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Photoelectron spectroscopy study of MC_n^- (M=Sc, Y, and La, $5 \leq n \leq 20$)

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Abstract

Photoelectron spectra of metal-attached carbon cluster anions MC_n^- (M=Sc, Y, and La, $5 \leq n \leq 20$) generated in a laser-vaporization ion source were measured using a magnetic bottle time-of-flight photoelectron spectrometer with 6.4 eV photon energy. The vertical detachment energy (vDE) of each species was estimated from the spectra and compared with the vDE of the linear and monocyclic ring forms of C_n. It was found that PES features of MC_n^- ($5 \leq n \leq 20$, n=odd) could be understood under the assumption that the π electronic structure of MC_n^- is similar to those of the linear carbon chains. However, the PES features of MC_n^- ($12 \leq n \leq 20$, n=even) indicate the presence of a π electronic structure similar to the isomers having ring form. Further possible electronic and molecular structures are presented and discussed for MC_n^- of odd n and even n, respectively.

Keywords: Photoelectron spectroscopy; Metal-attached carbon clusters; Vertical electron affinity π electronic structure

1. Introduction

Since the discovery of macroscopic generation and purification procedure of fullerenes and endohedral fullerenes, spectroscopic studies of them have been extensively performed with a lot of experimental technique such as EPR [1], NMR [2,3], UPS and XPS [4–6], EXAFS [7–9], X-ray [10], and so on. However, the formation mechanism of them has not yet been fully understood, even though it has been one of the most intriguing issues from the beginning of the fullerene research.

Recently, a laser vaporization technique has been extensively applied to a metal–carbon composite rod in the electric furnace under Ar atmosphere for making endohedral fullerenes [11]. It was found that the ambient temperature of the furnace was the most important physical parameter for making them. Additionally, it was suggested that the existence of the metal atom suitable for making endohedral fullerenes seemed to inhibit the formation process of empty fullerenes, because the yield of C_{60} and other higher

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fullerenes drastically decreased. On the other hand, a laser vaporization time-of-flight mass spectroscopy study using the same metal–carbon composite rod indicates that the easiness of the generation of the metal-attached carbon clusters (MC_n) in the vaporization cluster ion source is correlated to the easiness of the generation of endohedral fullerenes [12]. From these experimental findings it was suggested that the attachment of the metal atom to the carbon clusters might cause a drastic change in the molecular and electronic structure of them, and thus influence on the yield of fullerenes and endohedral fullerenes.

Recent ion chromatography studies indicated that there are several conformational isomers for the carbon clusters [13,14] and the metal-containing carbon clusters [15,16]. For example, von Helden et al. [15] studied about the structures of small mixed iron carbon cluster anions (FeC_n^-) and suggested that there are two kinds of conformational isomer (i.e. linear and ring forms) for FeC_n^-($n>4$). Their suggestion was further supported by another group using a photoelectron spectroscopy technique [17,18]. Shelimov et al. [16] examined LaC_n^+ ($n=2$–90) generated in a laser vaporization ion source by use of the ion drift tube apparatus. According to their interpretation, there exist at least two different kinds of ring conformers, i.e. 'open ring' structure (ring Ia: the metal atom is inserted into a carbon ring) and 'closed ring' structure (ring Ib: the metal atom is inside a carbon ring) for LaC_n^+ ($n \leq 20$). They also argued that LaC_n^+ ($n=2$–8) should not have a linear form, but should have a kind of ring form, in which La atom is inserted into a carbon ring, with a possible exception of LaC_2^+ and LaC_3^+. Additionally, they suggested that the annealing process of a ring conformer might play an important role in the formation of endohedral fullerene species. Several ab initio studies also discuss about the existence of linear, side-on form, 'open ring', 'closed ring', and another kind of 'closed ring' structure (ring Ic: the metal atom is attached outside of a monocyclic carbon ring) for the smaller MC_n and MC_n^+ [19,20].

Photoelectron spectroscopy (PES) is a powerful tool for the study of the electronic and vibrational states of neutral clusters and has been successfully applied to the carbon cluster anions (C_n^-) [21–24]. Using a laser vaporization cluster ion source, Yang et al. [21] first suggested that C_n^- has changed its form from linear to monocyclic ring at $n=10$, based on their PES results. On the other hand, a novel 'annealing' technique after laser vaporization was applied to C_n^- by Handschuh et al. [25] and a different mass distribution from that using a laser vaporization ion source was obtained. They found that the PES spectral features for the carbon clusters of different sizes could be classified into several groups, each of which has a different form (linear chain, monocyclic ring and fullerene-like structure) [25]. When the PES technique was applied to the C_n^- generated under several different laser vaporization ion source condition, where different mass distributions in the ion source could be obtained, it could be seen that the PES features changed drastically by the change of the relative abundance between linear and ring isomers [26,27]. Therefore, it is interesting to investigate what kind of species are involved in the metal–carbon cluster system, by a close inspection of the photoelectron spectra of metal–carbon binary cluster anions (MC_n^-) generated in a laser vaporization source. These spectra are also compared with those obtained by use of a pulsed arc cluster ion source (PACIS) [28,29].

2. Experimental

The details of the apparatus are described elsewhere [26] and are only briefly mentioned here. The apparatus consists of a cluster ion source, a time-of-flight mass spectrometer, and a magnetic-bottle type photoelectron spectrometer. Negatively charged carbon clusters and those attached with metal atom(s) were produced by use of a normal laser vaporization technique. A rotating/translating metal carbon composite rod (the molar ratio of metal/carbon is typically 1/130) was irradiated by the second harmonic of a Nd:YAG laser. Vaporized carbon is swept through a extender with helium carrier gas supplied from the pulsed injector operated at a backing pressure of 4 Atm. The anions produced in the plasma are then injected into a Wiley–Mclaren type time-of-flight mass spectrometer and accelerated with a pulsed electric field After the acceleration to the energy of 1.0 keV and traveling within a drift tube, negatively charged clusters were selected using a mass gate to ensure that only desired cluster ions could enter into the photodetachment region. The bunch of these cluster anions of a certain mass were then decelerated to 200 eV and irradiated by the ArF excimer laser (6.4 eV). The fourth harmonics of a Nd:YAG (4.66 eV) laser was also used for MC_n^- (M=La and Y, n=6, 8, 10, and 13), where the photoelectron signal intensity is quite low compared with the background electron signal generated by the ArF excimer laser. After photodetachment, kinetic energies of photoelectrons were analyzed by a magnetic-bottle type electron spectrometer (1600 mm long).

The photoelectron spectra presented in this paper are obtained typically with the accumulation of 2000–5000 laser shots. Background signals due to the scattering of the photodetachment laser with the surface of the chamber were collected as a reference in advance, smoothed and subtracted from the raw data. The kinetic energy of the photoelectrons was calibrated against the known data of C_5^-, C_8^-, and C_9^-. The background electron signal generated by scattered light interacting with the photodetachment chamber was subtracted from the data. The energy resolution of the spectrometer was typically $\Delta E/E = 0.1$.

3. Results and discussion

3.1. Mass distribution of negatively-charged carbon clusters C_n^- and metal-attached carbon clusters, MC_n^- (M=La, Y, and Sc)

Fig. 1a shows a typical mass spectrum for C_n^- and LaC_n^- obtained with a laser vaporization technique applied to a La–carbon composite rod. Similar mass spectra were obtained by use of Y–carbon and Sc–carbon composite rods. Throughout the experimental condition under investigation, it was confirmed that MC_n^- could be detected under a particular laser vaporization condition, where the mass distribution of C_n^- shows magic numbers of $n=5$, 8, 11 overlapping with that of no magic mass distribution from approximately $n=10$ in the spectrum. In the case of laser vaporization using a pure graphite rod, mass distribution obtained with high laser fluence condition is well characterized by the presence of magic numbers at C_n^- ($n=5$, 8 11), followed by an overlapping of no-magic mass distribution starting around $n=10$ (shown in Fig. 1b). However, with low laser fluence condition, the distribution changes into that showing magic numbers at $n=10$, 12, 16, and 18 (shown in Fig. 1c). In the present investigation, it is rather difficult to tune laser vaporization condition so that the mass distribution of C_n^- changed into that having magic numbers of $n=10$,12,16, and 18, where only few MC_n^- could be seen in the mass spectrum. Fig. 1 also demonstrates that the mass

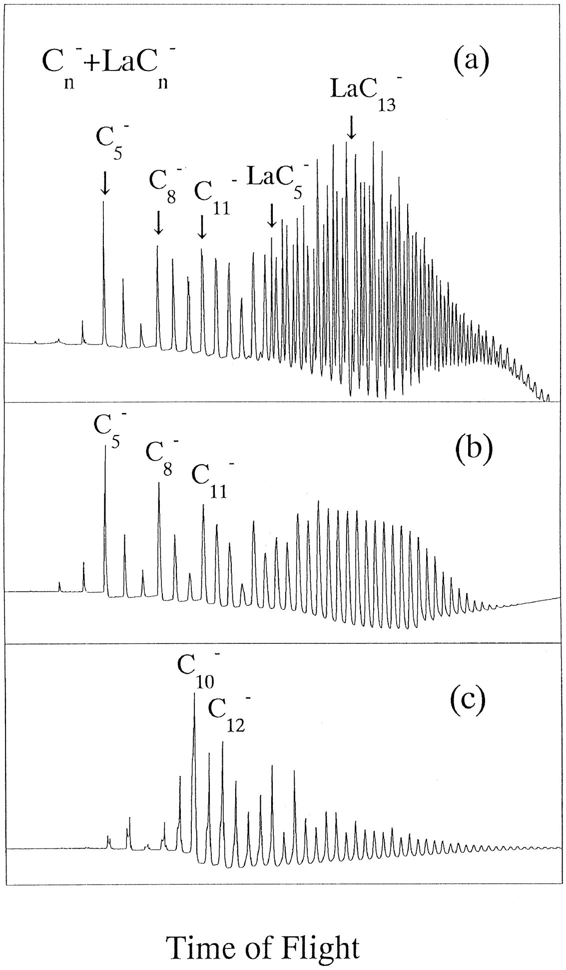

Fig. 1. (a) A time-of-flight mass spectrum obtained by laser vaporization of La–carbon composite rod; (b) a typical mass distribution of C_n^- obtained by laser vaporization of pure graphite rod with high laser fluence condition; (c) a typical mass distribution of C_n^- obtained by laser vaporization of pure graphite rod with low laser fluence condition.

distribution of MC_n^- is rather smooth except MC_{13}^-, which appears as a negative magic number in the spectrum.

Recent PES studies of C_n^- generated with high laser fluence condition clearly demonstrates that linear and ring forms of C_n^- can coexist for $10 \leq n \leq 16$, while only monocyclic ring form of carbon clusters can be generated for $n \geq 10$ [27] under low laser fluence condition. Since the mass distribution of C_n^- in the mass spectrum obtained with the vaporization of La–carbon composite rod becomes similar to that obtained with a laser vaporization of pure graphite rod with high laser fluence condition, it is highly likely that linear form of C_n^- $(10 \leq n \leq 16)$ in the vaporization source can coexist with monocyclic ring form of C_n^- when MC_n^- can be generated.

3.2. Photoelectron spectra of MC_n^- $(5 \leq n \leq 20)$: results

Only the PES for MC_n^- $(n \geq 5)$ could be obtained in the present investigation, since there is less or essentially no abundance for MC_2^-, MC_3^-, and MC_4^- in the mass distribution of MC_n^- (see Fig. 1). Already reported are the PES of these later species which could be measured when a PACIS (Pulsed Arc Cluster Ion Source) was used [28,29]. Figs. 2 and 3 show the PES of LaC_n^- $(5 \leq n \leq 20)$, $YC_n^-(5 \leq n \leq 20)$, and ScC_n^- $(5 \leq n \leq 20)$ of odd n and even n measured with 6.4 eV photon energy, respectively. From these spectra, the vertical detachment energy (vDE) of each MC_n^- species was determined using the value of the electron binding energy indicated by an arrow shown in these figures. Each peak position in these PES spectra was determined based on the careful comparison among the PES data obtained under several different laser vaporization condition. These values are summarized in Table 1 and also are used in Fig. 4 in the case of LaC_n^-. This figure also includes the data for linear and monocyclic ring forms of C_n^- [21–24,27,31] as reference.

Several characteristic features can be seen from Figs. 2 and 3. Fig. 2 shows that the vDE determined from the photoelectron spectra of MC_n^- $(n = \text{odd})$ increase monotonously towards higher electron binding energy as n increases (see also Fig. 4). Additionally, the spectral features for MC_n^- $(n = \text{odd})$ of different size are found to be similar to each other. On the other hand, PES features of MC_n^- $(n = \text{even})$ in Fig. 3 indicate that the intensity of the first photoelectron band is weak for MC_6^-, MC_8^-, and MC_{10}^- (M = La and Y) (indicated by arrows in Fig. 3). In the case of ScC_n^- $(n = 6, 8, \text{and } 10)$, this band was found to become too weak to be recognized. Additionally, another type of PES features (denoted by the symbol '×' in the Fig. 3) appear at the size of MC_{12}^-. The vDE of MC_{12}^- is approximately 0.2–0.4 eV lower than the value for MC_{10}^-, which is rather near to the vEA of C_{12}^- having a monocyclic ring form (see Fig. 4 and also Table 1). Fig. 3 also denotes that the first photoelectron band features of MC_{12}^- and MC_{16}^- resemble to each other, especially in the case of ScC_{12}^- and ScC_{16}^-.

There is an indication of an additional photoelectron band feature for MC_{13}^- (M = La, Y, and Sc) in the lower electron binding energy region (indicated by the asterisk in Fig. 2). Throughout the experimental condition under investigation, it was observed that the relative intensity of this band drastically changed, indicating the existence of some particular isomer for MC_{13}^-. In the following sections, the origin of the major recognizable photoelectron spectral features of MC_n^- (M = La,Y, and Sc, $5 \leq n \leq 20$) is discussed. The origin of the additional PES feature observed for the particular isomer of MC_{13}^- (M = La, Y, and Sc) is discussed in the last section of this paper.

3.3. The interpretation of the photoelectron spectra of MC_n^- $(5 \leq n \leq 20,\ n = \text{odd})$

In comparison with the vDE values obtained for MC_n^- $(5 \leq n \leq 8)$ in the present investigation and those obtained using the PACIS, it is very likely that the conformer of MC_n^- $(5 \leq n \leq 8)$ obtained here is the same as that having the higher vDE obtained in the case of the PACIS source. In the previous study, this conformer was considered to have a linear form where the metal atom is assumed to be attached to the end of the carbon chain [28,29]. In the PACIS study, however, there appears another conformer of MC_n^- $(2 \leq n \leq 8)$ having lower vDE (see Table 1), which was considered to be a side-on form where the metal atom was assumed to be attached to the side of carbon chain. Similar molecular structures have been proposed by several different groups for LaC_n [19,30], YC_n [19,20] and FeC_n [17,18], respectively.

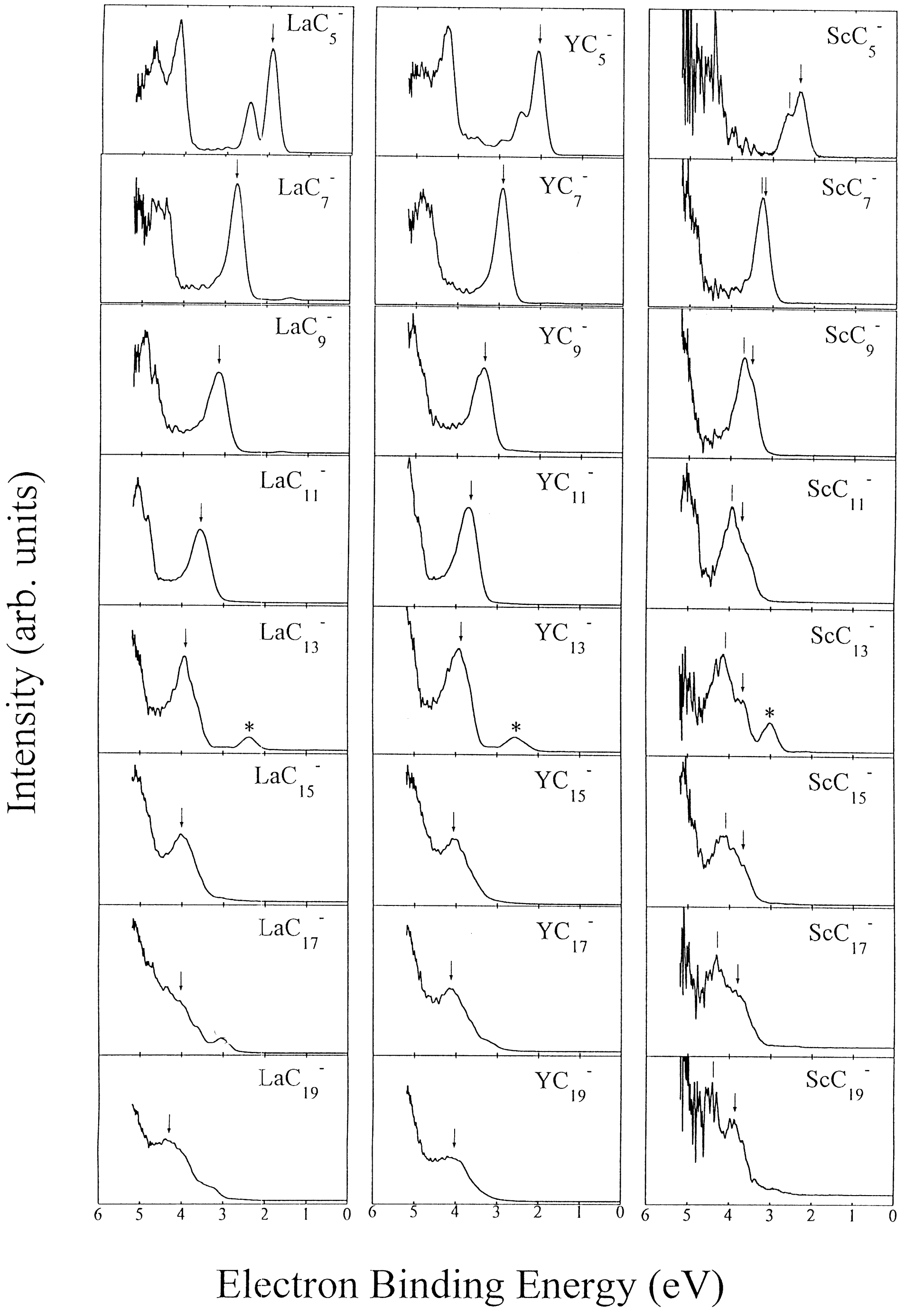

Fig. 2. Photoelectron spectra obtained for MC_n^- (M=La, Y, and Sc, $5 \leq n \leq 20$, n=odd) with 6.4 eV photon energy. The arrow indicates the position from which the vertical electron affinit for each species was determined. In the case of ScC_n^-, the dash line indicates the existence of another electronic state of ScC_n (see text). For peaks with *, see text.

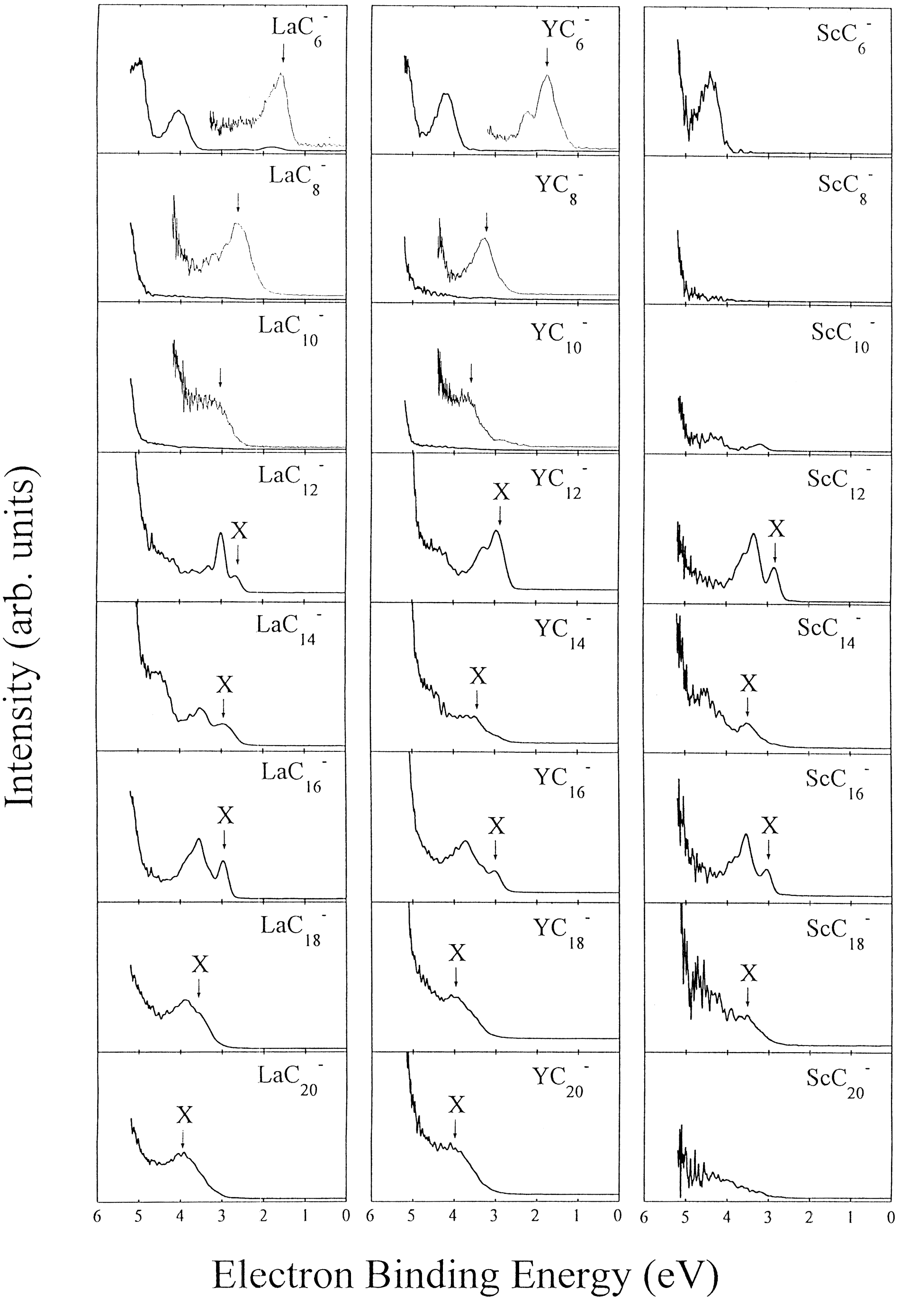

Fig. 3. Photoelectron spectra obtained for the linear MC_n^- (M = La, Y, and Sc, $5 \leq n \leq 20$, n = even) with 6.4 eV photon energy. The inserted spectra for MC_6^-, MC_8^- and MC_{10}^- (M = La and Y) are those obtained with 4.66 eV photon energy. The symbol '×' denotes a new PES band feature appearing for MC_n^-, (n = 12, 14, 16, and 18) (see text). The arrow indicates the position from which the vertical electron affinit for each species was determined.

Table 1
Summary of the vertical detachment energy (eV) of MC_n and C_n ($5 \leq n \leq 20$)[a]

n	LaC_n(s)[b]	LaC_n	YC_n	ScC_n	C_n(l)[c]	C_n(r)[c]
2	1.40				3.27	
3	1.30				1.99	
4	1.40				3.88	
5	1.37	1.95	2.04	2.32	2.87	
6	1.39	1.60	1.73	(n.a.)	4.19	
7	1.51	2.70	2.91	3.23	3.36	
8	1.67	2.61	3.27	(n.a.)	4.38	
9		3.15	3.36	3.45	3.68	
10		3.11	3.56	(n.a.)	4.50	2.38
11		3.55	3.70	3.63	3.85	3.09
12		2.68	2.94	2.85	4.55	2.56
13		3.91	3.87	3.62	4.07	3.61
14		3.00	3.47	3.51	4.64	2.54
15		4.00	4.00	3.65	4.20	3.29
16		3.00	3.00	3.06	4.70	2.51
17		4.00	4.11	3.58		3.74
18		3.49	4.00	3.51		2.73
19		4.29	4.17	3.89		3.50
20		3.94	4.02			2.56

[a] Abbreviations: s (side form); l (linear form); r (ring form).

[b] Data for LaC_n(s) were taken from Ref. [29].

[c] Data for C_n(l) and C_n(r) were taken from those in Refs. [25,28] and from the unpublished data obtained by M. Kohno [31].

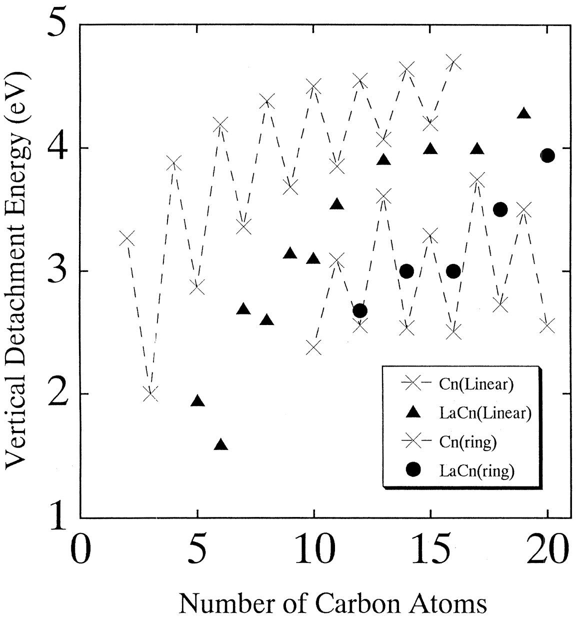

Fig. 4. Summary of the vertical detachment energy (vDE) of LaC_n^- ($5 \leq n \leq 20$) as a function of the number of the carbon atoms using the data shown in Table 1. The vEA of linear and ring forms of C_n^- (drawn by a dotted line) are also included as a reference.

As was pointed out in the previous section, the vDE and the photoelectron features of MC_n^- (n = odd) do not indicate any abruptness even though n is over 11. This finding strongly indicates that the π electronic structure of MC_n (n = odd) holds even when n is over 11, in contrast with the case of C_n^- where the abrupt change of vDE at $n = 10$ is clearly pronounced, because of the formation of ring conformers at $n \geq 10$ [21]. Therefore, if the PES features of MC_n^- (n = odd, $5 \leq n \leq 8$) are considered to be originated from linear form, it is natural to think that MC_n^- (n = odd, $9 \leq n \leq 20$) has also linear form, where the metal atom is considered to be attached to the end of carbon chain. It is interesting to point out that Fig. 4 clearly demonstrates that the vDE of MC_n (n = odd) gradually approaches to that for C_n^- of linear form as n increases.

The PES features of MC_n^- (M = La, Y, and Sc) with the same number of carbon atoms in Fig. 2 resemble to each other and also resemble to those of C_n^- of linear form. In other words, their photoelectron band features are essentially the same among themselves except with a slight shift in the electron binding energy. This indicates that the PES features of MC_n^- (n = odd) originate from the π electronic structure of C_n having a linear form.

In the case of ScC_n^- (n = odd), Fig. 2 shows that the first photoelectron band feature consists of two distinct sub-band structures and the peak positions of those (indicated by the arrow and the dashed line, respectively) seem to cross at ScC_7^-. It is rationalized that the apparent width of the first band feature for LaC_n^- (n = odd) and YC_n^- (n = odd) becomes broader than that for ScC_n^- (n = odd), considering that each of them also includes similar sub-band structures but the separation width is too small to be recognized in the spectra. From this finding and in consideration with the unpaired electrons in unoccupied πMO of linear form of MC$_n$ ($n=$odd), it is suggested that there are multiple electronic states (e.g. the doublet and quartet) for neutral MC$_n$ ($n=$odd) in the first electron binding energy region (see the next section).

3.4. The interpretation of the photoelectron spectra of MC$_n^-$ ($5 \leq n \leq 20$, $n=$even)

Fig. 4 indicates that the vDE of the LaC$_n^-$ ($5 \leq n \leq 11$) show an even–odd alternation, but the inversion phase is reversed to those obtained for C$_n^-$ of linear form. It was also found that the relative intensity of the first photoelectron band feature of MC$_6^-$, MC$_8^-$, and MC$_{10}^-$ (M = La and Y) becomes weak (indicated by arrows in Fig. 3). For ScC$_6^-$, ScC$_8^-$, and ScC$_{10}^-$, the intensity of the first band was found to be too weak to be recognized in the PES spectra of Fig. 3.

These findings are well rationalized when the molecular orbital (MO) of linear C$_n^-$ and MC$_n^-$ are qualitatively considered in the following way: In the case of linear C$_n^-$, the even–odd alternation in the electron binding energy is caused by that the πMO energy level of C$_n^-$ ($n=$odd) having the excess electron is higher than that of the adjacent C$_n^-$ ($n=$even) (see Fig. 5a). Fig. 5a also indicates that this πMO of C$_n^-$ ($n=$odd) is occupied with only one excess electron, while that of C$_n^-$ ($n=$even) is occupied with three electrons.

Group IIIa elements (La, Y, and Sc) have three valence electrons, two of them are in s-orbital and the other is in d-orbital. Thus these metal atoms have the capability of transferring electrons to the πMOs of C$_n^-$, when these metal atoms are attached to C$_n^-$. If it is assumed that two valence electrons are transferred from the metal atom to the πMOs of the linear form of carbon clusters in the case of MC$_n^-$ ($n=$odd), one can see that the π electronic structure does not change so much (see Fig. 5b). This seems to be the reason why the PES features of MC$_n^-$ ($n=$odd) resemble to those of C$_n^-$ having a linear form except with a shift in the electron binding energy.

Also, Fig. 5b indicates that, after photodetachment in the lowest electron binding energy, two electrons remain in the πMOs and the residual unpaired electron stays in the MO formed with the metal atom (not shown in Fig. 5b). Therefore, it is possible that there exist three unpaired electrons in total for MC$_n$ ($n=$odd), which can generate doublet and quartet electronic states. This is the reason why sub-band structure is seen in the case of ScC$_n$ ($n=$odd, $5 \leq n \leq 20$) in the lowest electronic binding energy region.

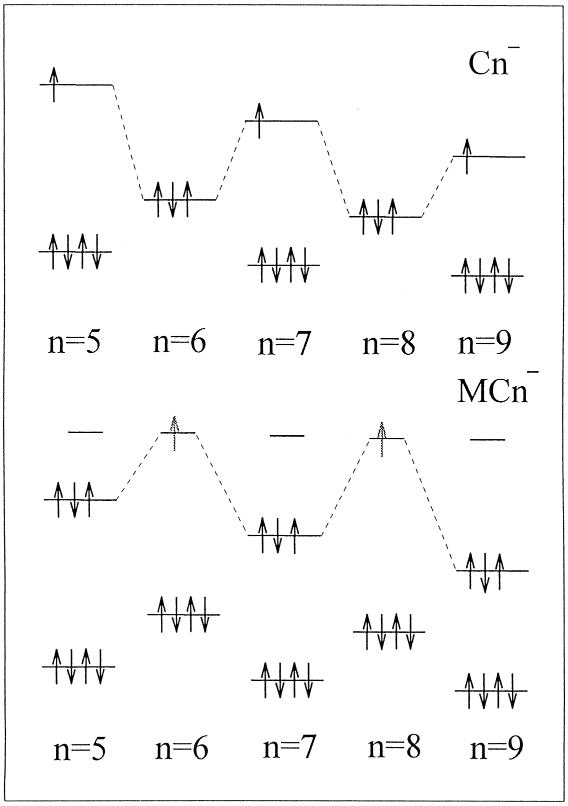

Fig. 5. The schematic drawing for the MO energy levels for C$_n^-$ of linear form (a) and MC$_n^-$ (b) ($5 \leq n \leq 9$). Note that (b) shows only MOs having π character.

On the other hand, in the case of MC$_n^-$ ($n=$even), the vacancy of the highest electron-filled πMO could accept only one excess electron from the metal atom. Therefore, if electron transfers further from the metal atom, it has to be accepted in the πMO shown as the uppermost MO of MC$_n^-$ seen in Fig. 5. This seems to be the reason why the even–odd alternation behavior in the EA of MC$_n^-$ reversed.

Fig. 3 shows that a different PES feature can be seen in the low electron binding energy region from the size of MC$_{12}^-$ (indicated by the symbol '×' in Fig. 3). It suggests that the electronic structure of MC$_n$ ($n=$even) may change from the size of MC$_{12}^-$. In the case of C$_n^-$, an abrupt change was observed in the PES features from C_9^- to C_{10}^-, which can be rationalized considering that ring structures are favored for C_n^- ($n \geq 10$) [22]. Fig. 3 shows that the value of vDE for MC_n ($12 \leq n \leq 20$, $n =$ even) is less than those expected for linear MC_n^- (see Fig. 4). It is assumed that the π electronic structure of MC_n ($12 \leq n \leq 20$, $n =$ even) has the character similar to those for C_n of ring form. This assumption is supported by the PES features between MC_{12}^- and MC_{16}^- which resemble each other, suggesting 4-fold periodicity characteristic of the π electronic structure of C_n having a ring form.

The discussion of the PES features for MC_6^-, MC_8^-, and MC_{10}^- in the previous paragraph suggests that the first band by MC_n^- ($12 \leq n \leq 20$, $n =$ even) of linear form probably is very weak. Therefore, it may not be clearly recognized when it is heavily overlapped by those of MC_n^- of ring form. This, in turn, implies that linear and ring forms of MC_n^- ($12 \leq n \leq 20$) may coexist in the present laser vaporization ion source. Fig. 3 indicates that the PES features of MC_n^- ($n =$ even, $12 \leq n \leq 20$) show a rather broad feature in the first band, especially for larger n. This may be rationalized by considering that MC_n^- in a ring form gives a minor contribution to the PES feature in the first electron binding energy region.

As was mentioned, it is difficult to tune laser vaporization condition so that monocyclic carbon ring clusters C_n ($n \geq 10$) are preferentially formed using a metal carbon composite rod as a target. Additionally, it was found that very few MC_n^- can be seen in the mass spectrum when monocyclic carbon clusters of ring form are preferentially formed in the source. These findings indicate that carbon clusters of ring form do not interact strongly with the metal atoms in the ion source. It suggests that the most probable ring form for MC_n^- ($12 \leq n \leq 20$, $n =$ even) observed in the present investigation is considered as that with the metal atom inserted into the carbon ring. This isomer is considered to be generated through the transformation of MC_n^- of linear form. Recent laser furnace experiment shows that an incorporation of metal atoms into graphite rods suitable for making endohedral fullerenes inhibits the formation of empty fullerenes, especially higher fullerenes [11]. Considering that laser vaporization of metal carbon composite rod seems to suppress the formation of carbon clusters of ring form, it is highly probable that the condition suitable for the formation of monocyclic carbon ring clusters C_n ($n \geq 10$) has an intimate correlation with that of the formation of C_{60} and other higher fullerenes.

3.5. The interpretation of an additional photoelectron feature of MC_{13}^-

Fig. 6 shows photoelectron spectra of LaC_{13}^- measured with different cluster ion source condition. Fig. 6a was obtained in the condition where the time delay between He injection valve and Q switch of vaporization laser was short, whereas Fig. 6b was obtained where this time delay was long. One can clearly see an additional PES feature (designated by

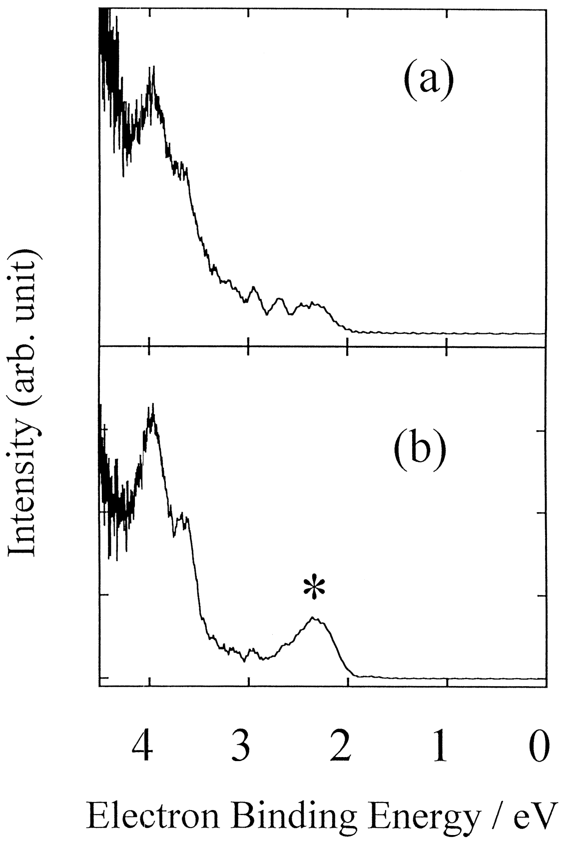

Fig. 6. Photoelectron spectra of LaC_{13}^- obtained with 4.66 eV photon energy. Note that (a) was obtained in the condition where the time delay between He injection valve and Q switch of vaporization laser was short, whereas (b) was obtained where this time delay was long.

asterisk) in Fig. 6b in low electron energy binding region, which indicates the existence of another conformational isomer of LaC_{13}^-, and its form is considered to be different from those for linear or ring forms discussed in the preceding sections.

An ab initio calculation using non-local density functional method (B3LYP/DZ, 6-31G*) suggests that the most stable isomer for LaC_{13}^- is considered as that with La atom inside the C_{13} ring, which gives low vertical detachment energy (1.9 eV) corresponding well to the observed vEA value (2.3 eV). This calculation also suggests that the charge density of La atom in LaC_{13}^- is +1.2, indicating that more than one electron transfers from the metal atom to the π electronic structure of the C_{13}^- ring, where the HOMO is occupied with three electrons in advance. This suggests that the PES feature of this isomer should be similar to that of the C_{14}^- ring. Actually, Fig. 7 demonstrates that the first PES band feature for this isomer of LaC_{13}^- resembles that of C_{14}^-. LaC_{13}^- thus seem to have a ring form.

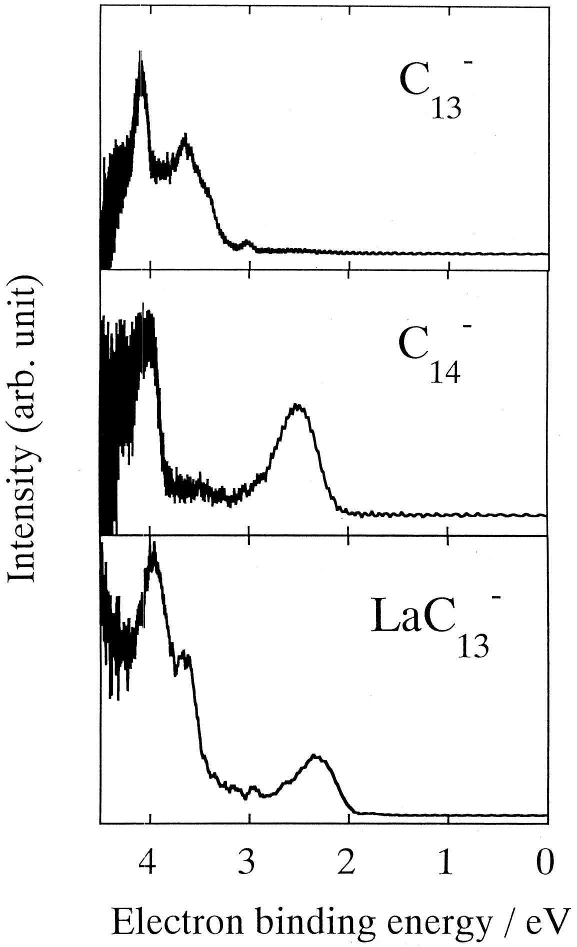

Fig. 7. Photoelectron spectra of C_{13}^-, C_{14}^-, and LaC_{13}^- obtained with 4.66 eV photon energy.

4. Conclusion

Photoelectron spectroscopy technique was applied to the mass selected metal-attached negatively charged carbon clusters MC_n^- (M = La, Y, and Sc, $5 \leq n \leq 20$) generated by a laser vaporization ion source. PES features obtained for MC_n^- (n = odd) suggest that the clusters have a linear form where the metal atom is considered to be attached to the end of carbon chain. While the PES features obtained for MC_n^- (n = 6,8,10) also suggest the linear form, those for MC_n^- ($n \geq 12$, n = even) indicate that another conformer may coexist. For those clusters, a ring form, where the metal atom is inserted into the carbon ring, was suggested and discussed. Finally, it was pointed out that in the case of MC_{13}^-, there is an additional PES feature which is very sensitive to the cluster ion source condition. With the help of ab initio calculations for this cluster, a ring form with La atom inside a C_{13} ring was proposed and discussed.

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