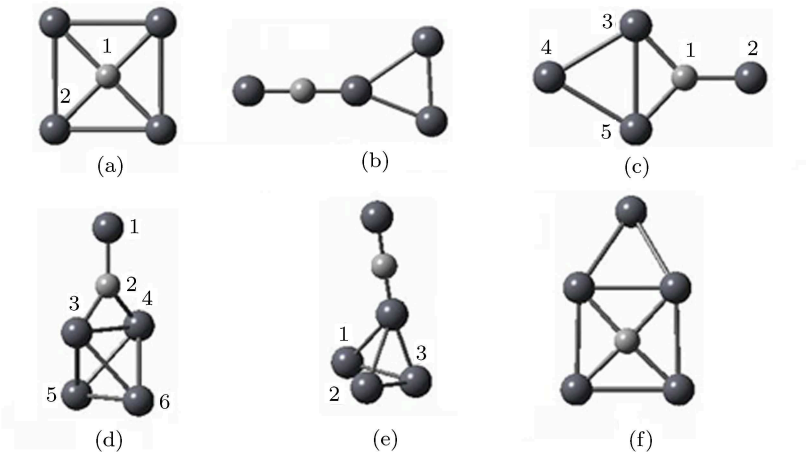


Fig.2. Low-lying isomers of (a, b, c) Al_4O and (d, e, f) Al_5O clusters.

3.1.6. . Al_6O

The most stable energetically state of Al_6O possesses a C_s ($^1A'$) geometrical form, Fig.3(a), which can be viewed as capping an Al atom over the atom (1,2) in Al_5O Fig.2(e). A C_{2v}($^1A_1$) isomer Fig.3(b) locates 0.11 eV above the Fig.3(a). The third in the energetic ordering is a planar C_{2v} ($^1A_1$) rearrangement Fig.3(c), lying 0.16 eV higher in energy. The energy ordering of the cationic species is partially changed. The C_s ($^2A'$) form Fig.3(a) is also stabilized, which is more stable than a planar C_{2v} ($^2B_1$) conformer by 0.14 eV. This planar can be viewed as bridging a triangle and a quadrangle with vertex Al–O atoms. The third is the isomer C_{2v}($^2A_1$) Fig.3(c), which is 0.24 eV above the cationic lowest energy state.

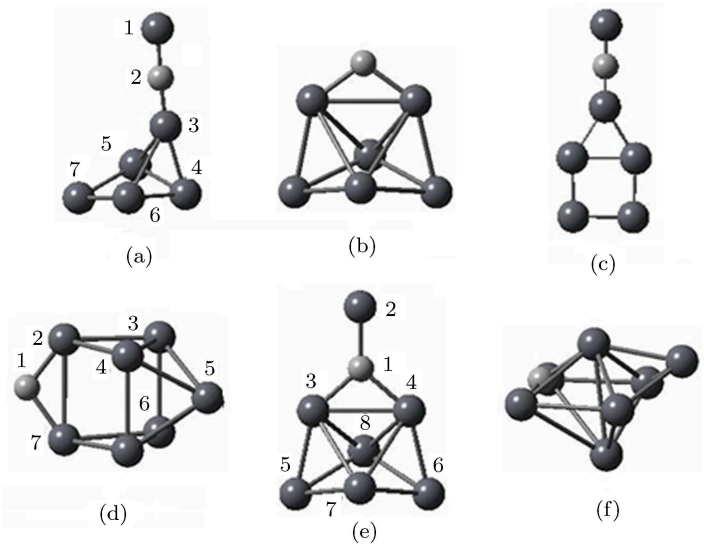


Fig.3. Low-lying isomers of (a, b, c) Al_2O and (d, e, f) Al_7O clusters.

3.1.7. . Al_7O

The ground state of Al_6O was found to be a C_{2v} ($^2A_1$) structure Fig.3(d), which can be viewed as an O atom capping over an Al_7 isomer.[16] This is followed by a C_{2v} ($^2B_1$) isomer Fig.3(e), which locates at 0.11 eV above Fig.3(d). The next structure in the energetic ordering is a C_s ($^2A''$) rearrangement, Fig.3(f), lying 0.36 eV higher in energy. The energy ordering of the cationic species is changed. A C_{2v} ($^1A_1$) form Fig.3(e) is stabilized. This is followed by a C_{3v} ($^1A_1$) isomer, located at 0.24 eV above Fig.3(e), which can be described as an Al-atom cage like Fig.3(d) containing a centred O atom. The third is a C_{2v} ($^1A_1$) geometrical configuration, Fig.3(d), lying 0.36 eV above the cationic lowest energy state.

We should note that the preferred spin multiplicity of Al_nO (even-numbered n) is a singlet whereas that of Al_nO (odd-numbered n) is a doublet. These revealed that clusters with even n are closed-shell systems whereas odd-numbered aluminium-oxide clusters are open-shell systems.

3.2. Vibrational frequency analysis

A vibrational frequency calculation is important to predict molecular stability. To determine the ground state of clusters, we tried all initial configurations with low total energies and then calculated vibrational frequencies for these clusters. We reported the lowest vibrational frequencies (LVF) of the ground states for each cluster in Table 2. It can be clearly seen that they are actually equilibrium states without imaginary frequencies.

Table 2. SCF energies, zero-point energies (ZPEs), point group (PG) and LVF of neutral (left) and cationic (right) Al_nCu.

n	PG	Energy/-a.u.	ZPEs/a.u.	LVF/cm^{-1}	PG	Energy/-a.u.	ZPEs/a.u.	LVF/cm^{-1}
2	$D_{\infty h}$	560.2575	0.0039	110.4	$D_{\infty h}$	559.9651	0.0038	150.4
3	C_{2v}	802.6766	0.0042	148.3	D_{3h}	802.4724	0.0040	136.9
4	D_{4h}	1045.1285	0.0054	94.2	C_{2v}	1044.9094	0.0048	40.9
5	C_{2v}	1287.5766	0.0067	47.0	C_{2v}	1287.3639	0.0065	54.0
6	C_s	1530.0471	0.0087	36.5	C_s	1529.8217	0.0081	37.6
7	C_{2v}	1772.5047	0.0105	27.8	C_{2v}	1772.2925	0.0090	40.5

3.3. Relative stability

The adiabatic ionization potentials (IPs) of neutral Al_nO ($n = 2-7$) are shown in Fig.4. There exists a conspicuous peaks at $n = 2$, which present a special relative stability. In the mass spectra of low energy ion beam measurement,[1,2] the intensities of Al_2O clusters are much higher than others in this series, which suggest that Al_2O clusters are more stable. These results agree well with our theoretical prediction. The IPs values corresponding to even number n are larger values, which correspond to relatively stable neutral state. For comparison, experimental IPs[17] of Al_n molecules have been shown in Fig.4. They have the same odd–even alternation as the Al_nO except Al_2. The oscillating behaviour of the IPs reflects the change of spin multiplicity of the ground state of this series. The clusters with even-numbered n present the higher values of the IP with respect to their neighbouring odd systems because it is more difficult to remove an electron from a closed-shell system than from an open-shell system.

To test the relative stabilities of cationic ions further, the following energy variation of reactions is considered: $2(Al_nO^+) \rightarrow (Al_{n+1}O^+) + (Al_{n-1}O^+)$. We define the energy variation in the formula as Delt $(E_n) = E_{n+1} + E_{n-1} - 2E_n$, which is the second difference in energy for cationic series. Hence we obtain the curves shown in Fig.5 corresponding to the energy variations in the formula as the number n of aluminium atoms. It is evident that the Delt (E_n) is larger for odd n and smaller for even n in Fig.5, which suggests that those Al_nO^+cationic species corresponding to odd n are more stable. The oscillating behaviour of the second difference in energy reveals the alternation of an open–closed shell system of the lowest energy state of this series. This conclusion can be extrapolated to Al_nO^+ ($n > 7$) cationic species. In the mass spectra of low energy ion beam measurement,[2] the strong signal intensities of Al_{15}^+, $Al_{17}O^+$, Al_{17}^+, and $Al_{19}O^+$ ions support our predictions on their stabilities.

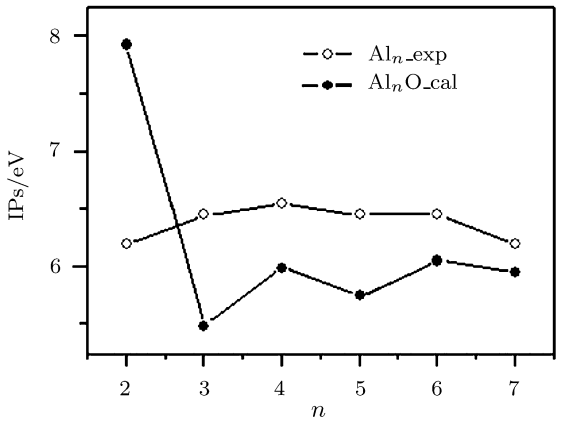


Fig.4. Ionization potentials vs. the number n of aluminium atom for Al_nO.

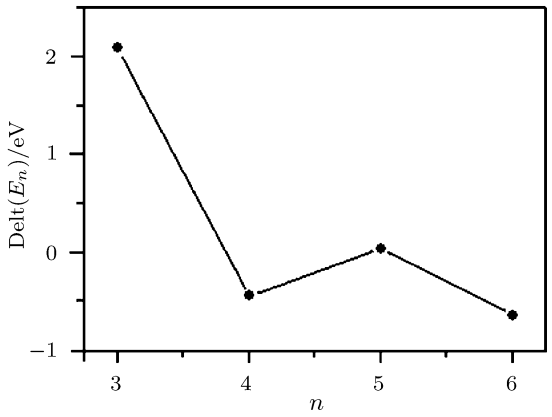


Fig.5. Delta (E_n) as a function of n.

4. General conclusions

Geometries, electronic states and energies of neutral and cationic Al_nO ($n = 2 - 7$) have been investigated by using the density functional theory. Structural optimization and frequency analyses were performed with the basis set of 6-311+G(3df). Our calculations predicted the existence of a number of previously unknown isomers. Al_nO ($n = 2 - 6$) can be viewed as capping an Al atom over the $Al_{n-1}O$ molecules. The ground states of neutral clusters correspond to the lowest spin multiplicities. The stabilities of the Al_nO ($n = 2 - 7$) clusters with even n are greater than those with odd n, however the stabilities of cationic ions have the opposite odd–even alternation. Our theoretical calculations on the neutral and cationic stabilities will be useful for the understanding of experimental observations.

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