



Investigation of Sc_mO_n^- ($m = 2-5, n = 2-3$) clusters using photoelectron spectroscopy and density functional calculations

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ABSTRACT

The Sc_mO_n^- ($m = 2-5, n = 2-3$) cluster anions were investigated using photoelectron spectroscopy and density functional theory (DFT) calculations. The adiabatic detachment energies (ADEs) and vertical detachment energies (VDEs) of these cluster anions were estimated from their photoelectron spectra. The most probable structures of Sc_mO_n ($m = 2-5, n = 2-3$) cluster anions and neutrals were determined by combining DFT calculations with the photoelectron spectroscopy experiments. The structures of Sc_mO_n^- ($m = 2-5, n = 2-3$) can be characterized as attaching oxygen atoms to the top sites, bridge sites, or hollow sites of Sc_m clusters. There is no direct interaction between the oxygen atoms.

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1. Introduction

Scandium oxides have potential applications in catalytic reaction, especially for heterogeneous catalysis [1–3]. Probing scandium oxide clusters may provide molecular level insight into the related catalytic reactions. Therefore, a number of experimental and theoretical studies have been carried out to investigate the properties of scandium oxides. The reaction of ScO^+ with D_2 has been studied in a guided ion beam tandem mass spectrometer [4]. The bond energies and ionization energies of ScO_2 were determined through the guided ion beam reaction between ScO^+ and NO_2 [5]. The ScO_n^- ($n = 1-4$) clusters were investigated by anion photoelectron spectroscopy [6]. The photoelectron spectra of ScO^- and ScO_2^- were analyzed using density functional calculations and coupled cluster theory [7]. That of ScO_2^- has also been investigated in more detail by *ab initio* calculations and Franck–Condon factor simulation [8]. Matrix-isolation infrared studies of ScO_n ($n = 1-4$) found that two forms of ScO_2 , bent OScO dioxide and $\text{Sc}(\text{O}_2)$ peroxide, coexist in the experiments [9,10]. A similar study of ScO_6 and ScO_8 showed that the trisuperoxo scandium complex ($\text{Sc}(\eta^2\text{-O}_2)_3$) and superoxo scandium bisozonide complex ($(\eta^2\text{-O}_2)\text{Sc}(\eta^2\text{-O}_3)_2$) were formed [11,12]. The electronic and geometrical structures of oxo, peroxy and superoxo isomers of scandium and other 3d-metal oxides were also investigated with density functional calculations by Jena and co-workers [13,14]. Recent theoretical calculations of larger oxygen-rich scandium oxides ScO_n ($n = 5-12, 15, 16, 18$) suggest that the lowest-energy isomers of ScO_n clusters with odd n always contain $\eta^2\text{-O}_3$ groups except for $n = 5$ [15].

The investigations of scandium oxides shown above, were mainly focused on single scandium atom and oxygen-rich species. On the other hand, the scandium oxides participating catalytic reactions are usually medium or large clusters containing multiple scandium atoms. Although density functional calculations suggested that ScO^+ and ScO are not good mediators for conversion of CH_4 into methanol [16,17], recent fast flow reactor experiments show that larger scandium oxide clusters with O^+ centers can activate the C–H bonds of hydrocarbon molecules [18,19]. Therefore, it is necessary to conduct detailed studies on the properties of Sc_mO_n ($m > 1$) clusters. There are a few theoretical studies on Sc_mO_n clusters with $m > 1$. For example, the structure and bonding properties of $\text{Sc}_2\text{O}_{2-4}$ were investigated using DFT calculations by Johnson and Panas [20]. The stability and electronic properties of Sc_mO ($m = 1-9$) clusters were studied by Li et al. [21]. The structure and magnetic properties of Sc_mO ($m = 2-14$) [22] and Sc_mO_n ($m = 1-2, n = 1-6$) [23] were studied using DFT by Wang and co-workers. The electronic properties of Sc_mO_n ($m = 1-3, n = 1-2$) were investigated using screened hybrid density functional theory by Yang et al. [24]. However, the experimental investigation of scandium oxides with multiple scandium atoms is quite rare except that the ionization potentials of Sc_mO ($m = 5-36$) were measured by Yang and Knickelbein [25]. In this work, we studied the structures and bonding properties of Sc_mO_n^- ($m = 2-5, n = 2-3$) clusters using mass-selected anion photoelectron spectroscopy and DFT calculations.

2. Experimental and theoretical methods

2.1. Experimental method

The experiments were conducted on a home-built apparatus consisting of a time-of-flight mass spectrometer and a magnetic-bottle

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photoelectron spectrometer, which has been described in detail elsewhere [26]. Briefly, the Sc_mO_n^- cluster anions were generated in a laser vaporization source in which a rotating, translating Sc_2O_3 target (13 mm diameter) was ablated with the second harmonic of an Nd:YAG laser (Continuum Surelite II-10) while helium gas with ~ 4 atm pressure was allowed to expand through a pulsed valve over the Sc_2O_3 target. The Sc_mO_n^- ($m = 2-5, n = 2-3$) cluster anions produced were mass-analyzed by the time-of-flight mass spectrometer. The resolution of the time-of-flight mass spectrometer is about 450 in term of $m/\Delta m$. The cluster anions of interests were each mass-selected by a mass-gate, decelerated by a momentum decelerator, then photodetached using the fourth harmonic (266 nm, 4.661 eV/photon) of a second Nd:YAG laser, respectively. The resultant electrons were energy-analyzed by the magnetic-bottle photoelectron spectrometer. The photoelectron spectra were calibrated using the known spectrum of Cu^- . The instrumental resolution was approximately 40 meV for electrons with 1 eV kinetic energy.

2.2. Theoretical method

The calculations were performed using density functional theory (DFT) with the hybrid B3LYP functional [27–30]. The 6-311+G (d) all-electron basis set implemented in Gaussian03 program package were used in all calculations [31]. In order to test the reliability of our calculations, benchmark calculations of the bond length and electron affinity (EA) of ScO were conducted using the hybrid B3LYP functional and 6-311+G (d) basis set. The bond length and electron affinity of ScO are calculated to be 1.659 Å and 1.26 eV respectively, in good agreement with the experimental measurements (1.668 Å [32], 1.35 eV [6]). In addition, Bauschlicher [33], Jena [34], Zhao [35] and their coworkers have investigated ScO using different density functional methods such as B3LYP, BPW91, and BLYP. They found that B3LYP method is the best for ScO, for the functionals used. Therefore, B3LYP method was used in this work. During the calculations, a variety of initial structures and all possible spin multiplicities of Sc_mO_n^- ($m = 2-5, n = 2-3$) were tried. All geometry optimizations were conducted without any symmetry constraint. Harmonic vibrational frequencies were performed on all optimized geometries to ensure that the structures correspond to real local minima. The zero-point vibrational energies and spin contamination were considered for all stable structures.

3. Experimental results

The photoelectron spectra of Sc_mO_2^- and Sc_mO_3^- ($m = 2-5$) obtained with 266 nm photons are shown in Figure 1. Each peak of the photoelectron spectra represents a transition from the ground state of the lowest or lower-lying isomers of the anions to the ground or excited state of the corresponding neutrals. The VDEs and ADEs of Sc_mO_n^- ($m = 2-5, n = 2-3$) cluster anions measured based on their photoelectron spectra were summarized in Table 1. The ADEs were determined by adding the value of instrumental resolution to the onset of the first peak in the photoelectron spectra. The onset of the first peak was found by drawing a straight line along the leading edge of the peak to cross the baseline of the spectra.

3.1. Sc_mO_2^- ($m = 2-5$)

As shown in Figure 1, the photoelectron spectrum of Sc_2O_2^- has three resolved features centered at about 1.20, 1.40 and 2.36 eV, respectively. Some features at the higher binding energy are also discernible. The photoelectron spectrum of Sc_3O_2^- has a strong peak centered at ~ 1.60 eV and a weak peak at about 2.40 eV. The photoelectron spectrum of Sc_4O_2^- has two well-resolved features cen-

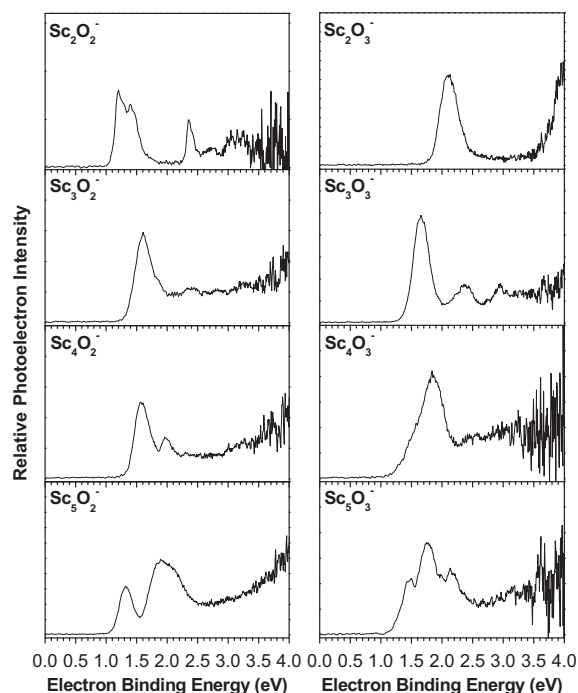


Figure 1. Photoelectron spectra of Sc_mO_2^- and Sc_mO_3^- ($m = 2-5$) cluster anions recorded with 266 nm photons.

Table 1

Experimentally observed VDEs and ADEs from the photoelectron spectra of Sc_mO_n^- ($m = 2-5, n = 2-3$).

Cluster	ADE	VDE	Cluster	ADE	VDE
Sc_2O_2^-	1.11	1.20	Sc_2O_3^-	1.84	2.10
Sc_3O_2^-	1.33	1.60	Sc_3O_3^-	1.43	1.66
Sc_4O_2^-	1.35	1.58	Sc_4O_3^-	1.26	1.84
Sc_5O_2^-	1.23	1.32	Sc_5O_3^-	1.16	1.27

The uncertainties of the experimental values are ± 0.08 eV.

tered at 1.58 and 1.99 eV. The photoelectron spectrum of Sc_5O_2^- exhibits two peaks centered at ~ 1.32 eV and 1.93 eV, respectively.

3.2. Sc_mO_3^- ($m = 2-5$)

The photoelectron spectrum of Sc_2O_3^- contains a strong peak centered at 2.10 eV. The onset of its second peak can be observed in the range of 3.7–4.0 eV. The spectrum of Sc_3O_3^- has an intense peak at ~ 1.66 eV and two weak peaks centered at about 2.39 and 2.95 eV. For Sc_4O_3^- , an intense peak centered at 1.84 eV is observed. Sc_4O_3^- also has a long tail at the low binding energy side, which may come from the excited states or other isomers of Sc_4O_3^- produced with low abundance. For Sc_5O_3^- , three features centered at ~ 1.45 , 1.76 and 2.13 eV are detected in the photoelectron spectrum. We also have taken the spectrum of Sc_5O_3^- with 532 nm photons (Figure 2). The 532 nm spectrum shows that the first feature is actually composed of two peaks centered at 1.27 and 1.41 eV respectively. Thus, the VDE and ADE of Sc_5O_3^- are determined to be 1.27 and 1.16 eV respectively based on the 532 nm spectrum.

4. Theoretical results and discussion

The optimized structures of the low-energy isomers of Sc_mO_n^- ($m = 2-5, n = 2-3$) clusters from DFT calculations were presented in Figure 3 with the most stable structures on the left. We have

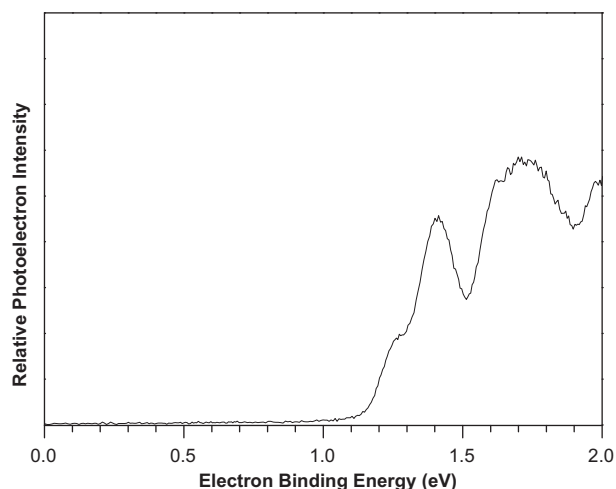


Figure 2. Photoelectron spectrum of Sc_5O_3^- cluster anion recorded with 532 nm photons.

considered several multiplicities and various initial structures including oxo (OMO), peroxy (MO_2), superoxo (MOO) and ozonide (MOOO) types of structures. The calculated results indicate that the most stable isomers of Sc_mO_n^- ($m = 2-5, n = 2-3$) clusters are in the form of oxo type of structures.

The low energy isomers of the neutral Sc_mO_n ($m = 2-5, n = 2-3$) clusters were optimized using their corresponding anionic structures as initial structures and presented in Figure 4. The calculated VDEs and ADEs of Sc_mO_n^- ($m = 2-5, n = 2-3$) cluster anions were listed in Table 2, in which the experimental values were also presented. The VDEs were calculated as the energy differences between the neutrals and anions at the geometry of the anionic species. For the anionic clusters with multiplicity M , the neutral species with multiplicities $M - 1$ and $M + 1$ were considered in the VDEs and ADEs calculations.

4.1. Sc_mO_2^- ($m = 2-5$)

The most stable isomer of Sc_2O_2^- (isomer 2A) is a rhombus structure with D_{2h} symmetry and in $^2B_{1u}$ electronic state. The Sc–O bond lengths are all 1.89 Å, similar to that calculated by Johnson and Panas [20]. The VDE of isomer 2A is calculated to be 1.16 eV, which is in agreement with the experimental measurement (1.20 eV). The structure of isomer 2B is similar to that of isomer 2A, but it is in $^4B_{2g}$ state. Isomer 2B is 0.72 eV higher in energy than isomer 2A. The calculated VDE of isomer 2B (0.44 eV) is much lower than the experimental value. As a result, its existence in the experiments can be excluded. Isomer 2C is much unstable than isomers 2A and 2B. It is higher in energy than isomer 2A by about 1.35 eV. Thus, the existence of isomer 2C in the experiments can be ruled out. Isomer 2A is likely the one produced in our cluster source.

The most stable isomer of Sc_3O_2^- (isomer 3A) is a structure composed of an isosceles triangle Sc_3 with one oxygen atom adsorbed on the surface and the other oxygen atom bridging a Sc–Sc bond of the triangular Sc_3 . Isomer 3B is a structure with two oxygen atoms bridging two Sc–Sc bonds of the triangular Sc_3 , and it is 0.14 eV higher in energy than isomer 3A. The calculated VDE of isomer 3B is 1.48 eV, much closer to the experimental value (1.60 eV) than that of isomer 3A (1.18 eV). Therefore, it is probable that isomer 3B is the major product generated in our experiments. Isomer 3A may also contribute to the photoelectron spectrum of Sc_3O_2^- since the first photoelectron feature of Sc_3O_2^- is quite broad and the VDE of isomer 3A is very close to the front

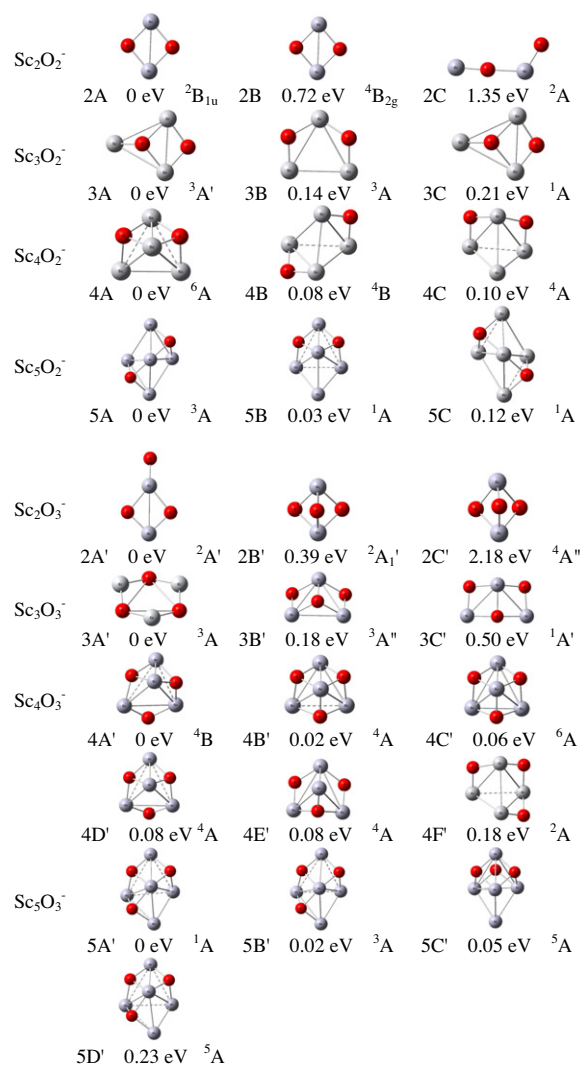


Figure 3. Low-lying isomers of Sc_mO_n^- ($m = 2-5, n = 2-3$) cluster anions.

part of that feature. Isomer 3C is higher in energy than isomer 3A by 0.21 eV and its theoretical VDE (0.94 eV) is not consistent with the experimental value. So its existence in the experiments can be ruled out.

Isomer 4A is the lowest-energy isomer of Sc_4O_2^- with 6A ground electronic state. It is a distorted tetrahedral Sc_4 adsorbing two oxygen atoms on its two surfaces. Isomers 4B and 4C are only 0.08 and 0.10 eV higher in energy than isomer 4A. The calculated VDE of isomer 4A (1.55 eV) is closer to the measured value of 1.58 eV than isomers 4B (1.35 eV) and 4C (1.24 eV). So isomer 4A is the most probable structure for Sc_4O_2^- cluster. Isomers 4B and 4C may also exist since they are very close to isomer 4A in energy. Isomer 4D with 6A electronic state is 0.21 eV higher in energy than isomer 4A. The calculated ADE and VDE of isomer 4D (1.35, 1.53 eV) are also in accordance with the experimental measurements. Therefore, it is suggested that isomers 4A–4D all contribute to the photoelectron features of Sc_4O_2^- .

The three most stable isomers of Sc_5O_2^- (isomers 5A–5C) differ in energy by only 0.03 and 0.12 eV. They all have two oxygen atoms adsorbed on two surfaces of the distorted triangular bipyramidal Sc_5 cluster, in which isomer 5B has two O atoms adsorbed on the same pyramid while isomers 5A and 5C have the O atoms on different pyramids. The calculated VDEs of isomers 5A and 5C (1.21, and 1.12 eV) are in agreement with the

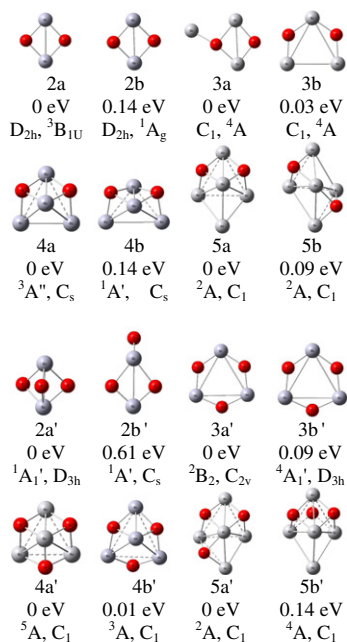


Figure 4. Low-lying isomers of neutral Sc_mO_n ($m = 2-5, n = 2-3$) clusters.

Table 2

Relative energies (REs) of the low-lying isomers of Sc_mO_n^- ($n = 2-5, m = 2-3$) as well as their VDEs and ADEs obtained by density functional calculations.

Isomer	Sym	State	$\langle S^2 \rangle$	RE (eV)	VDE (eV)		ADE (eV)		
					Theo.	Exp.	Theo.	Exp.	
Sc_2O_2^-	2A	D_{2h}	$^2B_{1u}$	0.75	0	1.16	1.20	1.16	1.11
	2B	D_{2h}	$^4B_{2g}$	3.75	0.72	0.44		0.43	
	2C	C_1	2A	0.75	1.35	1.54		1.38	
Sc_3O_2^-	3A	C_s	$^3A'$	2.02	0	1.18		1.13	
	3B	C_1	3A	2.01	0.14	1.48	1.60	1.24	1.33
	3C	C_1	1A	0	0.21	0.94		0.88	
Sc_4O_2^-	4A	C_1	6A	8.75	0	1.55	1.58	1.36	1.35
	4B	C_2	4B	3.75	0.08	1.35		1.32	
	4C	C_1	4A	3.75	0.10	1.24		1.17	
	4D	C_1	6A	8.75	0.21	1.53		1.35	
Sc_5O_2^-	5A	C_1	3A	2.02	0	1.21	1.32	1.17	1.23
	5B	C_1	1A	0	0.03	0.98		0.92	
	5C	C_1	1A	0	0.12	1.12		0.98	
Sc_2O_3^-	2A'	C_s	$^2A'$	0.75	0	2.05	2.10	1.80	1.84
	2B'	D_{3h}	$^2A'_1$	0.75	0.39	0.82		0.81	
	2C'	C_s	$^4A''$	3.75	2.18	1.36		1.35	
Sc_3O_3^-	3A'	C_1	3A	2.00	0	1.58	1.66	1.34	1.43
	3B'	C_s	$^3A''$	2.00	0.18	1.43		1.29	
	3C'	C_s	$^1A'$	0	0.50	1.08		0.97	
Sc_4O_3^-	4A'	C_2	4B	3.77	0	1.63	1.84	1.40	1.26
	4B'	C_1	4A	3.83	0.02	1.31		1.16	
	4C'	C_1	6A	8.75	0.06	1.58		1.13	
	4D'	C_1	4A	3.75	0.08	1.46		1.33	
	4E'	C_1	4A	3.76	0.08	1.32		1.22	
	4F'	C_1	2A	0.76	0.18	1.16		1.11	
Sc_5O_3^-	5A'	C_1	1A	0	0	1.07	1.27	1.00	1.16
	5B'	C_1	3A	2.09	0.02	1.02		0.98	
	5C'	C_1	5A	6.00	0.05	1.11		1.09	
	5D'	C_1	5A	6.00	0.23	1.13		1.06	

experimental value (1.32 eV). The calculated VDE (0.98 eV) of isomer 5B deviates much from that of the experimental measurements. Thus, we suggest that isomers 5A and 5C are the most probable ones generated in the experiments.

4.2. Sc_mO_3^- ($m = 2-5$)

The most stable isomer of Sc_2O_3^- (isomer 2A') is formed by attaching the third oxygen atom to one of the Sc atoms in the

Sc_2O_2 rhombus. The Sc–O bond lengths in the rhombus ring of isomer 2A' are 1.84 and 2.08 Å, respectively, and that of the terminal Sc–O bond in isomer 2A' is ~ 1.76 Å. The terminal Sc–O bond may be considered as a double bond since it is a little longer than the Sc–O triple bond (1.66 Å) of ScO cluster proposed in the literature [36,37], but shorter than the Sc–O single bond (1.87 Å) of Sc_2O_2 cluster [20]. The theoretical ADE and VDE of isomer 2A' are calculated to be 1.80 and 2.05 eV, very close to the experimental measurements (1.84 and 2.10 eV). Isomer 2B' has D_{3h} symmetry and is higher in energy than isomer 2A' by 0.39 eV. Isomer 2C' has a structure similar to isomer 2B' but with different spin multiplicity. Isomer 2C' is higher in energy than isomer 2A' by 2.18 eV, much less stable. The theoretical VDEs of isomer 2B' (0.82 eV) and isomer 2C' (1.36 eV) are much lower than the experimental value. Therefore, their existence in the experiments can be excluded. We suggest isomer 2A' to be the most probable one detected in the experiments.

The most stable isomer of Sc_3O_3^- (isomer 3A') is a chair-like structure formed by attaching three O atoms to the three edges of Sc_3 triangle with each O atom bridging two Sc atoms. Isomer 3B' and Isomer 3C' can be considered as an O atom capping the Sc_3 triangle and with the other two O atoms attaching to two edges of the Sc_3 triangle. Isomer 3B' is higher in energy than isomer 3A' by only 0.18 eV. The calculated ADEs and VDEs of isomer 3A' (1.34 and 1.58 eV) and 3B' (1.29 and 1.43 eV) are all consistent with the experimental values (1.43 and 1.66 eV). So we suggest that isomers 3A' and 3B' both contribute to the experimental photoelectron spectrum of Sc_3O_3^- . Isomer 3C' is higher in energy than isomer 3A' by 0.50 eV. Its VDE (1.08 eV) is much lower than the experimental value. Therefore, its existence in the experiments can be ruled out.

The first six low-lying isomers of Sc_4O_3^- are very close in energy, with energy separations of only 0.02, 0.06, 0.08, 0.08 and 0.18 eV. The structure of isomer 4A' can be viewed as two oxygen atoms capping two faces of a distorted Sc_4 tetrahedron and the third oxygen atom bridging one of the Sc–Sc bonds. The Sc–O bond lengths of isomer 4A' are in the range of 1.89–2.11 Å. The structures of isomer 4B' and 4C' can be viewed as three oxygen atoms capping three faces of a distorted Sc_4 tetrahedron. The structures of isomer 4D' has a Sc_4 tetrahedron capped by two O atoms and an oxygen atom bridging one of the Sc–Sc bonds. Isomer 4E' is a structure consisted of a distorted tetrahedral Sc_4 cluster with two oxygen atoms bridging two Sc–Sc bonds and the third oxygen atom capping a face of the tetrahedron. Isomer 4F' has a structure of three oxygen atoms bridging three Sc–Sc bonds of Sc_4 cluster. The calculated VDE of isomer 4F' (1.16 eV) deviates much from the experimental measurement (1.84 eV). Thus, the existence of isomer 4F' in the experiments can be excluded. The calculated VDEs of isomers 4A' and 4C' are in good agreement with the experimental VDE. They are the most probable products in the experiments. Since isomers 4B', 4D' and 4E' are very close to isomer 4A' in energy and their theoretical VDEs are consistent with the low electron binding energy tail in the range of 1.3–1.8 eV in the experimental spectrum of Sc_4O_3^- . Thus, the existence of these isomers in the experiments is also possible.

Isomer 5A' of Sc_5O_3^- has 1A ground electronic state. It is composed of three oxygen atoms adsorbed on three faces of the distorted bi-pyramidal Sc_5 cluster. The energies of isomer 5B', 5C' and 5D' are only 0.02, 0.05 and 0.23 eV higher than isomer 5A'. The calculated VDEs of these four isomers are all consistent with the experimental value (1.27 eV). So it is probable that isomers 5A', 5B', 5C' and 5D' all exist in the experiments.

As seen in Figure 4, the structures of neutral Sc_2O_2 , Sc_4O_2 , and Sc_5O_3 are very similar to those of their corresponding anions. It is found that the most stable structure of Sc_3O_2 neutral is different from that of Sc_3O_2^- . The anionic Sc_3O_2^- has an isosceles triangular

Sc₃ with one oxygen atom bridging a Sc–Sc bond and the other oxygen capping its face while the most stable structure of neutral Sc₃O₂ can be viewed as addition of a Sc atom to a distorted Sc₂O₂ rhombus. The first two isomers of Sc₃O₂ neutral are nearly degenerate in energy. They are similar to the first two degenerate structures of Sc₃O₂[−] but with the order switched. For Sc₃O₃ neutral, the most stable structure is similar to the second stable structure of Sc₂O₃[−] while its second stable structure is similar to the first isomer of Sc₃O₂[−]. The most stable structure of Sc₂O₃ neutral is in agreement with that reported by Johnson and Panas [20]. The structure of the most stable Sc₃O₃ neutral is different from its most stable anion as the anion is a chair-like structure and the neutral is planar. Similar to the case of Sc₅O₂, the first two isomers of Sc₄O₃ neutral are analogous to the first two structures of Sc₄O₃[−] but with the order switched.

From the structures of Sc_mO_n[−] clusters and their neutrals, we can see that oxygen atoms can be attached to the top sites, bridge sites, or hollow sites of Sc_m clusters. To further investigate the influence of oxygen atoms to Sc clusters, we examined the Sc–Sc distances in Sc_mO_n[−] (*m* = 2–5, *n* = 2–3) clusters. The Sc–Sc distances in the most stable isomers of Sc₂O₂[−] and Sc₂O₃[−] clusters are 2.79 and 2.88 Å respectively, a little longer than the Sc–Sc distance (2.65 Å) in Sc dimer [38] and much shorter than the Sc–Sc distance (3.21 Å) in metallic Sc [39]. The Sc–Sc bond lengths in the most stable isomer of Sc₃O₂[−] are 2.90, 3.25, and 3.25 Å, and those of Sc₃O₃[−] are 3.27, 3.27, and 3.28 Å respectively. In Sc₃O₂[−] and Sc₃O₃[−], the Sc–Sc bonds bridged by oxygen atoms are much longer than the Sc–Sc bond length in the Sc₃ cluster (2.84 Å) [38] and even a little longer than Sc–Sc bond distance (3.21 Å) in metallic Sc [39]. The Sc–Sc bond lengths of Sc₄O₂[−] and Sc₄O₃[−] clusters are in the range of 2.88–3.04 Å and 2.77–3.49 Å respectively while those of the distorted tetrahedral Sc₄ cluster in the ground state are in the range of 2.84–3.02 Å [38]. The shortest Sc–Sc bonds in the Sc₄O₂[−] and Sc₄O₃[−] clusters are almost the same as that in bare Sc₄ cluster. However, the longest Sc–Sc bonds in the Sc₄O₂[−] and Sc₄O₃[−] clusters are longer than that of Sc₄ cluster. The Sc–Sc bond lengths of Sc₅O₂[−] (2.90–3.13 Å) and Sc₅O₃[−] (2.87–3.34 Å) clusters, in general, are longer than those of the triangular bipyramid Sc₅ cluster (2.89–2.90 Å) [38]. On the basis of above analysis, we can see that Sc–Sc bonds of Sc_m[−] (*m* = 2–5) clusters are weakened due to adsorption of oxygen atoms.

It has been reported that Sc₄O₂ and Sc₄O₃ were successfully encapsulated in the C₈₀ cage to form endohedral fullerenes Sc₄O₂@C₈₀ and Sc₄O₃@C₈₀ [40–42]. These studies showed that the structures of Sc₄O₂ and Sc₄O₃ encapsulated in C₈₀ cages can be viewed as a distorted tetrahedral Sc₄ clusters capped by two or three oxygen atoms, respectively. These structures are quite similar to the low-lying isomers of Sc₄O₂ and Sc₄O₃ found in this work. However, the Sc–Sc bonds of the encapsulated Sc₄O₂ and Sc₄O₃ clusters are generally longer than those in the bare Sc₄O₂ and Sc₄O₃ clusters, probably due to their interactions with the carbon atoms in the C₈₀ cage.

5. Conclusions

Sc_mO₂[−] and Sc_mO₃[−] (*m* = 2–5) clusters were investigated with photoelectron spectroscopy and density functional calculations. Our studies show that the structure of Sc₂O₂[−] can be viewed as the attachment of two oxygen atoms to the edge of Sc₂ cluster and that of Sc₂O₃[−] as attachment of oxygen atoms to the top site and bridge sites of Sc₂ cluster. The structures of Sc₃O_n[−], Sc₄O_n[−], and Sc₅O_n[−] (*n* = 2–3) can be viewed respectively as attachment of oxygen atoms to the bridge sites, or hollow sites of Sc₃ triangle,

Sc₄ tetrahedron, and Sc₅ triangular bipyramid. In these Sc_mO_n[−] clusters, there is no direct interaction between the oxygen atoms. The addition of oxygen atoms weakens the Sc–Sc bonds of the Sc_m (*m* = 2–5) clusters.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cplett.2013.01.068>.

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