

# Time-of-flight mass and photoelectron spectroscopy study of $\text{LaC}_n^-$

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**Abstract.** Mass spectra of  $\text{LaC}_n^-$  were taken by using a laser-vaporization source (LVS) and pulsed arc cluster ion source (PACIS) applied to La-carbon composite rods (1:130 atomic ratio). The mass spectrum using the LVS with annealing procedure has shown several magic numbers for  $\text{LaC}_n^-$  ( $n = 44, 50, 60, \text{ and } 70$ ), whereas only small  $\text{LaC}_n^-$  (up to  $n = 14$ ) have been observed in the mass spectrum using the PACIS. Photoelectron spectra of some of these have been measured using a magnetic-bottle type time-of-flight electron spectrometer. These results indicate the existence of a few conformational isomers for small La-containing carbon cluster negative ions  $\text{LaC}_n^-$  ( $n = 5\text{--}8$ ).

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## 1 Introduction

Since the discovery of the endohedral fullerenes (the typical form is expressed by  $\text{M}@C_{82}$ ), the formation mechanism of them has been one of the most intriguing issues. A laser vaporization time-of-flight mass spectroscopy applied to metal-carbon composite rods, which have been used for the production of soot containing endohedral fullerenes, suggested that the metal-containing carbon clusters ( $\text{MC}_n$ ) might have an important role in the formation process of  $\text{M}@C_{82}$  [1].

Recent ion chromatography and photoelectron spectroscopy studies indicate the existence of several structural isomers for the metal-containing carbon clusters [2–5]. It is assumed that the attachment of the metal atom to the carbon clusters might cause a drastic change in the molecular and electronic structure.

Therefore it is interesting to investigate the photoelectron spectra for metal-containing carbon cluster negative ions ( $\text{MC}_n^-$ ), where the element M can be encapsulated into the fullerene cage, to shed light on the electronic and molecular structure of metal-containing carbon clusters ( $\text{MC}_n$ ).

## 2 Experimental

The experimental setup for the generation of  $\text{LaC}_n^-$  has already been described elsewhere [6, 7]. Briefly in the laser vaporization ion source (LVS), the negatively charged cluster ions were generated by laser vaporization of a La-carbon composite rod (La:C = 1:130 atomic ratio, c.a. 60 mm long and 6 mm in diameter). An annealing process right after vaporization and passing through the long extender (c.a. 30 cm) causes an enhancement of the relative intensities of the most stable isomers of the clusters. In the pulsed arc cluster ion source (PACIS), the La-carbon composite rod of 13 mm in diameter was used as an electrode. Typical current for arc burning was c.a. 5000 A for about 3–20  $\mu\text{sec}$ .

Photoelectron spectra for  $\text{LaC}_n^-$  have been measured by a magnetic bottle type photoelectron spectrometer, after selecting a specific  $\text{LaC}_n^-$  cluster by time-of-flight mass separation. Third (3.49 eV) and fourth (4.66 eV) harmonics of Nd:YAG laser in addition to XeCl laser (4.03 eV) were used for photodetachment.

## 3 Results and discussion

### 3.1 Mass spectrum of $\text{LaC}_n^-$

Figure 1 shows a typical mass spectrum of annealed carbon cluster negative ions ( $\text{C}_n^-$ ) and La-containing carbon cluster negative ions ( $\text{LaC}_n^-$ ) produced by the LVS. When the annealing process was not included, only carbon cluster negative ions ( $n \leq 40$ ) have been observed. With annealing, the mass spectrum shows several magic numbers for  $\text{LaC}_n^-$  ( $n = 44, 50, 60, 70$ ) and  $\text{C}_n^-$  ( $n = 5, 10, 32, 36$ ), respectively. In the higher mass region, only even numbered carbon cluster negative ions ( $\text{C}_{2m}^-$ ,  $32 \leq 2m$ ) and those with La ( $\text{LaC}_{2m}^-$ ,  $36 \leq 2m$ ) have been observed, whereas in the lower mass region, both even and odd numbered carbon cluster negative ions and those with La have been observed ( $\text{C}_n^-$ ,  $4 \leq n \leq 30$  and  $\text{LaC}_n^-$ ,  $4 \leq n \leq 17$ ).

The magic numbers for  $\text{LaC}_n^-$  are the same as those seen in the time-of-flight mass spectrum of annealed carbon cluster negative ions  $\text{C}_n^-$  [6, 8]. These magic numbers are also

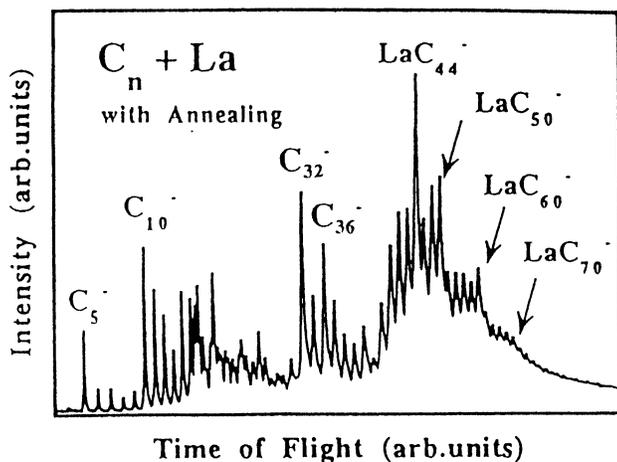


Fig. 1. Time-of-flight mass spectrum of annealed carbon clusters ( $C_n^-$ ) and metal-containing carbon clusters ( $LaC_n^-$ ) using LVS

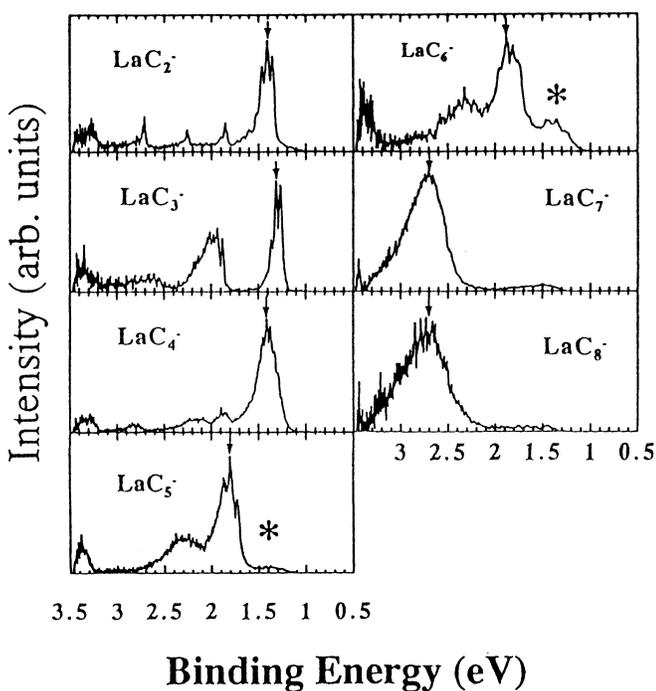


Fig. 2. Photoelectron spectra of  $LaC_n^-$  ( $n = 2-8$ ). Photodetachment energy is 3.49 eV

identical to the ones observed in the  $C_2$  loss photofragmentation pattern of higher fullerenes ( $C_{76}$ ,  $C_{82}$ , and  $C_{84}$ ) [9, 10]. The relative intensities between clusters in the smaller mass region and in the higher mass region depend to some extent on the source conditions and annealing parameters.

Using the PACIS we observed only small  $C_n^-$  ( $4 \leq n \leq 12$ ) and  $LaC_n^-$  ( $2 \leq n \leq 14$ ) throughout the experiment. Since the photoelectron spectra obtained for  $LaC_n^-$  of the same size (e.g.  $LaC_4^-$ ), produced by the LVS and the PACIS were identical, the PACIS was mainly used for measuring the photoelectron spectra of  $LaC_n^-$  ( $2 \leq n \leq 8$ ), while the LVS was mainly used for getting the photoelectron spectra of  $LaC_{44}^-$ ,  $LaC_{50}^-$ ,  $LaC_{60}^-$ , and  $LaC_{70}^-$ .

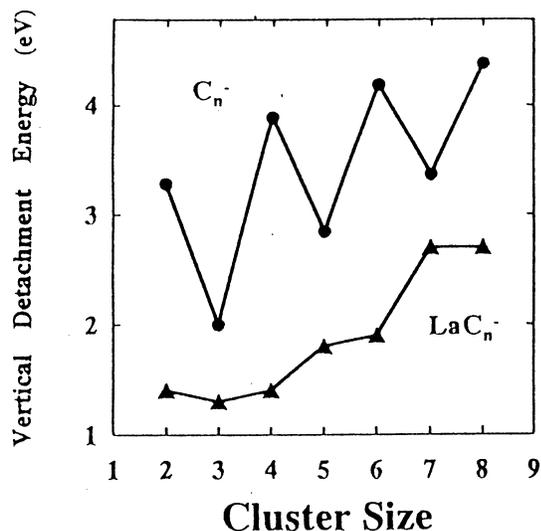


Fig. 3. Vertical detachment energies for  $LaC_n^-$  ( $n = 2-8$ ). As a reference, those for pure carbon cluster negative ions ( $C_n^-$ ) are also shown in the figure [12]

### 3.2 Photoelectron spectra of $LaC_n^-$ ( $2 \leq n \leq 8$ )

Figure 2 shows the photoelectron spectra (photodetachment energy: 3.49 eV) obtained for  $LaC_n^-$  ( $2 \leq n \leq 8$ ), which has been produced by the PACIS. The results indicate that all of the vertical detachment energies (VDEs) for  $LaC_n^-$  (the positions indicated by arrows in Fig. 2) are lower than those for  $C_n^-$  [11, 12]. Additionally, when the PACIS condition was varied during the experiment, another feature appeared in the spectra, (designated by the asterisk in Fig. 2 for  $LaC_5^-$  and  $LaC_6^-$ ), indicating the existence of another conformational isomer having a lower VDE value.

Figure 3 indicates the plot of the VDEs of  $LaC_n^-$  ( $2 \leq n \leq 8$ ) compared with those for  $C_n^-$  (from ref. 12). It can be clearly seen that the even-odd alternation of VDEs for  $C_n^-$  disappears in the case of  $LaC_n^-$ . As the size  $n$  increases, the VDE for  $LaC_n^-$  also gradually increases, but always is lower than that for  $C_n^-$  of the same size.

According to the recent ion chromatographic study, there are isomers of linear and monocyclic ring structure observed for  $C_n^-$  ( $10 \leq n \leq 30$ ) [13]. PES indicates that the VDE for linear structures is higher than that for ring structure [11]. Also Wang et al. suggested from the comparison of their photoelectron spectrum of  $FeC_n^-$  with the ion chromatography experiment [3], the existence of two different conformational isomers of linear and ring structure for  $FeC_n^-$  ( $4 \leq n$ ) [2, 4].

Based on the these observations, the features giving VDEs indicated by the arrow in Fig. 3 are attributed to the linear  $LaC_n^-$ . The features at low vertical detachment energies for  $LaC_5^-$  and  $LaC_6^-$ , (designated by asterisk in Fig. 2), can be attributed to the different conformational isomers, presumably due to those having ring structures. A preliminary ab initio calculation suggests that the VDE from  $LaC_4^-$ (chain) to  $LaC_4$ (chain) is c.a. 1 eV higher than that from  $LaC_4^-$ (ring) to  $LaC_4$ (ring) [14]. It also indicates that the LUMO of  $LaC_4$  is composed mainly of the La(6s) orbital, consistent with the the plot in Fig. 3 where even-odd

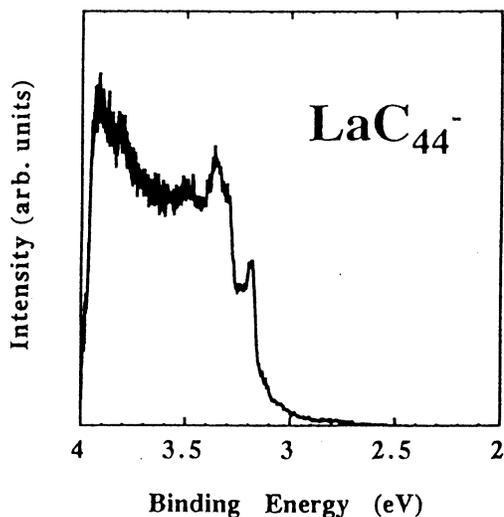


Fig. 4. Photoelectron spectrum of  $\text{LaC}_{44}^-$

alternation of VDEs characteristic to carbon clusters disappears.

### 3.3 Photoelectron spectra of $\text{LaC}_{44}^-$

Figure 4 shows the photoelectron spectrum of  $\text{LaC}_{44}^-$  produced by the LVS. The spectral feature looks quite similar to that due to  $\text{C}_{44}^-$  [6], showing an initial sharp peak followed by a more broader one. Also, in contrast to the difference between VDEs of  $\text{LaC}_4^-$  and  $\text{C}_4^-$ , or other small La-carbon clusters, the difference between the VDEs of  $\text{LaC}_{44}^-$  and  $\text{C}_{44}^-$  is very small.

In larger endohedral fullerenes (such as  $\text{LaC}_{82}$ ) the La donates its outer valence electrons into the fullerene orbitals [15]. Accordingly, the photoelectron spectra should be quite similar, but additional features due to the newly occupied orbitals are also expected, especially when two or more electrons are donated into the fullerene orbitals. It is interesting to note that Wang et al., when they discussed the resemblance between the photoelectron spectra of  $\text{C}_{60}^-$  and  $\text{CaC}_{60}^-$ , pointed out that the LUMO of  $\text{C}_{60}$  is triply degenerate, and two electrons are donated by the Ca [16].

The resemblance between the spectra of  $\text{LaC}_{44}^-$  and  $\text{C}_{44}^-$  suggests that there is a common molecular structure. Recent photofragmentation studies show common magic numbers ( $n = 44, 50, 60, 70$ ) for the photoionization/fragmentation of higher fullerenes  $\text{C}_n$  ( $n = 76, 82, \text{ and } 84$ ) [9, 10], and some of the endohedral fullerenes [10, 17–18]. However, since these fragment ions are considered to be produced via highly excited states of fullerenes, it is not conclusive whether these fragment ions seen in the mass spectra also have a closed-cage structure.

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